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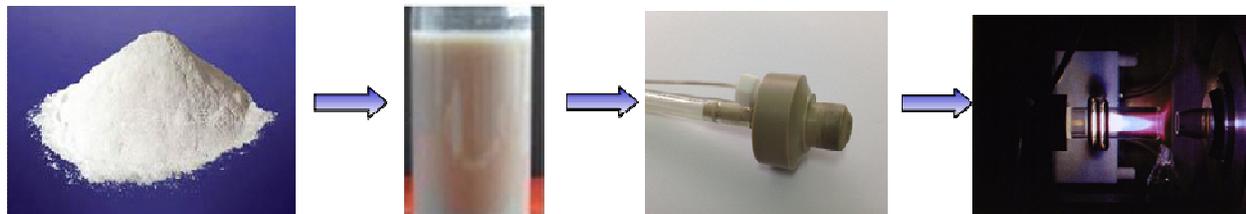
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Graphical Abstract



A simple, rapid and reliable method was developed for the determination of trace impurities in high-purity silicon nitride (nm- and μm -sized) by ICP-OES using a slurry nebulization technique .

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ARTICLE

Direct determination of trace impurities in high-purity silicon nitride by axial viewed inductively coupled plasma optical emission spectrometry using slurry nebulization technique

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Zheng Wang^{a*}, Junye Zhang^a, Guoxia Zhang^a, Deren Qiu^b and Pengyuan Yang^{b*}

The dispersive effect of polyacrylate amine (NH₄PAA) upon suspensions of silicon nitride (Si₃N₄) is considered. Slurry introduction for axial inductively coupled plasma optical emission spectrometry determination of Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni and Ti in powdered Si₃N₄ has also been investigated. Characterization by zeta potential measurement and slurry stability measurements shows that NH₄PAA is a good dispersant for the preparation of Si₃N₄ suspensions. The optimal concentration of NH₄PAA was 0.8 wt% for μm-sized Si₃N₄ and 1.2 wt% for nm-sized Si₃N₄. The analytical results obtained using nm and μm-sized Si₃N₄ by slurry introduction were in good accordance with results obtained by the high-pressure acid deposition method, thus verifying that calibration curves could be established using aqueous standards. By introducing a low amount of contamination in the sample preparation, an accurate result is obtained for the detection of contamination-risk elements such as K and Na, which cannot be accurately determined by the high-pressure acid deposition method. The limits of detection, which are in the range of 8–250 ng·g⁻¹, were shown to be superior to those of the conventional nebulization technique with ICP-OES or ICP-MS.

Introduction

Powdered silicon nitride (Si₃N₄) is being increasingly used as one of the basic materials for producing advanced ceramics.¹ Due to its special properties such as firmness, low density, chemical and thermal stability, low thermal expansion coefficient, and high conductivity resistance, silicon nitride is widely used in a number of industrial fields such as the manufacture of engine parts, bearings, cutting tools, crucibles, and even fusion reactor components. Furthermore, high-purity and nano-powdered silicon nitride is becoming important for applications in microelectronics and solar and space research. However, many of the desired properties of silicon nitride are influenced by trace impurities. Aluminum, magnesium, and iron influence the sintering behavior of silicon nitride powder;² alkali ions are known to decrease its resistance to oxidation by enhancing the mobility of oxide ions;³ and calcium, lithium, and sodium decrease the mechanical stability of silicon nitride ceramics at elevated temperatures.⁴ These effects necessitate appropriate analytical methods for the determination of trace impurities in powdered silicon nitride.

Inductively coupled plasma optical emission spectrometry or mass spectrometry (ICP-OES/MS) and atomic absorption spectrometry (AAS) are usually used for the analysis of trace elements in silicon nitride materials. Routine analysis with ICP-OES/MS and AAS requires converting the solid sample to a solution by chemical digestion and alkali salt fusion.⁵⁻⁷ However, Si₃N₄ is not easily completely solubilized, and the process is time-consuming and prone to contamination. In order to avoid these problems, direct solid analysis of the ceramics using solid sample introduction techniques has been investigated.^{3,8-11} With the use of electrothermal vaporization (ETV) ICP-OES,^{12,13} lower limits of detection could be achieved. However, the analyte matrix separation by vaporization is often incomplete, and, as a consequence, the difference in the behavior of Cu and Cr when processed from aqueous standards and from Si₃N₄ in the absence of fluorinating reagent means that calibration using an aqueous standard solution is not sufficiently accurate.

