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Determination of silicon and aluminum in silicon carbide nanocrystals by high-resolution continuum source graphite furnace atomic absorption spectrometry

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ABSTRACT

The determination of Al contaminant and the main component Si in silicon carbide (SiC) nanocrystals with the size-distribution of 1–8 nm dispersed in an aqueous solution was developed using high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS-GFAAS). The vaporization/atomization processes were investigated in a transversally heated graphite atomizer by evaporating solution samples of Al and Si preserved in various media (HCl, HNO_3). For Si, the best results were obtained by applying a mixture of 5 μg Pd plus 5 μg Mg, whereas for Al, 10 μg Mg (each as nitrate solution) was dispensed with the samples, but the results obtained without modifier were found to be better. This way a maximum pyrolysis temperature of 1200 °C for Si and 1300 °C for Al could be used, and the optimum (compromise) atomization temperature was 2400 °C for both analytes. The Si and Al contents of different sized SiC nanocrystals, dispersed in aqueous solutions, were determined against aqueous (external) calibration standards. The correlation coefficients (R values) of the calibrations were found to be 0.9963 for Si and 0.9991 for Al. The upper limit of the linear calibration range was 2 mg/l Si and 0.25 mg/l Al. The limit of detection was 3 μg/l for Si and 0.5 μg/l for Al. The characteristic mass (m_0) was calculated to be 389 pg Si and 6.4 pg Al. The Si and Al content in the solution samples were found to be in the range of 1.0–1.7 mg/l and 0.1–0.25 mg/l, respectively.

1. Introduction

The purity of SiC nanocrystals prepared for using in vivo biological applications [1–3] is essential. Depending on the Al content of the starting materials, the produced SiC nanocrystals can be contaminated by Al. According to human health studies [4–6], Al has been identified as a potential contributory factor for Alzheimer disease, amyotrophic lateral sclerosis, and dementia. Therefore, the accurate determination of the amount of Al in the SiC nanocrystals, - hopefully used for biological monitoring in the future, - is of paramount importance.

The Al contents of several liquid samples have been investigated by various analytical chemical methods [7–14]. Aluminum was determined by means of electrothermal atomic absorption spectrometry (ETAAS) in samples of oil [7], drinking water [8], infusions of different brands of teas [9], wines [10], and natural water [11], and by means of inductively coupled plasma mass spectrometry (ICP-MS) in biological samples [12], by means of kinetic-differentiation-mode high performance liquid chromatography (HPLC) in human serum [13] and by high resolution continuum source (HR-CS) GFAAS in pharmaceutical products [14].

Silicon is an essential trace element in humans and also quite important element in industry. Various methods have already been developed for the determination of the Si content in different biological and industrial samples. The Si content of biological and food samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) [15–17], and graphite furnace atomic absorption spectrometry (GFAAS) [18,19]. In the semiconductor and steel industry, Si was determined by ICP-MS [20,21]. Solid sampling GFAAS was used to determine trace amounts of silicon in polyamide [22] and HR-CS flame atomic absorption spectrometry to investigate the Si content of lubricating oil [23].

HR-CS-GFAAS allows detecting/determining more than 70 elements without the need for changing the primary light source. Another important advantage of this technique is that it can be used for measuring several non-metals [24,25]. Although commercial equipment for this technique has only been available for a

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Table 1
Optimal furnace programs for determining the Si and Al content in water-dispersed SiC samples.

Step	Temp. (°C)	Ramp (°C/s)	Hold (s)	Time (s)	Internal furnace gas (Ar) flow (l/min)
Drying 1	80	6	20	26.2	2
Drying 2	90	3	20	23.3	2
Drying 3	110	5	10	14	2
Pyrolysis 1	350	50	20	24.8	2
Pyrolysis 2	1200(Si) 1300(Al)	300	10	12.8(Si) 13.2(Al)	2
Gas adaption	1200(Si) 1300(Al)	0	5	5	0
Atomization	2400	1500	5	10.8	0
Clean-out	2500	500	4	4.2	2

