Electronic supplementary information for

Sample Loss in Asymmetric Flow Field-Flow Fractionation Coupled to Inductively Coupled Plasma-Mass Spectrometry of Silver Nanoparticles

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1. T-SEM Images

Transmission in scanning electron microscope (T-SEM) experiments were performed using a SEM ZEISS Supra 40 (Zeiss, Oberkochen, Germany) operated in transmission mode by using a so-called single-unit transmission set-up. For the sample preparation, the *Ag* NP dispersion was sonicated (5 min) in a bath. A volume of 0.5 μ L of the undiluted *Ag* NP sample was placed on a carbon foil coated copper grid (Plano, Wetzlar, Germany) and air-dried.



Fig. S1 Representative T-SEM image of the analyzed Ag nanoparticles.

A number of 2600 particles were analyzed with the software ImageJ (National Institutes of Health, Bethesda, MD, USA), resulting in an area equivalent particle diameter of 15 ± 5 nm.

2. AF4 scheme

The AF4 flows, such as the detector flow, the cross flow and the slot-outlet flow, are depicted in Fig S2.



Fig. S2 Scheme of the AF4 mechanism.

Through the slot-outlet shown in Fig. S2, the upper part of the channel flow is removed. Based on the FFF theory, the particle separation takes place in the lower few μ m of the channel. Therefore, no sample should be present in the slot-outlet flow.¹

At the end of each AF4 run, the AF4 channel is purged with a high tip flow of 3 mL min⁻¹ in order to remove sample residue from the channel. Simultaneously, a 4-port valve, which is connected to the slot-outlet port, is switched to the purge position. A capillary with an inner diameter of 750 μ m is connected to the purge position of the valve. This results in nearly 100 % of the channel flow to leave through the purge flow.

3. Calibration LA-ICP-MS

The integration of the signals for the LA-ICP-MS calibration droplets in Fig. 5 resulted in a linear calibration curve shown in Fig. S3.



Fig. S3 Calibration curve for quantification of Ag residue on the membrane.

A LOD of 4.2 pg was determined for the LA-ICP-MS experiments. The LOD was calculated using LOD = $B + 3 \cdot sB$, whereas B is the average of the background and sB the standard deviation.

Literature

1. J. C. Giddings, in Field-Flow Fractionation Handbook, ed. M. Schimpf, K. Caldwell, J. C. Giddings, Wiley, New York, 1 edn. 2000, vol. 1, ch. 1, p. 17-19.