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

## National foreword

This British Standard is the UK implementation of EN 15991:2015. It supersedes BS EN 15991:2011 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee RPI/1, Refractory products and materials.

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English Version

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

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

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

This European Standard was approved by CEN on 3 October 2015.

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EUROPÄISCHES KOMITEE FÜR NORMUNG

**CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels**

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# Contents

# European foreword

This document (EN 15991:2015) has been prepared by Technical Committee CEN/TC 187 “Refractory products and materials”, the secretariat of which is held by BSI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by May 2016 and conflicting national standards shall be withdrawn at the latest by May 2016.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 15991:2011.

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# 1 Scope

This European Standard defines a method for the determination of the trace element concentrations of Al, Ca, Cr, Cu, Fe, Mg, Ni, Ti, V and Zr in powdered and granular silicon carbide.

Dependent on element, wavelength, plasma conditions and weight, this test method is applicable for mass contents 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 (ICP OES) and electrothermal vaporization (ETV) 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 weight or by choosing lines with different sensitivity.

After adequate verification, the standard 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, $B_4C$, $Si_3N_4$, BN and several metal oxides as well as with the determination of P and S in some of these materials.

# 2 Principle

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 unit. The evaporation products containing the element traces are transported as a dry aerosol into the plasma of the ICP-torch and there excited for the emission of optical radiation. In a simultaneous emission spectrometer in, for example Paschen-Runge- or Echelle-configuration, the optical radiation is dispersed. The intensities of suited spectral lines or background positions are registered with applicable detectors like photomultipliers (PMT), charge coupled devices (CCD), charge injection devices (CID), and serial coupled devices (SCD). By comparison of the intensities of the element-specific spectral lines of the sample with calibration samples of known composition, the mass fractions of the sample elements are determined.

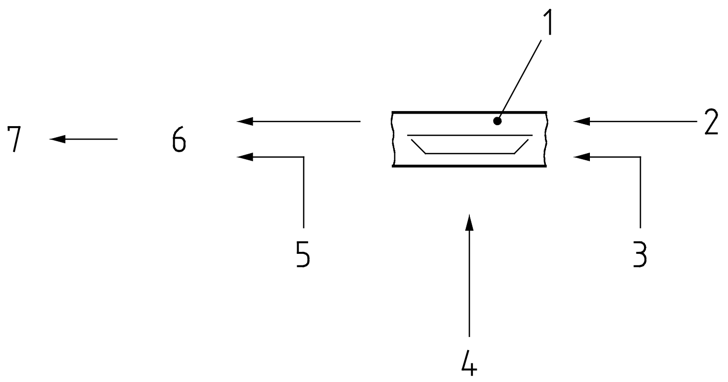
# 3 Spectrometry

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

Contrary to the wet chemical analysis from dilution in ICP OES the classical sample digestion is replaced by electrothermal vaporization at high temperatures in a graphite furnace.

By a suitable design of the furnace (see Figures 1 and 2) and a suited gas regime in the transition area graphite tube / transport tube (see Figure 1), it is ensured that the sample vapour is carried over into a form that is to transport effectively (see [5], [6], [7], [8], [10]). Carbide forming elements, for example titanium, zirconium, that are incompletely or not evaporating need a suitable reaction gas (halogenating agent) to be converted into a form that is easy to transport (see [1], [3], [5] and [10].) Dichlorodifluoromethane ($CCl_2F_2$) shall be used as halogenating agent. Compared to other halogen containing carbon compounds $CCl_2F_2$ provides optimum analyte release and transport efficiency. $CCl_2F_2$ is required for simultaneous determination of the elements listed in Clause 1. The results of the interlaboratory study (see Annex A) were obtained using $CCl_2F_2$ as reaction gas.

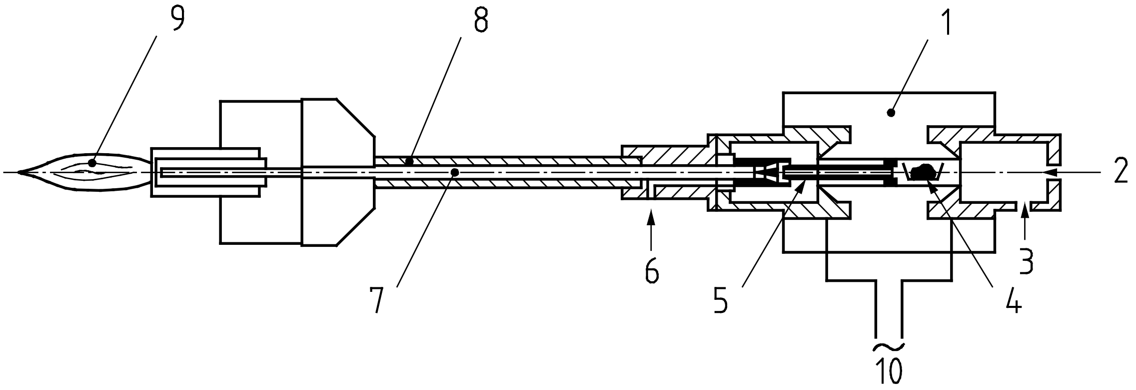
The dry aerosol is introduced into the ICP plasma by the injector tube and there excited for the emission of light (see Figure 1, Figure 2 and Figure 3).



