

# Direct Determination of Impurities in Powdered Silicon Carbide by Electrothermal Atomic Absorption Spectrometry Using the Slurry Sampling Technique

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A direct method of analysis of powdered silicon carbide for the determination of Al, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Ti, V and Zn based on electrothermal atomic absorption spectrometry (ETAAS) using the slurry sampling technique is described. Possible spectral interferences caused by the refractory matrix components were studied. The technique was optimized with regard to sample preparation, dispensing, thermal pre-treatment and atomization parameters. The accuracy was checked by comparison of the results with those obtained by ETAAS and inductively coupled plasma atomic emission spectrometry involving decomposition of the sample, and by instrumental neutron activation analysis. For most of the elements investigated the achievable limits of detection are at the sub-microgram per gram level.

**Keywords:** Silicon carbide direct analysis; slurry sampling technique; electrothermal atomic absorption spectrometry

Powdered silicon carbide has increasingly been used as a basic material for the production of advanced ceramics. The importance of trace element impurities for the quality of products and methods used for their determination was recently reviewed by Broekaert and co-workers.<sup>1,2</sup> Silicon carbide has been found to be a refractory and chemically resistant substance.<sup>3</sup> Its complete decomposition necessitates extreme chemical treatments which, from a trace analytical point of view, can have several disadvantageous consequences. The decomposition of silicon carbide by fusion with alkali metal salts<sup>4-6</sup> has proved to be rapid and efficient, and therefore attractive for routine analysis. However, the introduction of blank and high salt contents considerably limits its application, especially to samples of higher purity. Therefore, decomposition with high-purity mineral acids is, in general, preferred. A mixture of sub-boiled concentrated acids, HNO<sub>3</sub>-HF-fuming H<sub>2</sub>SO<sub>4</sub>, seems to be the most suitable reagent for this purpose.<sup>7-9</sup> However, the decomposition even when performed in a high-pressure autoclave lined with poly(tetrafluoroethylene) (PTFE) is time consuming and the resulting medium is inconvenient for some methods. These dissolution difficulties make simpler analytical methods desirable. Thus, in spite of some methodological limitations, it was possible to develop a technique for the direct analysis of nebulized slurries of powdered silicon carbide by inductively coupled plasma atomic emission spectrometry (ICP-AES).<sup>7,9</sup> Direct determination of 54 elements by instrumental neutron activation analysis (INAA) has also been reported.<sup>8</sup>

It was shown by Slovák and Docekal<sup>10</sup> that a very fine powder of aluminium oxide can be analysed for trace impurities up to the parts per million level by electrothermal atomic absorption spectrometry (ETAAS) using direct sampling of the aqueous sample suspensions. This technique was subsequently not adopted in the field of analysis of ceramic materials, but was taken up by us and investigated for its applicability to the determination of impurities in silicon carbide. However, in a direct analysis of silicon carbide by ETAAS, problems associated with the thermal stability of silicon carbide are expected, as a result of which

the matrix cannot be removed by thermal pre-treatment. Consequently, spectral interferences caused by the matrix and other particles formed during the atomization might be the reason for the substantial limitations of this method. Accurate calibration in this solid-sampling technique is another critical aspect. Finally, depending on the homogeneity, representative sampling of silicon carbide for slurry preparation and for dispensing can also be a problem.

In this paper, an optimized procedure for the direct determination of impurities in powdered silicon carbide by ETAAS using slurry sampling is presented. The technique is demonstrated by the determination of 11 elements in silicon carbide samples analysed recently by other analytical methods.

## Experimental

### Samples

Commercially available silicon carbide powders were supplied by H. C. Starck (Goslar, Germany, type A 10 and B 10), Lonza (Waldshut, Germany, type UF 15) and Elektroschmelzwerke (Kempten, Germany, type S 933); for simpler identification, they are henceforth denoted I-V. After ultrasonic pre-treatment, the typical average particle diameter and standard deviation of the grain size distribution were 0.41–0.48  $\mu\text{m}$  and 0.36–0.42  $\mu\text{m}$ , respectively. The particle size did not exceed 5  $\mu\text{m}$ . Except for the treatment in an ultrasonic bath, no further pre-treatment such as grinding or fractionation was applied.

### Apparatus

A Perkin-Elmer Model 5000 Zeeman-effect corrected atomic absorption spectrometer (inverse transversal AC system), equipped with an HGA-500 graphite furnace, an AS-40 autosampler and a Model 3600 Data Station, was used for the determination of Al, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Ti, V and Zn. In addition, the applicability of a continuum-source compensated spectrometer for this purpose was tested using a Perkin-Elmer Model 1100 B atomic absorption spectrometer equipped with a deuterium-arc correction system, an HGA-400 graphite furnace and an AS-40 autosampler. In order to minimize possible filtration effects by particles collected on the end of the capillary

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**Table 1** Experimental conditions used for the ETAAS slurry technique

