Hyphenation of Field-Flow Fractionation and ICP-MS to Overcome the Size Limitations of spICP-MS for the Analysis of Silica Nanoparticles

General Information ID0072

Application	Food, Cosmetics, Paints, Semiconductor
Technology	AF4-MALS-ICP-MS and spICP-MS
Info	Postnova AF2000, PN3621 MALS, Agilent 7900 ICP-MS, PN1650 Smart Stream Splitting
Keywords	Asymmetrical Flow Field-Flow Fractionation, Multi-Angle Light Scattering, Inductively Coupled Plasma-Mass Spectrometry, Single Particle ICP-MS, Nanoparticles, Silica

Introduction

Field-Flow Fractionation (FFF) comprises a family of techniques, which provide high-resolution separation of sample constituents in the size range from a few nanometers up to tens of microns [1]. Its most common subtype is Asymmetrical Flow FFF (AF4). AF4 hyphenated with Multi-Angle Light Scattering (MALS) and ICP-MS has proven to be a powerful analytical tool for the characterization of nanoparticle-containing samples enabling simultaneous access to size distribution as well as size-resolved elemental composition [2, 3]. A schematic of the AF4 separation principle is shown in Figure 1.

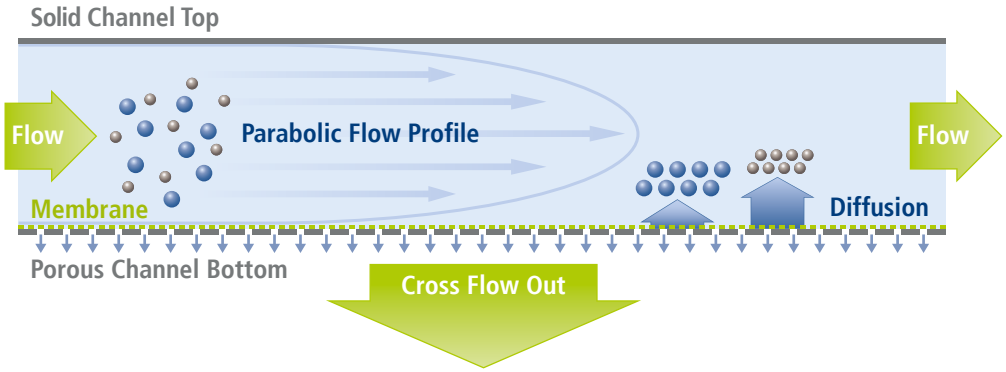

Figure 1: Schematic of the AF4 separation principle.

Within the last decade, single particle ICP-MS (spICP-MS) has emerged as a fast, highly sensitive and straightforward analytical technique that provides mass-, size- and number-based information of inorganic and metal nanoparticles at ppt concentration levels [4, 5].
In this application note we compare the performance of AF4-MALS-ICP-MS and spICP-MS for the characterization of silica nanoparticles particulary focusing on the lower size limit.

Experimental

In this study, a polydisperse colloidal silica mixture comprising five different sizes ranging from approx.10-300 nm (1 wt% each) was investigated. For spICP-MS measurements the suspension was diluted to 937 ng L^{-1} in ultrapure water. A single quadrupole ICP-MS (Agilent 7900 ICP-MS) was used with a dwell time of 100 µs. The nebulization efficiency was determined based on the size method and the ^{28}Si isotope was recorded.
For AF4-MALS-ICP-MS measurements the sample was used as received. The fractionation channel was equipped with a 5 kDa RC membrane and a mixture of 0.025 % NovaChem and 0.025 mM NaCl served as eluent. The separation method comprised a linear cross flow decay of 1.5 mL min^{-1} for 50 minutes followed by a smooth power gradient to end the separation field. To increase the sample concentration before reaching the detectors the channel flow was divided into a 0.1 mL min^{-1} pure solvent flow that was discarded and a 0.4 mL min^{-1} sample containing detector flow using the Postnova Postnova PN1650 Smart Stream Splitting device. Also the ^{28}Si isotope was monitored.