**Key**

| | | | |
|---|---|---|---|
| 1 | graphite tube with boat and sample | 5 | bypass gas (Ar) |
| 2 | carrier gas (Ar) | 6 | aerosol |
| 3 | reaction gas ($CCl_2F_2$) | 7 | to the ICP torch |
| 4 | shield gas (Ar) | | |

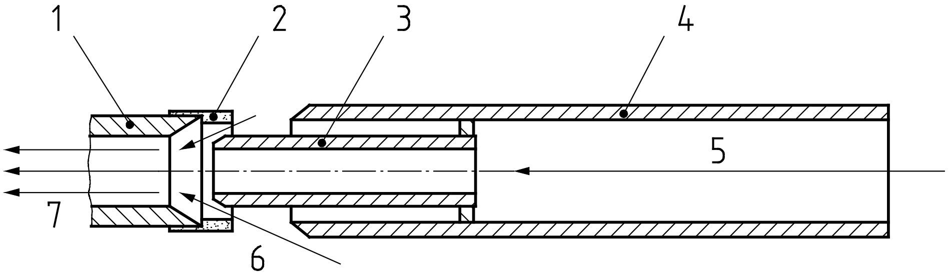
**Figure 1 — Schematic configuration of the ETV-gas regime with the gas flows carrier-gas, bypass-gas, reaction-gas and shield-gas**



**Key**

| | | | |
|---|---|---|---|
| 1 | graphite tube furnace | 6 | bypass-gas (Ar) |
| 2 | pyrometer | 7 | aerosol |
| 3 | carrier gas (Ar) + reaction gas ($CCl_2F_2$) | 8 | transport tube |
| 4 | solid sample | 9 | ICP-torch |
| 5 | vapour | 10 | power supply 0 A to 400 A |

**Figure 2 — Schematic design of the ETV-ICP-combination with an axial plasma (example)**



**Key**

| | | | |
|---|---|---|---|
| 1 | $Al_2O_3$-transport tube | 5 | carrier gas evaporated sample |
| 2 | $Al_2O_3$-transition ring | 6 | bypass gas |
| 3 | nozzle | 7 | gas mixture in laminar flow |
| 4 | graphite tube | | |

**Figure 3 — Schematic configuration of the transition area between graphite- and transport-tube**

NOTE Figure 1, Figure 2 and Figure 3 show a well-established commercial instrument.

# 4 Apparatus

**4.1 Common laboratory instruments** and laboratory instruments according to 4.2 to 4.7.

**4.2 ICP-emission spectrometer**, simultaneous, preferably with the possibility to register transient emission signals and suited for the synchronised start of ETV vaporization cycle and signal registration.

NOTE Especially for changing matrices the measurement of the spectral background near the analysis lines is beneficial, because by this the systematic and stochastic contributions of the analysis 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 a simultaneous background measurement, in addition to their possibility to save a lot of time in the analysis cycle.

**4.3 Electrothermal vaporization system** with graphite furnace with suited transition zone graphite tube / transport tube for optimised aerosol formation, to be connected to the injector tube of the ICP torch by a transport tube for example made of corundum, PTFE, PFA, PVC (cross-linked), with controlled gas flows (preferably with mass-flow-control) and furnace control (preferably with continuous online-temperature control of the graphite boat) for a reproducible control of the temperature development.

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

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

**4.6 Microbalance**, capable of reading to the nearest 0,01 mg.

NOTE A microbalance with a direct reading of 0,001 mg is advantageous.

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

# 5 Reagents and auxiliary material

Only analytical grade reagents shall be used unless stated otherwise.

**5.1 Sample boats** of graphite (spectral grade) adapted in size to the graphite tube of the ETV, baked out for the necessary purity.

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

NOTE For silicon nitride, silicon carbide and boron carbide certified reference material is available for main-, minor- and trace-components. (For CRMs, see Annex E.)

**5.3 Calibration solutions**, made of tested stock solutions of the elements to be analysed.

**5.4 Reaction gas,** Dichlorodifluoromethane ($CCl_2F_2$)..

NOTE Dichlorodifluoromethane is the most effective reaction gas, some alternative reaction gases have serious disadvantages. According to the EU-regulation (see [12]) of materials influencing the ozone layer, this chemical product is allowed for laboratory use and for the use as a starting substance. $CCl_2F_2$ 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 subject to registration at the European Commission.

**5.5 Argon** purity ≥ 99,99 % (volume fraction).

# 6 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, using for example ISO 5022 [13], ISO 8656-1 [14], EN ISO 21068-1 [15], but this list is not exhaustive.

If the sample is not received in a dry state, it shall be dried at (110 ± 10) °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.

It is critical that the sample material is on hand at a particle size of ≤ 50 µm; eventually it shall be broken up and homogenized, if necessary. For this a crushing device suited for the analysis goal shall be applied.

For porous materials, it shall be checked out if it is necessary to break them up. Breaking up is necessary if the transient analysis signals show an unusual long decay (tailing).

# 7 Calibration

The calibration shall be performed for each measuring cycle with calibration samples with defined analyte concentrations. The procedure shall be carried out in accordance with Clause 8. 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 analyte concentration or by a combination of both possibilities.

Because of the low weights used and therefore the resulting spread, the number of (calibration) measurements should take account of the desired accuracy. Practically about 10 to 15 standards have been found to be ideal; e.g. for 10, five weights of two different calibration samples with different analyte concentrations 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 trace concentrations of 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 standards with or without matrix adaptation may be used (see [1], [6] to [9] and Annex F). In the concrete case this shall be documented by calibration substances 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, i.e. materials with the same matrix as the sample and with concentrations negligible compared to the expected analyte concentration in the sample. The blank sample is weighed with a mass comparable to the sample to be analysed, then the aqueous calibration solution is added.

NOTE 3 The calculation of the calibration function is usually carried out as linear regression. The calculated data are displayed graphically as calibration function. Eventually also a quadratic regression is applicable. The continuous slope of the calibration function with a sufficient gradient is important.

# 8 Procedure

Use the sample prepared according to Clause 6 and weigh, preferably between 1 mg and 5 mg with a precision of 0,01 mg into the sample boats; baked out in advance. The baking-out temperature for cleaning the boats shall be approximately 100 °C above the highest temperature of the analysis run.

Dependent on the material, the analyte, the analyte concentration, the chosen lines and the ETV-system higher weights may be used.

The applied part sample weight shall be documented.

The ICP-emission-spectrometer (4.2) shall be set up in accordance with its operations manual. After an adequate waiting time (20 min is normal) the first boat is applied into the furnace of the ETV-system by tweezers (4.4) or by an auto sampler device.

The analysis programme is started, while the control of the temperature run of the furnace of the ETV-system and the registration of the emission signals in the spectrometer shall be triggered simultaneously.

After the end of the analysis programme the sample boat is removed from the furnace of the ETV by tweezers or by an automatic auto sampler device and the next one is brought in.