Experimental conditions	Element										
	Al	Cd	Cr	Cu	Fe	Mn	Mg	Ni	Ti	V	Zn
<i>Instrumental parameters—</i>											
Wavelength/nm	256.8 396.1	228.8*	357.9	324.7	305.9 372.0* 373.7 252.7† 248.3*	279.5*	285.2 202.5 383.8†	352.5 232.0†	364.3	318.4	213.9*
Spectral bandwidth/nm	0.7	0.7	0.7	0.7	0.2	0.2	0.7	0.2	0.2	0.7	0.7
Source/ mA, W	HCL‡ 25	EDL 4	HCL 25	HCL 15	HCL 30	HCL 20	HCL 4	HCL 20	HCL 30	HCL 40	HCL 10
<i>Temperature programme§—</i>											
Drying¶	320 °C, ramp 10 s, hold 20 s, for all elements										
Charring	Ramp 20 s, hold 20 s, for all elements										
Temperature/°C	1700	300	1500	1200	1400	900	900	1400	1400	1700	300
Atomization temperature	2700 °C, maximum power heating, hold 5 s, for all elements										
Read/s	5	1	5	5	5	5	5	5	5	5	1.5
Internal gas flow (argon)/ ml min <sup>-1</sup>	300	300	300	100	300	300	300	300	300	50	100
Cleaning	2700 °C, hold 2 s, for all elements										
Cooling	20 °C, hold 20 s, for all elements										
Modifier**/mg	0.2	no	0.2	0.2	no	no	no	no	no	no	no
<i>Linear working range††—</i>											
Up to concentration (ppm)	350	—	20	10	400 (60)	10	35	30	150	90	0.8
Atomic line/nm	256.8	—	357.9	324.7	305.9 (372.0)	279.5	285.2	352.5	364.3	318.4	213.9
Slurry composition (% m/v)	0.5	2.5	0.5	0.5	0.5	0.5	0.01	2.5	0.5	0.5	2.5

\*Possible spectral interference, see text and Table 5.

†Not recommended because of spectral interference.

‡Hollow cathode lamp.

§Internal gas flow 300 ml min<sup>-1</sup> Ar, except in atomization step.

¶Sampling volume 20 µl.

||Recorder and magnet and READ commands are on for 5 and 1 s, respectively, before starting the atomization step.

\*\*Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Suprapur (Merck).

††Linear working range up to concentration in ppm at the specified wavelength and slurry composition assuming dispensing of 20 µl aliquots.

during pipetting, the common sampling capillary of the autosampler (Part No. 101161, i.d. 0.5 mm) was replaced with another one of i.d. 0.8 mm. Pyrolytic graphite coated graphite ringed tubes with fork-shaped platforms<sup>11</sup> (see Fig. 1) supplied by Ringsdorfwerke (Bonn, Germany) were used. For a few comparative measurements, ordinary electrographite (Part No. 070699) and pyrolytic graphite coated graphite (Part No. 091504) tubes without platforms were also utilized. The instrumental parameters used are summarized in Table 1.

### Procedure

For the preparation of sample slurries, 0.1–0.5 g of silicon carbide powder was mixed in a cleaned plastic beaker (30 ml) with 20 ml of doubly distilled water previously checked for the blank value. Suspensions were pre-treated in a Sonorex RK 255 H ultrasonic bath (Bandelin Electronic, Berlin, Germany) for 15 min in order to disintegrate particle agglomerates. Under continuous stirring with a PTFE-covered magnetic bar, from the position usually assigned to a beaker containing the modifier solution, 20 µl aliquots of the homogenized slurries were automatically dispensed into the cavity of the platform. Stirring was

performed by a remote-controlled rotating magnet situated (because of steric hindrance) over the covered sample beaker.<sup>12</sup> A concentrated solution of Suprapur-grade magnesium nitrate as chemical modifier was added to the suspension and the mixture was introduced into the furnace, or it was separately dispensed into the cavity of the platform, *via* the sample volume mode of an autosampler prior to the sample suspension. For standardization by the standard additions technique, the suspensions were spiked with aqueous standard solutions.

For the analysis of the silicon carbide powders by ICP-AES and ETAAS, the samples were decomposed in an autoclave with a mixture of concentrated HNO<sub>3</sub>, HF and fuming H<sub>2</sub>SO<sub>4</sub>. A more detailed description of the decomposition procedure and of the INAA used as an additional independent method can be found elsewhere.<sup>7–9</sup>

### Scanning Electron Microscopy

Scanning electron micrographs of the platform surface were obtained with a Philips SEM 500 microscope with magnification ranging from 10 to 2500 times at an accelerating voltage of 20 kV. The same microscope equipped with a

Philips EDAX 9800 microprobe system was used for element-specific surface analysis of the platform.

## Results and Discussion

### Thermal Decomposition of Silicon Carbide

According to the thermodynamic data,<sup>3</sup> the total decomposition of silicon carbide requires thermal treatment at temperatures above 2500 °C, whereby the decomposition mechanism can be affected by impurities. During the decomposition process, elemental silicon and carbon are produced. Owing to its higher volatility, silicon vaporizes from the mixture, whereas carbon is expected to form mainly a solid residue. From the practical point of view, this phenomenon can limit the maximum applicable sample amount and, consequently, can also affect the limits of detection.

