SVENSK STANDARD
SS-EN 15991:2015

Fastställd/Approved: 2015-11-30
Publicerad/Published: 2015-12-21
Utgåva/Edition: 2
Språk/Language: engelska/English
ICS: 81.060.10

SWEDISH STANDARDS INSTITUTE

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)

Standarder får världen att fungera

SIS (Swedish Standards Institute) är en fristående ideell förening med medlemmar från både privat och offentlig sektor. Vi är en del av det europeiska och globala nätverk som utarbetar internationella standarder. Standarder är dokumenterad kunskap utvecklad av framstående aktörer inom industri, näringsliv och samhälle och befrämjar handel över gränser, bidrar till att processer och produkter blir säkrare samt effektiviserar din verksamhet.

Delta och påverka
Som medlem i SIS har du möjlighet att påverka framtida standarder inom ditt område på nationell, europeisk och global nivå. Du får samtidigt tillgång till tidig information om utvecklingen inom din bransch.

Ta del av det färdiga arbetet
Vi erbjuder våra kunder allt som rör standarder och deras tillämpning. Hos oss kan du köpa alla publikationer du behöver – allt från enskilda standarder, tekniska rapporter och standard-paket till handböcker och onlinetjänster. Genom vår webbtjänst e-nav får du tillgång till ett lättnavigerat bibliotek där alla standarder som är aktuella för ditt företag finns tillgängliga. Standarder och handböcker är källor till kunskap. Vi säljer dem.

Utveckla din kompetens och lyckas bättre i ditt arbete
Hos SIS kan du gå öppna eller företagsinterna utbildningar kring innehåll och tillämpning av standarder. Genom vår närhet till den internationella utvecklingen och ISO får du rätt kunskap i rätt tid, direkt från källan. Med vår kunskap om standarders möjligheter hjälper vi våra kunder att skapa verklig nytta och lönsamhet i sina verksamheter.

Vill du veta mer om SIS eller hur standarder kan effektivisera din verksamhet är du välkommen in på www.sis.se eller ta kontakt med oss på tel 08-555 523 00.

Standards make the world go round

SIS (Swedish Standards Institute) is an independent non-profit organisation with members from both the private and public sectors. We are part of the European and global network that draws up international standards. Standards consist of documented knowledge developed by prominent actors within the industry, business world and society. They promote cross-border trade, they help to make processes and products safer and they streamline your organisation.

Take part and have influence
As a member of SIS you will have the possibility to participate in standardization activities on national, European and global level. The membership in SIS will give you the opportunity to influence future standards and gain access to early stage information about developments within your field.

Get to know the finished work
We offer our customers everything in connection with standards and their application. You can purchase all the publications you need from us - everything from individual standards, technical reports and standard packages through to manuals and online services. Our web service e-nav gives you access to an easy-to-navigate library where all standards that are relevant to your company are available. Standards and manuals are sources of knowledge. We sell them.

Increase understanding and improve perception
With SIS you can undergo either shared or in-house training in the content and application of standards. Thanks to our proximity to international development and ISO you receive the right knowledge at the right time, direct from the source. With our knowledge about the potential of standards, we assist our customers in creating tangible benefit and profitability in their organisations.

If you want to know more about SIS, or how standards can streamline your organisation, please visit www.sis.se or contact us on phone +46 (0)8-555 523 00

Europastandarden EN 15991:2015 gäller som svensk standard. Detta dokument innehåller den officiella engelska versionen av EN 15991:2015.

Denna standard ersätter SS-EN 15991:2011, utgåva 1.

The European Standard EN 15991:2015 has the status of a Swedish Standard. This document contains the official English version of EN 15991:2015.

This standard supersedes the Swedish Standard SS-EN 15991:2011, edition 1.

Upplysningar om sakinnehållet i standarden lämnas av SIS, Swedish Standards Institute, telefon 08-555 520 00. Standarder kan beställas hos SIS Förlag AB som även lämnar allmänna upplysningar om svensk och utländsk standard.

Information about the content of the standard is available from the Swedish Standards Institute (SIS), telephone +46 8 555 520 00. Standards may be ordered from SIS Förlag AB, who can also provide general information about Swedish and foreign standards.