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Results

Especially for silica nanoparticles, spICP-MS measurements are challenging due to the presence of spectral interferences coming from elements ubiquitously present in the plasma (e.g. $^{14}N^{14}N^{+}$ and $^{12}C^{16}O^{+}$) overlapping with the signal of the most abundant Si isotope at m/z = 28 [6]. As a result, the background at m/z 28 is very high which makes the detection of silica nanoparticles difficult and causes a high size detection limit. With spICP-MS one large size fraction of around 295 nm was identified as shown in Figure 2. The high ionic background signal for silica resulted in a rather high lower size detection limit of 135 nm.

In contrast the AF4 technique was able to separate the sample into five distinct size fractions (Figure 3). The MALS detector delivered the corresponding radii of gyration of 6 nm, 11 nm, 28 nm, 43 nm and 117 nm (red dots) and the ICP-MS detection identified silicon in the particles.

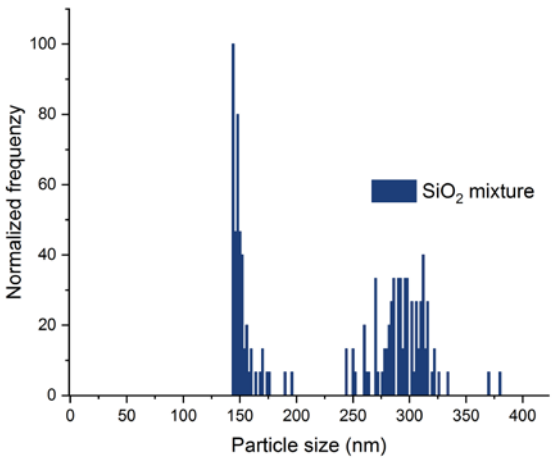

Figure 2: Obtained particle size distribution for the polydisperse colloidal silica mixture from spICP-MS analysis.

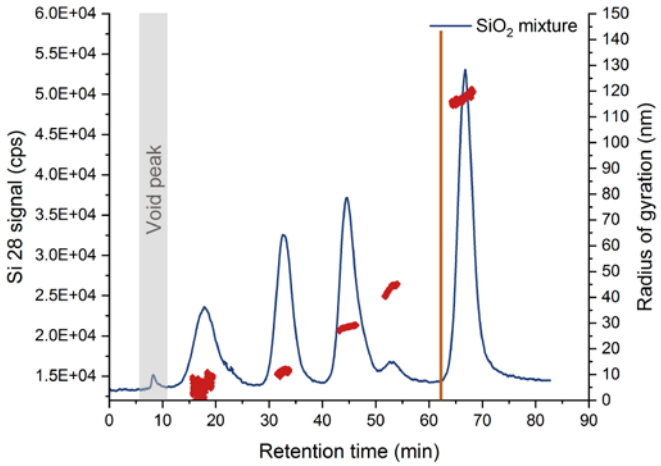

Figure 3: Obtained AF4-MALS-ICP-MS fractogram indicating five different silica particle size populations in the sample (blue trace: ^{28}Si signal; red dots: Radius of Gyration from MALS; orange line: lower size limit of spICP-MS).

Conclusion

While spICP-MS can provide fast access to particle mass- and number distribution of the larger silica particle size fraction (302 nm), it struggles with the smaller size fractions (< 135 nm) due to the high ionic background present in the sample and significant polyatomic interferences generated in the plasma torch.

AF4-MALS-ICP-MS is a powerful tool to overcome the size limitations that spICP-MS faces with metal oxide particles enabling accurate sizing of the investigated silica particles down to 15 nm (geometric diameter). Hyphenation of AF4 with single or even triple quadrupole spICP-MS is a promising route to further improve the size limit of spICP-MS. [7]

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Acknowledgements

Brant Kim from Entegris Koreo is gratefully acknowledged for providing the silica samples.

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