

Simultaneous Direct Determination of Aluminum, Calcium and Iron in Silicon Carbide and Silicon Nitride Powders by Slurry-Sampling Graphite Furnace AAS

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A fast and accurate analytical method was established for the simultaneous direct determination of aluminum, calcium and iron in silicon carbide and silicon nitride powders by graphite furnace atomic absorption spectrometry using a slurry sampling technique and a Hitachi Model Z-9000 atomic absorption spectrometer. The slurry samples were prepared by the ultrasonication of silicon carbide or silicon nitride powders with 0.1 M nitric acid. Calibration curves were prepared by using a mixed standard solution containing aluminum, calcium, iron and 0.1 M nitric acid. The analytical results of the proposed method for aluminum, calcium and iron in silicon carbide and silicon nitride reference materials were in good agreement with the reference values. The detection limits for aluminum, calcium and iron were 0.6 µg/g, 0.15 µg/g and 2.5 µg/g, respectively, in solid samples, when 200 mg of powdered samples were suspended in 20 ml of 0.1 M nitric acid and a 10 µl portion of the slurry sample was then measured. The relative standard deviation of the determination of aluminum, calcium and iron was 5 – 33%.

(Received June 2, 2003; Accepted December 8, 2003)

Introduction

Silicon carbide and silicon nitride are known to be very hard ceramics, and have thus been used in wear guides, cutting tools, valves and so on. Furthermore, these ceramics have been used in engines, turbines and heat-transfer parts because of their strength at high temperatures.^{1,2} Although silicon carbide and silicon nitride exhibit outstanding strength and hardness at high temperatures, these characteristics are reported to be degraded by a concomitance of impure elements, such as aluminum, calcium and iron.³⁻⁸ In order to produce strictly controlled sintered products, therefore, fast and accurate analytical methods are needed to measure the concentrations of impure aluminum, calcium and iron in silicon carbide and silicon nitride powdered raw materials.

Aluminum, calcium and iron in silicon carbide and silicon nitride powders have been determined by various methods, such as inductively coupled plasma atomic emission spectrometry (ICP-AES),⁹⁻¹⁴ graphite furnace atomic absorption spectrometry (GF-AAS)^{12,13} and inductively coupled plasma mass spectrometry (ICP-MS).¹³ All of these techniques use sample solutions prepared by acid digestion methods under high-pressure conditions, or by alkaline fusion methods. In Japan, ICP-AES analysis using a sample solution has been prescribed as the official method to determine aluminum, calcium and iron in silicon carbide¹⁵ and silicon nitride powders for fine ceramics.¹⁶ The sample digestion procedure, however, is generally complicated and time-consuming.

On the other hand, a few studies of solid sampling techniques that avoid the sample digestion process have been conducted. Barth *et al.* reported a simultaneous direct determination of aluminum, calcium and iron in silicon nitride powders by electrothermal vaporization-ICP-AES (ETV-ICP-AES) using slurry samples.¹⁷ However, that study required both a laboratory-made ETV device and an interface to the ICP-AES. Docekal *et al.* reported a simultaneous determination of aluminum, calcium and iron in silicon carbide by ICP-AES with slurry samples.¹⁸ In that study, however, the analytical results obtained by using slurry samples were 5 – 24% lower than those obtained using acid-decomposed sample solutions.

A few studies have been reported on the direct determination of aluminum and iron in silicon carbide and silicon nitride by GF-AAS using slurry sampling techniques. Docekal and Krivan reported a direct, though not simultaneous, determination of aluminum and iron in silicon carbide.¹⁹ Likewise, Friese and Krivan reported a direct, but not simultaneous, determination of aluminum and iron in silicon nitride.²⁰ The direct determination of iron in silicon carbide and of iron in silicon nitride were reported by Morita *et al.*²¹

Although calcium is one of the most important impure elements to analyze, there have been no reports on the direct determination of calcium in silicon nitride and silicon carbonate by GF-AAS. Furthermore, no studies have appeared on the simultaneous direct determination of aluminum, calcium and iron in silicon carbide and silicon nitride by GF-AAS.