In order to ensure a fast and complete decomposition and vaporization of the sample in the graphite furnace, the maximum available atomization temperature of 2700 °C and maximum power heating mode were chosen in all experiments, with consideration of the lifetime of graphite tube or the stabilized temperature platform furnace (STPF). Dispensing a sample portion of 0.1 mg caused no significant interference during the over-all tube lifetime, reaching approximately 400–500 atomization shots of 5s duration. After this number of shots, a small residue identified as the carbon matrix was observed in the centre of the platform, as can be seen in the scanning electron micrograph shown in Fig. 1. Repeated introduction of 0.5 mg of sample, however, gave rise to considerable accumulation of carbonaceous matter on the platform, which had to be removed mechanically after approximately 60–80 determinations. The use of full internal gas flow (300 ml min<sup>-1</sup>) during the atomization stage reduced the amount of deposited matter on the platform. Neither silicon nor other main impurity elements were detected by the EDAX microprobe in the residue remaining on the surface of the platform. The conclusion can be drawn that the decomposition of silicon carbide is complete and that trace elements trapped in the bulk are released during the atomization stage. The tube and/or platform should not be significantly corroded by interaction with silicon carbide, as was manifested by the long lifetime of both components.

### Spectral Interferences

Owing to its refractory properties, the sample matrix cannot be removed during the charring treatment. Therefore, considerable interferences by non-specific attenuation and/or emission<sup>13</sup> caused by particles and molecules produced during the atomization stage can be expected. The levels of the background attenuation shown in Fig. 2 were measured over the wavelength range 200–450 nm with an atomic absorption spectrometer equipped with a deuterium-arc lamp in the background mode and by the two-line method at the following non-sensitive lines: Cu 249.2, 282.4 and 323.1 nm, Al 307.0 nm, Zn 212.5 nm, Fe 358.1 and 421.6 nm and Ni 231.4 and 362.5 nm. More pronounced or even negative absorbance background values were observed if the two-line method was used. The background increased proportionately only if small sample portions up to 50 µg were injected, followed by a slight increase for larger sample amounts. These differences and the shape of the non-specific spectra indicate that the attenuation is caused by molecules with fine-structured molecular band spectra. According to literature data,<sup>14,15</sup> C<sub>2</sub>, C<sub>3</sub> and Si<sub>2</sub> seem to be the most probable interfering species, but other molecules such as SiC<sub>2</sub> and Si<sub>2</sub>C can also be produced.<sup>3</sup> For example, the Mulliken system for a C<sub>2</sub> molecule shows a headless

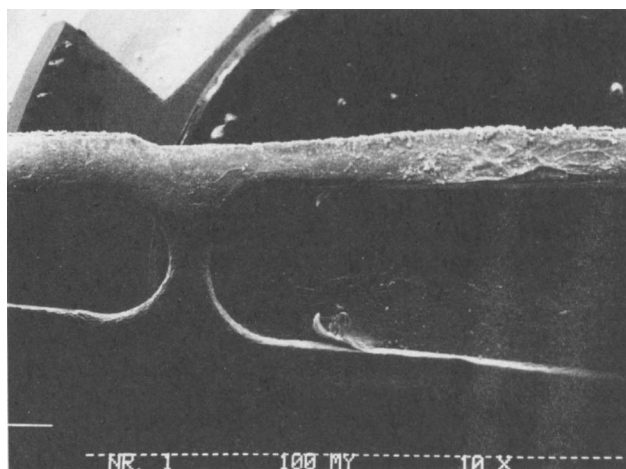


Fig. 1 Fork-shaped platform with the carbonaceous residue in the central part of the cavity after 400 repeated atomizations of 0.1 mg of silicon carbide (sample IV); final magnification of 6.2