Before the actual analysis run the blank value of the system shall be determined with an empty, cleaned boat. With another empty, clean boat and a certain amount of calibration sample or dried calibration solution the integration intervals of the chosen emission lines and the background positions shall be checked for their optimum position and eventually are corrected.

For each material a special temperature programme shall be created depending on the analyses.

The programme creation preferably should be done using available calibration standards. They also should be used to choose the suitable emission lines.

Before configuring the integration – respectively the analysis – interval the release of the analyses shall be observed by recording the transient emission signals.

EXAMPLE Furnace programme for the matrix SiC:

Conditioning step: 3 s heating-up from room temperature to 450 °C, dwell 27 s at 450 °C;

Vaporization step: 3 s heating-up to 2 300 °C, dwell 27 s at 2 300 °C;

Cooling-off time: 50 s cooling down to room temperature.

The cooling-off rate is dependent on the performance of the used chillier. Before changing the boat the temperature should be < 200 °C.

Integration interval: 31 s to 52 s after the start of the furnace programme;

Total integration time: 21 s.

Each sample shall be measured several times, but at least 3 times. If the single values of the multiple analysis of the analyte concentrations deviate by more than a given degree, depending on the repeatability of the method, then the analysis shall be repeated according to Clause 8.

If poor reproducibility of the spectral intensities of one or more analytes of the sample persists, it is necessary to homogenize the sample further, e.g. in a mortar. For low concentrations, near the limit of determination (see [16]) this additional step is not necessary.

## 9 Wavelength and working range

When selecting the wavelength of analytes, it should be borne in mind that these shall be inference free with respect to sample matrix and further impurities. Only spectral lines shall be selected where under the chosen working conditions neither self-absorption nor self-reversal can occur.

NOTE 1 Proposal for choosing of wavelength and information about working ranges, see Annex B.

NOTE 2 A summary description of interferences and possibilities to reduce these is in Annex C.

When setting up the analytical programme for a specific material, ensure via suitable pre-tests that the analytical ranges lie above the limit of determination of the analytes. The upper working range is restricted by decrease of sensitivity (slope of calibration graph) to about 80 % of its initial value. Where appropriate the line used can be changed to a less sensitive spectral line.

## 10 Calculation of the results and evaluation

The intensities of spectral lines measured by the emission spectrometer are to be corrected to net-intensities via background intensities measured at the background measuring points. Using the analytical functions the corrected net-intensities are to be converted into the corresponding masses of the respective analyte (see Clause 8). Using the sample weight of sub-sample the mass fractions of analytes in the sample shall be calculated.

NOTE To improve precision and trueness the method of internal standard (reference element) can be applied. For this purpose, the ratio of intensities of spectral lines of analyte elements to the intensity of the spectral line of a reference element (e.g. Si in analysis of SiC) is used.

The wavelengths of used spectral lines and background measuring points for calibration and for measurement of the sample itself shall always be the same.

## 11 Reporting of results

The concentration shall be reported as the mean of the individual determinations carried out, expressed as a % *m/m*. Results shall be rounded to the nearest 0,01 % or the uncertainty of measurement (see Annex D), whichever is the greater.

## 12 Precision

NOTE See ISO 5725-2 [17] for definitions.

### 12.1 Repeatability

The repeatability limit *r* will not be exceeded in more than 5 % of cases by the absolute difference between two single test results independent of each other and determined at the same sample material by the same analyst using the same analytical procedure and the same equipment in the same laboratory within a short time.

The data of repeatability determined at three different silicon carbide samples in the frame of an interlaboratory comparison are listed in Annex A.

### 12.2 Reproducibility

The reproducibility limit *R* will not be exceeded in more than 5 % of cases by the absolute difference between two single test results determined by different analysts analysing the same sample material using the same analytical procedure and different equipment in different laboratories.

The reproducibility data determined using three different silicon carbide samples in the frame of an interlaboratory comparison are listed in Annex A.

## 13 Test report

Test reports shall include the following information:

a) designation of the sample tested;

b) a reference to this European Standard;

c) test results, expressed as mean of the single values of multiple determinations according to Clause 11;

d) if required, uncertainty of mean (see Annex D) or standard deviation;

e) if required, information for calibration;

f) if any discrepancy from this standard (observed during the test);

g) name and address of laboratory, analysis date and, if required, signature of the responsible person.

# Annex A
(informative)

# Results of interlaboratory study

The interlaboratory study was carried out using six different SiC samples. The analyte concentration (mass fractions) of each individual sample was calculated on the basis of the analytical functions obtained by the other five samples. This procedure was carried out for three selected silicon carbide samples and the results were used for evaluation of statistical data. The maximum grain size of all samples was less than 50 µm. The evaluation of results was carried out according to ISO 5725-2 [17].

## Table A.1 — Data of precision determined at the SiC-sample nmp1

| Analyte | | Total mean values | Variance of Repeat-ability | Repeatabilitystandard deviation | Repeatability limit | Coefficient of variation of repeatability | Reproducibility standard deviation | Reproducibility limit | Coefficient of variation of reproducibility |
|---|---|---|---|---|---|---|---|---|---|
| | $p$ [a] | $w_A$ | $s_r^2$ | $s_r$ | $r$ | $v_r$ | $s_R$ | $R$ | $v_R$ |
| | | mg/kg | mg/kg | mg/kg | mg/kg | % relative | mg/kg | mg/kg | % relative |
| **Al** | 10 | 94,47 | 79,59 | 8,92 | 24,98 | 9,44 | 12,35 | 34,57 | 13,07 |
| **Ca** | 9 | 3,13 | 0,34 | 0,58 | 1,62 | 18,49 | 0,89 | 2,50 | 28,51 |
| **Cr** | 8 | 2,48 | 0,13 | 0,36 | 1,01 | 14,52 | 0,51 | 1,43 | 20,55 |
| **Cu** | 10 | 0,82 | 0,03 | 0,18 | 0,50 | 21,53 | 0,27 | 0,74 | 32,26 |
| **Fe** | 10 | 279,45 | 316,15 | 17,78 | 49,79 | 6,36 | 23,76 | 66,51 | 8,50 |
| **Mg** | 10 | 3,18 | 0,18 | 0,43 | 1,20 | 13,50 | 0,49 | 1,37 | 15,40 |
| **Ni** | 10 | 71,69 | 54,12 | 7,36 | 20,60 | 10,26 | 9,47 | 26,51 | 13,21 |
| **Ti** | 9 | 141,63 | 123,51 | 11,11 | 31,12 | 7,85 | 18,04 | 50,51 | 12,74 |
| **V** | 10 | 138,61 | 296,52 | 17,22 | 48,21 | 12,42 | 22,21 | 62,18 | 16,02 |
| **Zr** | 10 | 22,00 | 3,55 | 1,88 | 5,28 | 8,57 | 1,85 | 5,18 | 8,41 |

[a] Number of participants for the element.