As a method of direct solid analysis, laser ablation-ICP-MS (LA-ICP-MS) has been used for quantitative determination of

trace metals in high-purity powders for the production of ceramics.¹⁴⁻¹⁶ However, the lack of appropriate standards or certified reference materials for a wide variety of samples of interest is problematic when using LA-ICP-MS for quantitative analysis. Furthermore, it is rather expensive for routine use.

The problems encountered with solution and solid sample introduction technology have led to the development of an alternative approach, which is to prepare the sample as slurry. Slurry introduction technology has been applied in atomic absorption spectrometry for many years.^{3,17} However, it cannot be used to conduct simultaneous multi-element analyses, and the process is time-consuming.

Slurry nebulization ICP-OES is simple to implement, it is inexpensive, and requires only minor instrument modification. Consequently, slurry introduction techniques for ICP-OES have been used for the analysis of many materials such as titanium dioxide,¹⁸ zirconium oxide,¹⁹ silicon carbide,²⁰ boron carbide,²¹ and magnesium niobate.²² Graule *et al.*³ analyzed high-purity Si₃N₄ powder by atomic emission and atomic absorption spectrometry. However, due to the particle size distribution of the powders and the stability of the slurry was not investigated in detail by this method, large deviations in the values obtained from the results of other analytical methods occurs, especially for Fe. Kim *et al.*⁵ conducted the analysis of Si₃N₄ using high-pressure acid digestion and slurry nebulization ICP-OES, but reported no detailed results for the technique. Zaray *et al.*²³ added Freon-12 (CCl₂F₂) to the plasma as a halogenation agent in order to increase the degree of evaporation of the slurry particles. However, negative deviation was observed in the results and it could not be completely eliminated because of the difference in the nebulization efficiency of the solution and the slurry. Therefore, this technique is only applicable for the quality control of well-defined types of materials, rather than high-accuracy analysis.

It is well known that transport and nebulization efficiency are strongly influenced by particle size and the stability and homogeneity of the aqueous slurries.²⁴⁻²⁷ For preparing stable and homogeneous aqueous slurries, the addition of a dispersing agent is generally recommended.^{18,25}

In this work, Si₃N₄ powders with various particle sizes, from the μm scale to the nm scale, were selected. Stable and homogeneous suspensions were prepared and characterized by various methods. The prepared slurries were nebulized and carried into an axially viewed ICP torch for determining their impurities. The results are presented and discussed.

Experimental

Instrumentation and operating conditions

All analyses were conducted on a ICP-OES spectrometer configured for axial viewed (VISTA AX, Varian, American). The sample introduction system consisted of a V-groove nebulizer and a reduced-volume Sturman-Masters Type spray chamber made of polytetrafluorethylene (PTFE). Zeta potentials of the suspensions were measured by a Zeta-Plus Analyzer (ZetaPALS, Brookhaven Instruments, USA). All the

ultrasonic processing operated on an ultrasonic bath (DS-3510DTH, Kincaid Shanghai Analytical Instruments Co., China). The operating parameters and selected analytical spectral lines are given in **Tables 1** and **2**, respectively.

Table 1. Instrumentation and operating conditions

Spectral range	167-785 nm
Viewing	Axial
RF generator	40 MHz
Torch	All-quartz
Injector tube diameter	2.3 mm
Power	1.25 kW
Plasma flow	15 L·min ⁻¹
Auxiliary flow	1.5 L·min ⁻¹
Nebulizer flow	0.65 L·min ⁻¹
Replicate read time	3 s
Replicates	3
Instr. Stabilization delay	20 s
Sample uptake delay	25 s
Rinse time	10 s
Sample uptake rate	0.8 mL·min ⁻¹

Table 2. Selected analytical lines

Element	Spectral lines/nm
Al	396.152
Ca	422.673
Co	238.863
Cr	267.716
Cu	324.754
Fe	238.204
K	766.491
Mg	285.213
Mn	257.610
Na	589.592
Ni	216.556
Ti	334.188
Si	288.158

Reagents and materials

All reagents were of guaranteed grade. The solutions were prepared with Milli-Q water (18 MΩ·cm). The multi-element working standards were prepared from 1000 mg·L⁻¹ aqueous standards (Shanghai Institute of Measurement and Testing Technology, Shanghai, China). The blank and calibration standards were prepared containing the same amount of dispersant.

