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Capability of Asymmetrical Flow Field-Flow Fractionation (AsFlFFF) for Separation and Characterization of SiO_2 Nanoparticles†

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Asymmetrical flow field-flow fractionation (AsFlFFF) provides information on the size distributions of colloidal nanoparticles. Asymmetrical flow field-flow fractionation was employed to determine the size and size distribution of SiO_2 nanoparticle samples having the nominal mean sizes of 20, 60 and 238 nm. Asymmetrical flow field-flow fractionation results showed the samples have size distributions broader than those provided by the particle manufacture. The same SiO_2 nanoparticles were also analyzed by transmission electron microscopy (TEM) and dynamic light scattering (DLS) and the results were compared with those from AsFlFFF. Transmission electron microscopy images clearly showed the presence of aggregated particles, which seems to be the main reason why the size distributions obtained by AsFlFFF were broader. Results suggest that, particularly for particle samples having broad size distributions, AsFlFFF seems to provide a useful tool for size characterization.

Key Words: Asymmetrical flow field-flow fractionation (AsFlFFF), SiO_2 nanoparticles, Particle size distribution.

INTRODUCTION

The mobility, fate and bioavailability of natural nanoparticles in the environment depend on their size, shape and the electrical charge among others[1,2]. Natural particles in the nanometer size range play a significant role in environmental processes because of their role in pollutant and trace element mobility and bioavailability[3,4].

Unfortunately, the characterization and quantification of colloidal nanoparticles are not simple tasks since the measurements are highly dependent upon several parameters including the particle size and the size distribution, the sample concentration and the physicochemical nature of the suspending media. Among those, the size and the shape are believed to be important characteristics that control their environmental behaviour, for example, adsorption, aggregation, sedimentation, fate and transport. In order to obtain accurate information on the size and the shape of the nanoparticles, it is sometimes necessary to minimize their polydispersity by fractionating them, thus preventing the artifacts in the particle size measurements[5,6].

Field-flow fractionation (FFF) is a separation technique that is based on coupling of a laminar flow in a ribbon-like channel and an external field applied perpendicular to the flow direction. Field-flow fractionation is useful for separation and characterization of colloidal particles, polymers and biological macromolecules[7-14].

In this work, an asymmetrical flow field-flow fractionation (AsFlFFF), one of sub-techniques of field-flow fractionation, was employed to determine the size and size distribution of SiO_2 nanoparticles, which were taken as a model particles for environmental particles. Results obtained from AsFlFFF were compared with those from transmission electron microscopy (TEM) and dynamic light scattering (DLS).

Theory: In AsFlFFF, the hydrodynamic diameter (d_H) of the particles is related with their retention time t_r by Wittgren *et al.*[15]:

$$d_H = \frac{2V^o kTt_r}{\pi\eta w^2 F_c t^o} \qquad (1)$$

In eqn. 1, V^o is the void volume of the AsFlFFF channel, k the Boltzmann constant, T the absolute temperature (K), η the viscosity of the carrier liquid, w the channel thickness, F_c the volumetric cross-flow rate and t^o the void time (the elution time of the species that are not retained). Using eqn. 1, an AsFlFFF fractogram of the particles in a colloid can be converted directly to a size distribution.

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EXPERIMENTAL

Polystyrene latex beads having the nominal diameters of 50, 100, 200 and 300 nm were obtained from Duke Scientific (Palo Alto, CA, USA). SiO2 nanoparticles having nominal diameters of 20, 60, 238 nm were purchased from Corpuscular inc. (Cold Spring, NY, USA).

Asymmetrical flow field-flow fractionation: The AsFlFFF system used in this study was the Eclipse AF4 (Wyatt Tech., Europe GmbH, Dernbach, Germany) assembled with a 250-µm-thick Mylar spacer and a regenerated cellulose membrane (Millipore, Bedford, MA, USA) having the cut-off molecular weight of 10,000 Da.