### Table A.2 — Data of precision determined at the SiC-sample 628

| **Analyte** | | **Total mean values** | **Variance of Repeatability** | **Repeatabilitystandard deviation** | **Repeatability limit** | **Coefficient of variation of repeatability** | **Reproducibility standard deviation** | **Reproducibility limit** | **Coefficient of variation of reproducibility** |
|---|---|---|---|---|---|---|---|---|---|
| | $p$ [a] | $w_\mathrm{A}$ | $s_r^2$ | $s_r$ | $r$ | $v_r$ | $s_R$ | $R$ | $v_R$ |
| | | mg/kg | mg/kg | mg/kg | mg/kg | % relative | mg/kg | mg/kg | % relative |
| **Al** | 10 | 284,21 | 516,50 | 22,73 | 63,63 | 8,00 | 34,45 | 96,45 | 12,12 |
| **Ca** | 9 | 22,33 | 1,69 | 1,30 | 3,64 | 5,82 | 1,96 | 5,48 | 8,77 |
| **Cr** | 8 | 3,76 | 0,11 | 0,33 | 0,93 | 8,86 | 0,57 | 1,60 | 15,18 |
| **Cu** | 10 | 3,13 | 0,09 | 0,29 | 0,82 | 9,37 | 0,32 | 0,89 | 10,20 |
| **Fe** | 10 | 414,90 | 798,73 | 28,26 | 79,13 | 6,81 | 27,23 | 76,26 | 6,56 |
| **Mg** | 10 | 2,14 | 0,20 | 0,45 | 1,25 | 20,86 | 0,56 | 1,57 | 26,19 |
| **Ni** | 10 | 99,66 | 59,59 | 7,72 | 21,61 | 7,75 | 8,66 | 24,25 | 8,69 |
| **Ti** | 9 | 88,52 | 56,52 | 7,52 | 21,05 | 8,49 | 8,13 | 22,76 | 9,18 |
| **V** | 10 | 418,52 | 2488,61 | 49,89 | 139,68 | 11,92 | 48,81 | 136,66 | 11,66 |
| **Zr** | 10 | 13,79 | 2,91 | 1,71 | 4,78 | 12,37 | 1,95 | 5,46 | 14,14 |

[a] Number of participants for the element.

**Table A.3 — Data of precision determined at the SiC-sample 8517 certified later as reference material BAM-S003**

| Analyte | $p$ [a] | Total mean values<br>$w_A$<br>mg/kg | Variance of Repeatability<br>$s_r^2$<br>mg/kg | Repeatability standard deviation<br>$s_r$<br>mg/kg | Repeatability limit<br>$r$<br>mg/kg | Coefficient of variation of repeatability<br>$v_r$<br>% relative | Reproducibility standard deviation<br>$s_R$<br>mg/kg | Reproducibility limit<br>$R$<br>mg/kg | Coefficient of variation of reproducibility<br>$v_R$<br>% relative | Certified values for comparison<br>mg/kg | Certified expanded uncertainty<br>$U$<br>($k$ = 2) [b]<br>mg/kg |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Al** | 10 | 352,51 | 476,02 | 21,82 | 61,09 | 6,19 | 26,33 | 73,71 | 7,47 | 372 | 20 |
| **Ca** | 9 | 27,30 | 4,92 | 2,22 | 6,21 | 8,13 | 2,56 | 7,17 | 9,38 | 29,4 | 1,8 |
| **Cr** | 8 | 3,46 | 0,17 | 0,42 | 1,17 | 12,07 | 0,47 | 1,31 | 13,49 | 3,5 | 0,4 |
| **Cu** | 10 | 1,22 | 0,01 | 0,10 | 0,27 | 7,88 | 0,15 | 0,41 | 11,94 | 1,5 | 0,4 |
| **Fe** | 10 | 161,20 | 103,88 | 10,19 | 28,54 | 6,32 | 14,49 | 40,58 | 8,99 | 149 | 10 |
| **Mg** | 10 | 5,62 | 0,21 | 0,46 | 1,30 | 8,24 | 0,61 | 1,70 | 10,83 | 6,3 | 0,6 |
| **Ni** | 10 | 36,17 | 4,69 | 2,17 | 6,07 | 5,99 | 3,02 | 8,47 | 8,36 | 32,9 | 2,7 |
| **Ti** | 9 | 91,56 | 30,35 | 5,51 | 15,42 | 6,02 | 10,32 | 28,90 | 11,27 | 79 | 4 |
| **V** | 10 | 41,99 | 46,40 | 6,81 | 19,07 | 16,22 | 9,50 | 26,59 | 22,61 | 41,4 | 2,8 |
| **Zr** | 10 | 23,06 | 3,15 | 1,77 | 4,97 | 7,69 | 2,36 | 6,60 | 10,23 | 25,2 | 2 |

[a] Number of participants for the element.

[b] CRM BAM-S003.