Si₃N₄ samples with various particle sizes were selected for testing. The sub-μm particle sized Si₃N₄ (OBE10 (mean size = 0.27 μm)) and ED101 (mean size = 0.25 μm) (Federal institute for materials research and testing, Germany) were directly utilized without grinding. The distribution of particles is illustrated in **Figure 1(a)** and **(b)**. The particle sizes of the Si₃N₄ were determined by a Photo-Sedimentometer (SICAS-4800, Shanghai Institute of Ceramics, CAS). Another sample source was nm-sized Si₃N₄ (Hefei Kiln Nanometer Technology Development Co. Ltd, China). The particle size was gained from Field emission scanning electron microscope (SEM) (SU-8220, Hitachi, Japan) image (**Figure 1(c)**).

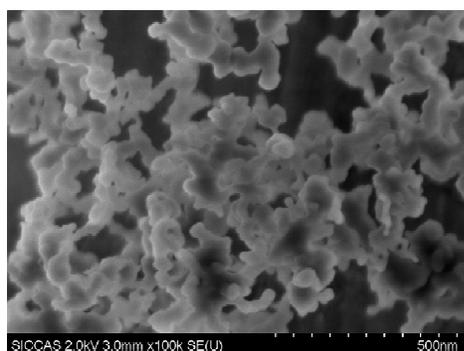
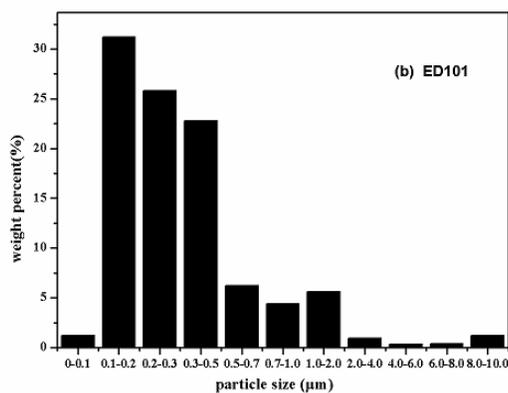
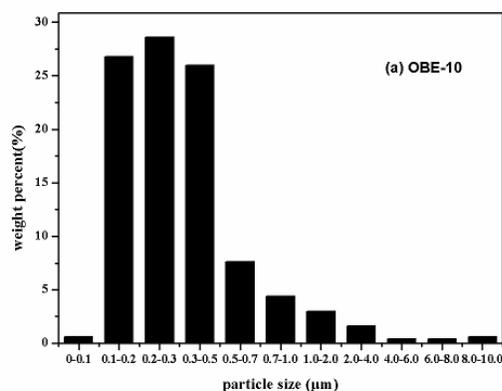


Figure 1. Bar diagram for silicon nitride particle size distribution in (a) OBE10 and (b) ED101; SEM micrographs of distribution of nm-size Si_3N_4 particles (c)

Sample preparation

A slurry was prepared by weighing the Si_3N_4 sample, and then transferring it to a 100 mL volumetric flask containing the dispersant NH_4PAA (Aldrich Chemical Co., USA). The pH was adjusted to 6 with aqueous HCl or NH_3 . The slurry was mixed ultrasonically before measuring particle size distributions to ensure that only the mobility of single particle was measured.

For the ICP-OES analysis of the solution, 0.2 g sample was digested with 5 mL of HNO_3 and 5 mL of HF in an autoclave system for 10 h at 180 °C. The resulting sample solution was then evaporated to dryness under an IR lamp, and the residues

were transferred to a polyethylene volumetric flask and made up to 20 mL with 5% HNO_3 .

Results and discussion

Influence of pH on the slurry stability

A highly stable and homogeneous slurry is critical to obtaining accurate analytical results. Therefore, it is necessary to optimize the conditions of the slurry preparation. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory,^{28,29} there are two factors in effect on the particle surface: van der Waals attraction and electrostatic repulsion. Slurry flocculation occurs if the van der Waals attraction overcomes the electrostatic repulsion. The zeta potential of the slurry represents the electrostatic interaction between particles in the dispersion. To obtain a stable and homogeneous slurry, preparation conditions such as the pH of the solution and the type and amount of the dispersant can be optimized.