In this paper we report on a fast and accurate method for the simultaneous direct determination of aluminum, calcium and iron in silicon carbide and silicon nitride powdered raw materials by GF-AAS using slurry samples. The slurry samples were prepared by 30 min of ultrasonication with 0.1 M nitric

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Table 1 Optimized temperature program used in the simultaneous direct determination of aluminum, calcium and iron

Step	Temperature/°C	Time/s	Ar flow rate/ml min ⁻¹
Drying	80 - 150 ^a	30	200
Pyrolysis	700	30	200
Atomization	2900	17	30 (200) ^b
Cleaning	3000	3	200

a. Ramp mode.

b. Ar gas was not interrupted for R022 silicon carbide analysis.

acid. We investigated the extraction behavior of impure aluminum, calcium and iron as analytes from solid samples to 0.1 M nitric acid. The temperature program needed to perform the simultaneous analysis was investigated and then optimized. Accurate analytical results were successfully obtained not only by the standard addition method, but also by calibration curves prepared using a standard solution mixed with aluminum, calcium and iron.

Experimental

Apparatus and reagents

A Hitachi Model Z-9000 (Hitachi Ltd., Japan), polarized Zeeman atomic absorption spectrometer equipped with a tube-type graphite furnace was used for the simultaneous determination of aluminum, calcium and iron.

A Model 3200 ultra-sonic cleaner (Branson, USA) and a Model G-560 vortex mixer (Scientific Ind., USA) were used for the ultrasonication and mixing of slurry samples, respectively. Teflon or polypropylene bottles were used to prepare slurry samples.

Silicon carbide powdered reference materials (Ceramics Society of Japan, R021, R022 and R023) and silicon nitride powdered reference materials (*ditto*, R003 and R004) were used after drying for 4 h at 85°C.

An aluminum, calcium and iron mixed standard solution was prepared by mixing each standard solution: aluminum (1000 mg/l solution, Al(NO₃)₃ in 0.5 M HNO₃, Wako Pure Chemical Industries Co., Japan), calcium (1000 mg/l, CaCO₃ in 1.0 M HNO₃, *ditto*) and iron (1000 mg/l, Fe(NO₃)₃ in 0.1 M HNO₃, *ditto*). Nitric acid was of super-special grade (Wako Pure Chemical Industries Co., Japan) without further purification. Deionized water was purified by a Milli-Q water purification system (Millipore, USA). Argon gas was used as a carrier and interrupted gas for a GF-AAS measurement.

GF-AAS measurement with slurry samples

Slurry samples were prepared as follows. A sample of 20 - 200 mg dried silicon carbide or silicon nitride powder was placed in a Teflon or polypropylene bottle. A 20 ml portion of 0.1 M nitric acid was added to the bottle, in which the mixture was then suspended by the ultrasonication for 30 min. There are several reasons why 0.1 M nitric acid was used in preparing the slurry samples: (1) iron(III) precipitates above pH = 2.2 as iron hydroxide, and (2) the absorbances of iron, aluminum and calcium were constant when the concentration of nitric acid was between 0.01 and 0.15 M (figure not shown).

The slurry sample was introduced into a graphite furnace by using a micro pipette. Prior to pipeting, the slurry sample in the bottle was mixed for a few seconds using a vortex mixer. The sample introduced into the furnace was then dried, pyrolyzed

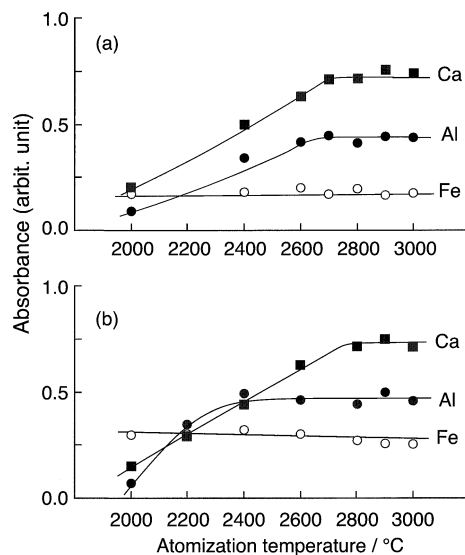


Fig. 1 Relationship between the atomization temperature and the absorbances of analytes. Sample: (a) R021 silicon carbide slurry, (b) R004 silicon nitride slurry.