The channel geometry was trapezoidal with the tip-to-tip length of 26.5 cm and breadths at the inlet and the outlet of 2.2 and 0.6 cm, respectively. Due to the swelling of the membrane, the actual channel thickness is usually smaller than the thickness of the spacer. To measure the actual channel thickness, a 20 nm polystyrene beads having a narrow size distribution were used with the carrier solution of water containing 0.1 % FL-70 and 0.02 % NaN_3. The actual channel thickness determined from the retention time of 20 nm polystyrene beads was 163 µm.

A HPLC pump (Young-Lin SP930D, Anyang, Korea) was used to deliver the carrier liquid into AsFlFFF channel. The channel and the cross-flow rates were measured respectively using liquid flow meters (Optiflow 1000, Agilent Technologies, Palo Alto, CA, USA). Eluted particles were monitored using a Young-Lin M720 UV detector (Anyang, Korea) with the wavelength set at 254 nm. The 20 µL sample suspension were injected into the channel using a 20 µL loop injector (Rheodyne, Cotati, CA, USA). The syringe pump (Model 100, KD Scientific, USA) was used with flow rate of 0.2 mL/min for 60 s to inject the sample through injector loop to the channel inlet.

Dynamic light scattering (DLS): The DLS system used in this study was a Zetasizer Nano ZS90 from Malvern inc. (Worcestershire, UK) equipped with a He-Ne laser (wavelength of 633 nm) as the light source. Experimental parameters were: viscosity = 0.009 cp, refractive index = 1.33 and the collection angle = 90º.

Transmission electron microscopy (TEM): A JEOL model JEM-2000FXII (Tokyo, Japan) a transmission electron microscope (TEM) were used for electron microscopy of SiO_2 nanoparticles.

RESULTS AND DISCUSSION

Fig. 1(a) shows the asymmetrical flow field-flow fractionation (AsFlFFF) fractograms of the same mixture of four polystyrene latex beads having nominal diameters of 50, 100, 200 and 300 nm obtained at three different channel flow rates (F_{out}) of 1.02, 1.33 and 1.54 mL/min, respectively. The cross-flow rate (F_c) was fixed at 0.52 mL/min. The carrier liquid was water containing 0.1% FL-70 and 0.02 % NaN_3. As shown in Fig. 1(a), as the channel flow rate decreases, the separation time and the resolution gradually increases.

As mentioned earlier, an AsFlFFF fractogram can be converted to a size distribution using eqn. 1. The size distributions obtained for the fractograms shown in Fig. 1(a) are shown in

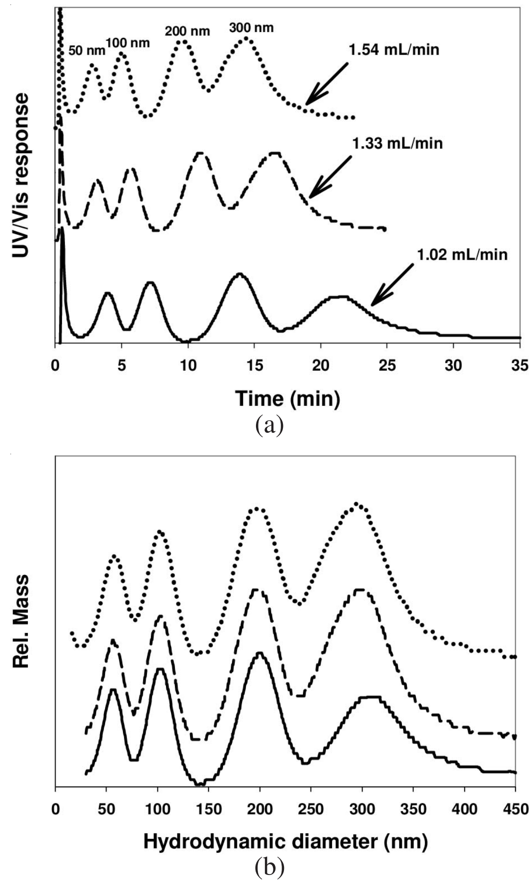


Fig. 1. AsFlFFF fractograms (a) and size distributions (b) of a mixture of four polystyrene latex beads obtained at various channel flow rate (F_{out}). F_c was fixed at 0.52 mL/min. The carrier liquid was water containing 0.1 % FL-70 and 0.02 % NaN_3

