

Membrane- particle interactions in asymmetric flow field flow fractionation (A4F) – The influence of the ζ -potential

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ABSTRACT

Using Asymmetric Flow Field Flow Fractionation (A4F) as a method for nanoparticle characterization, unspecific nanoparticle-membrane interactions must be taken into consideration. These interactions have a significant negative influence on the fractionation efficiency and the recovery rates due to unspecific deposition of the nanoparticles on the membrane surface. A possible explanation for the unspecific interactions could be the ζ -potential of the membrane. Therefore typically used A4F membrane materials are investigated by ζ -potential measurements of the membrane to provide a simple method for qualitative prediction of unwanted interactions.

Keywords: Asymmetric Flow Field Flow Fractionation (A4F), ζ -Potential, membrane, nanoparticles

1 INTRODUCTION

Asymmetric flow field flow fractionation (A4F) is a powerful and promising technique for the separation of nanoparticles. Operated in a multi-detector approach, i.e. in combination with UV/Vis detection, light scattering (LS) and plasma mass spectrometry (ICP-MS) it can become a fast and quantitative analytical method providing information on particle size, size-distribution and elemental composition at the same time. Even some information on coating of nanoparticles are accessible. A main advantage is also the broad measurable size range reaching from 1 nm to 1 μ m with a size resolution of about 10 nm. For a representative amount of nanoparticles an injection volume of only 20 to 100 μ L is necessary. Nevertheless there are also some limitations of the technique. Not understood but often observed are e.g. unpredictable particle losses in the A4F channel attributed to occurring particle-membrane-interactions¹⁻⁴. Visible deposition of particles on the membrane occurs especially in the focus area. Thus, poor recovery rates are observed especially during the first 5 to 10 injections after a membrane or sample type change. Moreover, membrane particle interactions might lead to certain shifts in retention time, which influences size calibration by standard particles like poly styrene.

Thus, this and further study focuses on a detailed investigation of such particle-membrane-interactions and discusses possible influence factors such as material type (e.g. PVDF, RC or PES), cut-off, surface morphology as well as ζ -potential of the particles and the membrane material itself. First results have been already published⁵ treating investigations considering the charge of the membrane surface (streaming potential) dependent on the type and cut-off. Moreover, influence factors like possible surfactants, pH or ionic strength are studied. Variation of similar membrane types from different producers are compared as well as homogeneity within one membrane. Besides, surface morphology was studied by scanning electron microscopy (SEM). Hypothesis which explain possible particle-membrane- interactions are proposed and critically evaluated for real A4F measurements.

The streaming potential describes the difference in electrical potential occurring between both sides of a membrane, when a pressure is applied carrying the surrounding liquid from one side to the other. The ζ -potential appears at the shear plane of the electrochemical double layer.

Some previous studies are already dealing with this topic, but not for A4F membranes, but for fouling of filtration membranes^{6,7}. This generates the idea to study the ζ -potential of typical used A4F membranes. Table 1 gives an overview over often used membranes.

NP Type	Membrane Material	Cut-off [kDa]	Literature
Ag@Citrate	Regenerated Cellulose	1	8
Ag@Citrate	Regenerated Cellulose	1	9
Ag	Regenerated Cellulose	1	10
Ag	Regenerated Cellulose	1	11
Ag@PVA	Regenerated Cellulose	10	12
Ag@PVP	Regenerated Cellulose	10	13

Ag	Polyethersulfone	1	11
Ag	Polyethersulfone	0.3	14
Ag@Carbonate	Polyvinylidendifluoride	30	15

Table 1: Literature overview for typically used A4F membranes.

2 EXPERIMENTAL SECTION

2.1 Instrumentation

SEM measurements. The surface of the FFF membranes was analyzed using a Philips XL30 ESEM-FEG SEM (XL Series, Philips, USA) equipped with an EDX unit (15 kV for EDX, 1kV for imaging). Before microscopy analysis the membranes were covered with a 0.5 nm thick platinum coating to make them conductive (MED 020 Coating system, BAL-TEC).