and atomized according to the temperature program given in Table 1. The number of temperature values given in Table 1 corresponds to the values shown by the instrument used in this study. The wavelengths used were as follows: aluminum, 309.3 and 396.2 nm; calcium, 422.7 nm; iron, 248.3 nm. The slit width was 1.3 nm for all analytes, and was not changeable, but fixed for this instrument.

When the standard addition method was applied, the slurry samples, containing the standard solution mixed with appropriate concentrations of aluminum, calcium and iron were introduced into the graphite furnace.

Results and Discussion

Optimization of instrumental conditions

In order to obtain accurate and reproducible analytical results, it was necessary to optimize the conditions of both pyrolysis and atomization as important factors for the GF-AAS measurement with the slurry sampling technique. Especially, it was essential to use a simultaneous multi-element determination to figure out the common optimized measurement conditions. Therefore, examinations to optimize the temperature-time program were carried out by using silicon carbide and silicon nitride slurry samples and the mixed standard solution containing aluminum, calcium and iron.

Figure 1(a) shows the relationship between the atomization temperature and the analyte absorbances for the R021 silicon carbide slurry sample. Since the absorbances of all analytes became constant above 2700°C, an atomization temperature of 2900°C was selected. A pyrolysis temperature of 700°C was selected, because the absorbances of all analytes were constant between 500°C and 1100°C when the atomization temperature was fixed at 2900°C (figure not shown).

Figure 1(b) shows the relationship between the atomization temperature and the analyte absorbances for the R004 silicon nitride slurry sample. Since the absorbances of all analytes became constant above 2800°C, an atomization temperature of 2900°C was selected. A pyrolysis temperature of 700°C was selected, because the absorbances of all the analytes were

Table 2 Extraction efficiency of aluminum, calcium and iron from silicon carbide and silicon nitride

Sample	Extraction efficiency, %		
	Al	Ca	Fe
Silicon carbide			
R021	— ^a	98	38
R022	— ^a	76	50
R023	— ^a	9	37
Silicon nitride			
R003	— ^a	49	24
R004	— ^a	23	— ^a

a. Analyte absorbance was not detected.

constant between 500°C and 1100°C when the atomization temperature was fixed at 2900°C (figure not shown).

For the temperature-dependent absorbance, almost the same behavior was seen between the silicon carbide slurry sample and the mixed standard solution containing aluminum, calcium and iron. Based on these results, the heating program for the simultaneous multi-element GF-AAS measurement was optimized, as shown in Table 1.

Relationship between the ultrasonication time and the absorbances of analytes

In order to obtain accurate and precise results by the slurry sampling GF-AAS, slurry samples should be suspended as uniformly as possible. Therefore, the relationship between the ultrasonication time and the absorbances of the analytes was investigated by using an R023 silicon carbide slurry sample to optimize the ultrasonication time. As shown in Fig. 2, the absorbances of aluminum, calcium and iron in the slurry sample obtained by ultrasonication of more than 15 min were about twice those obtained without ultrasonication. Therefore, 30 min of ultrasonication was selected to prepare the slurry samples. On the other hand, the absorbance behavior of calcium in R021 silicon carbide, as shown in Fig. 2(b), suggested an extraction of calcium from the sample, even without ultrasonication.

The effect of ultrasonication on the diameter of silicon carbide powder was examined by scanning electron microscopy. The diameter of this powder without ultrasonication ranged from 10 to 200 µm, whereas it was less than 3 µm in slurry prepared by 30 min ultrasonication. Ultrasonication also improved the relative standard deviation (RSD) of the analyte absorbances obtained by using the slurry samples, from ca. 40–60% without ultrasonication to ca. 5–30% with it. These results showed that ultrasonication dissociated the aggregated sample powders, apparently allowing relatively uniform slurry samples to be prepared.

