Asymmetrical Flow Field-Flow Fractionation coupled with ICP-MS for Trace Analysis of Engineered Silver Nanoparticles in River Water

General Information

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Application Nano, Environmental

Technology AF4-ICP-MS

Info Postnova AF2000 MT, PN3211 UV-Vis, PN1650 Smart Stream Splitter, Agilent 7900 ICP-MS

Keywords Asymmetrical Flow Field-Flow Fractionation, Inductively-Coupled Plasma Mass Spectrometry, Smart Stream Splitting, High Volume Injection, Trace Analysis, Silver Nanoparticles, River Water

Introduction

Due to the lack of powerful and appropriate analytical tools, the fate and behaviour of engineered silver nanoparticles (AgNP) in the environment is still widely unexplored. One promising approach to overcome this knowledge gap is the hyphenation of Asymmetrical Flow Field-Flow Fractionation with Inductively-Coupled Plasma Mass Spectrometry (AF4-ICP-MS). The AF4 separates the particles from the matrix and delivers them in increasing size order to the ICP-MS which gives highly sensitive and element-selective detection. Furthermore, this sensitivity can be enhanced further by High Volume Injection [1] and Smart Stream Splitting (S3, also known as slot outlet) [2,3] enabling the enrichment of the sample directly in the AF4 fractionation channel. This means AF4-ICP-MS is a powerful combination for trace analysis of AgNP even in complex environmental matrices such as river water.

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

High Volume Injection

During the injection step in AF4 the sample is introduced into the system via the injection flow, which is counteracted by the focus flow. The incoming sample particles are held in the lower part of the channel where the flows meet and are washed, equilibrated and focused prior to fractionation (Figure 2). One of the most prominent advantages of AF4 is that this step allows for a practically unrestricted volume of sample introduction. In fact the only limitation is the available sample volume. In this way, even very low-concentration samples can be enriched directly in the fractionation channel.

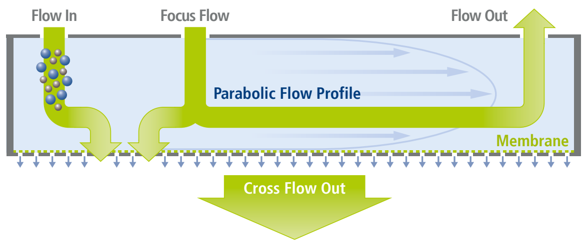
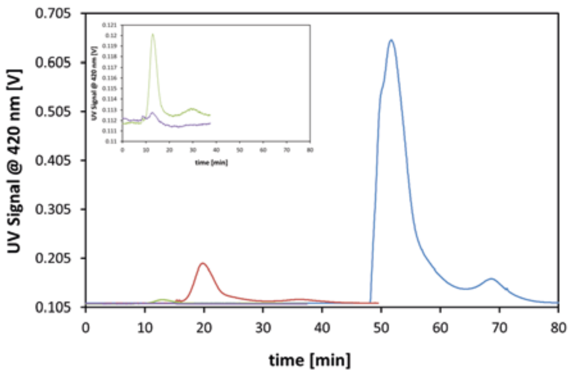


Figure 2: Schematic illustration of High Volume Injection in AF4.

In this study, we investigated increasing injection volumes of AgNP and determined both recovery rates and the achieved increase in sensitivity using an AF4 equipped with a UV detector. The results show that comparing an injection volume of 10 µL with one of 8000 µL, a sensitivity increase by a factor of 660 could be achieved while the recovery rate remained excellent (Figure 3).



Injection Volume [µL]	Recovery [%]	Sensitivity Factor increase
10	100 ± 20	-
100	87 ± 15	7
1000	102 ± 5	83
8000	99 ± 5	660

Figure 3: The AF4-UV-fractograms, recoveries and sensitivity enhancements for different injection volumes (10 - 8000 µL).

