Asymmetrical Flow Field-Flow Fractionation for Trace Level Analysis of Engineered Silver Nanomaterials in River Water

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Introduction

Due to the lack of powerful and appropriate analytical tools, the fate and behavior of engineered silver nanomaterials (AgNM) in the environment is still widely unexplored. Up to now, quantitative data are first and foremost derived from computational modeling studies [1,2].

We herein present the application of Asymetrical Flow Field-Flow Fractionation (AF4) for the quantification of AgNM in river water. By taking advantage of Slot-Outlet [3], High-Volume-Injection and hyphenation with ICP-MS [4], limits of quantification in river water down to 14 ± 4 ng/L could be achieved.

Asymmetrical Flow Field-Flow Fractionation

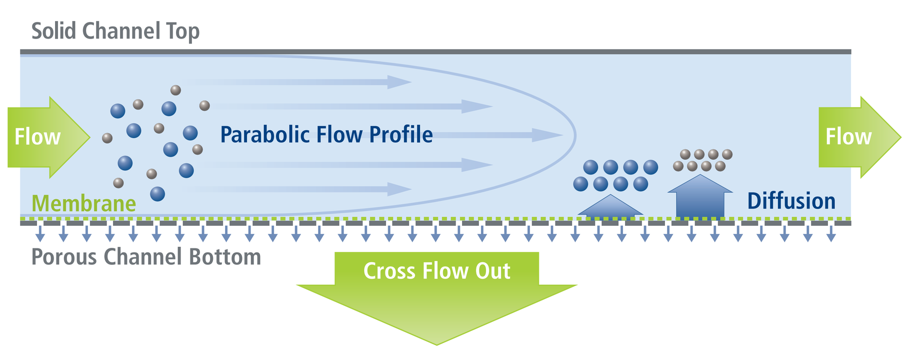

Figure 1: Schematic of the general separation principle in AF4.

- Cross-flow (hydraulic pressure gradient) controlled separation
- Fractionation according to hydrodynamic size

Slot-Outlet (Smart-Stream-Splitting - SSS)

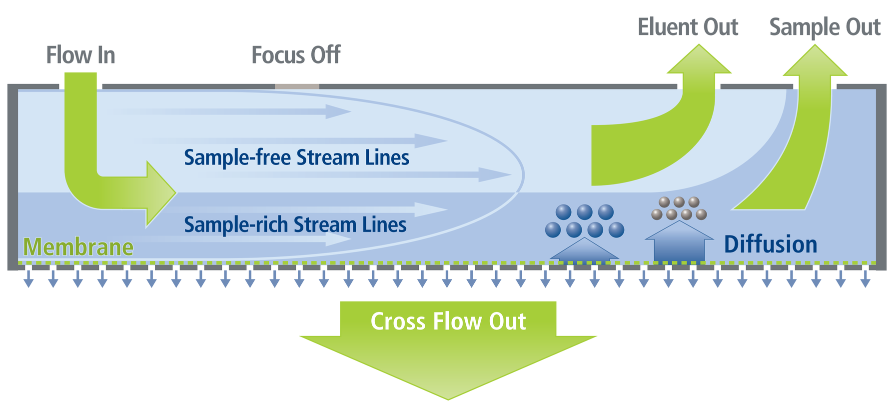

Figure 2: Principle of Slot-Outlet.

- Removal of upper, sample-free channel flow
- Reduced sample dilution in the separation channel

