Sizing of Polydisperse Silver Nanoparticle Suspensions - Comparison of Asymmetrical Flow FFF Coupled to Online DLS with Batch Mode DLS

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Introduction

Dynamic Light Scattering (DLS) is a well-established and powerful analytical technique for sizing of nanoparticles in suspensions. Due to its easy applicability it has found its place in analytical laboratories all around the world. However, DLS has significant drawbacks when it comes to the characterization of polydisperse samples. This is due to the Rayleigh approximation that states that the intensity of the scattered light (I) is proportional to the particle diameter (d) to the power of six ($I \propto d^6$). That means, for example, a 60 nm particle scatters one million times as much light as a 6 nm particle, thereby heavily biasing the measurement towards any larger particles present in a mixture, ultimately leading to overestimated particle sizes [1]. One possibility to overcome this drawback is the separation of polydisperse samples by Field-Flow Fractionation prior to DLS analysis and then using DLS as an online detector to accurately measure each monodisperse size fraction as it elutes.
We herein present a comparison of DLS in batch mode with Asymmetrical Flow Field-Flow Fractionation coupled with DLS (AF4-DLS) for the measurement of a mixture of silver nanoparticles (AgNP) of different sizes (20 nm, 40 nm, 60 nm). The results obtained clearly highlight the advantage of using a powerful fractionation technology prior to DLS analysis for polydisperse samples.

Asymmetrical Flow Field-Flow Fractionation

In AF4, fractionation is induced in a narrow, ribbon-like channel by the counteraction of a cross-flow separation force against the Brownian motion of the particles or molecules introduced. Under equilibrium conditions, the particles align in the different velocity streams of the parabolic flow profile of the channel according to their hydrodynamic size. This results in the elution of the particles in size order from small to large (Figure 1) [2].

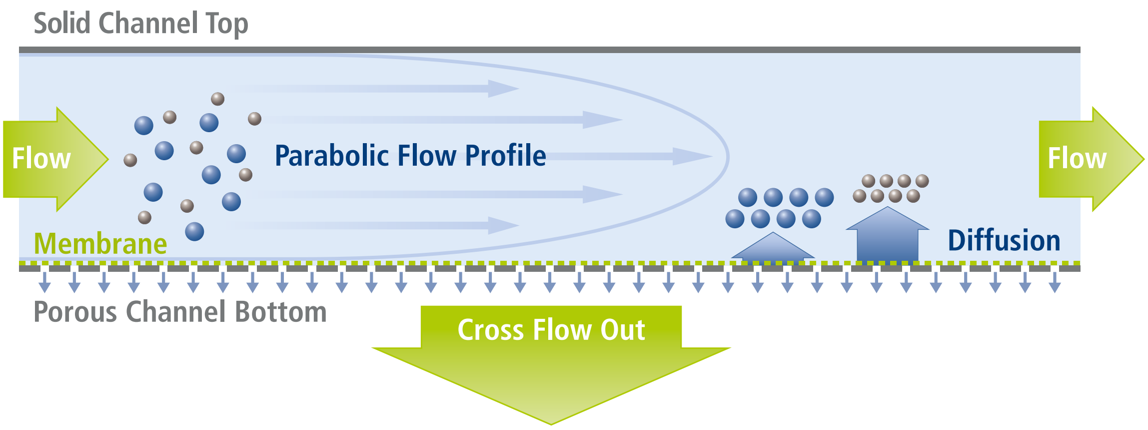

Figure 1: AF4 separation principle

AF4-DLS Versus DLS in Batch Mode

In order to investigate the performance of both AF4-DLS and DLS in batch mode for sizing of AgNP, stock suspensions were prepared containing either AgNP of one single size (20 nm, 40 nm or 60 nm) or a mixture of all three sizes at comparable weight percentages. While sizes obtained for suspensions containing only one AgNP size were in good agreement with the nominal values provided by the manufacturer, DLS in batch mode failed to resolve the three particle size populations in the mixture while clearly discriminating against the smaller particle sizes (Figure 2).

