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BSI Standards Publication

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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National foreword

This British Standard is the UK implementation of EN 15979:2011.

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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

Essai 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 l'excitation d'arc DC

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

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

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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of an identical text or by endorsement, at the latest by July 2011, and conflicting national standards shall be withdrawn at the latest by July 2011.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.

Annex A
(informative)

Results of inter-laboratory study

The inter-laboratory study was carried out using six different SiC samples. The analyte concentrations (mass fractions) of one 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]. (For the results of the inter-laboratory study see [5].)

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

Element	p_j [a]	**Total mean values** γ_j mg/kg	**Repeatability standard deviation** s_r mg/kg	**Repeatability limit** r mg/kg	**Coefficient of variation of repeatability** v_r % relative	**Reproducibility standard deviation** s_R mg/kg	**Reproducibility limit** R mg/kg	**Coefficient of variation of reproducibility** v_R % relative
Al	13	83,54	10,95	30,66	13,11	30,37	85,03	36,35
B	11	6,03	0,89	2,49	14,76	2,47	6,92	40,99
Ca	12	3,35	0,87	2,43	25,88	1,45	4,05	43,10
Cr	7	3,42	0,24	0,68	7,12	1,41	3,93	41,05
Cu	12	1,22	0,29	0,82	24,00	0,64	1,79	52,15
Fe	13	274,56	22,61	63,32	8,24	77,55	217,13	28,24
Mg	13	3,50	0,30	0,83	8,47	1,05	2,94	30,01
Ni	13	64,71	4,54	12,72	7,02	17,99	50,38	27,80
Ti	13	155,58	16,14	45,20	10,38	45,16	126,45	29,03
V	12	141,74	17,46	48,87	12,31	42,86	120,00	30,24
Zr	10	21,96	2,13	5,97	9,72	6,99	19,56	31,82

[a] Number of participants for the element j

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

Element	p_j [a]	**Total mean values** γ_j mg/kg	**Repeatability standard deviation** s_r mg/kg	**Repeatability limit** r mg/kg	**Coefficient of variation of repeatability** v_r % relative	**Reproducibility standard deviation** s_R mg/kg	**Reproducibility limit** R mg/kg	**Coefficient of variation of reproducibility** v_R % relative
Al	13	286,28	19,67	55,07	6,87	30,12	84,33	10,52
B	12	38,67	3,09	8,65	7,98	3,75	10,50	9,69
Ca	12	22,37	2,35	6,58	10,50	3,07	8,60	13,72
Cr	7	3,94	0,33	0,93	8,39	0,41	1,14	10,34
Cu	12	2,97	0,48	1,36	16,34	0,67	1,87	22,58
Fe	13	408,41	23,75	66,51	5,82	44,36	124,21	10,86
Mg	13	2,21	0,19	0,53	8,60	0,37	1,04	16,77
Ni	13	101,41	6,17	17,27	6,08	10,07	28,20	9,93
Ti	13	95,40	9,02	25,26	9,46	11,44	32,04	11,99
V	12	434,35	31,81	89,08	7,32	51,45	144,06	11,85
Zr	10	15,24	1,33	3,71	8,70	1,59	4,46	10,46

[a] Number of participants for the element j

Table A.3— Data of precision determined at the SiC-sample 8517[a]

Element	p_j [b]	Total mean values γ_j mg/kg	Repeatability standard deviation s_r mg/kg	Repeatability limit r mg/kg	Coefficient of variation of repeatability v_r % relative	Reproducibility standard deviation s_R mg/kg	Reproducibility limit R mg/kg	Coefficient of variation of reproducibility v_R % relative	Certified values for comparison mg/kg	Certified expanded uncertainty U ($k = 2$) mg/kg
Al	13	384,67	23,11	64,71	6,01	24,21	67,77	6,29	372	20
B	11	35,08	2,68	7,49	7,63	4,73	13,25	13,49	63	7
Ca	12	25,01	2,75	7,70	10,99	3,59	10,06	14,36	29,4	1,8
Cr	8	3,46	0,45	1,25	12,86	0,63	1,77	18,25	3,5	0,4
Cu	12	1,11	0,27	0,77	24,67	0,39	1,09	35,09	1,5	0,4
Fe	13	166,28	14,02	39,26	8,43	23,57	65,99	14,17	149	10
Mg	13	5,34	0,34	0,95	6,37	0,63	1,76	11,79	6,3	0,6
Ni	13	33,36	3,71	10,39	11,12	4,35	12,18	13,04	32,9	2,7
Ti	13	79,84	8,81	24,67	11,03	11,76	32,93	14,73	79	4
V	11	41,20	7,58	21,23	18,41	11,79	33,00	28,61	41,4	2,8
Zr	11	21,95	2,60	7,28	11,84	2,73	7,66	12,46	25,2	2