The particles in the agglomerated form have a static charge originating from the intrinsic charged groups or from the adsorption of charged molecules or groups coexisting in the medium, such as H^+/OH^- . The charge on the particles is characterized in terms of zeta potential and can be determined by electrophoretic mobility. The zeta potential of the particles depends on their chemical form and varies with the medium, especially the pH conditions therein. The case where the zeta potential of a particulate matter reaches zero is defined as the isoelectric point (IEP) of the matter and is identified in terms of the pH value of the sample. The reader is directed to Farinas *et al.*²⁷ and Ebdon *et al.*³⁰ for a more detailed treatment of this subject. At the IEP, the slurry will be unstable and the particles will be agglomerated. The slurry is stable only when the zeta potential is significantly different from the IEP.

Figure 2 shows the relationship of the zeta potential vs. pH. It is clear that the zeta potential varies with pH. The IEP of the nm- and μm -sized Si_3N_4 particle are observed at pH 3.0–4.0. The stability could be achieved in alkaline media for both nm- and μm -sized Si_3N_4 particles, as the zeta potential is high and sufficiently separated from the IEP in this pH range (**Figure 2**). However, the viscosity of the slurry became very high under basic conditions, making comparison to the aqueous standards difficult.²⁷ Bearing these factors in mind, pH 6.0 was selected for this research.

Effect of dispersant type and amount on stability

Polyelectrolytes are widely used as dispersants for the preparation of ceramic powder suspensions. Owing to the combined effect of both electrostatic and steric stabilization, absorbed polyelectrolytes create a large energy barrier, which prevents the colloid particles from flocculating. However, it is well known that the surface charge properties of different

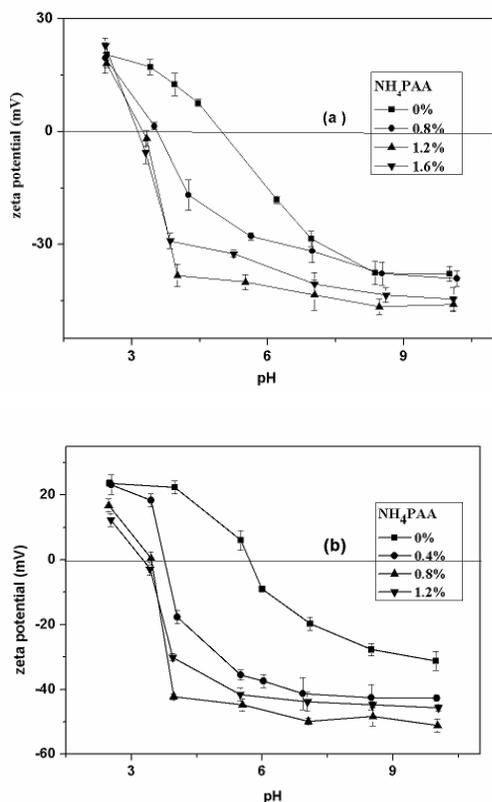


Figure 2. Zeta potential vs. pH for Si₃N₄ slurries at different NH₄PAA concentrations. (a. nm size, b. μm size)

ceramic powders vary with the type of powder, and in some cases even with the manufacturer. Accordingly, an adequate dispersant should be properly selected for each individual ceramic sample.^{25,27}

Figure 2 shows the zeta potential of nm- and μm-sized Si₃N₄ slurry vs. pH at different NH₄PAA concentrations. The IEP is shifted to the acidic zone with NH₄PAA addition. However, the concentration of the dispersant should also be controlled because excessive dispersant decreases the stability of the slurry and increases its viscosity.²⁷ From **Figure 2**, it is clear that 1.2 wt% NH₄PAA is suitable for dispersing the nm-Si₃N₄ powder, while 0.8 wt% NH₄PAA is suitable for the μm-Si₃N₄ powder. The zeta potential was essentially less than -40 mV at pH 6.0 (**Figure 2**).

The dispersion effect can also be illustrated by comparing the slurry intensity. Slurry stability was investigated as shown in **Figure 3**. The nm-sized Si₃N₄ slurry with no dispersant at IEP displayed instability, as shown in **Figure 3(a)**. The normalized intensities of matrix Si and impurities Fe and Al in a nm-Si₃N₄ slurry with 1.2 wt% NH₄PAA (**Figure 3(b)**) showed good stability with time. Thus, NH₄PAA plays an important part in stabilizing the slurry.

