SLOVENSKI STANDARD
SIST EN 15979:2011

01-november-2011

Preskušanje keramičnih surovin in osnovnih materialov - Neposredno določevanje masnih frakcij nečistoč v prahu in zrnih silicijevega karbida z OES in DC obločnim vzbujanjem

Testing of ceramic raw and basic materials - Direct determination of mass fractions of impurities in powders and granules of silicon carbide by OES by DC arc excitation

Prüfung keramischer Roh- und Werkstoffe - Direkte Bestimmung der Massenanteile an Verunreinigungen in pulver- und kornförmigem Siliciumcarbid mittels OES und Anregung im Gleichstrombogen

Essais des matières premières et matériaux de base céramiques - Détermination directe des fractions massiques d'impuretés dans les poudres et granulés de carbure de silicium par OES à excitation d'arc DC

Ta slovenski standard je istoveten z: **EN 15979:2011**

ICS:

81.060.10	Surovine	Raw materials

SIST EN 15979:2011 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 15979

January 2011

ICS 81.060.10

English Version

Testing of ceramic raw and basic materials - Direct determination of mass fractions of impurities in powders and granules of silicon carbide by OES by DC arc excitation

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COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Ref. No. EN 15979:2011: E

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Foreword

This document (EN 15979:2011) 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of an identical text or by endorsement, at the latest by July 2011, and conflicting national standards shall be withdrawn at the latest by July 2011.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 describes the method for the analysis of mass fractions of the impurities Al, B, Ca, Cr, Cu, Fe, Mg, Ni, Ti, V and Zr in powder- and grain-shaped silicon carbide of ceramic raw and basic materials. This application can also be extended to other metallic elements and other similar non-metallic powder- and grain-shaped materials such as carbides, nitrides, graphite, carbon blacks, cokes, carbon, as well as a number of further oxidic raw and basic materials after appropriate testing.

NOTE There are positive interferences for materials such as e.g. graphite, B_4C, BN, WC and several refractory metal oxides.

This testing procedure is applicable to mass fractions of the impurities mentioned above from approximately 1 mg/kg up to approximately 3 000 mg/kg, after verification. In some cases it may be possible to extend the range up to 5 000 mg/kg depending on element, wavelength, arc parameter, and sample weight.

2 Principle

The combustion and evaporation of the crushed sample material takes place in the arc in an atmosphere of mixed argon and oxygen or in air. The metallic traces in the arc plasma are excited to emission of light. The light is guided into a simultaneous emission spectrometer (e.g. by coupling via fibre-optics or directly). The light is split in its spectral lines and measured by applicable detectors like a photomultiplier, charge coupled device (CCD), and charge injection device (CID). The mass fractions of elements in the sample are calculated by comparison of the intensities of the element-specific spectral line with those of a calibration sample of identical material.

3 Spectrometry

The optical emission spectrometry is based on generation of line spectra of excited atoms or ions, in which each spectral line can be definitely related to an element and the line intensities are proportional to the mass fractions of elements in the measured sample (see [6], [7] & [12]).

Contrary to wet-chemical methods via solution the classical sample decomposition is replaced by evaporation end excitation in DC-Arc.

4 Apparatus

Ordinary laboratory apparatus and the following:

4.1 Emission spectrometer, simultaneous, preferably with time resolved registration of signal, and connected to DC-Arc-equipment.

4.2 Gas flushing device, for shielding gas and/or reaction gas of DC-Arc, e.g. gas-mixer with mass-flow controller and Stallwood-jet

NOTE When working with air, the shielding gas unit can be omitted.

4.3 Tweezers, self-locking.

4.4 Balance, an analytical balance at least capable of reading to the nearest 0,1mg. However, for small weight <10 mg, a five figure balance at least capable of reading to the nearest 0,01 mg shall be used.

4.5 Pressing tool, for compacting the sample into the electrode.

4.6 Drying cabinet

NOTE A drying cabinet will only be necessary if wet mixed and subsequently dried samples are used.

4.7 Stirring balls made out of polytetrafluoroethylene (PTFE), diameter 6 mm.

NOTE Stirring balls will be necessary if wet mixed and subsequently dried samples are used.

4.8 Plastic flasks, sealable, nominal volume 25 ml.

NOTE Plastic flasks will be necessary if mixed and subsequently dried samples are used.