[a] CRM BAM-S003

[b] Number of participants for the element j

Table A.4 — Statistical results summarised in intervals

Element	p_j	Interval of mass fractions mg/kg	Repeatability standard deviation s_r mg/kg	Repeatability limit r mg/kg	Coefficient of variation of repeatability v_r % relative	Reproducibility standard deviation s_R mg/kg	Reproducibility limit R mg/kg	Coefficient of variation of reproducibility v_R % relative
Al	13	80 - 390	11 - 23,1	31 - 65	6,0 - 13,1	24 - 30,4	68 - 85	6,3 - 36,4
B	11 - 12	6,3 - 43	0,9 - 3,1	2,5 - 8,7	7,6 - 14,8	2,5 - 4,7	6,9 - 13,3	9,7 - 41
Ca	12	3,6 - 25	0,9 - 2,8	2,4 - 7,7	10,5 - 26	1,5 - 3,6	4,0 - 10,1	13,7 - 43,1
Cr	7 - 8	3,7 - 4,0	0,2 - 0,5	0,7 - 1,3	7,1 - 12,9	0,4 - 1,4	1,1 - 3,9	10,3 - 41
Cu	12	1,1 - 3,0	0,3 - 0,5	0,5 - 0,8	1,4 - 24,7	0,4 - 0,7	1,1 - 1,9	22,6 - 52,2
Fe	13	170 - 401	14,0 - 23,8	39 - 67	5,8 - 8,4	24 - 78	66 - 217	10,9 - 28,2
Mg	13	2,3 - 5,3	0,2 - 0,3	0,5 - 1,0	6,4 - 8,6	0,4 - 1,0	1,0 - 2,9	16,8 - 30,0
Ni	13	34 - 101	3,7 - 6,2	10,4 - 17,3	6,1 - 11,1	4,4 - 18,0	12 - 50,4	9,9 - 27,8
Ti	13	81 - 159	8,8 - 16,1	24 - 45	9,5 - 10,4	11,4 - 45,2	32 - 127	12 - 29
V	11 -12	42 - 450	7,6 - 31,8	21 - 89	7,3 - 18,4	11,8 - 51,5	33 - 144	11,9 - 30,2
Zr	10 -11	15 - 22	1,3 - 2,6	3,7 - 7,3	8,7 - 11,8	1,6 - 7,0	4,5 - 19,6	10,5 - 31,8

Annex B
(informative)

Wavelength and working range

Table B.1 lists the suggested emission lines and working ranges for silicon carbide.

Table B.1 — Suggestions for emission lines and working range, applicable for SiC

Element	Wavelength nm		Working range mg/kg
Aluminium	257,5	308,2	20 - 3 000
	394,4	396,1	
Boron	249,6	–	1 - 100
Calcium	317,9	393,9	1 - 500
Chromium	283,5	284,3	5 - 1 000
	425,4	–	
Copper	324,7	327,3	1 - 100
Iron	238,2	259,9	20 - 3 000
	302,0	371,9	
Magnesium	279,5	280,2	1 - 500
	285,2	–	
Nickel	300,2	305,0	20 - 2 000
	341,4	349,2	
Titanium	323,4	334,9	10 - 2 000
	336,1	337,2	
Vanadium	290,8	310,2	10 - 2 000
	318,5	–	
Zirconium	339,1	–	10 - 2 000

The suggested wavelength and working ranges are obtained by an inter-laboratory study using SiC as the sample material. Mostly spectrometers with CID detector and external DC-Arc systems, connected via fibre optics, were used.

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

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

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

To ensure accuracy when increasing the working range, preferably more than one spectral line per element shall be used. Normally, this is possible only with a spectrometer with free choice of lines (area or array detectors).

Annex C
(informative)

Possible interferences and their elimination

C.1 General

This annex gives an overview about possible occurring spectral and non-spectral interferences and partly take into account basic principles of DC-Arc excitation and optical emission spectrometry. For more detailed information, the following references are recommended ([6], [7] and [12]).

In practice, line interferences (spectral interferences) and interferences in volatilising the sample and by impacting the Arc-plasma by accompanying or matrix elements (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 coinciding lines. The result of this effect is dependent on the type and spectral resolution of the spectrometer.