**Table A.4 — Statistical results summarized in intervals**

| Analyte | $p$ [a] | Interval of mass fractions<br>mg/kg | Repeatability standard deviation<br>$s_r$<br>mg/kg | Repeatability limit<br>$r$<br>mg/kg | Coefficient of variation of repeatability<br>$v_r$<br>% relative | Reproducibility standard deviation<br>$s_R$<br>mg/kg | Reproducibility limit<br>$R$<br>mg/kg | Coefficient of variation of reproducibility<br>$v_R$<br>% relative |
|---|---|---|---|---|---|---|---|---|
| **Al** | 6 | 92 - 353 | 9,4 - 26,6 | 26 - 75 | 7,5 - 10,2 | 14,3 - 41,7 | 40 - 117 | 8,9 - 15,5 |
| **Ca** | 5 | 3,0 - 27,6 | 0,7 - 2,9 | 1,9 - 8,1 | 8,1 - 22,0 | 1,1 - 3,3 | 3,1 - 9,1 | 11,8 - 36,6 |
| **Cr** | 4 | 2,6 - 3,9 | 0,23 - 0,47 | 0,7 - 1,3 | 8,9 - 13,4 | 0,47 - 0,58 | 1,3 - 1,6 | 12,3 - 17,9 |
| **Cu** | 6 | 0,9 - 3,1 | 0,12 - 0,39 | 0,3 - 1,1 | 9,5 - 23,6 | 0,15 - 0,40 | 0,4 - 1,1 | 12 - 37 |
| **Fe** | 6 | 164 - 414 | 11,3 - 31,8 | 32 - 89 | 6,6 - 7,7 | 17,8 - 31,4 | 50 - 88 | 7,6 - 10,8 |
| **Mg** | 6 | 2,2 - 5,5 | 0,53 - 0,58 | 1,48 - 1,62 | 9,9 - 25,8 | 0,62 - 0,72 | 1,7 - 2,0 | 13,1 - 30,1 |
| **Ni** | 6 | 37,3 - 99 | 2,8 - 9,8 | 7,7 - 27,5 | 7,4 - 12,2 | 3,4 - 11,6 | 9,4 - 32,6 | 9 - 15,9 |
| **Ti** | 5 | 88,4 - 145 | 6,7 - 14,1 | 18,6 - 39,4 | 7,1 - 11,2 | 10,5 - 23,5 | 29,4 - 65,7 | 11,9 - 16,2 |
| **V** | 6 | 41,8 - 421 | 8,1 - 58,2 | 22,5 - 163 | 13,8 - 19,3 | 11,7 - 58,0 | 33 - 163 | 13,8 - 28,1 |
| **Zr** | 6 | 13,8 - 22,7 | 2,2 - 2,6 | 6,1 - 7,3 | 9,6 - 18,8 | 2,4 - 3,5 | 6,7 - 9,8 | 10,8 - 21,2 |

[a] Number of participants for the element.

# Annex B
(informative)

## Wavelength and working range

Table B.1 shows emission lines and working rages suggested for silicon carbide.

**Table B.1 — Recommended spectral lines and working ranges for SiC**

| **Analyte** | **Wavelength**<br>nm | | **Working range**<br>mg/kg |
|---|---|---|---|
| Aluminium | 237,3 | 257,5 | 1 - 1 000 |
| | 396,1 | – | |
| Calcium | 317,9 | 318,1 | 0,1 - 1 000 |
| | 393,3 | – | |
| Chromium | 267,7 | 283,5 | 0,3 - 300 |
| | 284,3 | – | |
| Copper | 324,7 | 327,3 | 0,1 - 100 |
| Iron | 271,4 | 274,3 | 1 - 1 000 |
| | 274,6 | 304,7 | |
| | 371,9 | – | |
| Magnesium | 280,2 | 285,2 | 0,1 - 300 |
| Nickel | 231,6 | 349,2 | 0,3 - 300 |
| Titanium | 253,1 | 308,8 | 0,5 - 500 |
| | 315,2 | 337,2 | |
| Vanadium | 271,5 | 291,0 | 0,5 - 1 000 |
| | 318,5 | 339,1 | |
| Zirconium | 256,8 | 273,4 | 0,1 - 300 |
| | 339,1 | – | |

The suggested wavelength and working ranges are obtained by an interlaboratory study using SiC as sample material.

The working ranges mentioned in Table B.1 may vary depending on the sample materials, samples weight and calibration samples.

The suggested lines were used in the interlaboratory study and proved to be good. This cannot exclude the occurrence of spectral interferences at the mentioned lines using other sample compositions or other matrices.

The working ranges are derived from the interlaboratory study and are based experiences. By choice of other lines the working range can be shifted. The limit of determination is given often by laboratory conditions, e.g. use of micro balance or clean room conditions.

To ensure trueness and for increasing the working range, preferably more than one spectral line per element shall be used. Obviously this is only possible with spectrometer with free choice of analytical lines (area- or array detectors).

# Annex C
(informative)

# Possible interferences and their elimination

## C.1 General

This annex gives an overview about possible spectral and non-spectral problems (interferences) and partly take into account basic principles of ETV ICP OES. For more detailed information's the literature ([1] and [2]) is recommended.

In practice line interferences (spectral interferences) and those interferences in volatilising the sample and by impacting the plasma with the dry aerosol (non spectral interferences) are critical.

## C.2 Spectral interferences

### C.2.1 Line coincidences

Line coincidences occur by superposition or overlapping of spectral lines. They are not noticeable below a critical concentration ratio between the disturbing and the analytical element. This ratio is calculated from the intensities of the analyte and of their interfering coincident lines. The result of this effect is dependent on the type and spectral resolution of the spectrometer.

Because newer tables of element emission lines are not available and the development of modern ICP-spectrometers (for example with CID- or CCD-detectors) has to be accommodated, during process development preparing tests should be performed with the spectrometer used for the analysis. It should also be ensured that the analyte is not being determined with disturbed analytical lines. It is recommended to check this when changing the matrix. Using CID- and CCD-spectrometers imaging two-dimensional Echelle-spectra special attention should be paid to different order interferences.

NOTE Herein order disturbances do not mean classical order interferences, but interferences resulting from the design principle of modern Echelle-spectrometers. On the two-dimensional display of the Echellogram the orders are partly located on the CID or CCD and, related to the pixel-distance, often this is a similar distance from each other like well-known line coincidences within an order but separated by wavelength. By this interferences may occur in a way that element lines are separated by the order and so by the wavelength, but are located within the same or adjacent columns of pixels.