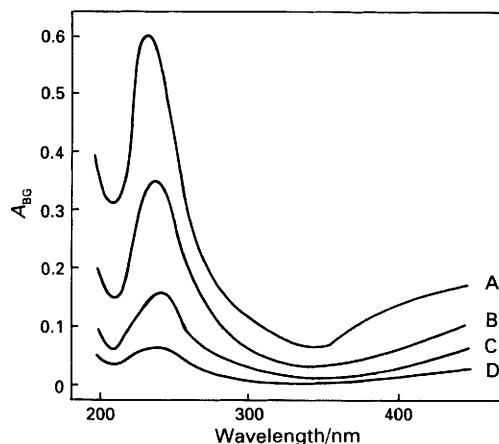
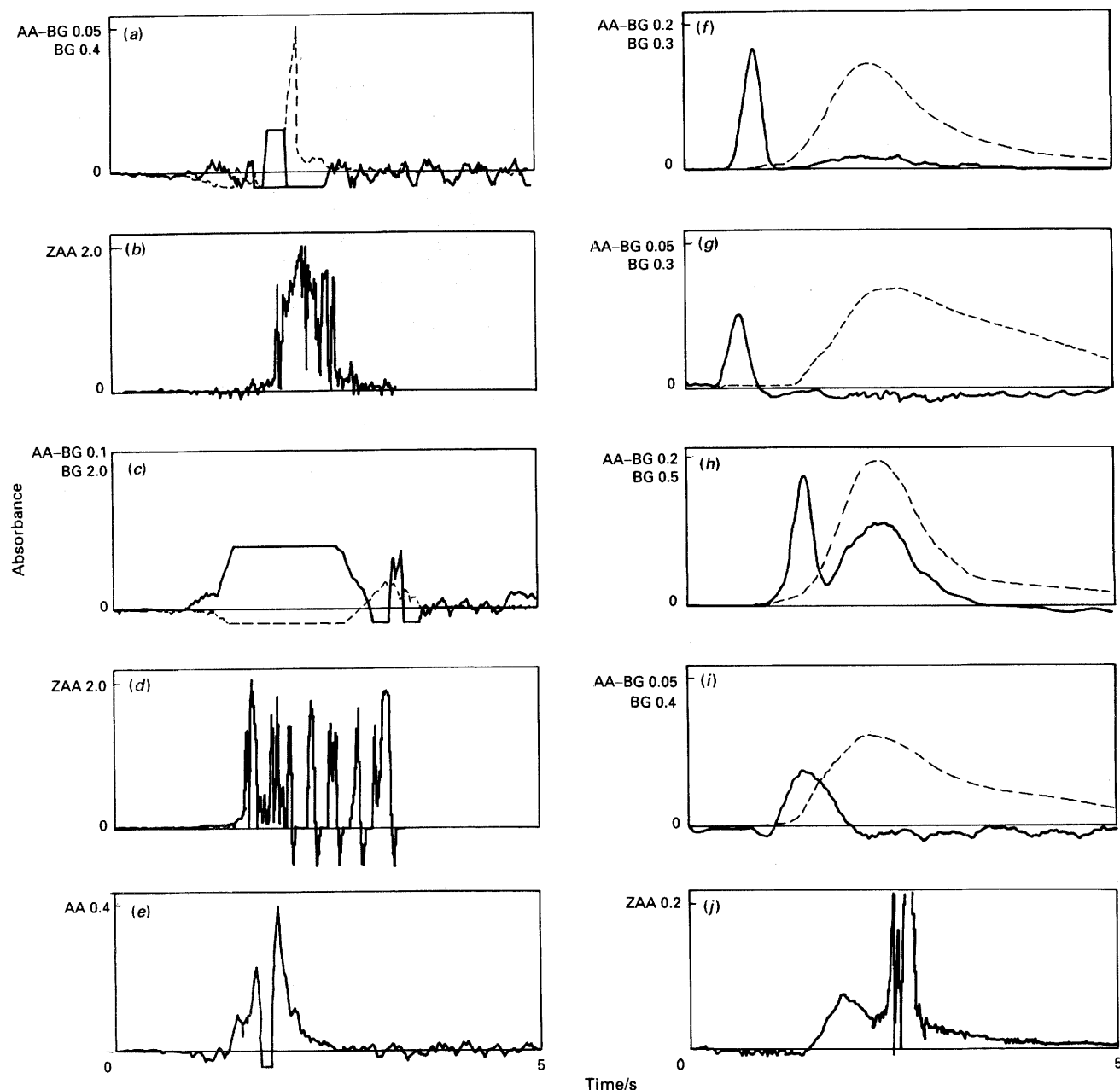


Fig. 2 Spectra of non-selective attenuation measured with deuterium-arc continuum for a 2.0 nm spectral bandwidth, at an argon flow rate of: A, 0; B, 50; C, 100; and D, 300 ml min<sup>-1</sup> and for 0.1 mg of dispensed sample IV

band with a maximum at 232.5 nm and the comet-head group of the C<sub>3</sub> molecule appears at 404.9 nm as a red degraded band.<sup>14</sup> Owing to the fine structure of the bands, over- and under-correction errors especially for continuum-source compensated spectrometers are to be expected.

In fact, these interferences were observed at several lines of interest for a number of analyte elements (see Fig. 3). For example, double peaks were observed for the lines of Zn at 213.9 nm and Fe at 252.7 nm, and over-corrections occurred at the lines of Cd at 228.8 nm, Ni at 231.1 nm and Ni at 232.0 nm if deuterium-arc corrected signals were measured. Second peaks (Zn, Fe) and negative signals (Cd, Ni) coinciding in time with the background attenuation do not occur (see Fig. 4) if other analytical lines are used in the continuum-source compensated measurement [see Figs. 3(a) and 4(a), 3(h) and 4(g), and 3(i) and 4(h)] or if Zeeman-effect background correction is applied at the same line [see Figs. 3(f) and 4(e)]. The volatilization of Zn and Cd prior to the matrix enables this problem to be overcome using time-separated measurements [see Figs. 3(f) and (g)]. However, this procedure is not applicable to the measurement of Ni and Fe at the lines given above. Therefore, for these elements, other analytical lines have to be chosen (see Table 1).



**Fig. 3** Under- and over-correction errors caused by silicon carbide decomposition products. Signal traces: AA-BG, continuum source corrected; BG (dotted line), background attenuation; AA, uncorrected; and ZAA, Zeeman-effect corrected. Internal gas flow rate, 300 ml min<sup>-1</sup> Ar, except for Cu (50 ml min<sup>-1</sup>). Amount of sample injected: 0.5 mg for Cd, Ni and Zn; 0.1 mg for Ca (AA), Cu, Fe and Mg; no sample for Ca (ZAA, AA-BG). (a) Mg, 383.3; (b) and (e) Ca, 239.9; (c) and (d) Ca, 422.7; (f) Zn, 213.8; (g) Cd, 228.8; (h) Fe, 252.7; (i) Ni, 232.0; and (j) Cu, 324.7 nm