In contrast to DLS in batch mode, AF4-DLS was able to separate and correctly size all three AgNP populations even within the mixture in one single run (Figure 3).

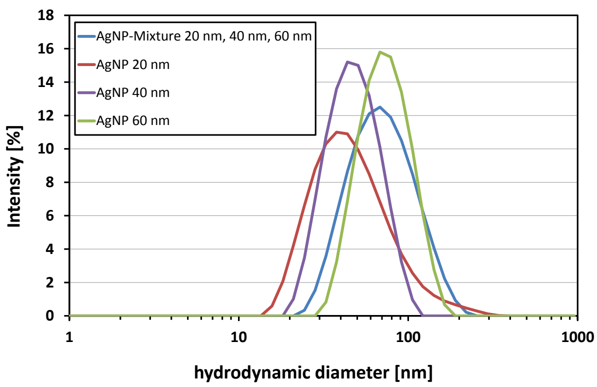

Figure 2: Comparison of intensity-based particle size distributions for single AgNP and AgNP in a 1:1:1 (w%) mixture obtained from DLS in batch mode.

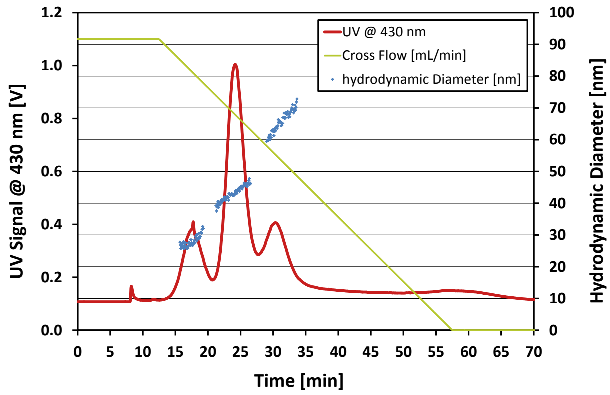

Figure 3: AF4-DLS fractogram of a 1:1:1 (w%) mixture of AgNP (20 nm, 40 nm, 60 nm).

The particle sizes obtained are summarized in Table 1. The measured size for the mixture by DLS in batch mode clearly overestimates the average size due to the bias of the measurement towards the 60 nm particles.

D(h) z-average mean [nm]				
AgNP-Std.	**BatchDLS**	**mean dev.**	**AF4-DLS**	**mean dev.**
20 nm	31.1	0.6	30.6	0.6
40 nm	42.8	0.2	47.2	0.6
60 nm	65.3	0.8	62.5	1.1
20 nm + 40 nm + 60 nm Mix	61.2	0.9	28.7	0.3
			44.0	0.4
			65.1	0.6

Table 1: Particle sizes obtained for the three AgNP-standards by DLS in batch mode and by AF4-DLS.

Conclusion

In this comparative study, both AF4-DLS and DLS in batch mode were applied for the investigation of a suspension composed of a mixture of AgNP of three different sizes. The results obtained clearly highlight the superiority of a fractionation step prior to DLS analysis over DLS as a standalone technique. DLS in batch mode was not able to resolve all three AgNP populations and moreover significantly discriminated against smaller particle sizes. In contrast, the coupled technique of AF4-DLS was able to resolve all three AgNP populations within one single run and therefore provide the true particle size distribution of a polydisperse sample.

References

[1] Dynamic Light Scattering: An Introduction in 30 Minutes, Technical Note, 2017, Malvern Pananalytical.
[2] Heinzmann G. and Meier F., Field-Flow Fractionation: A powerful technology for the separation and advanced characterization of proteins, antibodies, viruses, polymers and nano-/microparticles, 2017, http://www.chemeurope.com/en/whitepapers/126566/field-flow-fractionation-a-powerful-technology-for-the-separation-and-advanced-characterization.html