Using these detectors for element-mass fractions of more than 1 mg/kg up to 10 mg/kg for the registration of the most sensitive lines of transient emission signals, saturation of individual pixels may be observed. So the well-known main lines of the elements sometimes cannot be used and less sensitive lines should be taken into account. Of course it is likely that such interferences are not well documented.

### C.2.2 Band coincidences

The interferences by molecular bands are caused by excited molecules and molecule fragment (e.g. $N_2^+, CN^-, CO^-$), which are formed in the plasma by carbon, entering air, the used gases or incompletely dissociated components of the matrix. The emitted bands may coincide with the analysis lines analogue to the line interferences.

These band interferences are of less importance for the lower wavelengths but sometimes seriously interfere with the analysis in the range above 350 nm.

### C.2.3 Background influence

The spectral background is caused by recombination continuum and is dependent on the matrix and on the wavelength.

The background influence is partly distinctive and results in a strong intensification of the background. It may result in the fact that it is impossible to work in certain wavelength regions because of the increased background to signal ratio.

### C.2.4 Line reversal, self-absorption

If the concentration of the analysed elements strongly increases in the outer cooler zones of the plasma the analyte radiation from the hotter zones is absorbed. So the registered intensities are lower than the corresponding analyte concentrations.

Radial and axial plasma observations have different results. Because line reversal and self-absorption can be recognized at the behaviour of the analytical function it should be made sure that the measurements are within the linear range.

For the linear range of ETV ICP OES under normal conditions not more than four orders of magnitude are possible.

### C.2.5 Unspecific radiation

Stray radiation should be avoided by the manufacturer as far as possible. It is caused by reflections in the spectral apparatus (stray light) and by radiation from other orders (not the same as order interferences (see C.2.1, NOTE). It may result in an apparently element specific contribution of the signal.

## C.3 Non-spectral interferences

### C.3.1 Interferences by the physical characteristics of the sample

This disturbance can be caused by different chemical composition of the reference and the analytical sample. It becomes identifiable by differences in the evaporation behaviour, in the transport efficiency or in influences on the plasma.

This disturbance can only be reduced by changing the calibration sample or, with limitations, by switching to dried reference solutions added to the sample (addition method).

In the ideal situation reference standards and analysis samples need to be matched.

### C.3.2 Interferences by depositions

By formation of depositions in the transition region between graphite tube and transport tube, for example in the so-called nozzle (see Figure 3), the gas flow to the ICP torch can be strongly changed. This can be identified by a drift in the signal intensities.

### C.3.3 Interferences by carry-over

With interferences by carry-over the analysis is influenced by residues in the ETV system (memory-effect). In an ETV sometimes there are distinct memory-effects. So it is possible that analytes that have been the main components of a sample before cannot be determined as trace elements.

Changing the graphite parts (contacts, tube, boat) and cleaning of the transition area graphite tube / transport tube and the transport tube itself will be necessary.

### C.3.4 Ionization interferences

Elements easy to ionize (e.g. alkali and alkaline-earth elements) to a small extent can cause a relocation of the ionization-balance for the detected element.

If there is a problem of this kind and if there is no calibration sample of the same matrix the respective alkali- or alkaline-earth element should be added to the sample in the existing form. If calibration samples of the same matrix are used, this kind of interference is not expected.

### C.3.5 Changing of the electrical coupling efficiency

Strong changes in the mass concentrations can have an influence on the efficiency of the coupling of electrical energy. By this the plasma temperature and the excitation conditions for the analyte are changed.

Changes of the electrical coupling efficiency and of ionization interferences can be avoided by reducing the sample weight or by matrix adaptation of analyte- and calibration-sample.

## C.4 Conclusion

For all possible interferences, except spectral interferences that have to be examined matrix-dependent, the best solution is to use calibration samples of the same matrix as the analysis sample, ideally the use of certified reference materials (CRM).

# Annex D
(informative)

# Information regarding the evaluation of the uncertainty of the mean value

The specification of the measurement uncertainty of the results may be desired by the customer. The specification of the expanded uncertainty $U$ is recommended and can be calculated by multiplication of the combined measurement uncertainty $u_{\mathrm{comb}}$ with the expanding factor $k = 2$. The calculation of the combined uncertainty can be carried out by a mathematical summarization of all contributions to the uncertainty as described in detail by the ISO/IEC Guide 98-3 [18] and as specified for analytical measurements by the Eurachem-Citac-Guide [19]. However, other possibilities can be used to estimate the measurement uncertainty as an alternative to that procedure of calculation of the measurement uncertainty based on a detailed analysis and modelling of the entire measurement process. To do so, laboratory internal data of validation processes or data of interlaboratory comparisons can be used [20]. In this case, a detailed knowledge of all contributions to the combined uncertainty is not necessary. A practical way is the analysis of a certified reference material (CRM) with similar properties to the investigated analytical samples. In this case, the combined measurement uncertainty can be calculated based on the standard deviation of the mean value determined by measurement of the CRM in the laboratory, the uncertainty of the certified value and the deviation of the measured and the certified value. (For more information, see [20], [21], [22], [23] as well as [24]).

# Annex E
(informative)

## Commercial certified reference materials

There are various commercial reference materials for a wide spectrum of materials. In the biggest international database COMAR (Code d'Indexation des Matériaux de référence) organized by the BAM there are 10 223 CRM's of 193 manufacturers from 23 countries which are listed for the moment.

For the reference materials suited for this standard there should exist as many data as possible for the mass concentrations of metallic trace contaminations. For the following reference materials these data are available. According to the possible use there are also other materials mentioned besides silicon carbide.

| | |
|---|---|
| ERM®-ED 101 1) | silicon nitride powder |
| CRM BAM-S003 1) | silicon carbide powder |
| ERM®-ED102 1) | boron carbide powder |
| Euronorm-CRM No. 781–1 2) | silicon carbide refractory |
| BCS-CRM No. 359 2) | nitrogen bearing silicon carbide |
| BCS-CRM No. 360 2) | SiAlON bonded silicon carbide |

---

1) ERM®-ED 101, CRM BAM-S003 and ERM®-ED102 are the trade names of products supplied by Bundesanstalt für Materialforschung und –prü-fung (BAM), Berlin. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the products named. Equivalent products may be used if they can be shown to lead to the same results.

