SLOVENSKI STANDARD
SIST EN 15991:2011

01-november-2011

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

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)

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

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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)

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This European Standard was approved by CEN on 10 December 2010.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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Foreword

This document (EN 15991:2011) 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of an identical text or by endorsement, at the latest by July 2011, and conflicting national standards shall be withdrawn at the latest by July 2011.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 vaporisation (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.

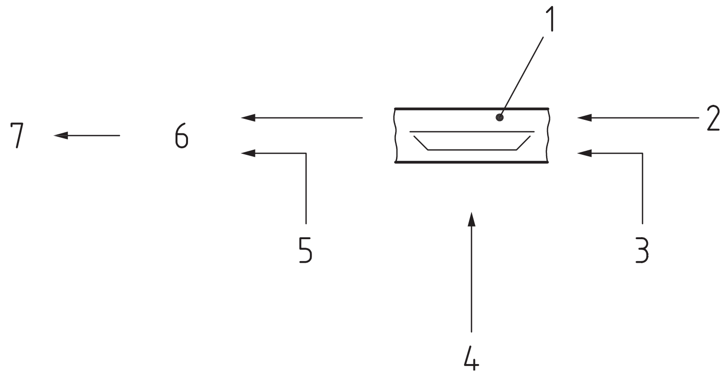
3 Spectrometry

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.

In contrary to the wet chemical analysis from dilution in ICP OES the classical sample digestion is replaced by electrothermal vaporisation 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 not or incompletely evaporating need a suited modifier, like a halogenation agent, preferably dichlorodifluoromethane, to be converted into a form that is easy to transport (see [1], [3], [5] and [10].)

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



Key

1 graphite tube with boat and sample

2 carrier gas (Ar)

3 reaction gas (Freon)

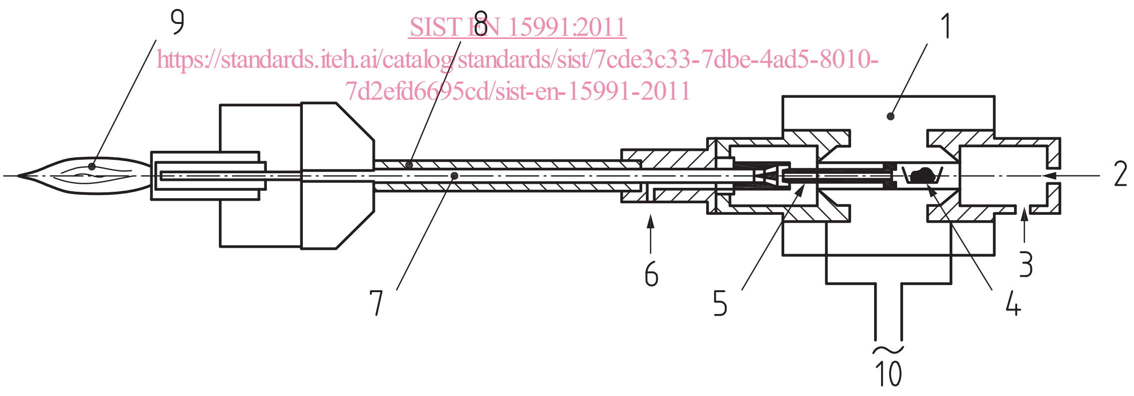
4 shield gas (Ar)

5 bypass gas (Ar)

6 aerosol

7 to the ICP torch

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



Key

1 graphite tube furnace

2 pyrometer

3 carrier gas (Ar) + reaction gas

4 solid sample

5 vapour

6 bypass-gas (Ar)

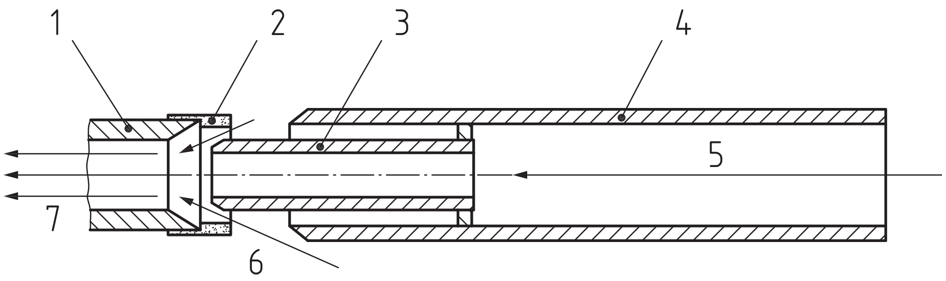
7 aerosol

8 transport tube

9 ICP-torch

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

2 Al_2O_3-transition ring

3 nozzle

4 graphite tube

5 carrier gas evaporated sample

6 bypass gas

7 gas mixture in laminar flow

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

NOTE Figures 1 to 3 show a well established commercial instrument.

4 Apparatus

4.1 Common 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 vaporisation 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 Echelle or similar CID systems are 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 vaporisation 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 measurement of the graphite boat connected to a feed forward control of the power supply) 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 Modifier, halogenation agents, for example in form of halocarbons, preferably dichlorodifluoromethane.

NOTE Dichlordiflouromethane is the most effective modifier, some alternative modifiers 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.

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

6 Sampling and sample preparation

Sampling has to 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 has to be broken up and homogenised, if necessary. For this a crushing device suited for the analysis goal shall be applied.

For porous materials it has to 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 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 analyte concentration or by a combination of both possibilities.

NOTE 2 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.

NOTE 3 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 has to 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 4 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 5 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 7 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 by tweezers 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 are normally triggered and run automatically in a synchronised way.

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 has to be created depending on the analyses.

NOTE 1 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 have to 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;
Vaporisation 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

NOTE 2 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 homogenise 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 may be 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 Additionally generate the ratio of net-intensities of analyte lines to the spectral line of a reference element of the same mass fraction (e.g. Si in analysis of SiC). This method of interior standard (reference element) can lead to an increase of precision but also to improve the accuracy of the method.

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