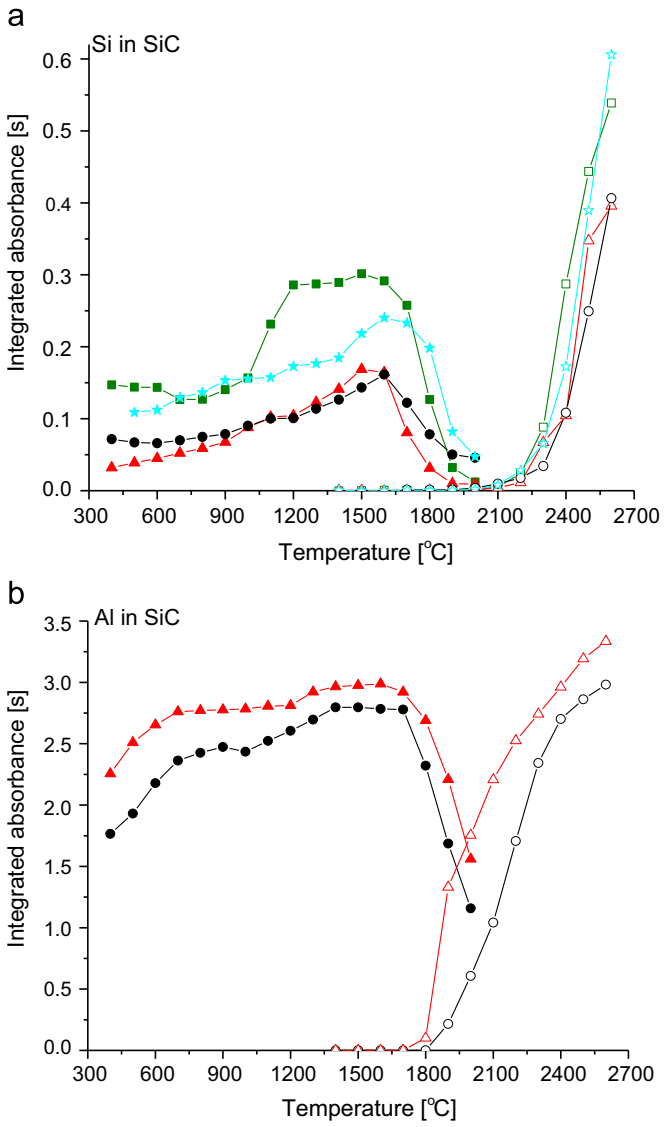

Fig. 1. Pyrolysis and atomization curves of (a) Si and (b) Al, recorded with sample SiC-1 using different various chemical modifiers. Square legends corresponds to the curves using Pd/$Mg(NO_3)_2$ modifier, round legends to $Mg(NO_3)_2$ modifier, the stars to Pd modifier and triangle ones obtained without any modifier. The full legends denote the pyrolysis while empty legends the atomization curves.

few years, several methods for measuring various elements have been already studied. The technique has been successfully applied in the analysis of halogens in their molecular forms [26–30], in

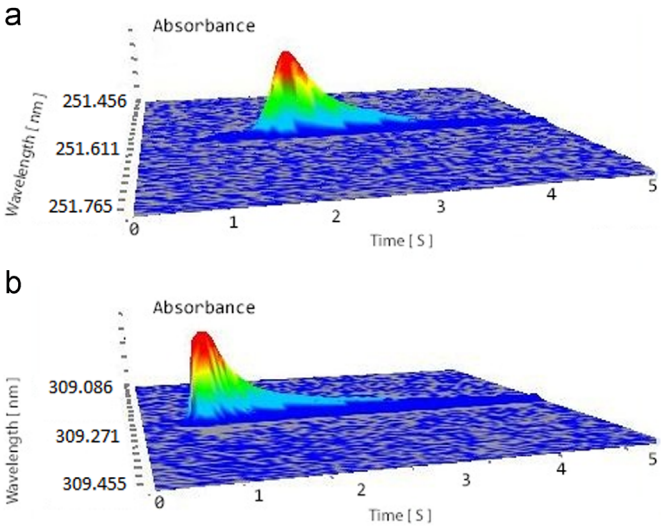

Fig. 2. Typical 3D GFAAS spectrum of 24.8 ng Si (a) and 4 ng Al (b) in SiC-1 solution.

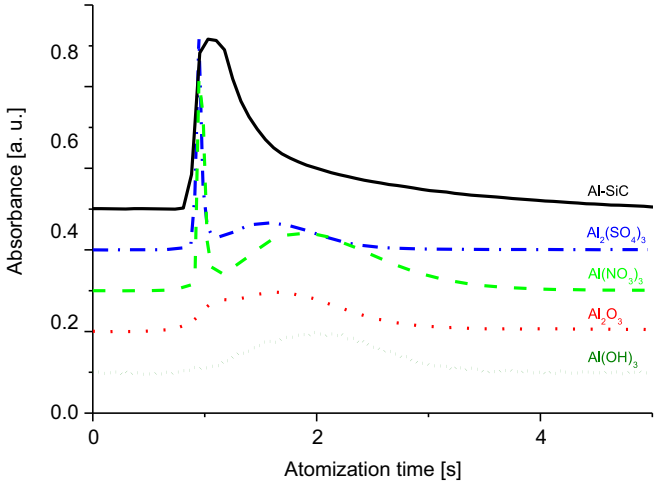

Fig. 3. GFAAS spectra of various aluminum compounds, dissolved or dispersed in distilled water, each with ~4 ng Al (baselines are shifted by 0.1 absorbance unit for better visualization).

food analysis [31,32], as well as in environmental applications [33,34].

In our laboratories, SiC nanocrystals are prepared by wet chemical etching techniques [35]. Due to the limitations of the synthesis, low volumes of the host material can be manufactured in a batch (1–2 ml). The primary goal of the present work was to develop an accurate method for determining the Si and Al content of SiC nano-materials by means of HR-CS-GFAAS, utilizing low amounts (some micrograms) of solid materials in small sample volumes (microliters).

2. Experimental

2.1. Instrumentation

The HR-CS-GFAAS measurements were carried out on a ContrAA-700 tandem spectrometer (Analytik Jena AG, Jena, Germany) equipped with a transversally heated graphite atomizer (THGA) tube. Sample and standard solutions were injected by an MPE-60 (Analytik Jena AG) autosampler throughout a dosing hole into the PIN-platform of the pyrolytic graphite coated graphite tubes