Relationship between the standing time of slurry samples and the absorbances of analytes

In order to confirm the stability of a slurry sample prepared by 30 min ultrasonication, the relationship between the standing time of the R021 silicon carbide slurry and the absorbances of the analytes in the sample was investigated, as shown in Fig. 3. The absorbance of calcium did not lessen even after 2 h. On the other hand, the absorbances of aluminum and iron gradually lessened after 1 and 30 min, respectively. If the analytes were still in and/or on the sample particles, the behavior of absorbances of analytes must be identical. Therefore, the individual behaviors of the absorbances shown in Fig. 3 were

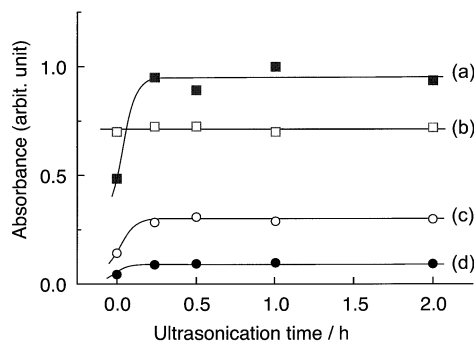


Fig. 2 Relationship between the ultrasonication time and the absorbances of analytes in the slurry samples. Element/sample: (a) calcium/R023 silicon carbide, (b) calcium/R021 silicon carbide, (c) iron/R023 silicon carbide, (d) aluminum/R023 silicon carbide.

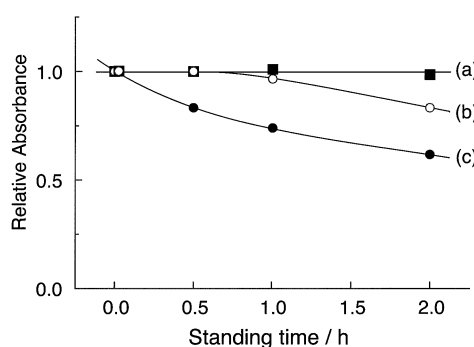


Fig. 3 Relationship between the standing time and the absorbances of analytes. (a) Calcium, (b) iron and (c) aluminum absorbance obtained by R021 silicon carbide slurry.

thought to be based on the individual extraction behaviors of analytes from the sample particles to the aqueous phase containing 0.1 M nitric acid.

Extraction behavior of analytes from samples

The extraction efficiency of analytes from silicon carbide and silicon nitride powders by 0.1 M nitric acid, which was used to prepare a slurry sample, was investigated. The extraction efficiency is defined in this study as $E = B/A$, where E is the extraction efficiency, A is the absorbance of an analyte obtained by measuring a slurry sample prepared by the proposed method and B is the absorbance of the analyte obtained by measuring the supernatant separated by centrifugation, at 3000 r.p.m. for 20 min, of the slurry sample which was used to measure A .

As shown in Table 2, both calcium and iron were partially extracted from silicon carbide and silicon nitride samples, while aluminum was not extracted at all. These phenomena were consistent with the absorbance behavior of analytes, as described above. Calcium in R021 silicon carbide was thought to exist at the surface of the particle as in some water-soluble species, because calcium can be extracted even by pure water. In order to enhance the extraction efficiency of analytes from the samples, it might be necessary to increase the nitric acid concentration, to use other acids or to adopt other strategies; however, these approaches were not investigated in this study.

Absorption profiles

In order to ascertain the thermal program, the absorption-time profiles for aluminum, calcium and iron were investigated.

Table 3 Analytical results for aluminum, calcium and iron in silicon carbide and silicon nitride

Sample	Found ^{a/} $\mu\text{g g}^{-1}$		
	Al	Ca	Fe
Silicon carbide R023	23	27	146
Reference value/wt%	0.003	0.003	0.015
Silicon nitride R003	3 ^b	2	40
Reference value/wt%	<0.0001 - <0.0006	<0.0001 - <0.0013	0.0042 \pm 0.0004

a. Calibration curve was prepared by standard addition method.

b. Analytical line of 309.3 nm for aluminum was used.