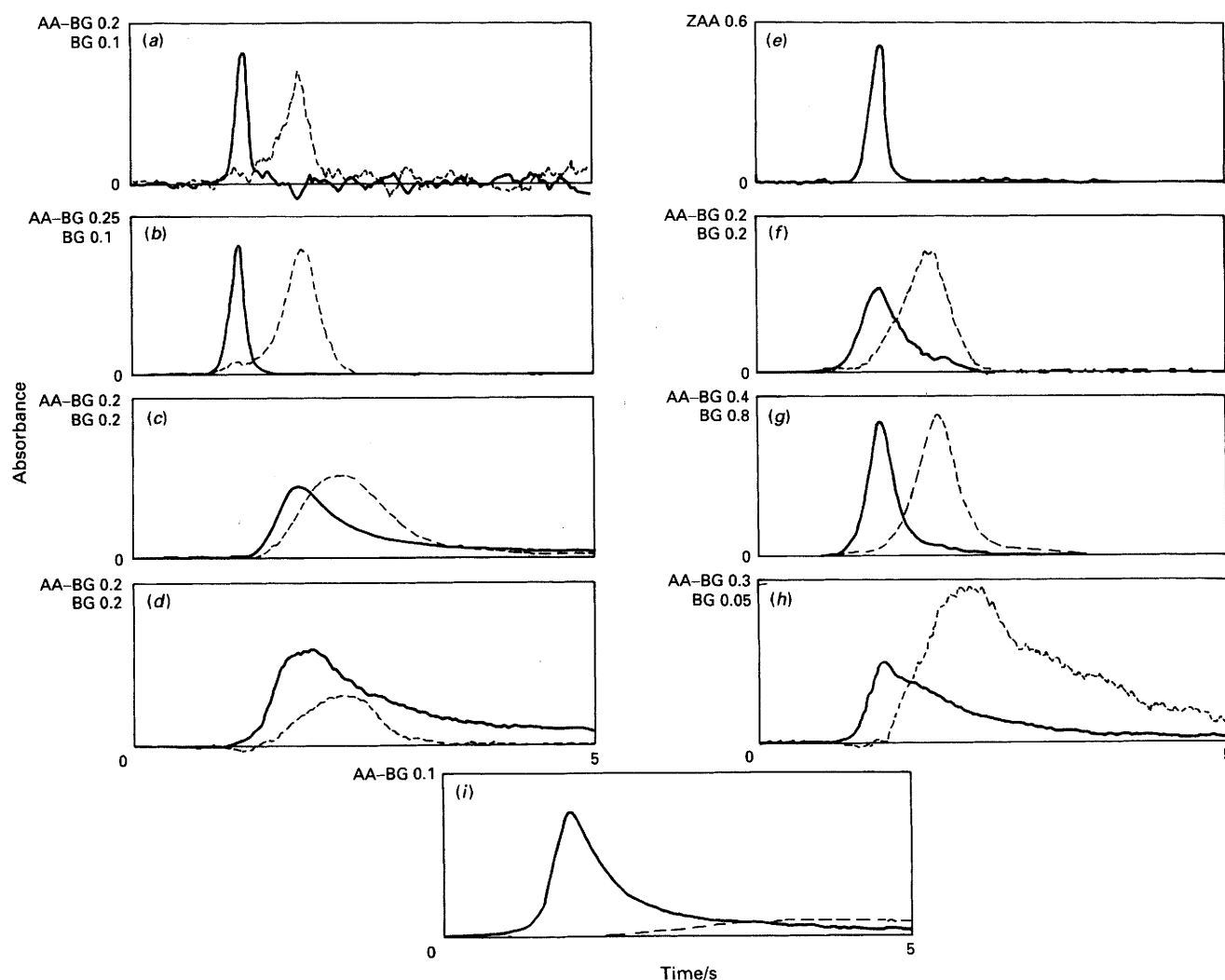
A large interference (disturbed signals) was observed with and without dispensed samples (new tube) for the main Ca lines at 422.7 and 239.9 nm, using both the continuum-source and the Zeeman-effect background correction systems [see Fig. 3(b)–(e)]. This interference might be due to contamination of the tube and/or platform material with diffusively distributed thermally stable calcium carbide or emission<sup>13</sup> of carbonaceous species ejected from the surface. This interference made the determination of Ca impossible. At internal gas flow rates of lower than 200 ml min<sup>-1</sup> of argon, especially on the tailing part of the Zeeman-effect corrected signals for Cu, Fe, Mn, Ni, Ti and V, an interfering effect manifested in the spike-like form of the absorbance record [see Fig. 3(j)] occurred. This interference is probably caused by a discontinuous vaporization or release of carbonaceous residue and its emission. Therefore, atomization with the full gas flow rate (300

ml min<sup>-1</sup>) proved to be the best for the analysis of this material.

### Standardization and Analysis of Samples

The direct analysis of solid samples by ETAAS requires suitable matrix-containing solid standards with known concentrations of the trace elements of interest. However, reference standard materials for silicon carbide with certified trace element contents are not available and the thermochemical aspects make a standardization using synthetic standard materials, as is applied to the analysis of aluminium oxide,<sup>10</sup> impossible. The formation of silicon carbide requires treatment of the starting substrates in an electric oven at very high temperatures. It can be expected that several of the spiked elements will be lost during this procedure, as can also be deduced from the low content of





**Fig. 4** Typical signal shapes for some elements. For absorbance specification see Fig. 3. Internal gas flow rate, 300 ml min<sup>-1</sup>. Amount of sample injected: 0.5 mg for Cr, Ni, Ti, V and Zn; 0.1 mg for Al, Fe and Mn; and 0.025 mg for Mg. (a) Mg, 202.5; (b) Mn, 279.5; (c) V, 318.4; (d) Ti, 364.3; (e) Zn, 213.8; (f) Al, 256.8; (g) Fe, 248.3; (h) Ni, 352.5; and (i) Cr, 357.9 nm

the volatile elements (Cd, Zn, Cu, *etc.*) generally found in this material (see Table 2). Hence, the standard additions technique based on spiking the suspensions with aqueous standard solutions is considered as a very useful standardization method. However, this standardization technique has to be verified for accuracy.<sup>16</sup> The results obtained by the slurry technique were compared with those of ETAAS and ICP-AES after sample decomposition and with those of INAA.