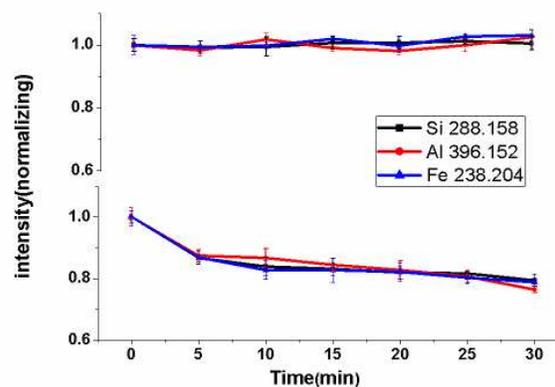


Figure 3. Intensity vs. time for Si₃N₄ slurries at pH 6.0. (a. nm without dispersant; b. nm with 1.2 wt% NH₄PAA)

Calibration

Technically, the physicochemical processes of the slurry will be comparable with an aqueous solution while the particles in the slurry are small enough, and the slurry is stable. This affords the possibility of calibration with aqueous standards. Most of the published reports indicate that the particle size distribution of a slurry is an important factor in such calibration. These studies reported that slurry particles larger than 5 μm (in some reports 2 μm) do not reach the plasma and result in a loss of signal.³⁰ For the analysis of advanced ceramic materials by using slurry nebulization ICP-OES with aqueous standard calibrations, incomplete vaporization caused negative deviations from published values.

The particle size is the limiting parameter for efficient slurry nebulization, and the maximum particle size of the slurry must be such that any single solid particle can occupy an aerosol droplet. To achieve a particle size distribution that would yield results similar to those of an equivalent equimolar aqueous solution, preparing slurries in an aqueous solution alone is unsuitable for the majority of samples owing to flocculation effects, which result in a rapid sedimentation of the finely powdered material. To obtain accurate analytical results, it is therefore essential to prepare a stable and homogeneous slurry that will yield a stable, homogeneous aerosol spray for introduction into the plasma. This is achieved by employing stabilizing agents, commonly termed “dispersants” or “surfactants.”

Figures 1 (a) and **(b)** show that the particle size of the OEB10 and ED101 Si₃N₄ powder is less than 5 μm, while the specification **Figures 1(c)** shows that the size of the nm particles is far less than 1 μm. The dispersing effect of NH₄PAA can also be verified by comparing the SEM micrographs of the sediments. The SEM micrographs of μm particle has been chosen and shown in **Figure 4**. Large flocs are observed in the sediments of suspensions without any dispersant (**Figure 4(a)**), while particles of the sediments with 0.8 wt% NH₄PAA (**Figure 4(c)**) are well dispersed and not

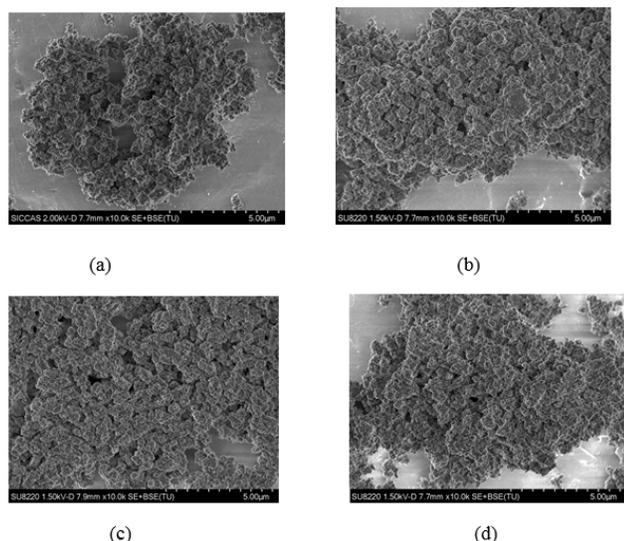


Figure 4. SEM micrographs of sediments from a 2 wt% Si_3N_4 μm particle suspension at pH 6.0 (a) Without dispersants at $\times 20000$, (b) with 0.4 wt% NH_4PAA dispersant at $\times 20000$, (c) with 0.8 wt% NH_4PAA dispersant at $\times 20000$, and (d) with 1.5 wt% NH_4PAA dispersant at $\times 20000$.

associated with each other. Large flocs are also observed in the sediments of suspensions with 0.4 wt% NH_4PAA (Figure 4(b)) and with 1.5 wt% NH_4PAA (Figure 4(d)) because of less and excessive dispersant. The dispersing effect of NH_4PAA for nm-sized Si_3N_4 was the similar to μm -size Si_3N_4 .