Membrane ζ -potential. The streaming zeta potentials of typical types of membranes for the A4F have been analyzed using a flow-through zeta potential analyzer Müttek(TM) System SZP-06 (BTG Instruments GmbH, Germany). Round membrane segments of 2 cm diameter were placed in the flow through cell of the zeta potential analyzer and measured. Conductivity and pH were additionally determined using a MultiLine P3 (WTW, Germany) separate sensors. Membrane materials were provided by Wyatt Technology. The measurements were performed with tap water, DI water, DI water + NH_4NO_3 , DI water + NaOH, DI water + HNO_3 and DI water + SDS, or $\text{Na}_6\text{P}_6\text{O}_{18}$.

A4F setup. The A4F system is composed of a separation channel and a flow control (Eclipse3, Wyatt Technology Europe, Germany) connected to a metal-free HPLC system (DGU-20A3 degasser, LC-10Ai pump, SIL-20AC autosampler, CBM-20A control unit) from Shimadzu Europe (Germany). The A4F system was coupled to an UV/Vis diode array detector (SPD-M20A, Shimadzu GmbH, Germany), followed by a multiangel laser-light scattering (18 angel MALLS) detector (DAWN Heleos2, Wyatt Technology Corporation, USA), which operates at a laser wavelength of 658 nm. At an angel of 108° of the MALLS detector, an online DLS NanoStar (Wyatt Technology Corporation, USA) was connected via a glass fibre cord. The eclipse channel had the dimension of 145 mm in length and 50 mm in width and a channel height of 350 μm . A 30 kDa polyvinylidendifluoride (PCDF, GE Osmonics Germany, Sepa CF-PVDF-UF-JW) channel membrane was used and DI water was applied as carrier.

Data from the light scattering detector were processed with the ASTRA software (Wyatt, Version 6.0) and UV/vis data using the LC solution software (Shimadzu, Version 1.22 SP1).

2.2 Chemicals

Nitric acid (65 % w/w, sodium hydroxide, sodium hexametaphosphate and ammonium nitrate were purchased in suprapur/pro Analysis quality from Merck (Merck GmbH). Sodium dodecyl sulfate (SDS) was purchased from Sigma Aldrich (Sigma Aldrich Chemie GmbH). A Milipore, Mili-Q A-10 water unit (Milipore AG) was used for the production of 18 M Ω cm deionised water (DI-water). All solutions used as carrier for the A4F system were degassed prior use in an ultrasonic bath. For A4F method validation, certified reference material Au particles purchased from National Institute of Standards and Technology (NIST SRM® 8011, 8012 and 8013) were used. After opening, the standards were transferred to nitrogen flushed and pre-cleaned (ethanol p.a.) PE-LD vessels and then stored in the dark. Before measurements, the standards were always freshly prepared, diluting from the stock with carrier solution directly in the 2 mL HPLC (PE-LD) vials.

Silver nanoparticles with citrate coating were provided by NanoSys GmbH - Fluids and Consulting, Switzerland.

3 RESULTS AND DISCUSSION

3.1 A4F measurements

After changing of an A4F membrane usually significant particle losses can be observed. However, recovery rates often improve after several injections (usually about up to 10 injections). An Ag@citrate nanoparticle suspension was injected 6 times directly after changing the membrane. Figure 1 shows the increase in intensity after 6 successive injections. Also a small shift in the retention time can be observed.

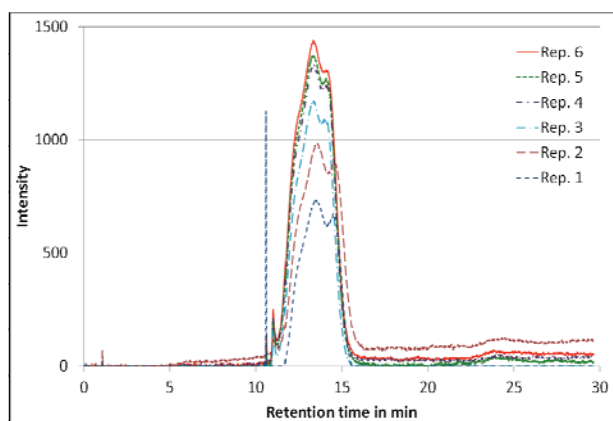


Figure 1: A4F fractogram og nano Ag@citrate after 6 successive injections ⁵.

The increase of the signal and therefore the increase of the recovery rate might be explained with particle deposition

preferably occurring in the focus zone. This deposition can be caused on the one hand by an uneven structure of the surface of the membrane or on the other hand by attractive forces between the particles and the membrane surface due to the electrostatic attraction. To prove this hypothesis it is of interest to study the surface morphology of the A4F membranes as well as their ζ -potential.

