A Movable Asymmetrical Flow Field-Flow Fractionation System for Size Characterization of Nanoparticles

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1. Introduction

Natural particles in nanometer size range play a significant role in mobility and bioavailability of pollutants and trace elements [1]. The mobility and bioavailability of nanoparticles depend on their chemical and physical properties such as size, shape, density, electrical charge and etc. [2, 3]. Among those, the size and shape of nanoparticles are important characteristics that control their behavior such as adsorption, aggregation, sedimentation, and transport.

Dynamic light scattering (DLS) is usually fast and easy to determine particle size. It is often difficult, however, to obtain accurate size distributions for samples having broad or multimodal size distributions. Electron microscopy (EM) can be used for determining sizes of nanoparticles but requires measuring a large number of particles especially those having broad size distributions. Field-flow fractionation (FFF) are useful for separation and size determination of colloidal nanoparticles, polymers, and biological macromolecules [4].

In this study, a movable asymmetrical flow FFF (AF4) system using a UV-Vis detector, which is the most universal method for the analysis of colloidal nanoparticles of various types, was developed for the field measurement of nanoparticles in natural water. AF4 provides separation of nanoparticles based on their sizes, and allows determination of the particle size distributions. The performance test of the established AF4 system was carried out with polystyrene or silver reference nanoparticles. In order to investigate trace amounts of natural nanoparticles using AF4, highly sensitive detection method or pre-concentration of samples are necessary [5, 6]. In the present work, liquid waveguide capillary cells (LWCCs) with longer optical path length than 1 cm are adopted for enhancing sensitivity of absorption measurement. The optimum separation conditions of AF4 coupled with LWCC system and the limit of detection (LOD) of different cells will be discussed.

2. Method and Results

2.1 Materials

Polystyrene nanoparticles having the nominal mean diameters of 20, 50, and 100 nm were obtained from Duke Scientific (Palo Alto, CA, USA). Polyvinylpyrrolidone-coated silver nanoparticles (PVP-AgNP) having nominal diameters of 30, 60 nm were purchased from nanoComposix, Inc. (San Diego, USA).

2.2 AsFlFFF system

The separation channel for AF4 system was the Eclipse AF4 (Wyatt Tech., Europe GmbH, Germany) assembled with a 350-μm-thick Mylar spacer and a regenerated cellulose membrane filter (10 kD, Millipore, USA). The geometry of the channel was trapezoidal with the tip-to-tip length of 17.5 cm and breadths at the inlet and the outlet of 2.2 and 0.3 cm, respectively. The carrier liquid was delivered into the channel using a HPLC pump (Shimadzu LC-20AD, Japan). The rate of cross-flow was measured using liquid flow meters (Optiflow 1000, Agilent Technologies, USA). The sample suspensions 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 at the flow rate of 0.2 mL/min for 40 s to inject the sample through the loop injector into the channel. Eluted particles were monitored using a UV-Vis detector (SPD-20A, Shimadzu, Japan) at 254 nm for polystyrene nanoparticles. The whole AF4 system is setup in a compact rack ((w) × (d)×81(h) cm³) can be transported by a van for the field experiment. Liquid waveguide capillary cell with an optical path length of 10 (LWCC-M-100, WPI, USA) or 100 cm (LWCC-3100, WPI, USA) was directly connected with the outlet of the separation channel using Teflon tubes. A spectrophotometer (Cary 5, Varian) was coupled with LWCC using a fiber optic interface (Hellma, Germany) and fiber optic cables (600 μm in a core diameter, Hellma, Germany).

2.3 Size determination using AF4

In AF4 system, the hydrodynamic diameter (d_H) of a particle is related with its retention time (t_r) by

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

, where V^o is the void volume of the AF4 channel, k is the Boltzmann constant, T is the absolute temperature (k), η is the viscosity of the carrier liquid, w is the channel thickness, F_c is the volumetric cross-flow rate (mL/min), and t^o is the void time (the elution time of nonretained species). Using Eq. (1), an AF4 fractogram of a sample can be converted directly to its particle size distribution.
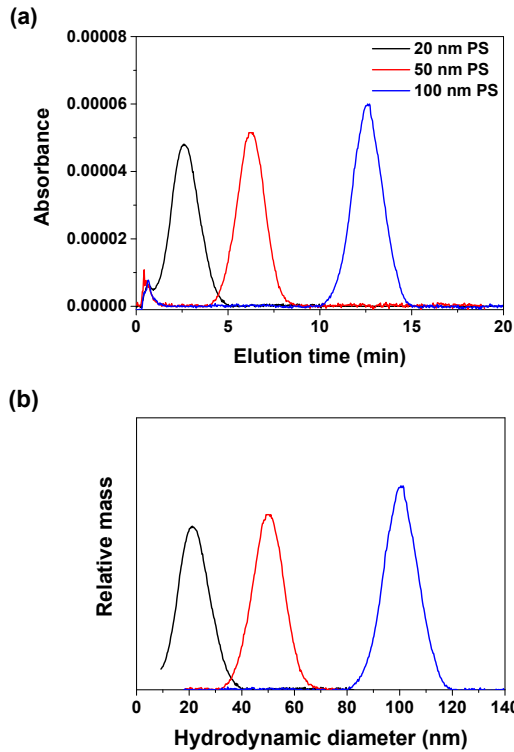
(a)

(b)

Fig. 1. AF4 fractograms (a) and size distributions (b) of polystyrene nanoparticles with nominal mean diameters of 20, 50 and 100 nm.