For the slurry to be efficiently nebulized, vaporized, and atomized, the particle size distribution is crucial. When the introduced slurry is completely desolvated by evaporation and the mean particle size is less than $5 \mu\text{m}$,³¹ simple aqueous standards can be used to establish the calibration curves, because the atomization process experienced by the slurry particles is the same as that experienced by aerosols. Slurry sampling for Si_3N_4 has already been reported, but not all of the reports gave accurate results. This may be the reason that previous research work showed that a slurry cannot be calibrated with aqueous standards, even when the particle is small.

Micro and trace elements (Al, Ca, Cr, Cu, Fe, Mg, Mn, Na, Ni and Ti) in μm -sized Si_3N_4 and (Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni and Ti) in nm-sized Si_3N_4 were determined by using a slurry method, and the results were compared with those obtained by using the established acid digestion method. In our analysis, we obtained accurate results for impurities in two different particle-sized Si_3N_4 slurries determined by calibration with aqueous standards. The results determined by the slurry introduction method were in good accordance with the reference values, thus verifying that calibration curves can be accurately established with aqueous standards.

Limits of detection (LOD)

The LODs expressed as three times the standard deviation (SD) of the blank control samples obtained from high-purity Si_3N_4 are given in **Table 3**. The LODs are compared with those obtained by other methods (Nebulization-ICP-OES (Neb-ICP-OES),³² Slurry neb-ICP-OES,³ slurry sample-Electrothermal AAS (SS-ETAAS),¹⁷ Solution-ETAAS,¹⁷ radiation neutron activation analysis (RNAA),³³ and ICP-MS³²). The superiority of our slurry nebulization technique is evident. Due to the possibility of controlling the blank water sample prior to the preparation of the slurry, extremely low limits of detection are obtained for the contamination risk elements Ca, Fe, K, Na, being 2–50 times lower than those of the solution method. Thus, mainly due to the limitation of the control, the instrumental detection power of ICP-MS cannot be exploited using wet chemical procedures. In these cases, a low amount of contamination was introduced during the sample preparation, and has good S.D. values for stable suspension. Comparatively, SS-ETAAS was consistently better than all other methods owing to the extremely low blanks, large applicable sample volumes, high transport efficiency, and the addition of Freon-12.

Table 3. Limits of detection ($\text{ng}\cdot\text{g}^{-1}$) for high-purity Si_3N_4 using slurry ICP-OES, with comparisons to those reported by other methods

Element	This work	Other Methods					ICP-MS ³²
		Neb-ICP-OES ³²	Slurry neb-ICP-OES ³	SS-ETAAS ¹⁷	Solution-ETAAS ¹⁷	RNAA ³³	
Al	100	300	2500	90	90	--	150
Ca	20	1000	80	--	--	--	300
Co	60	200	--	--	--	--	3
Cr	100	50	--	6	70	1	20
Cu	80	20	500	50	20	60	10
Fe	80	200	700	90	300	50	600
K	200	1000	--	4	150	35	500
Mg	120	200	50	7	60	--	25
Mn	8	10	--	6	6	2	10
Na	100	200	--	12	1200	0.6	200
Ni	250	500	--	--	--	--	10
Ti	8	50	400	--	--	--	10

SS : slurry sample introduction

Analysis of Si_3N_4 samples and comparison with reference values

The results obtained using our slurry nebulization and using solution nebulization for the analysis of Si_3N_4 powders with various particle sizes are summarized in **Tables 4** and **5**. For the nm-sized Si_3N_4 the values are compared with those from the acid digestion method. The ED101 μm -sized Si_3N_4 is also compared with the reference values (**Table 5**). The good agreement in the results for this technique proves that satisfactory accuracies are achievable with this technique. The RSD of results in **Table 4** and **Table 5** ranged from 1.1% (Al) to 4.9% (Ni). As can be seen in **Table 5**, the experimentally

determined concentrations were in agreement with reference values at the 95% confidence level in all cases. In the case of Al, the experimentally determined value of $471 \pm 21 \mu\text{g}\cdot\text{g}^{-1}$ is in agreement with the reference value of $469 \pm 12 \mu\text{g}\cdot\text{g}^{-1}$ at the 95% confidence level using a Student's t-test ($t_{\text{calc}}=1.25$, $t_{\text{table}}=2.44$). The results show that K and Na can only be determined directly by slurry introduction rather than acid decomposition for some samples, this being due to the fact that slurry introduction is loss less and avoids contamination.