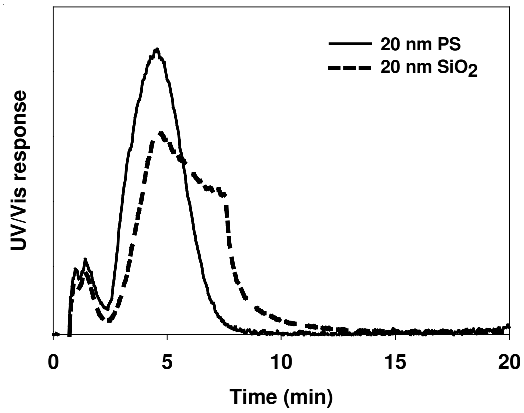
Fig. 1(b). It can be seen in Fig. 1(b) that, even though the channel flow rate (and thus the separation time and the resolution) was different, the hydrodynamic diameters corresponding to the peak maxima are close to each other.

The diameters calculated for the retention times at the peak maxima of the polystyrene latex bead using eqn. 1 obtained at the channel flow rate of 1.02 mL/min are shown in Table-1. As expected, the sizes measured by AsFlFFF are in good agreements with the nominal mean diameters. The relative errors were less than about 10 %. Fig. 1 and Table-1 shows AsFlFFF is capable of separating colloidal nanoparticles based on their sizes.

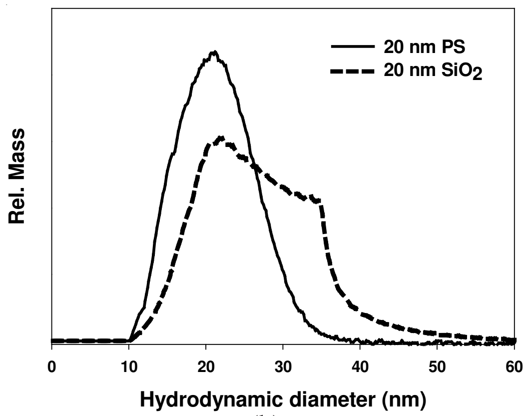
TABLE-1
DIAMETERS MEASURED BY AsFlFFF FOR POLYSTYRENE LATEX BEADS SHOWN IN Fig. 1

Nominal diameter (nm)	Diameter measured by AsFlFFF (nm)	Relative error (%)
52	58	10.3
102	104	1.9
200	199	0.5
300	291	3.0

Fig. 2(a) shows AsFlFFF fractograms and size distribution of polystyrene latex beads and SiO_2 nanoparticle overlaid. Both samples have nominal mean diameters of 20 nm. The channel flow rate F_{out} was 0.52 mL/min and the cross-flow rate F_c was 1.52 mL/min, respectively. The carrier liquid was the same as that used in Fig. 1. The size distributions obtained as in Fig. 1 are shown in Fig. 2(b). As shown in Fig. 1(a) and (b), the polystyrene beads have a near-symmetrical size distribution with the diameter measured at the peak maximum close to the nominal diameter. Unlike the polystyrene beads, the SiO_2 nanoparticles have a broader and non-symmetrical size distribution.



