Field-Flow Fractionation with Single Particle ICP-MS as an Online Detector

General Information ID0039

Application	Nano
Technology	AF4-spICP-MS
Info	Postnova AF2000 MT, Postnova PN9050 ICP-MS Interface, Agilent 7900 ICP-MS
Keywords	Asymmetrical Flow Field-Flow Fractionation, Single Particle ICP-MS, Particle Number Size Distribution

Introduction

One of the challenges in characterization of complex nanomaterials in the environment is to obtain number based information such as concentration and size distribution at environmentally relevant concentrations.
The combination of Field-Flow Fractionation and Inductively Coupled Plasma Mass Spectrometry (FFF-ICP-MS) has been proven to be an essential analytical technique for characterization of environmental samples [1-3], but it lacks direct measurement of particle number. Single Particle ICP-MS (spICP-MS) is a new analytical technique to provide number based information for mono-dispersed metal and metal oxide nanoparticles at parts per trillion (ppt) concentration levels [4,5].
This application note reports direct hyphenation of spICP-MS to the Asymmetrical Flow FFF (AF4) system for size- and number-based characterization of a mixture of gold nanoparticles.

Experimental

A Postnova AF2000 Multiflow Asymmetrical Flow Field-Flow Fractionation (AF4) system was interfaced directly to an Agilent 7900 ICP-MS system. The AF4 effluent was directed into the ICP-MS nebulizer using a capillary connecting the outlet of the AF4 channel to the inlet of the ICP-MS nebulizer. A dilute mixture of 30 nm (NIST, RM8012, 27.6 nm (TEM)) and 60 nm gold nanoparticles (NIST, RM8013, 56.0 nm (TEM)) was used in the coupling experiment. The concentration of 30 nm and 60 nm nanoparticles in the mixture were 250 ppt and 1000 ppt, respectively. The ICP-MS system was operated in the spICP-MS mode.

A sequence of 54 replicates with an analysis time of 30 sec was constructed for the spICP-MS analysis. The time delay between each consecutive replicate was 14 sec. The sequence was started upon injection of the mixture into the AF4 system. Each replicate was stored separately and analyzed for particle number and size using Agilent MassHunter Workstation software. The number of counted nanoparticles and average diameter of the replicates were compiled and graphed manually using Microsoft Excel and OriginPro.

Figure 1: Postnova AF2000 MT and Agilent 7900 ICP-MS.

POSTNOVA

info@postnova.com
www.postnova.com

Postnova Analytics GmbH
86899 Landsberg, GERMANY
T: +49 8191 985 688 0

Postnova Analytics UK Ltd.
Worcestershire, WR14 3SZ, UK
T: +44 1684 585167

Postnova Analytics Inc.
Salt Lake City, UT 84102, USA
T: +1 801 521 2004

Postnova Northern Europe
01630 Vantaa, FINLAND
T: +358 9 8545 510

Results and Discussion

The number of counted nanoparticles in each replicate was plotted against runtime, and showed two distinct peaks (Figure 2). The first peak eluted between 12.5 and 18.3 min and the second peak eluted between 18.3 and 25 min. The first peak represents the most abundant population in the mixture comprising 2/3 of the total number of the counted particles. The results of the size analysis of the replicates across the peaks (red circles) obtained by AF4-spICP-MS are also shown in Figure 2. The nanoparticles counted during the elution have an average diameter across the first peak of 28.6 ± 0.6 nm and of 59.5 ± 0.6 nm across the second peak, respectively. The measured average diameters are in good agreement with the nominal values of the nanoparticles. Using the peak area, the number of nanoparticles in the mixture was calculated as 6.2×10^8 and 2.9×10^8 for 30 nm and 60 nm nanoparticles, respectively. These values are about 35 % lower than the number of the nanoparticles present in the mixture, therefore representing a recovery rate of 65 % for both nanoparticle sizes, which is in good agreement with recovery rates for gold nanoparticles described in literature [6]. The sample loss is non-specific since the ratio of 30 nm to 60 nm nanoparticles obtained by the method (2.13) differed by only 1.9 % from the ratio of the nanoparticles in the mixture (2.09). The sample loss can be attributed to either the adsorption of nanoparticles to the membrane and/or tubings, or to underestimation of the peak area. The non-specific recovery of the nanoparticles can be enhanced by adding volatile salts such as ammonium acetate to the running carrier solution. Peak area estimation can be improved by increasing the number of data points, which can be achieved by decreasing the analysis time per replicate.