Because newer tables of arc emission lines are not available and the development of modern ICP-spectrometers (e.g. Echelle- -optics, CID- and CCD-detectors) has to be accommodated, preliminary tests should be performed with the spectrometer used for the analysis during process development. It should be also ensured that the analyte is not determined using interfered (disturbed) analytical lines. It is recommended to check this always when changing the matrix. Using CID- and CCD-spectrometers imaging two-dimensional Echelle-spectra special attention should be paid on 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.

During registration of transient emission signals saturation of individual pixels may be observed for the most sensitive emission lines at higher element mass-fractions. So the well known main lines of the elements sometimes cannot be used and less sensitive lines should be taken instead. Possible line interferences for these less sensitive lines are sometimes not well documented.

C.2.2 Band coincidences

The interferences by molecular band are caused by excited molecules or molecule fragments e.g. C-C, C-N, C-O, which are formed in the Arc-plasma by carbon, circumfluent air, used shielding gas or incompletely dissociated components of matrix. The emitted bands may coincide to the analysis lines analogue to the line interferences.

These band disturbances are of less importance for the lower wavelengths but sometimes seriously complicate the analysis in the range above 350 nm. In particular the strong CN-bands with their edges at

359 nm, 388,3 nm and 421,6 nm can be effectively reduced with the aid of so called "Stallwood-jet" using shielding gas. As shielding gas mainly Argon is used in different ratios with oxygen.

C.2.3 Background influences

The spectral background is caused by recombination continua and is dependent on the matrix and on the wavelength. Another cause can be a continued radiation of igneous particles in the Arc-plasma or radiation coming from the glowing electrodes, if this is not gated out.

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. Background influences can be reduced using special-filters. This will be particularly necessary when because of the use of fibre optics only the visual wavelength range can be used (utilized).

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.

Because line reversal and self absorption can be recognised at the behaviour of the analytical function it should be assured that the measurements are within the linear range.

Under normal conditions not more than four orders of magnitude are possible for the linear range of DC-Arc excitation. The linear calibration range often covers only two to three orders of magnitude, sometimes even less.

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 disturbances (see C.2.1, NOTE). It may result in an apparently element specific part of the signal.

C.3 Non spectral interferences

C.3.1 Interferences by the physical characteristics of the sample

Difficulties can occur if the sample contains out-gassing components or if crystalline fractions of the sample explosively burst during the heating by the arc-plasma. The effect can be a deflagration or sputtering of the sample. Similarly problems can arise if the sample forms melting balls and which may drop out of the cup during burn-off of the electrode.

C.3.2 Interferences by depositions

This kind of interference can take place especially if the counter electrode is not changed.

C.3.3 Ionisation interferences

Elements easy to ionise e.g. alkali metals alkaline-earth metals can cause already in small contents a relocation of the ionisation-balance of the arc-plasma and change the excitation conditions and therefore the intensity of the analytical lines significantly.

If problems of this kind are existing and there are no calibration samples of the same material available it is possible to add the appropriate easy to ionise element, if possible in the same form as in the sample and in the same concentration. Another possibility consists in the addition of greater portions of an easy ionisable element to the analysis- as well as calibration sample ("spectrochemical buffer“).

C.3.4 Change of electric arc-plasma

In principle calibration samples with a composition as far as possible to the analysis samples should be used. In most cases this is, however, only possible as an approximation.

In this case interferences can occur because of the different chemical composition between calibration- and analysis sample. This can be observable by different evaporation behaviour or different influence on the plasma. Strong changes in mass concentration shift the electron pressure and temperature of the plasma and therewith the excitation conditions of the analytes.

Influences on the arc plasma and ionisation interferences can be reduced by less sample weight, matrix matching of analysis- and calibration sample or by dilution with graphite powder.

Another disturbance can be seen in the fluctuation of the arc observable by erratic movement of the arc burning spot on the edge of cup electrode. Depending on sample conductivity and evaporation behaviour this arc fluctuation can be more or less pronounced. It can be eliminated by application of a magnetic field (magnetic field arc). State of the art DC-Arc systems are using double- or triple-optics to reduce the effect of arc fluctuation.

C.3.5 Conclusion

The best solution to avoid most interferences 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_{comb} with the expanding factor $k = 2$. The calculation of the combined uncertainty can be carried out by a mathematical summarisation 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, also other possibilities can be used to estimate the measurement uncertainty alternatively 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 inter-laboratory 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 largest international database COMAR (Code d'Indexation des **Matériaux de référence**) organised 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 used for this standard there should exist as much 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-S002 [1]	tungsten 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

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[1] ERM®-ED 101, CRM BAM-S002, CRM BAM-S003 and ERM®-ED102 are the trade names of products supplied by Bundesanstalt für Materialforschung und –prüfung (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.

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