In general, an accurate standardization requires that the analyte element added as a standard to the sample and the indigenous analyte element in the sample behave similarly during the charring and atomization stages. According to this stipulation, a 'generalized standard additions method' reported recently<sup>17</sup> could not be applied to this slurry technique. In this work, the trace impurities might be trapped in the sample bulk, they might be physically sorbed or chemically bound as a result of the production processes applied (smelting, zone melting, grinding) on the surface of the particles or they might be present as discrete particles disseminated throughout the silicon carbide powder. Hence the kinetics and efficiency of vaporization and atomization are, in general, influenced by the physical and chemical form of the analyte element, which, consequently, affects the analyte signal. An equalization of the behaviour of different forms of the analyte element can be achieved by a suitable matrix-analyte modification.

Preliminary experiments using wall atomization from ordinary and pyrolytic graphite coated graphite tubes showed large discrepancies between the expected and found contents, even if the signals were evaluated from integrated absorbances (peak areas). These experiences and the above considerations suggested the application of the STPF concept to this problem. Therefore, in subsequent experiments a fork-shaped platform in a ringed tube and integrated absorbance (s) evaluation were used.

Suspensions of powdered silicon carbide were prepared in water in order to achieve hydrolysis of the spiked analytes followed by retention of the hydrolysis products on the very large particle surface (approximate specific surface area 15 m<sup>2</sup> g<sup>-1</sup>). The sorption of the analyte elements in the added form should eliminate the physical separation of the spiked analyte present originally in the aqueous phase from the sample particles by being sucked into the graphite or by drying processes during the first stage of the temperature programme. In special experiments, the leaching behaviour of the elements and their distribution between the two phases of the suspension were studied. For this purpose, after ultrasonication, the phases were separated and the liquid phase was analysed. The results of these experiments showed that neither the analytes contained in the samples nor the analyte spikes were significantly leached from the silicon carbide particles into the solution.

The modifiers used for the equalization of the behaviour

**Table 2** Element contents determined in different silicon carbide samples by the slurry technique (A) and comparison with results obtained by ETAAS or ICP-AES after sample decomposition (B) and INAA (C)

Element	Method*	Content/ $\mu\text{g g}^{-1}$				
		I UF 15 Lonza	II B 10 Starck	III A 10 Starck	IV A 10 Starck	V ESK S 933
Al	A	251 $\pm$ 14	338 $\pm$ 15	480 $\pm$ 40	224 $\pm$ 15	177 $\pm$ 19
	B	267 $\pm$ 3	347 $\pm$ 2	461 $\pm$ 2	198 $\pm$ 5	178 $\pm$ 4
Cd	A	<0.02	<0.02	<0.02	<0.02	<0.02
	B	0.23 $\pm$ 0.04	<0.07	<0.07	n.d. <sup>†</sup>	<0.5
	C	<0.25	<2	<0.1	<0.2	<0.09
Cr	A	3.1 $\pm$ 0.3	18.5 $\pm$ 1.5	2.6 $\pm$ 0.3	5.5 $\pm$ 0.3	7.1 $\pm$ 0.5
	B	3.0 $\pm$ 0.1	18.2 $\pm$ 0.2	2.4 $\pm$ 0.1	5.6 $\pm$ 0.2	6.9 $\pm$ 0.5
	C	2.6 $\pm$ 0.2	15.1 $\pm$ 1.0	1.9 $\pm$ 0.15	4.4 $\pm$ 0.8	7.1 $\pm$ 0.2
Cu	A	3.4 $\pm$ 0.3	8.9 $\pm$ 0.4	2.3 $\pm$ 0.1	1.3 $\pm$ 0.1	3.2 $\pm$ 0.6
	B	5.3 $\pm$ 0.4	8.0 $\pm$ 0.8	1.9 $\pm$ 0.1	$\approx$ 1	2.9 $\pm$ 0.3
Fe	A	260 $\pm$ 10	650 $\pm$ 30	15.3 $\pm$ 0.2	150 $\pm$ 10	340 $\pm$ 20
	B	251 $\pm$ 4	656 $\pm$ 16	17.0 $\pm$ 0.7	134 $\pm$ 1	320 $\pm$ 1
	C	239 $\pm$ 5	646 $\pm$ 39	16.1 $\pm$ 1.2	132 $\pm$ 2	322 $\pm$ 14
Mg	A	30.8 $\pm$ 0.5	17.6 $\pm$ 1.0	5.6 $\pm$ 0.5	4.0 $\pm$ 1.1	5.2 $\pm$ 0.8
	B	33.6 $\pm$ 0.6	12.6 $\pm$ 0.3	5.0 $\pm$ 0.1	1.7 $\pm$ 0.1	3.7 $\pm$ 0.2
Mn	A	6.9 $\pm$ 0.6	3.7 $\pm$ 0.2	0.14 $\pm$ 0.08	0.78 $\pm$ 0.06	0.72 $\pm$ 0.08
	B	7.0 $\pm$ 0.2	3.8 $\pm$ 0.2	$\approx$ 0.2	0.69 $\pm$ 0.02	0.73 $\pm$ 0.14
	C	7.9 $\pm$ 0.2	3.9 $\pm$ 0.2	0.16 $\pm$ 0.01	0.74 $\pm$ 0.01	0.70 $\pm$ 0.01
Ni	A	21.4 $\pm$ 0.8	12.4 $\pm$ 0.5	3.0 $\pm$ 0.4	4.6 $\pm$ 0.5	4.8 $\pm$ 0.7
	B	24 $\pm$ 0.1	12.9 $\pm$ 0.1	$\approx$ 2	$\approx$ 2	<3
	C	21.7 $\pm$ 0.3	13.0 $\pm$ 0.3	0.81 $\pm$ 0.04	1.6 $\pm$ 0.2	3.8 $\pm$ 0.2
Ti	A	107 $\pm$ 3	82 $\pm$ 1	61 $\pm$ 1	40 $\pm$ 3	130 $\pm$ 13
	B	102 $\pm$ 2	82 $\pm$ 2	65 $\pm$ 1	41 $\pm$ 2	158 $\pm$ 1
V	A	34 $\pm$ 1	29 $\pm$ 1	29 $\pm$ 2	9 $\pm$ 2	84 $\pm$ 1
	B	36 $\pm$ 1	26 $\pm$ 1	28 $\pm$ 1	9.6 $\pm$ 3.3	84 $\pm$ 2
Zn	A	0.68 $\pm$ 0.02	0.12 $\pm$ 0.02	0.43 $\pm$ 0.04	0.18 $\pm$ 0.02	0.31 $\pm$ 0.03
	B	0.8 $\pm$ 0.15	<0.15	0.11 $\pm$ 0.01	n.d.	n.d.
	C	<0.5	<0.5	<0.1	<0.6	<0.5