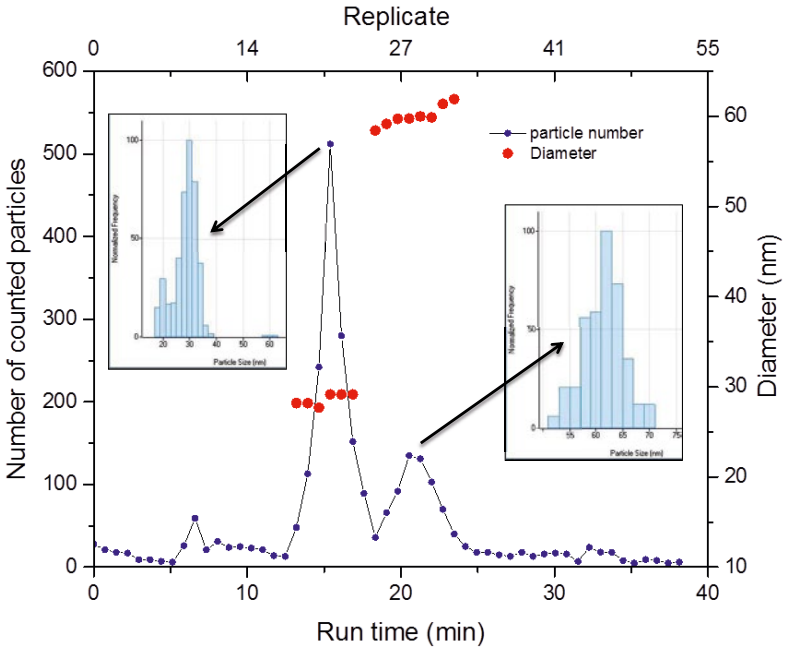

Figure 2. Particle number-based fractogram of the mixture of 30 nm and 60 nm Au gold nanoparticles obtained by AF4-spICP-MS. The red circles represent the average replicate diameter measured by spICP-MS. The shown histograms representing the particle size distribution at the respective peak maxima are directly obtained from the Agilent MassHunter Workstation software.

Conclusion

The data presented in this study show the successful interfacing of two particle characterization techniques, AF4 and spICP-MS, to determine number and size of nanoparticles in a mixture. In this combination, AF4 is essential to provide sample sub-streams that are sufficiently purified and simplified for the spICP-MS analysis. The partnership of the two techniques will give unique measurement capabilities for characterization of complex matrices that would not be possible by either technique alone. For example, the hyphenated technique can be utilized for characterization of dissolved and non-dissolved metallic mixtures. As a result of the AF4 separation, the dissolved or ionic component will be completely removed from the particulate form, which simplifies the spICP-MS analysis of the non-dissolved component. This feature can be beneficial in studies such as nanoparticle toxicology where differentiation between the dissolved and particulate components is of essential importance.

References

[1] Taylor, H.E., et al., Analytical Chemistry, 1992, 64(18), 2036-2041.
[2] Lesher, E., et al., S.K.R. Williams and K.D. Caldwell, Editors, 2012, Springer Vienna, 277-299.
[3] v. d. Kammer, F., et al., Acta Hydrochimica et Hydrobiologica, 2003, 31(4-5), 400-410.
[4] Pace, H.E., et al., Environmental Science & Technology, 2012, 46(22), 12272-12280.
[5] Mitrano, D.M., et al., Journal of Analytical Atomic Spectrometry, 2012, 27(7), 1131-1142.
[6] Gray, E.P., et al., Journal of Analytical Atomic Spectrometry, 2012, 27, 1532-1539.