2) Euronorm-CRM No. 781-1, BCS-CRM No. 359 and BCS-CRM No. 360 are the trade names of products supplied by Bureau of Analysed Samples Limited (BAS), Newham Hall, Middlesbrough, England. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the products named. Equivalent products may be used if they can be shown to lead to the same results.

# Annex F
(informative)

## Information regarding the validation of an analytical method based on liquid standards in the example of SiC and graphite

By calibration with dried aqueous calibration solutions, preferably dried under an IR-lamp, the ETV method gets more universal. This ensures that it is possible to achieve common calibration functions with dried aqueous calibration solutions as well as with suited powdered calibration material (see Clause 8). This means that not in every case can a successful calibration by aqueous solutions be possible.

The possibilities to use dried aqueous calibration solutions are strongly dependent on the sample character, especially on the matrix and on the performance of the ETV system, regarding the aerosol formation and the transport efficiency. Also the choice of lines and the use of an additional gas (en: sheet gas) between ETV and ICP-torch can be essential for a success. So atom lines compared to ion lines can react less dependent on matrix effects in the plasma (for example cooling of the plasma) and so can show less matrix-dependent intensity changes (at same analyte concentrations but different matrix), what is a precondition for common calibration functions.

In Figure F.1 a) and Figure F.1 b) for some elements common calibration functions are shown. Based on the good correlation of the calibration functions which have been achieved using aqueous calibration samples, graphite and SiC it can be expected that the calibration using dried aqueous standard solutions for graphite and SiC is successful or that both of these solid materials can be used for calibrating each other. This conclusion is only valid for tested materials, when for the chosen and tested elements and lines and for the adjusted instrument conditions (temperature program, gas flows, mechanical adjustments in the transition area) are identical.

In cases of doubt calibration samples with the same or with an adapted matrix should be preferred, especially certified reference materials.

For the generation of the calibration functions shown in Figure F.1 a) and Figure F.1 b) SiC and graphite calibration samples were used that had been analysed in round robin exercises. For the aqueous calibration solutions commercial liquid standards were used.

The following instruments were applied for the measurements:

a) ICP-OES-Spectrometer with CID-camera;

b) commercial ETV-system according to schematics 2 and 3 with the following adjustments:

  1) Gas flows:

    i) 370 ml/min Ar-bypass gas, 170 ml/min Ar-carrier gas and 2,3 ml/min dichlorodifluoromethane (reaction gas);

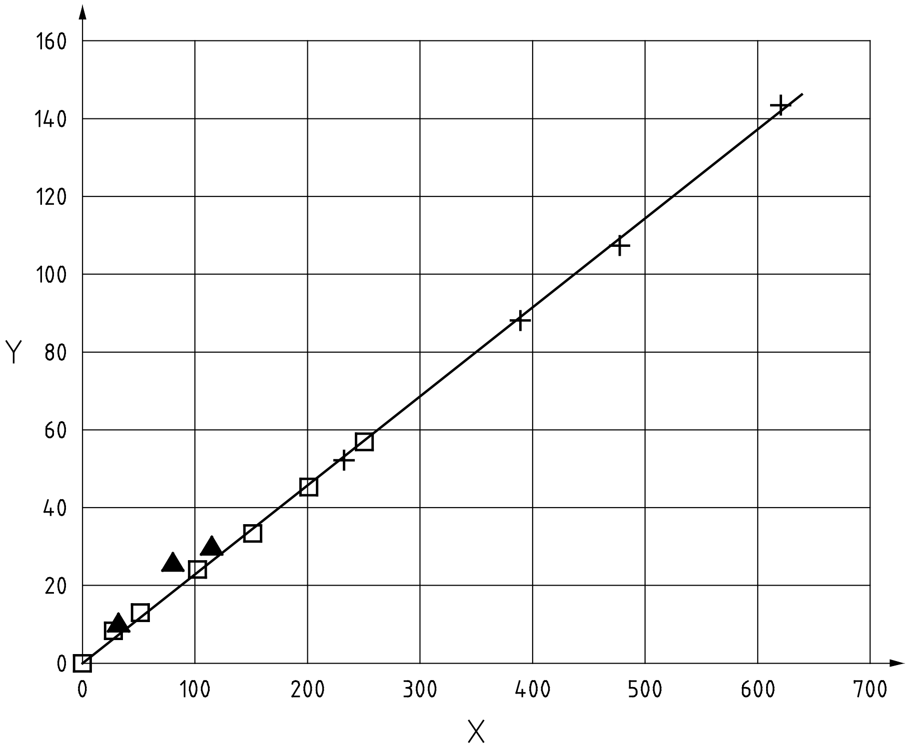
  2) Temperature program:

    i) 5 s heating up to 450 °C, 25 s holding time at 450 °C;

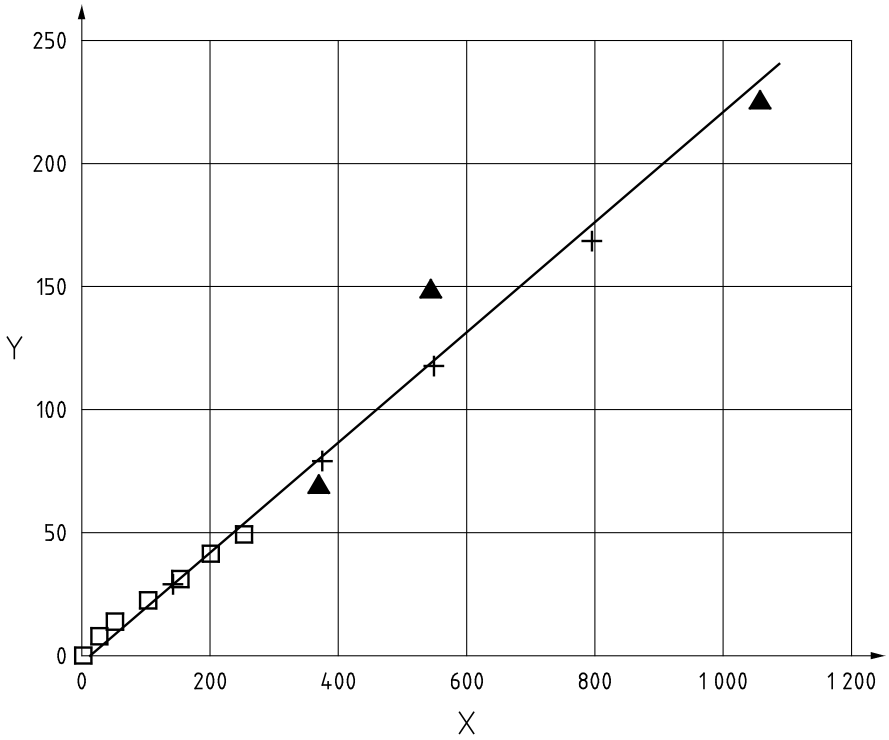
    ii) 3 s heating up to 2 200 °C, 27 s holding time at 2 200 °C;

