Asymmetrical Flow Field-Flow Fractionation (AF4) Coupled with Liquid Waveguide Capillary Cell for Size Determination of Nano-Colloids in Groundwater

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1. Introduction

Field-flow fractionation (FFF) is a separation technique useful for analysis of nanoparticles and macromolecules based on their diffusion coefficients [1]. Among FFF subtechniques, asymmetrical flow field-flow fractionation (AF4) is the most universal technique useful for natural or manufactured nanoparticles, macromolecules and bio-nanoparticles. In FFF, an (or more) on-line detector is connected to the outlet of the FFF channel to produce informations on the sample, such as the particle size distribution. FFF has been combined with sensitive detectors such as light scattering (LS) [2], inductively coupled plasma mass spectrometry (ICP-MS) [3] and laser-induced breakdown detector (LIBD) for characterization of trace amount of nano-colloids [4]. These detection methods have some disadvantages including high cost and operational difficulties. An UV-vis detector has also been used widely for detection of nanoparticles, proteins and biomacromolecules due to its low cost, convenience and operational simplicity. Recently, a liquid waveguide capillary cell (LWCC) connected to an UV-vis spectrophotometry was developed for improvement of detection sensitivity of trace organic and inorganic species using flow injection analysis [5].

In the present study, AF4-LWCC system was developed to improve the limit of detection (LOD) for analysis of nano-colloids. LWCC with longer path length than 1 cm is coupled with AF4 system to enhance the detection sensitivity. Also, online sample enrichment in the AF4 channel was performed to determine the size and size distributions of colloids in KAERI Underground Research Tunnel (KURT) groundwater.

2. Method and Results

2.1 AF4 system

The geometry of the AF4 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). Eluted particles were monitored by a UV-vis detector (SPD-20A, Shimadzu, Japan). A LWCC with the optical path length of 10 or 100 cm was directly connected to the outlet of the FFF channel using Teflon tubes. A spectrophotometer (Cary5, Varian) was coupled with the LWCC using a fiber optic adaptor (Hellma, Germany) and fiber optic cables (600 μm in a core diameter, Hellma, Germany).

2.2 Analysis of silver nano-colloids using AF4

Fig. 1 shows AF4 fractograms and size distributions of a mixture of 30 and 60 nm silver nano-colloid samples. The cross-flow rate (F_c) and the channel-flow rate (F_{out}) were 0.50 and 1.01 mL/min, respectively. The carrier liquid was water containing 0.01% SDS and 0.02% NaN_3. As shown in Fig. 1, the mean diameters of 30 and 60 nm silver nano-colloids were 40.3 and 66.2 nm, respectively. The comparison of various particle size techniques such as TEM, DLS and AF4 will be discussed for size analysis of silver nano-colloids.

To improve the detection sensitivity, optical path lengths were increased from 10 cm to 100 cm. Absorbance at 405 nm was increased approximately 10 times for both 30 nm silver nano-colloids (from 0.066 to 0.672) and 60 nm silver nano-colloids (from 0.027 to 0.290) when an optical path length of a LWCC was increased from 10 to 100 cm.

Results show that LOD for analysis of silver nano-colloids is improved with increasing optical path length.

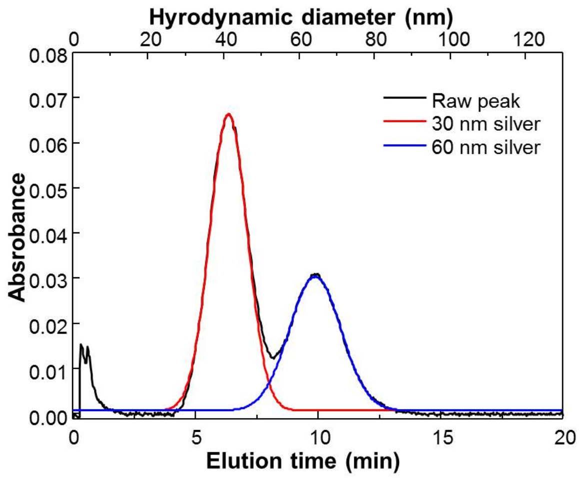

Fig. 1. AF4 fractogram and size distribution of silver nano-colloids.

2.3. Determination of size distribution of colloids in KURT groundwater

An on-line enrichment method was applied for separation and size determination of colloids in KURT groundwater. Fig. 2 shows a schematics diagram of AF4 setup for analysis of colloids in KURT groundwater. The injection volume was increased to be 10 mL and the injected sample was focused in the FFF channel for enrichment of the colloids. Size distributions were determined for colloids in the KURT groundwater collected at various depths. The size of nano-colloids in KURT groundwater was ranging from 3 to 30 nm in diameter.

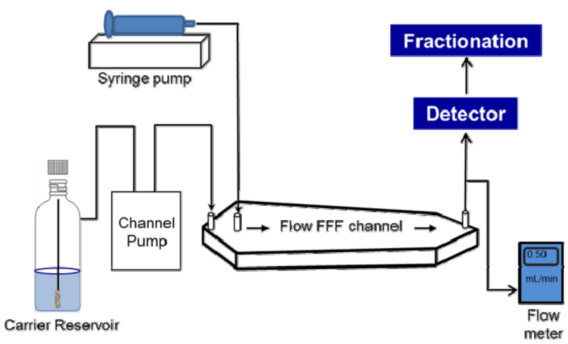

Fig. 2. Schematics of on-line enrichment of KURT groundwater colloid in AF4 channel.

3. Conclusion

In this study, AF4-LWCC system was successfully employed for separation and size determination of nano-colloids and colloids in KURT groundwater. The characteristic of AF4-LWCC system for determining U(IV) nano-colloid and colloids in KURT groundwater will be discussed.

4. References

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