APPLICATION NOTE

ICP - Mass Spectrometry

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Analysis of SiO_2 Nanoparticles in Reaction Mode with Single Particle ICP-MS

Introduction

With the development of nanotechnology and the increased use of nanoparticles in various products and processes, the need to characterize nanoparticles has also increased. Nanoparticles of various compositions are manufactured and used in a variety of products and processes, including paint, strengthening of materials, fine polishing in semiconductor processes, as well as moisture absorption prevention of medicine and food. Silicon dioxide (SiO_2) nanoparticles are the second largest domestically produced nanomaterials in Japan after carbon black.[1]

Measuring silicon (Si) with ICP-MS is challenging. The presence of $^{14}N_2^+$ and $^{12}C^{16}O^+$ polyatomic ions, which form in the plasma, have the same *m/z* as the most abundant Si isotope ($^{28}Si \approx 92\%$ abundance). As a result, the background at *m/z* 28 is very high when polyatomic ions are not removed (Standard mode). This background inhibits low-level Si determination and makes detection of SiO_2 nanoparticles difficult. In addition, the relatively high ionization potential of Si makes it more challenging to ionize, resulting in an intensity lower than other easily ionized elements, such as Na.

However, if the signal-to-background (S/B) ratio can be improved, there is the possibility to detect smaller SiO_2 nanoparticles. In a previous application note,[2] we reported that the 100 nm SiO_2 nanoparticle standard can be analyzed using SP-ICP-MS without interference removal (Standard mode). However, if the interference can be removed in Reaction mode, it is expected that smaller SiO_2 nanoparticles will be accurately measured.

This work will discuss the ability of SP-ICP-MS to detect, measure, and characterize SiO_2 nanoparticles using Reaction mode.

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Experimental

Sample Preparation

A known 50 nm SiO_2 nanoparticle standard, NanoXact™, was purchased from nanoComposix™ (San Diego, California, USA). The certified size is 50 ± 3 nm, as determined by transmission electron microscopy (TEM). Sample preparation involved sonicating the solutions for two minutes to break up any agglomerated particles, followed by dilutions with deionized water to yield final concentrations of about 100,000 particles/mL. The final solutions were sonicated again prior to analysis. Dissolved calibration curves were made by serial dilutions of a 1000 mg/L dissolved silicon standard. The silicon concentrations of the dissolved standards were 0, 5 and 10 µg/L Si. For the determination of nanoparticle transport efficiency (TE), 50 nm Au nanoparticles (PerkinElmer Part No. N8151035) at concentrations of 50,000 particles/mL were used. This study's determined TE was 8.9%.

Analysis and Instrumentation

All analyses were performed on a PerkinElmer NexION® 2000S ICP-MS equipped with Universal Cell Technology, using the Nano Application Module within Syngistix™ for ICP-MS software.

Optimal cell gas, cell gas flow and RF power for nanoparticle analysis have been determined from the results acquired in Standard mode. The dwell time was set to 50 microseconds because it is reported that the particle diameter and particle concentration can be measured more accurately at less than 100 microseconds.[3] The instrument parameters of Standard mode are shown in Table 1 and of Nano mode are shown in Table 2.

Table 1. NexION 2000S ICP-MS Instrument Parameters - Non-Nano Mode.

Parameter	Value
Sample Uptake Rate	100 µL/min
Nebulizer	PFA Concentric
Spray Chamber	Quartz Cyclonic
RF Power	1600 W
Analyte	^{28}Si
Cell Mode	Reaction
Cell Gas	NH_3, H_2+Ar (9:1), H_2

Table 2. NexION 2000S ICP-MS Instrument Parameters - Nano Mode.

Parameter	Value
Sample Uptake Rate	100 µL/min
Nebulizer	PFA Concentric
Spray Chamber	Quartz Cyclonic
RF Power	1600 W
Analyte	^{28}Si
Cell Mode	Reaction
Cell Gas	H_2
Dwell Time	50 µsec
Settling Time	0 sec
Analysis Time	60 sec/sample

Results and Discussion

Measurement of silicon (Si) with ICP-MS is challenging due to the polyatomic ions $^{14}N_2^+$ and $^{12}C^{16}O^+$ present at *m/z* 28. There are two types of interference removal techniques: collision cell technology using helium (He) gas and reaction cell technology using a reactive gas. Collision cell technology is a method of removing the interference ions by generating an energy difference between the analyte ion and the interference ion by collision of the He gas and establishing an energy barrier at the exit of the cell. On the other hand, reaction cell technology is a method of removing interferences by utilizing the difference in the reactivity between the analyte and interference with the cell gas. For these reasons, collision cell technology results in a large decrease of the intensity of the analyte ions, whereas the reaction cell technology maintains the intensity. Since nanoparticles produce a small signal intensity, reaction cell technology is the preferred technique to remove polyatomic ions.