  3) Measuring interval / Integration interval:

    i) from 31 s to 56 s synchronized with the temperature program.



**a) Analyte: Al, analytical line 237,3 nm**



**b) Analyte: Fe, analytical line 304,7 nm**

**Key**

| | | | |
|---|---|---|---|
| Y | intensity of the spectral line in counts | + | standard solution, LSTD-05, dried |
| X | analyte mass in nanograms | ☐ | silicon carbide, SiC 628 resp. SiC 933 |
| ▲ | graphite, SGL2 | | |

**Figure F.1 — Comparison of the calibration function of liquid calibration solutions and powdered calibration samples**

# Bibliography

[1] KURFÜRST U., ed. *Solid Sample Analysis, Direct and Slurry Sampling using GF-AAS and ETV-ICP*. Springer Verlag Berlin Heidelberg New York, 1998

[2] BOUMANS P.W.J.M. *Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometry*. Pergamon Press, Oxford, New York, Toronto, Sydney, Paris, Frankfurt, Vol. 1 and 2, 1980

[3] KANTOR T. Interpreting some analytical characteristics of thermal dispersion methods used for sample introduction in atomic spectrometry. *Spectrochim. Acta*. 1988, **43B** pp. 1299–1320

[4] ZARAY GY., LEIS F., KANTOR T., HAßLER J., TÖLG G. Analysis of silicon carbide powder by ETV-ICP-AES. *Fresenius J. Anal. Chem.* 1993, **346** pp. 1042–1046

[5] REN J.M., SALIN E.D. Direct solid sample analysis using furnace vaporization with Freon modification and inductively coupled plasma atomic emission spectrometry-I, Vaporization of oxides and carbides. *Spectrochimica Acta*. 1994, **49B** pp. 555–566

[6] Schäffer, U., Krivan, V.: *Multielement analysis of graphite and silicon carbide by inductively coupled plasma atomic emission spectrometry using solid sampling and electrothermal vaporisation*, Anal. Chem. 71 (1999) 4, 849-854

[7] HAßLER J., DETCHEVA A., FÖRSTER O., PERZL P.R., FLORIAN K. Working with a modern ETV-device and an ICP-CID-spectrometer. *Ann. Chim.* 1999, **89** pp. 827–836

[8] SCHRÖN W., LIEBMANN A., NIMMERFALL G. Direct solid sample analysis of sediments, soils, rocks and advanced ceramics by ETV-ICP-AES and GF-AAS. *Fresenius J. Anal. Chem.* 2000, **366** pp. 79–88

[9] Haßler, J., Förster, O., Schwetz, K. A.: *Moderne chemische Analysenverfahren von keramischen Werkstoffen, direkte Feststoffspurenanalytik von SiC mittels ETV-ICP-OES und DC-Arc-OES*, cif/Ber. DKG 77 (2000) 7, D11-D17

[10] KÁNTOR T. Electrothermal vaporization and laser ablation sample introduction for flame and plasma spectrometric analysis of solid and solution samples [Review]. *Spectrochimica Acta*. 2001, **56B** pp. 1523–1563

[11] MATSCHAT R., HAßLER J., TRAUB H., DETTE A. Multielement trace determination in SiC powders: assessment of interlaboratory comparisons aimed at the validation and standardization of analytical procedures with direct solid sampling based on ETV ICP OES and DC arc OES. *Anal. Bioanal. Chem.* 2005, **383** pp. 1060–1074

[12] Regulation (EG) Nr. 2037/2000 of the European Parliament and the Council, dated June 29, 2000 about materials leading to the decomposition of the ozone layer

[13] ISO 5022:1979, *Shaped refractory products — Sampling and acceptance testing*

[14] ISO 8656-1:1988, *Refractory products — Sampling of raw materials and unshaped products — Part 1: Sampling scheme*

[15] EN ISO 21068-1:2008, *Chemical analysis of silicon-carbide-containing raw materials and refractory products - Part 1: General information and sample preparation (ISO 21068-1:2008)*

[16] IUPAC Technical Report: *A statistical overview of standard (IUPAC and ACS) and new procedures for determining the limits of detection and quantification: Application to voltammetric and stripping techniques. Pure Appl. Chem.* 1997, **69** (2) pp. 297–328

[17] ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[18] ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

[19] EURACHEM/CITAC GUIDE CG 4: *Quantifying Uncertainty in Analytical Measurement*, 2. Auflage, 2000, ISBN 0 948926 15 5

[20] Eurolab Technical Report 1/2006 *Guide to the Evaluation of Measurement Uncertainty for Quantitative Tests Results*

[21] ISO 5725-4:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 4: Basic methods for the determination of the trueness of a standard measurement method*

[22] EUROLAB Technical Report 1/2007: *Measurement Uncertainty Revisited: Alternative Approaches to Uncertainty Evaluation*

[23] IUPAC Technical Report: *Harmonized guidelines for single-laboratory validation of methods of analysis. Pure Appl. Chem.* 2002, **74** (5) pp. 835–855

[24] GUIDE E.U.R.A.C.H.E.M. *The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics*. First Edition, 1998

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