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Smart Stream Splitting

In AF4 the separation mechanism naturally results in the sample being located in the lower part of the fractionation channel. This means that at the detector outlet the sample gets diluted by the upper, sample-free, part of the flow. Using Smart Stream Splitting (S3) removes the upper, sample-free part of the channel flow and allows only the lower, sample-rich flow to go to the detectors. The result is that the detectors see an increased sample concentration and therefore give higher signals (Figure 4).

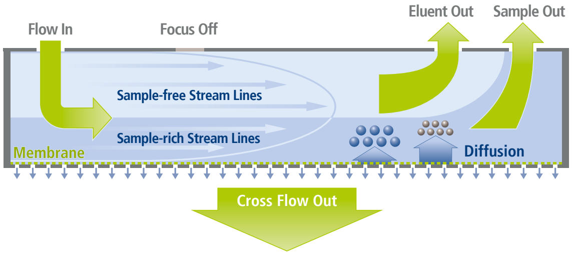
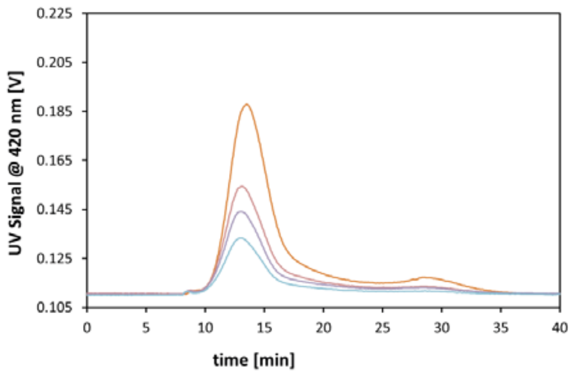


Figure 4: Schematic illustration of S3 in AF4.

In the case of the AgNP under investigation, removal of 60 % of the upper-channel flow by S3 resulted in a 2.4 fold increase in sensitivity while the recovery of the AF4 remained close to 100 % (Figure 5).



Splitting Rate [%]	Recovery [%]	Sensitivity Factor increase
0	100 ± 3	-
20	98 ± 2	1.2
40	99 ± 2	1.6
60	97 ± 1	2.4

Figure 5: AF4-UV-fractograms, recoveries and sensitivity enhancements by S3 for different channel flow splitting ratios.

AF4-ICP-MS Analysis of AgNP-spiked Rhine Water

After the successful proof-of-concept study performed in ultrapure water, the AF4 was hyphenated with ICP-MS and applied to the investigation of Rhine river water spiked with trace amounts of AgNP (321 ng/L and 628 ng/L) (Figure 6). Following on from the above development work an 8000 µL injection volume and a 60 % S3 were applied resulting in both an excellent recovery rate of 98 ± 8 % and a Limit of Quantification of 14 ± 4 ng/L (according to DIN32645) for AgNP in this challenging environmental matrix of river water.

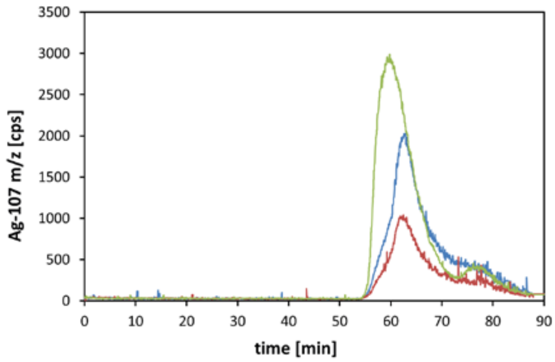


Figure 6: AF4-ICP-MS fractograms of AgNP spiked in Rhine water (628 ng/L, blue trace; 321 ng/L, red trace) and ultrapure water (1037 ng/L, green trace).

Conclusion

The results presented here clearly highlight the excellent applicability of AF4 for trace analysis of AgNP. By taking advantage of High Volume Injection and Smart Stream Splitting along with the hyphenation with ICP-MS, AF4 is a powerful tool for the investigation of low levels of AgNP in complex environmental matrices.

References

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