In this study, various reaction gases were evaluated in Reaction mode: NH_3, H_2+Ar (9:1), and H_2. The relationship of the cell gas flow rate and intensity of blank and 50 ppb Si at *m/z* 28 are shown in Figure 1, along with the background equivalent concentration (BEC). All three cell gases can reduce the polyatomic interferences, resulting in improved BECs. Although the Si BECs are similar with all three gases, the Si intensity is lower with NH_3 than other gases.

These results can be explained by looking at the reaction chemistries.[4] Following are the reactions with ammonia:

$$N_2^+ + NH_3 \rightarrow NH_3^+ N_2 \qquad k \approx 10^{-9}$$

$$CO^+ + NH_3 \rightarrow NH_3^+ + CO \qquad k \approx 10^{-9}$$

$$Si^+ + NH_3 \rightarrow SiNH_2^+ + H \qquad k \approx 10^{-10}$$

While ammonia reacts faster with the interferences than Si^+ and improves the BEC, Si^+ intensity will be reduced because it also reacts with ammonia.

Following are the reactions with hydrogen:

$$N_2^+ + H_2 \rightarrow N_2H^+ H \qquad k \approx 10^{-9}$$

$$CO^+ + H_2 \rightarrow COH^+ + H \qquad k \approx 10^{-9}$$

$$Si^+ + H_2 \rightarrow \text{No Reaction}$$

Hydrogen reacts with the interferences at the same rate as ammonia, but because it does not react with Si^+, there is more sensitivity for Si^+ than with ammonia. Therefore, hydrogen is a more effective reaction gas.

The H_2/Ar gas mixture is less effective than pure hydrogen because of scattering losses as a result of collisions between Si^+ and Ar, due to the physical size of Ar, which is much larger than Si^+.

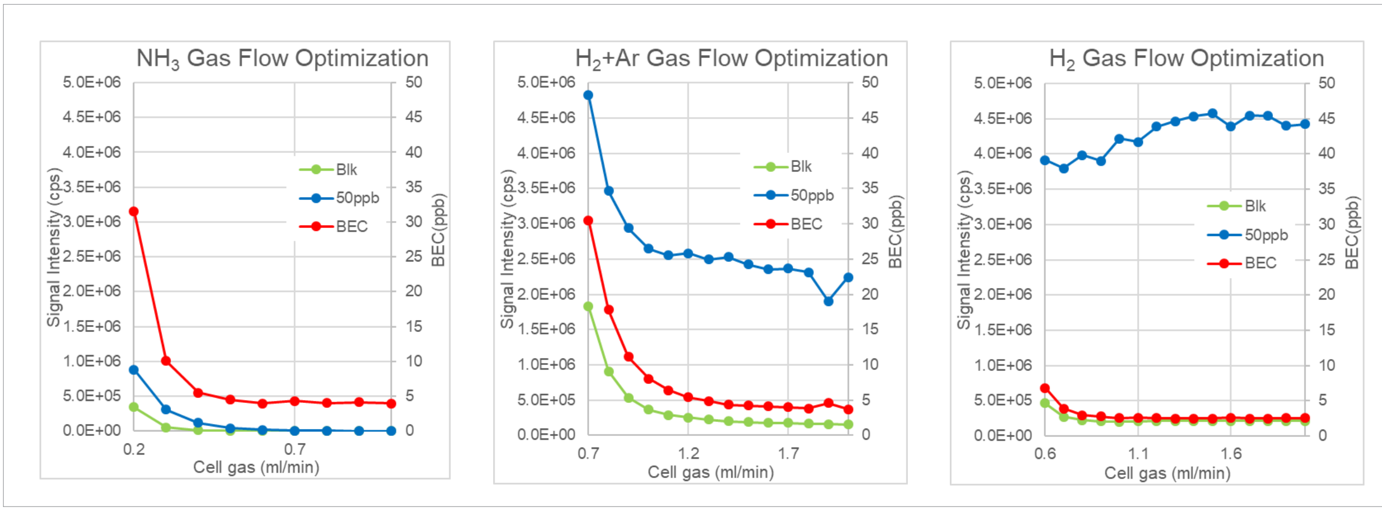

Figure 1. Cell gas flow rate vs. intensity and BEC of m/z 28 for NH_3, H_2+Ar (9:1), and H_2.

For SP-ICP-MS analysis, a Si calibration curve was first created, and then the SiO nanoparticle sample was measured three times. The obtained particle size histogram of SiO_2 nanoparticles is shown in Figure 2, with the x-axis representing particle size and the y-axis showing the number of particles measured. This histogram shows a symmetrical particle size distribution, centered at 49 nm. Table 3 shows that the measured particle size agrees with the certificate value, demonstrating the ability of SP-ICP-MS to accurately measure 50 nm SiO_2 nanoparticles.