Har du synpunkter på innehållet i den här standarden, vill du delta i ett kommande revideringsarbete eller vara med och ta fram andra standarder inom området? Gå in på www.sis.se - där hittar du mer information.

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 15991

November 2015

ICS 81.060.10

Supersedes EN 15991:2011

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.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

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

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

Ref. No. EN 15991:2015 E

Contents

Page

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.

According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

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.

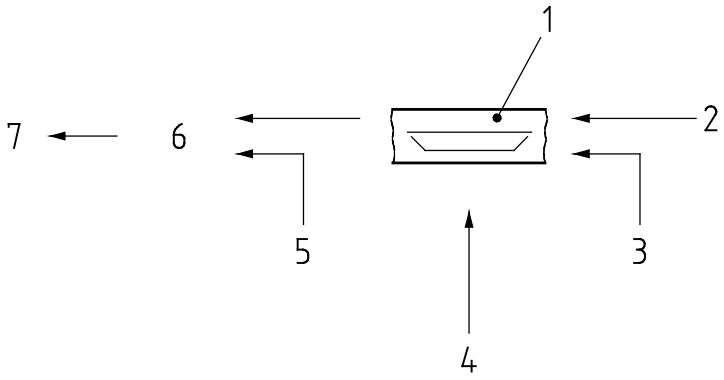
3 Spectrometry

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.

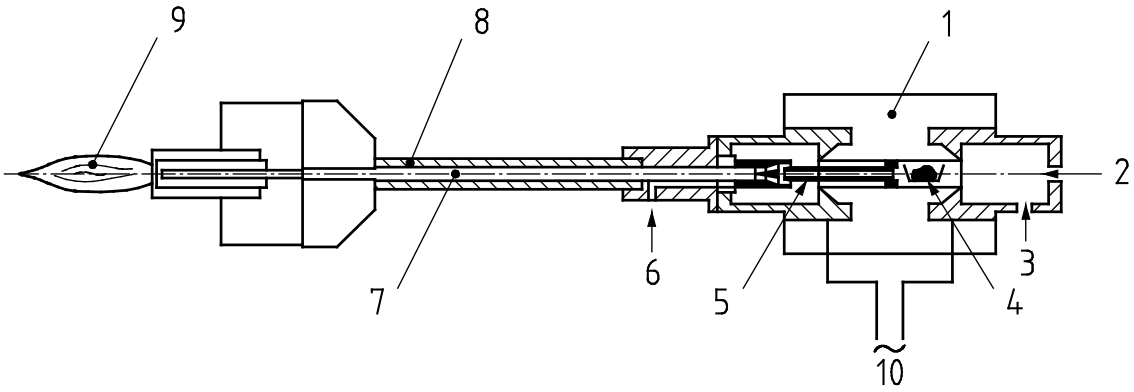
The dry aerosol is introduced into the ICP plasma by the injector tube and there excited for the emission of light (see Figure 1, Figure 2 and Figure 3).



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)		

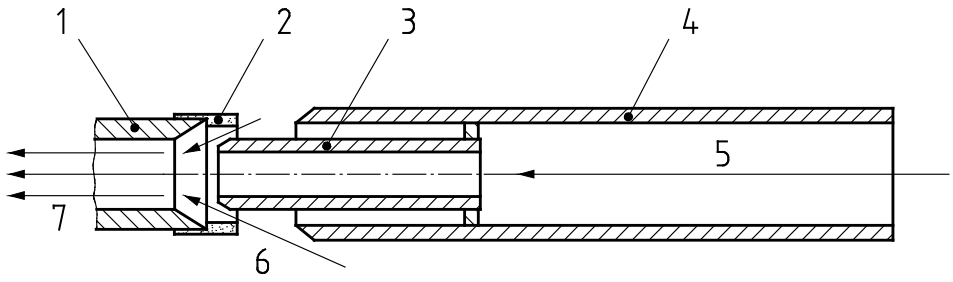
Figure 1 — Schematic configuration of the ETV-gas regime with the gas flows carrier-gas, bypass-gas, reaction-gas and shield-gas



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.