5 Reagents

Only analytical grade reagents shall be used unless stated otherwise.

5.1 High resistance carbon electrodes or graphite electrodes, spectral-grade, peak-shaped or elliptical counter electrode (cathode), cup-shaped carrier electrode (anode) with groove or taper.

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

NOTE Certified reference materials for main- minor- and trace constituents are available for e.g. silicon nitride, Silicon Carbide and Boron Carbide. A listing of certified reference materials is given in Annex E.

5.3 Oxygen purity ≥ 99,99 % (volume fraction)

5.4 Argon purity ≥ 99,99 % (volume fraction)

6 Sampling and preparation of test samples

Sampling of test samples shall be representative for the total quantity 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.

The particle size of sample material shall be ≤ 160 µm. If necessary it has to be crushed and homogenized. Choose the crushing device according to the analysis task.

7 Calibration

Calibration shall be carried out for each measuring cycle (minimum once per day) with calibration samples (5.2) of defined mass fractions of traces-impurities in accordance with Clause 8. Calibration shall be performed at the beginning and at the end of the measuring cycle. Within the calibration range at least a three-point calibration shall be performed (see [4], [8]).

Calibration samples (5.2) of identical or similar material, if possible certified reference materials or matrix matched synthetic calibration samples, shall be used. The mass fractions of trace-impurities in the calibration samples should be in the range of the sample material (see Annex E).

The analytical function shall be calculated using the known mass fractions of calibration samples (5.2) and the measured net intensities of spectral lines of the analytes (see Clause 10). See also IUPAC Technical Report: A statistical overview of standard (IUPAC and ACS) and new procedures for determining the limits of detection and quantification [16].

Calculation of analytical functions shall be performed by linear regression. All important correlation data shall be calculated and depicted via analytical functions graphically. It is possible to use a quadratic regression too. A monotonic slope of the analytical function at the best possible sensitivity is critical.

8 Procedure

8.1 Standard procedure

The sample prepared in accordance with Clause 6 is filled into the carrier electrode. Alternatively the three following procedures (a to c) can be applied.

a) The sample material is filled into the carrier electrode using a small, precisely tailored funnel and applying mechanical compression;

b) The carrier electrode is filled by repeatedly pressing the cup (orifice downwards) onto the sample material which is lying on a clean carrier (e.g. filter paper);

c) A sub-sample of the sample material is weighed to the nearest ± 0,1 mg into the carrier electrode in a defined narrow weighing range (e.g. between 4,5 to 5,5 mg). The mass of the weighed sub-sample has to be documented.

Depending on dimension and shape of the carrier electrode the mass of the sub-sample can vary. The sample mass can be reduced in case of elements, e.g. with mass fractions above the calibration range (minimum circa 1 mg). In this case, the weighed sub-sample has to be mixed in the electrode with a material of the same type, which does not contain the respective analytes. The total mass of material in the electrode shall correspond to that of the calibration sample (5.2). Instead of a pure material of the same type-spectral-grade carbon powder can be used.

Subsequently, the sub-sample has to be compacted in the cup of the carrier electrode by slightly striking it on a rigid underlay or by knocking with a spatula at the tweezers holding the carrier electrode.

The electrodes shall be touched in the clamp-region of the electrode holder using tweezers (4.3)

The carrier electrode has to be fixed in the optical path using the electrode holder of the DC-Arc equipment. The distance to the upper counter electrode (cathode) has to be adjusted to the nearest ± 0,1 mm at a value of 3,5 mm to 4,0 mm.

NOTE 1 The distance between the electrodes can vary according to the diameter of the electrodes.

The position of the electrodes, and thus the arc discharge, has to be constant with respect to the optical axis of the optical system. Any change of the optical adjustment will lead to different results. Parts of the electrodes shall not be visible to the emission spectrometer. This is especially true for the upper electrode (cathode) whereas the lower electrode (anode), because of the high burn-off rate, normally remains a significantly shorter time in the optical path.

NOTE 2 Electrodes visible in the optical path result in a strong enhancement of the spectral background in some spectral ranges.

The arc discharge has to be started synchronous to the data acquisition of the spectrometer (4.1).