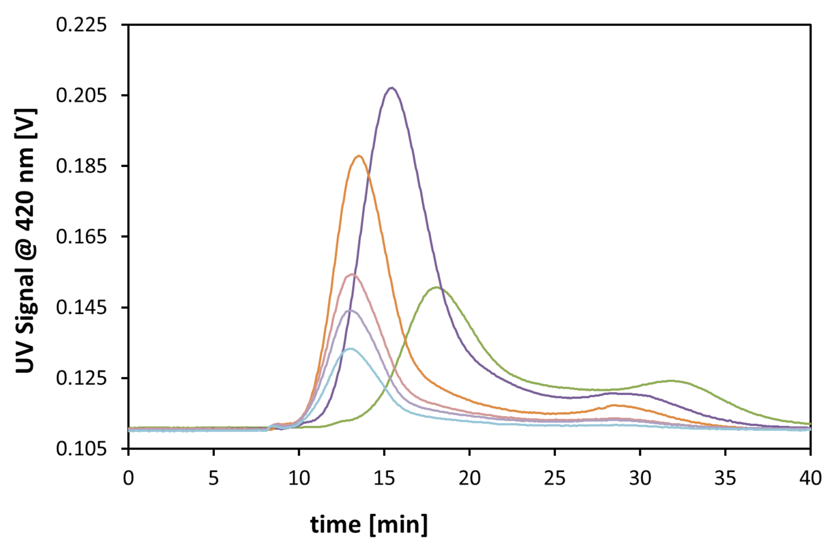

Figure 3: AF4-fractograms of AgNM obtained with different Slot-Outlet flows (0-90%).

SSS [%]	Recovery [%]	Sensitivity Factor ↑
0	99.6 ± 2.5	---
20	97.7 ± 1.6	1.2
40	98.5 ± 1.8	1.6
60	96.6 ± 0.2	2.4
80	83.4 ± 2.1	4.2
90	46.5 ± 3.0	/

Table 1: Obtained recoveries and sensitivity enhancements for different Slot-Outlet flows.

High-Volume-Injection

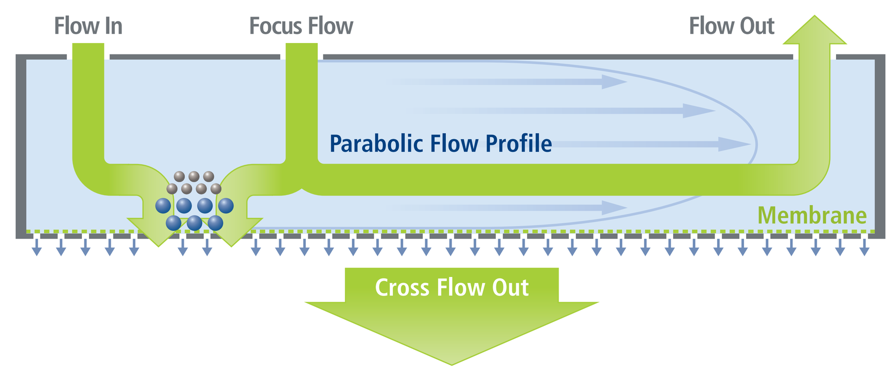

Figure 4: Principle of High-Volume-Injection in AF4.

- Unlimited sample introduction possible
- Online sample enrichment and cleaning

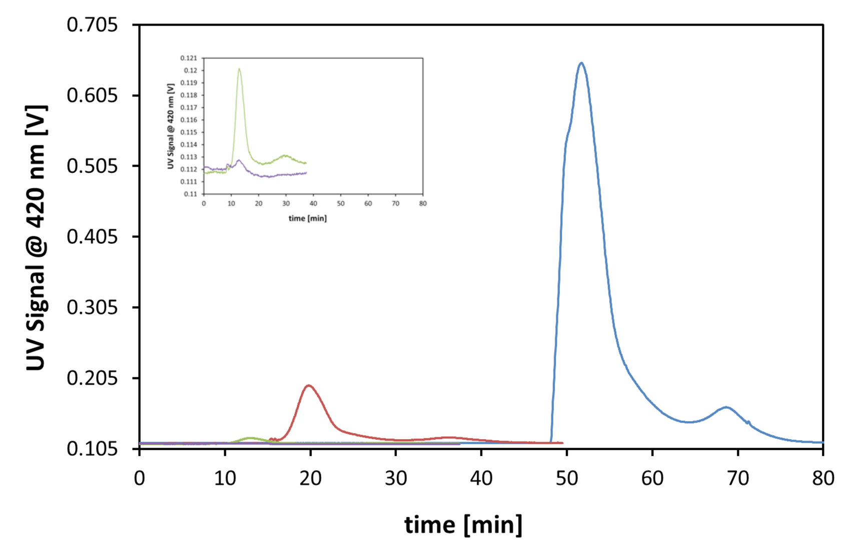

Figure 5: AF4-fractograms of AgNM obtained with different injection volumes (10-8000 µL).

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

Table 2: Obtained recoveries and sensitivity enhancements for different injection volumes.

Hyphenation of AF4 and ICP-MS

Figure 6: Postnova AF2000MT and Agilent 7900 ICP-MS.