3.2 ζ -potential of the membranes

Selected membrane materials, due to the ones mainly used in literature were studied. This study focuses on the influence of different carrier solutions, pH values or ionic strength on the ζ -potential of the membrane, as well as of the particles of interest. Additionally the variation of the ζ -potential at different positions of the membrane surface is studied as well as the influence of different cut-offs for the same material and the variation of membranes manufactured by different producers. Since further data will be published soon^{8,9} here only the influence of different pH values will be discussed. As most typical membrane materials regenerated cellulose (RC) with a cut-off of 30 kDa, polyethersulfone (PES) with a cut-off of 10 kDa and polyvinylidene-difluoride (PVDF) with a cut-off of 30 kDa were selected. The pH was adjusted using NaOH or HNO₃. Figure 2 presents the determined ζ -potential of all three membranes over the whole pH range.

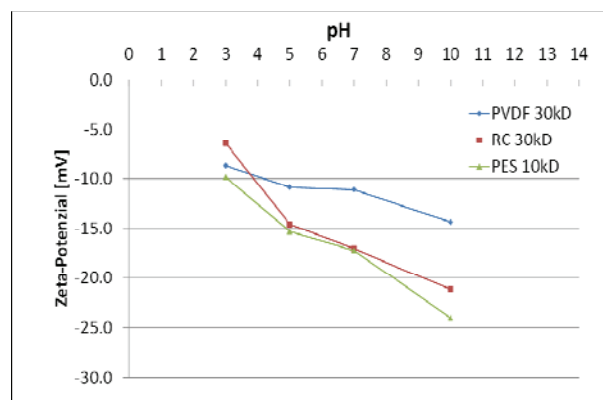


Figure 2: Influence of the pH on the ζ -potential of different A4F membranes⁵.

It demonstrates that a pH change results in a significant change in the ζ -potential for membranes with pH sensitive groups like OH, or COOH as it is the case in RC and PES. PVDF membrane with covalent fluor carbon bonds shows much less sensitivity towards pH changes. All these results can be found in the publication of Ulrich et al⁵.

3.3 Morphology of the membranes

Beside the ζ -potential also the surface morphology can have an important influence on the separation efficiency inside the A4F channel. Therefore, all membranes were also investigated using a scanning electron microscope (SEM).

Figure 3 shows an image of a representative surface of a PES 10 kDa membrane. It is obvious, that the surface is not completely even and smooth. Some rougher parts and even some holes in the μm size range were observed. This might also explain some of the particles losses occurring especially in the focus zone. The separation principle of A4F is based on a parabolic channel flow profile, which ensures a laminar flow inside the channel. The actual separation takes place close to the membrane surface. Thus, a A4F separation is probably highly demanding in terms of smoothness and evenness of the membrane surface. Therefore, rough and uneven surface morphology probably disturbs the laminar flow and increases the likelihood of particle deposition on the surface.

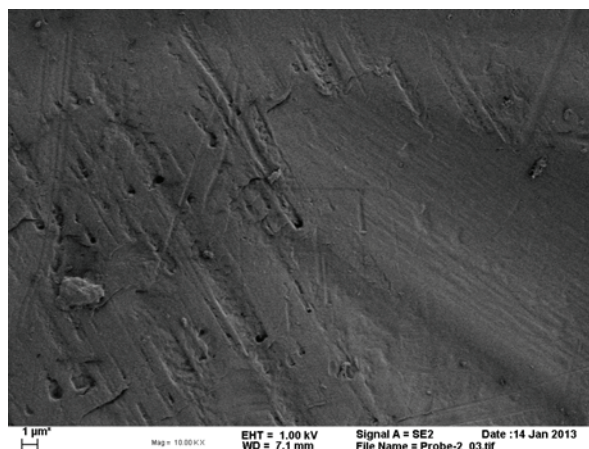


Figure 3: SE-SEM image of a PES 10 kDa membrane.

4 CONCLUSION

The performed experiments show that the ζ -potential of the membrane depends on the material, surface variations, the pH, and much more influencing factors. By measuring the ζ -potential of both the membrane and the nanoparticles of interest A4F measuring conditions and setup can be adjusted in such way that the particle-membrane interactions are minimized. A detailed study for such optimisation is under progress and will be published soon by Bendixen et al¹⁶.

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