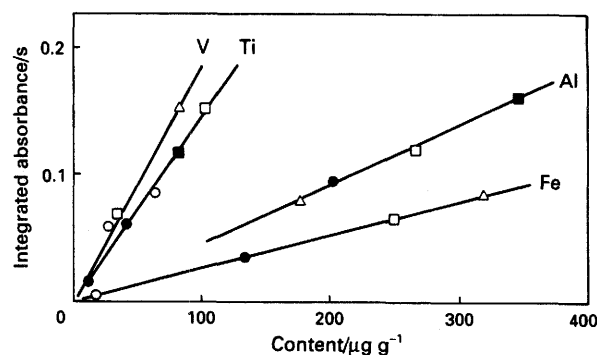
\*A, ETAAS using slurry sampling technique;  $n=5$ . B, ETAAS or ICP-AES after high-pressure decomposition of the sample (refs. 8 and 9);  $n=6$ . C, INAA (ref. 8).

<sup>†</sup>n.d.=Not determined.

of all analyte forms should react with silicon carbide at sufficiently low temperatures. Palladium and magnesium nitrate seemed to be well suited for this purpose,<sup>3</sup> when applied in sufficiently large amounts. For example, 0.6 mg of magnesium nitrate is needed for complete decomposition of 0.1 mg of silicon carbide. Nevertheless, utilization of larger amounts of these modifiers is mainly limited by their purity (affecting the blank) and by their chemical interaction with graphite. Proceeding from the relatively well known properties of magnesium nitrate as a universal modifier,<sup>18</sup> the modifying efficiency for this matrix was studied in more detail.

Although silicon carbide cannot be removed during the charring stage, the determination of a suitable charring temperature plays a decisive role in the standardization. Thermal treatment at too high temperatures can give rise to losses of the spiked analytes from the unmodified suspension and, consequently, higher results would be obtained. On the other hand, at too low pre-treatment temperatures, giving rise to no loss of the analyte, the reaction of the modifier with the matrix might be insufficient or it might not take place at all. In this instance, there would be a risk of obtaining lower results owing to easier atomization of the spiked analyte.

The optimum experimental conditions for the determination of the main impurity elements Al, Cr, Fe, Mn, Ti and V, the content of which in various samples was verified by other methods, are summarized in Table 1. The contents determined in silicon carbide powders of different origin by this slurry technique and the other independent methods



**Fig. 5** Standardization by using samples analysed after decomposition; 0.1 mg of sample introduced. Samples:  $\square$ , I;  $\blacksquare$ , II;  $\circ$ , III;  $\bullet$ , IV; and  $\triangle$ , V

are compared in Table 2. Surprisingly, for most of the elements investigated no addition of modification agents was necessary. This is obviously due to the utilization of the STPF concept and the evaluation of integrated absorbance data and probably also to the convenient form of the analyte elements in the sample.

Excluding some few instances where the analyte element contents were low, the results obtained by the slurry technique are in good agreement with those obtained by INAA and by ICP-AES or ETAAS after sample decomposition.

**Table 3** Reproducibility of sampling and dispensing procedure in the determination of Cr in silicon carbide (sample IV)

Sampling sequence No.	Relative standard deviation* (%)	
	Sampling	Dispensing
1	—	3.3
2	—	2.2
3	—	3.8
4	—	3.4
5	—	4.0
6	—	3.9
Average	6.4	3.4

\*Based on dispensing 20  $\mu\text{l}$  aliquots of 0.5% m/v sample suspensions and using integrated absorbance evaluation;  $n=6$ .