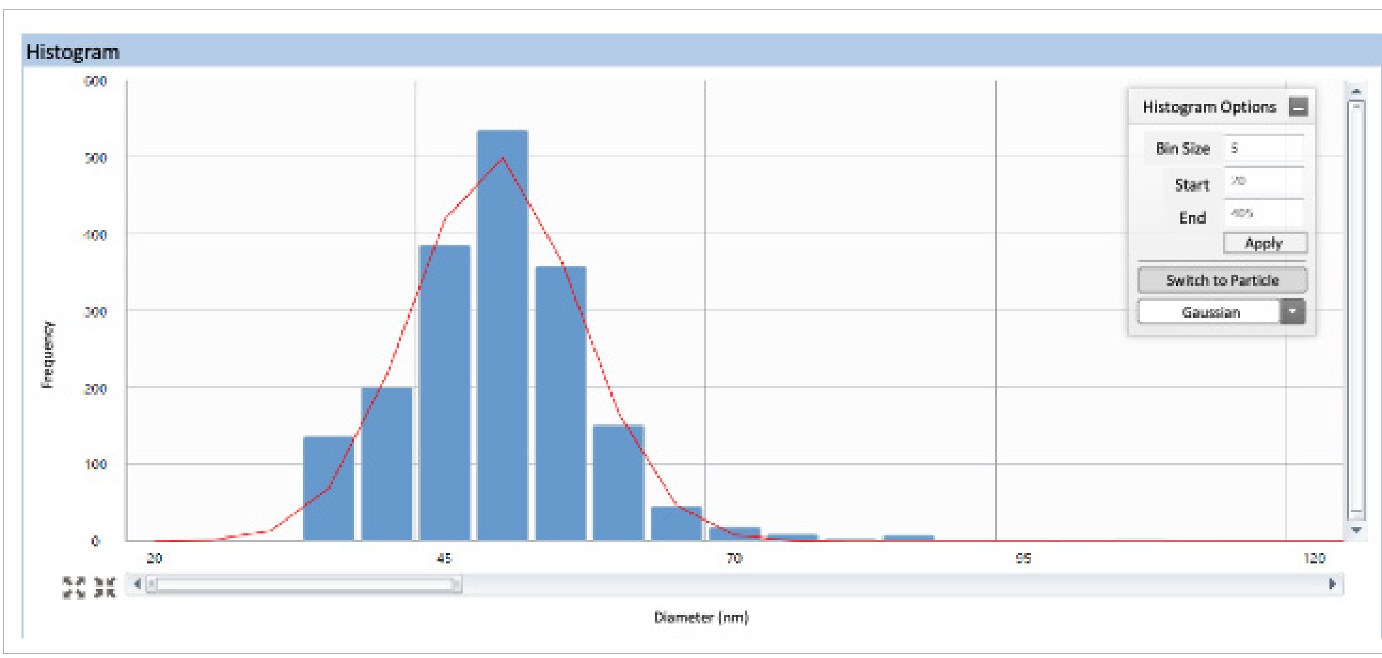

Figure 2. Size histogram of 50 nm SiO_2 nanoparticles analyzed by SP-ICP-MS.

Table 3. Size and Particle Concentration Results of 50 nm SiO_2 Nanoparticles Analyzed by SP-ICP-MS

Analyte	Mode	Mean Size (nm)	Certificate* (nm)	Particle Concentration (E+5 particle/mL)
28Si	H_2 Reaction	49 ± 0.29	50 ± 3	1.1 ± 0.065

* *as determined by transmission electron microscopy*

Conclusion

This work has demonstrated the ability to measure SiO_2 nanoparticles in Reaction mode using SP-ICP-MS. With the combination of short dwell times (< 100 µs) and Reaction mode, the NexION ICP-MS Single Particle Analyzer accurately measures 50 nm SiO_2 nanoparticles by reducing interferences while maintaining analyte intensity.

References

1. 2017 Nanomaterial Information Sheet, Changes in Nanomaterial Production Volume, METI Web Site (2018) https://www.meti.go.jp/policy/chemical_management/files/nanomaterial/2018suii.pdf (Final confirmation, September 11, 2019).
2. "Analysis of SiO_2 Nanoparticles in Standard Mode with Single Particle ICP-MS", PerkinElmer Application Note, 2015.
3. Hineman et al., "Effect of Dwell Time on Single Particle Inductively Coupled Plasma Mass Spectrometry Data Acquisition Quality" (J. Anal. At. Spectrom., 2014).
4. Anicich, V.G. "An Index of the Literature for Bimolecular Gas Phase Cation-Molecule Reaction Kinetics", Jet Propulsion Laboratory, 2003.

Consumables Used

Component	Part Number
Drain Tubing, Gray/Gray (1.30 mm id), Santoprene, (12)	N8152415
PFA-100 PFA Nebulizer, Self-Aspiration at 100 µL/min	N8152584
50 nm Au Nanoparticles	N8151035
Si Standard, 1000 µg/mL, 125 mL	N9303799
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)

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