The evaporation or combustion of the sample in the DC-Arc has to be carried out preferably under shielding gas excluding any nitrogen. The mixing ratio of the shielding gas is about 70 parts by volume argon and 30 parts by volume oxygen at a constant gas flow of about (4 ± 1) l/min. The evaporation or combustion in air is principally possible, but then one has to pay attention to spectral interferences, e.g. CN-bands. In addition, degradation of the reproducibility can be expected.

CAUTION — It is not safe to look into the arc plasma without eye protection (UV- and IR-radiation). Reflections on reflective areas can be dangerous too.

Each sample shall be measured a minimum of three times.

8.2 Procedure using addition of carrier

This procedure is especially suitable for low analyte concentrations.

The sample shall be weighed together with carrier and spectral-grade carbon or graphite. The mixture is homogenised using an easy volatile solvent. The optimal relation of quantities as well as the selection of an appropriate carrier (see [2] and [11]) shall be investigated for each sample material experimentally.

NOTE 1 The power of detection is advanced by addition of carrier. Suitable carriers are halides like AgCl, $BaCl_2$.

NOTE 2 For materials such as SiC and WC and also for oxides such as MoO_3, WO_3, Ta_2O_3, Nb_2O_3, it is recommended to use $BaCl_2$ as carrier and a mass-ratio of sample/graphite/$BaCl_2$ of 10/4/1. In the individual case the ratio should be checked and, if necessary, be optimized.

NOTE 3 The sample mix can be homogenized in a plastic bottle (4.8) after addition of 6 ml dichloromethane and about 20 stirring balls (4.7). Shake the bottle for a minimum of 10 min. The dichloromethane can be completely removed by placing the opened plastic bottle in a drying cabinet for approximately 1 h at 60 °C. The dried mixture is loosened by gently shaking the plastic bottle. After that, the stirring balls can be removed.

CAUTION — To avoid exposure to dichloromethane, the appropriate safety regulations shall be obeyed.

Filling of the carrier electrode shall be carried out in accordance with 8.1.

The samples used for calibration (5.2) shall be treated in the same manner.

Each sample has to be measured a minimum of three times. If the deviation of the single values of the analyte concentrations is greater than the specified value of repeatability, the procedure has to be repeated according to Clause 8.

In the case of continued insufficient reproducibility of spectral line intensities of one or more analytes the sample has to be homogenised additionally (e.g. mortar). For low concentrations near the limit of determination (see [16]) this further step is not necessary.

8.3 Wavelength and working range

It is critical that all selected analyte wavelength are interference-free with respect to sample matrix and further impurities.

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

Only spectral lines shall be selected where under the chosen working conditions neither self-absorption nor self-reversal will occur. Order-interferences mainly occur when combining Echelle optics with plane solid-state detectors (CID- or CCD-detectors).

NOTE 2 A comprehensive description of possible interferences and their reduction can be found in Annex C.

Ensure that the concentrations to be analyzed lie above the limits of determination of the analytes. The upper working range is limited by a decrease of sensitivity (slope of calibration function) to about 80 % of its initial value. If applicable, less sensitive spectral lines can be used.

9 Calculation

The intensities of spectral lines measured by the emission spectrometer (4.1) shall be corrected to net-intensities using the background intensities measured at the background measuring points. The net-intensities shall be converted into the corresponding masses of the respective analytes using analytical functions. These include the weight of the sub-samples, so the mass fractions of the analytes in the original sample can be calculated.

Additionally, the ratio of the net-intensities of the analyte lines to the intensity of an emission line of a reference element with constant mass fraction (e.g. Si in analysis of SiC) can also be calculated.

NOTE This so called method of interior standard (reference element) can increase precession and accuracy of the analysis method.

The wavelength of spectral lines and the background measuring points used for calibration and sample analysis have always to be the same.

10 Expression of results

The concentration of the analytes as mean of the single values of the multiple determinations shall be expressed in mass fractions and rounded to the decimal place resulting from uncertainty of measurement (for more information about uncertainty see Annex D).

11 Precision

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

11.1 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 each other and determined on the same sample material by the same analyst using the same analytical procedure and the same equipment in the same laboratory within a short period of time.

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

11.2 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 at the same sample material using the same analytical procedure and different equipment in different laboratories.

The reproducibility data determined at three different silicon carbide samples in the frame of an inter-laboratory comparison are listed in Annex A.

12 Test report

The 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 10;

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.