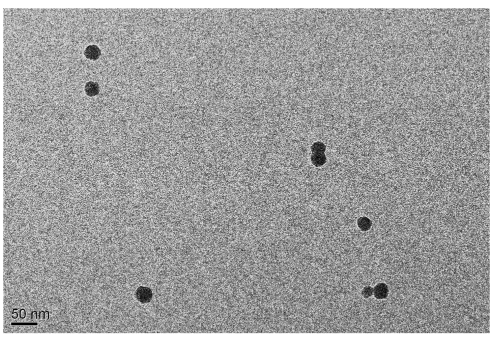
(a)



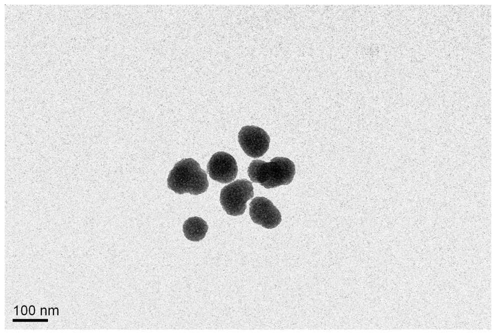
(b)

Fig. 2. AsFlFFF fractograms (a) and size distributions (b) of polystyrene latex beads and SiO_2 nanoparticles having nominal mean diameters of 20 nm. Flow rate were F_{out} = 0.52 and F_c = 1.52 mL/min. The carrier liquid was the same as that used in Fig. 1

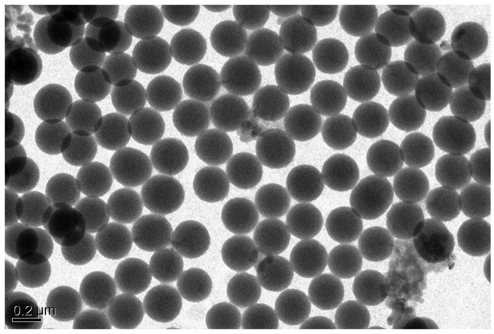
Fig. 3 showed the transmission electron microscopy (TEM) images of SiO_2 nanoparticles having nominal mean diameters of 20 (a), 60 (b) and 238 nm, respectively. It is seen in Fig. 3(a) that some of the 20 nm SiO_2 nanoparticles are aggregated, which may explain why the size distribution of the SiO_2 nanoparticles have a nonsymmetrical and broad size distribution as shown in Fig. 2.



(a)



(b)

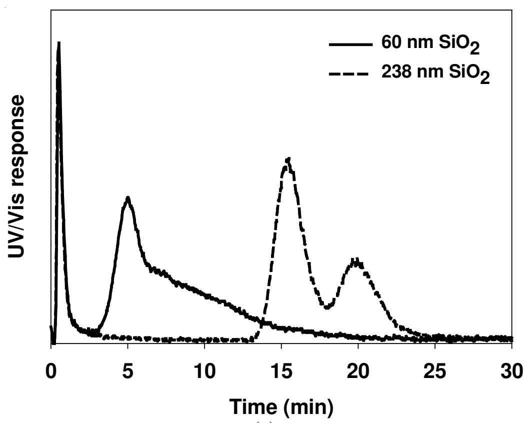


(c)

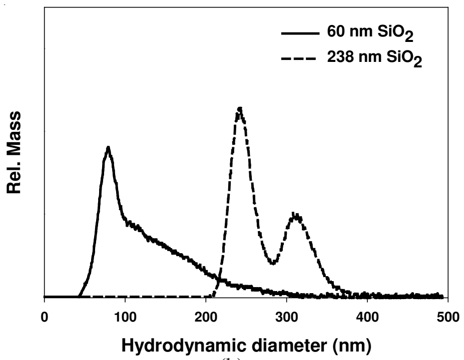
Fig. 3. TEM images of SiO_2 nanoparticle having nominal diameters of 20 (a), 60 (b) and 238 nm (c)

Fig. 4 shows AsFlFFF fractograms (a) and size distributions (b) of SiO_2 nanoparticles having nominal diameters of 60 and 238 nm, respectively. The channel flow rate F_{out} was 1.02 mL/min and the cross-flow rate F_c was 0.52 mL/min, respectively. The carrier liquid was the same as that used in Fig. 1. Fig. 4 shows the 60 nm SiO_2 sample have a broad size distribution ranging in hydrodynamic diameter from 40 up to about 300 nm. The measured mean hydrodynamic diameter was 124 nm. The 238 nm SiO_2 sample show a bimodal size distribution ranging in hydrodynamic diameter from about 200 up to about 400 nm. The measured mean hydrodynamic diameter was 273 nm.