Table 4. Comparison of analytical results ($\mu\text{g}\cdot\text{g}^{-1}$) for two different sizes of Si_3N_4 particles, determined with slurry introduction and calibrated with aqueous standards

Element	Kaier (mean size < 50 nm)		OBE10 (mean size = 0.27 μm)	
	Slurry	Acid digestion	Slurry	Acid digestion
Al	2.7 ± 0.3	2.6 ± 0.2	9.7 ± 0.3	10.1 ± 0.3
Ca	9.4 ± 0.1	9.4 ± 0.2	2.5 ± 0.2	2.6 ± 0.2
Cr	2.1 ± 0.2	2.1 ± 0.05	2.3 ± 0.2	2.5 ± 0.3
Cu	5.1 ± 0.2	5.0 ± 0.4	0.1 ± 0.02	—
Fe	47.2 ± 5.2	46.5 ± 1.8	10.4 ± 0.3	10.6 ± 0.4
K	0.2 ± 0.1	—	—	—
Mg	1.4 ± 0.2	1.6 ± 0.1	1.1 ± 0.1	1.1 ± 0.1
Mn	0.7 ± 0.1	0.7 ± 0.1	0.2 ± 0.02	0.2 ± 0.04
Na	0.23 ± 0.06	—	0.40 ± 0.03	—
Ni	2.2 ± 0.2	2.2 ± 0.1	1.4 ± 0.1	1.4 ± 0.1
Ti	2.6 ± 0.1	2.6 ± 0.3	1.2 ± 0.1	1.3 ± 0.1

Table 5. Comparison of analytical results ($\mu\text{g}\cdot\text{g}^{-1}$) for Si_3N_4 , determined by slurry introduction, calibrated with aqueous standards and published reference values

Element	ED101 (mean size = 0.25 μm)		
	Slurry	Acid digestion	Reference values
Al	471 ± 21	474 ± 18	469 ± 12
Ca	14.2 ± 0.8	14.2 ± 1.0	14.4 ± 0.5
Co	42.6 ± 1.0	43.1 ± 1.2	43.5 ± 0.8
Cr	1.4 ± 0.1	1.3 ± 0.2	—
Cu	0.2 ± 0.1	0.2 ± 0.1	—
Fe	79.7 ± 1.4	80.0 ± 1.2	79.5 ± 1.3
K	2.2 ± 0.4	2.2 ± 0.4	—
Mg	4.1 ± 0.3	4.2 ± 0.5	4.3 ± 0.4
Mn	0.2 ± 0.1	0.3 ± 0.1	—
Na	7.64 ± 0.26	8.84 ± 0.39	7.59 ± 0.27
Ni	3.0 ± 0.2	2.7 ± 0.3	—
Ti	3.2 ± 0.3	3.0 ± 0.2	—

Mean value \pm 3 SD (n = 5)
 — : Not-detected

Conclusions

A simple, rapid, and reliable method was developed for the determination of trace impurities, including Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, and Ti in high-purity silicon nitride using a slurry nebulization ICP-OES method. The stable and homogeneous slurry can be prepared by the addition of only 0.8 wt% NH_4PAA for μm -sized Si_3N_4 and 1.2 wt% for nm-sized

Si_3N_4 , both at pH 6.0. The analytical results obtained with slurry introduction were compared with those via nebulization of aqueous solutions prepared by the acid decomposition method. The nm- and μm -sized Si_3N_4 can be directly and accurately analyzed using slurry nebulization into ICP-OES with aqueous standard calibration. Using a small contamination introduced in the sample preparation, the LODs, which are in the range of 8–250 $\text{ng}\cdot\text{g}^{-1}$, were shown to be superior to those of the conventional nebulization technique with ICP-OES or ICP-MS.

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Notes and references

^aShanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.

^bDepartment of Chemistry, Fudan University, Shanghai 200433, China.

*Corresponding author: Fax: (+86)21-52413016; E-mail: wangzheng@mail.sic.ac.cn

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