Table 4 Analytical results for aluminum, calcium and iron in silicon carbide and silicon nitride

Sample	Found ^{a,b/} $\mu\text{g g}^{-1}$		
	Al	Ca	Fe
Silicon carbide			
R021	415 \pm 32	76 \pm 3	184 \pm 59
Reference value/wt%	0.039	0.007	0.018
R022 ^c	569 \pm 84	270 \pm 21	512 \pm 88
Reference value/wt%	0.058	0.025	0.051
R023	27 \pm 9	34 \pm 3	150 \pm 43
Reference value/wt%	0.003	0.003	0.015
Silicon nitride			
R003	2 \pm 0.4 ^d	2 \pm 0.3	40 \pm 4
Reference value/wt%	<0.0001 - <0.0006	<0.0001 - <0.0013	0.0042 \pm 0.0004
R004	328 \pm 16	35 \pm 2	284 \pm 57
Reference value/wt%	0.035 \pm 0.002	0.0036 \pm 0.0005	0.028 \pm 0.001

a. Calibration curves were prepared by mixed standard solution.

b. Number of measurements was 4 - 5.

c. Ar gas was not interrupted at atomization stage.

d. Analytical line of 309.3 nm for aluminum was used.

Typical absorption patterns of these analytes in various samples are illustrated in Fig. 4. All absorption-time profiles showed symmetric patterns and no shoulder. Accordingly, it was thought that a single chemical species of each analyte might be produced in the pyrolysis process under the proposed experimental condition. Based on these absorption-time profiles, it was found that 17 s of atomization time was sufficient.

Simultaneous direct determination of aluminum, calcium and iron in silicon carbide and silicon nitride powders

In order to confirm the accuracy of the proposed method, silicon carbide and silicon nitride powdered reference materials were analyzed. The calibration curves were prepared using the standard addition solution containing aluminum, calcium and iron. The analytical results given in Table 3 are in good agreement with the reference values. Furthermore, the slopes of the calibration curves prepared by the standard addition method were almost the same as those prepared by the mixed standard solution, containing aluminum, calcium and iron. Therefore, it was found that an accurate determination could be made by using calibration curves prepared by the mixed standard solution, thus allowing for a quicker analysis. Table 4 gives the analytical results obtained by using calibration curves prepared by the mixed standard solution. They are in good agreement with the reference values.

The detection limits for aluminum, calcium and iron were 0.6

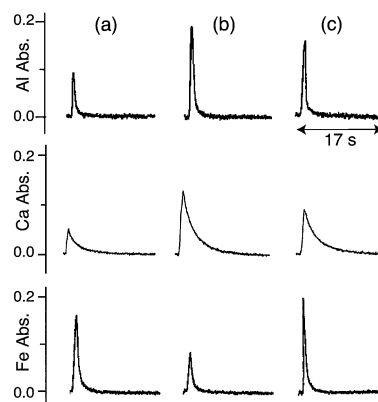


Fig. 4 Absorption-time profiles of analytes in various samples: (a) a 10 μl portion of 0.1 mg/l mixed standard solution, (b) a 5 μl portion of R021 silicon carbide slurry, 20 mg/20 ml, (c) a 5 μl portion of R004 silicon nitride slurry, 20 mg/20 ml.

$\mu\text{g/g}$, 0.15 $\mu\text{g/g}$ and 2.5 $\mu\text{g/g}$, respectively, in solid samples, when 200 mg of powdered sample was suspended in 20 ml of 0.1 M nitric acid and a 10 μl portion of the slurry sample was then measured. Although the highest sensitive wavelength for iron, 248.3 nm, was chosen in this study, the actual sensitivity was lower than expected. We attributed this to the fixed slit width of this instrument, 1.3 nm; also, the sensitivity might be affected by the less-sensitive line, 248.8 nm. The RSD precision of the determination of aluminum, calcium and iron was 5 - 33%.

In conclusion, the proposed method has proved to be a fast and accurate means for the simultaneous direct determination of aluminum, calcium and iron impurities in silicon carbide and silicon nitride powders.

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