The size distributions were measured by dynamic light scattering (DLS) for the same SiO_2 samples and the results are shown in Fig. 5. The mean diameters measured by DLS were 26.9, 129.9 and 289 nm for 20, 60 and 238 nm samples, respectively. The DLS results are listed in Table-2 with the results obtained by AsFlFFF and by TEM together.



(a)



(b)

Fig. 4. AsFlFFF fractograms (a) and size distributions (b) of SiO_2 nanoparticles having nominal mean diameters of 60 and 238 nm overlaid. Flow rate were F_{out} = 1.02 and F_c = 0.52 mL/min. The carrier liquid was the same as that used in Fig. 1

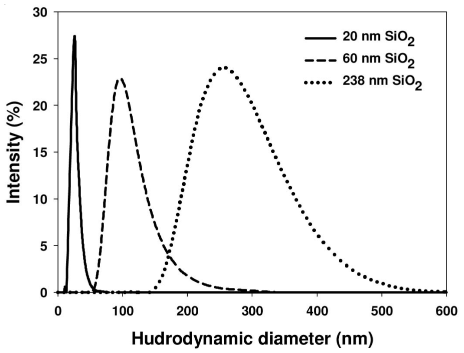


Fig. 5. Size distribution of 20, 60 and 238 nm SiO_2 nanoparticles obtained by DLS

TABLE-2
DIAMETERS MEASURED BY VARIOUS TECHNIQUES FOR SiO_2 NANOPARTICLES

Nominal diameter (nm)	Diameter measured by nm		
	AsFlFFF	DLS	TEM
20	26.8	26.8 ± 0.2	26.9 ± 4.2
60	124.3	129.9 ± 3.6	78.0 ± 14.5
238	273.1	289.0 ± 2.1	267.0 ± 16.0

Although the underlying mechanisms are very much different, both the AsFlFFF and the DLS measurements are based on the Brownian motion (or mass diffusion) of the particles in a medium, yielding the hydrodynamic diameters based on the Stokes-Einstein equation[16,17]. Thus the results from AsFlFFF and DLS are expected to agree to each other. As expected and as shown in Table-2, the results obtained by AsFlFFF and DLS are in good agreements for all three SiO_2 samples. It is noted however that, as shown in Fig. 5, DLS fails to show the details of the size distributions. All the size distributions obtained by DLS are unimodal, unlike the size distributions obtained by AsFlFFF (Fig. 2 and 4).

For the 20 and 238 nm samples, the TEM results are also in good agreements with those from AsFlFFF and DLS. For the 60 nm sample, however, the TEM results are much lower than those from other two techniques. TEM provides the images of the particles and is an excellent tool to see through the particles. However, during TEM measurements, the sample suspension is dried and put on a high-vacuum, which may cause shrinkage and agglomeration of particles. It also requires measuring a great number of particles to obtain accurate and representative size distributions, which is tedious and time-taking. Thus the size distribution and the mean sizes measured by TEM may not be accurate[18]. In Table-2, the numbers of the particles analyzed in the TEM measurements were 70 for the 20 and 60 nm sample and 260 for 238 nm sample, respectively.

Conclusion

Asymmetrical flow field-flow fractionation (AsFlFFF) was tested for its capability for separation and size characterization of SiO_2 nanoparticles, which were employed as a model particle for environmental particles. AsFlFFF provides separation of nanoparticles based on their sizes and allows determination of the particle size distributions. The diameters obtained by AsFlFFF were in good agreements with those obtained by DLS. This is probably because the both techniques are based on the Brownian motion of the particles in a suspension. It is noted however that the DLS may not provide accurate size distributions for samples having broad or multimodal size distributions[19-21]. TEM results did not agree well with those from AsFlFFF or DLS. Results indicate that AsFlFFF is a potentially useful and a convenient tool for size characterization of environmental particles.

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