Table 1. Mean diameters of polystyrene nanoparticles measured by AF4

Nominal diameter (nm)	Measured diameter (nm)	Relative error (%)
20	20.5	2.5
50	49.5	1.0
100	99.5	0.5

Fig. 1 shows AF4 fractograms (Fig. 1(a)) and the size distributions (Fig. 1(b)) obtained by Eq. (1) for 20, 50, and 100-nm polystyrene reference nanoparticles. The cross-flow rate (F_c) and channel-flow rate (F_{out}) were 0.50 and 1.01 mL/min, respectively. The carrier liquid was water containing 0.02% FL-70 and 0.02% NaN_3. The mean sizes calculated with the measured retention times shown in Fig. 1(a) were represented in Fig. 1(b) and summarized in Table 1. The AF4 data are in excellent agreement with the nominal diameters with the relative errors less than 3%.

Fig. 2 shows AF4 fractograms (Fig. 2(a)) and size distributions (Fig. 2(b)) obtained by Eq. (1) for PVP-AgNP having nominal diameters of 30 and 60 nm. The separation conditions such as flow rates and carrier liquid were same as those for the separation of polystyrene nanoparticles. The mean diameters of 30 and 60-nm PVP-AgNP's shown in Fig. 2(b) were 40.3 and 66.2 nm, respectively. The mean diameters determined by TEM and DLS were 32.7 and 51 nm for 30-nm PVP-AgNP and 60.8 and 74.7 nm for 60-nm PVP-AgNP, respectively. The TEM results may not be

accurate as only limited numbers of particles could be measured. It was also difficult to obtain reliable and reproducible size data using DLS, due to a bias in the light scattering intensity toward large particles [7].
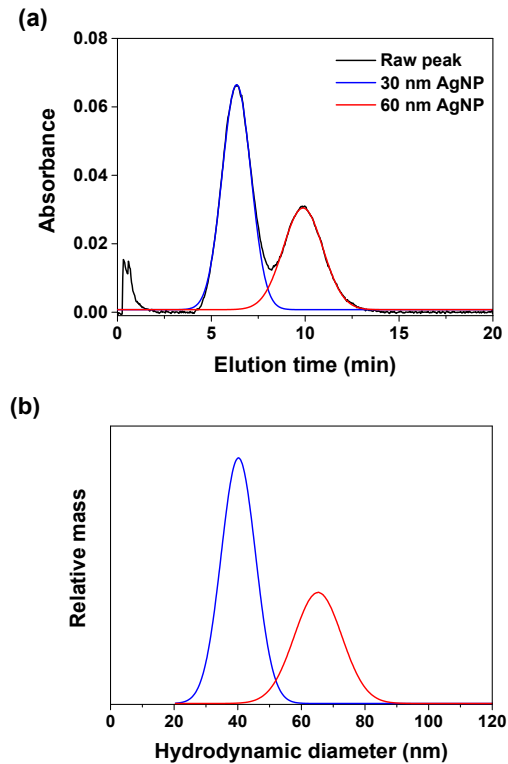
(a)

(b)

Fig. 2. AF4 fractograms (a) and size distributions (b) for PVP-AgNP with nominal mean diameters of 30 and 60 nm obtained using LWCC with optical path length of 10 cm.
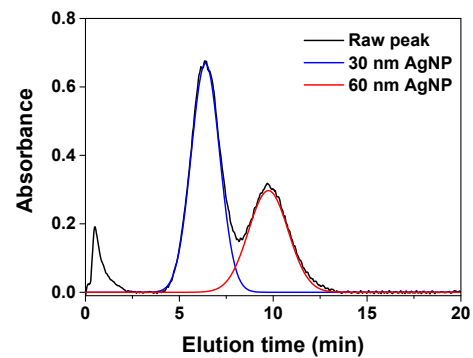

Fig. 3. AF4 fractogram of PVP-AgNPs a mixture of 30 and 60-nm PVP-AgNP and mathematical deconvolution obtained using LWCC with optical path length of 100 cm.

Fig. 3 shows an AF4 fractogram of a mixture of 30 and 60-nm PVP-AgNP observed using LWCCs with optical path length of 100 cm. Absorbance at 405 nm was increased about 10 times for both 30-nm PVP-AgNP (from 0.066 to 0.672) shown in Fig 2(a) and 60-nm PVP-AgNP (from 0.027 to 0.290) shown in Fig 3 when an optical path length of a LWCC was increased

from 10 to 100 cm. It seems clear that the use of LWCC with longer optical path length yields better detection sensitivity. The signal-to-noise ratio (S/N) depends on kinds of carrier liquids. The optimized separation condition for AF4-LWCC system with various carrier liquids is investigated and the results will be presented.

3. Conclusions

In this study, a movable AF4 system was developed and tested for separation and size characterization of polystyrene and silver reference nanoparticles. For the enhancement of sensitivity on absorption measurement, LWCC with longer optical path length than 1 cm was coupled with the developed AF4 system and the optimized condition of AF4-LWCC system was obtained. The developed AF4 system will be combined with laser-induced breakdown detection (LIBD) for analysis of trace nanoparticles in natural water.

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