**Table 4** Reproducibility of dispensing in the determination of Fe for various silicon carbide samples

Sample No.	Relative standard deviation* (%)	Concentration level/ $\mu\text{g g}^{-1}$
I	3.7	250
II	5.1	650
IV	8.3	130
V	6.8	320

\*See Table 3.

The wide range of the element contents in the silicon carbide samples analysed by other methods permits the use of these materials for standardization purposes. An example is shown in Fig. 5, in which the integrated absorbances of Al, Fe, Ti and V measured for 0.1 mg of each of the five samples are plotted against the content determined by ETAAS after decomposition of the sample. Another possible approach is to apply various amounts of one well characterized silicon carbide material, either by dispensing suspensions of various concentrations or by repeating the introduction and drying step. If solid silicon carbide standards are used, the analysis can be performed also by the wall atomization technique. In this manner,

tailing (memory) effects might be decreased for carbide-forming elements, and integrated absorbance can be used for the evaluation.

### Sampling Errors

Sampling errors with the slurry technique are generally associated with variance of the analyte mass sampled resulting from the variances of the particle mass, number of particles present in the volume injected, concentration of the analyte element (homogeneity) and volume pipetted.<sup>19</sup> Ceramic powders obtained by grinding can be expected to have good homogeneity. Therefore, sample portions of 0.1 g of silicon carbide for analyses should normally be sufficient for the preparation of the suspension. However, the dispensing of relatively small volumes of slurries might cause considerable fluctuations of signals owing to the irregular distribution of particles and impurities, as discussed under Standardization and Analysis of Samples. From this point of view, suspensions as concentrated as possible should be introduced into the atomizer. However, the maximum dispensable amount of silicon carbide is limited by the accumulation of carbon-aceous residue on the platform and by spectral interferences, as mentioned above.

The standard deviation of the sampling procedure, including the preparation of the slurry and its dispensing with the autosampler, was determined for some elements by analysing 0.5 and 2.5% m/v (0.01% m/v for Mg) aqueous suspensions. Results for the reproducibility for Cr at the 5 ppm level in silicon carbide (sample IV) and for Fe in various samples are given in Tables 3 and 4, respectively. It can be seen that good reproducibilities for both sampling and dispensing are achieved for 20  $\mu\text{l}$  aliquots of 0.5% m/v sample slurry (for an average number of particles analysed of about  $1 \times 10^9$ ). These reproducibilities are similar to those usually found in the analysis of homogeneous solutions. In addition, they proved that the stirring technique with the remote-controlled magnetic bar was sufficient for homogenization of the suspensions also with respect to the dispensing procedure used, being superior to dispensing by hand. The good agreement of the results obtained directly by the slurry technique and by other methods (see Table 2)

**Table 5** Detection limits achieved in the analysis of silicon carbide powders by ETAAS using the slurry sampling technique

Element	Wavelength/nm	Internal gas flow/ml min <sup>-1</sup>	Detection limit*/ $\mu\text{g g}^{-1}$	Comments†
Al	256.8	300	—	Not determined owing to high content
Ca	422.7	300	—	Impossible to determine
Cd	228.8	50	0.02	Determined for a spiked slurry
Cr	357.9	50	0.2	m
Cu	324.7	0	0.05	v
Fe	372.0	300	2	s
	248.3	100	0.4	s
Mg	285.2	300	—	Not determined owing to high content
Mn	279.5	50	0.02	s
Ni	352.5	50	0.8	m
Ti	364.3	100	5	m
V	318.4	50	2	m
Zn	213.9	0	0.01	v

\*Based on three times the standard deviation of the blank fluctuation evaluated from integrated absorbance applying 20  $\mu\text{l}$  aliquots of a 2.5% m/v suspension of a silicon carbide sample with low trace element contents.

†Detection limit determined by: m, memory effect; v, maximum vaporizable amount of sample; and s, spectral interference, high background level.

is evidence for a high degree of homogeneity of the samples, and it also proves that no significant separation processes take place during the slurry agitation or dispensing (e.g., sedimentation or filtration effects).

### Detection Limits

In most practical instances, the detection limits are determined by the fluctuation of the blank values. In our experiments, chemical contamination could be minimized by the proposed batch technique. The laboratory ware (beakers and stirrer bars) could be cleaned effectively. Water of extremely high purity was used for the preparation of suspensions and modifier solutions. A further advantage of this technique is that the actual blank level can be easily controlled by analysis of the dispensing medium prior to the addition of the sample. If, owing to fluctuations, too large blanks are determined, a new dispensing liquid can be prepared and checked again.

The main factors determining the limits of detection include memory effects, especially for carbide-forming elements, spectral interferences, fluctuation of the baseline and the maximum applicable sample amount. As can be seen from Table 5, the detection limits for many elements are at the sub-microgram per gram level.

### Conclusions

In spite of its refractory properties, powdered silicon carbide can be directly analysed by ETAAS for Al, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Ti, V and Zn using the slurry sampling technique. In this technique, the risk of introducing contaminants is much lower and can be controlled and reduced more easily than in solution ETAAS. Thus, detection limits, being at the sub-microgram per gram level, are determined not by the blank but by spectral interferences and by the maximum vaporizable sample amount dispensed for atomization. Using the STPF concept and, if necessary, suitable modification, standardization can be performed by spiking the slurries with aqueous standard solutions. The method developed is adequate for routine analysis.

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