- Element-selective detection
- Extremely high sensitivity for metallic nanomaterials including AgNM

Rhine Water Sample Preparation

- Sampling spot at Rheingütestation Worms
- High natural particular background (mostly Mg, Al, Ca, Fe, Si)
- Filtration (0.22 µm PVDF) prior to spiking
- Spiking with sub-µg/L AgNM (Ag10-COOH, PlasmaChem GmbH)
- AF4-ICP-MS analysis using 60% Slot-Outlet and 8 mL High-Volume-Injection
- Tracing of Ag-107 m/z

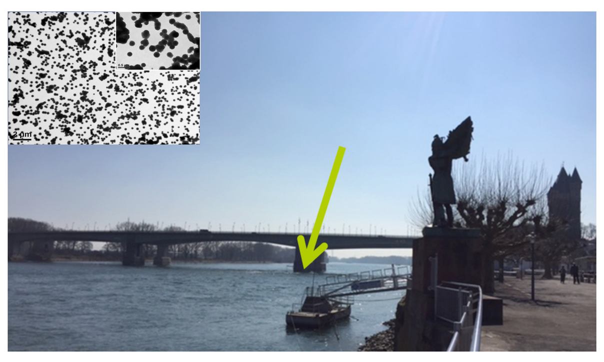

Figure 7: Sampling spot at Rheingütestation Worms and TEM-picture of Rhine water containing natural submicroparticles. (© University of Frankfurt)

AF4-ICP-MS-Analysis of Rhine Water

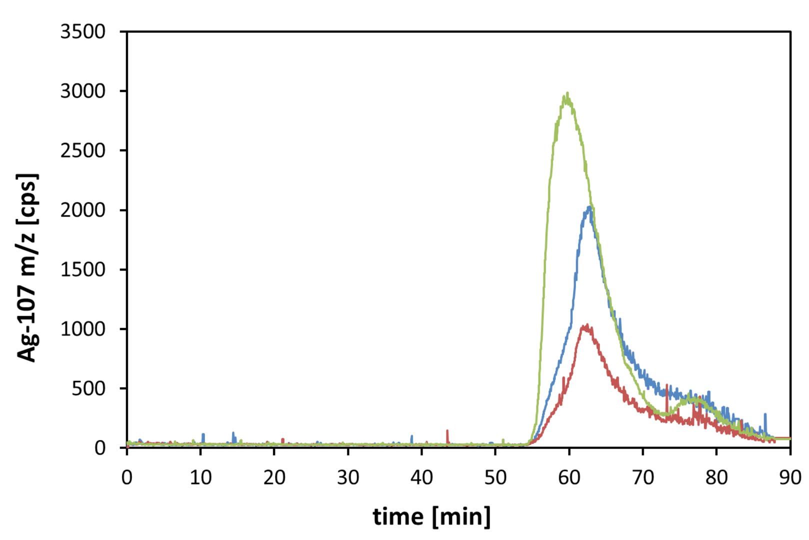

Figure 8: AF4-ICP-MS fractogram of AgNM spiked in Rhine water (628 ng/L, 321 ng/L) and ultrapure water (1037 ng/L).

- No silver observed in unspiked Rhine water: LOQ ICP-MS: < 5 ng/L
- LOQ AF4-ICP-MS: 14 ± 4 ng/L for spiked samples
- 5 min retention time shift in comparison to UPW
- Sample alteration ((hetero)-agglomeration etc.)

Conclusions

In this study, we successfully demonstrate the applicability of AF4 for trace level analysis of AgNM in river water. AF4 hereby reveals to be a promising tool to study the fate and behavior of AgNM in the environment.

Acknowledgements

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References

[1] Gottschalk F., Sun T., Nowack B., *Environmental Pollution*, **2013**, 181, 287-300.
[2] Su T., Bornhöft N.A., Hungerbühler K., Nowack B., *Environmental Science & Pollution*, **2016**, 50(9), 4701-4711.
[3] Giddings J.C., Lin H.C., Caldwell K.D., Myers M.N., *Separation Science and Technology*, **1983**, 18(3), 293-306.
[4] Mudalige T.K., Qu H., Linder S.W., *Analytical Chemistry*, **2015**, 87, 7395-7401.

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