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Characterization of Asian dust using steric mode of sedimentation field-flow fractionation (Sd/StFFF)

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Steric 모드의 침강장-흐름 분획법을 이용한 황사의 특성분석

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Abstract: Asian dust particles are known to have sizes ranging from a few nanometers up to about a few micrometers. The environmental and health effects depend on the size of the dust particles. The smaller, the farther they are transported, and the deeper they penetrate into the human respiratory system. Sedimentation field-flow fractionation (SdFFF) provides separation of nano to microparticles using a combination of centrifugal force and parabolic laminar flow in a channel. In this study, the steric mode of SdFFF (Sd/StFFF) was tested for size-based separation and characterization of Asian dust particles. Various SdFFF experimental parameters including flow rate, stop-flow time and field strength of the centrifugal field were optimized for the size analysis of Asian dust. The Sd/StFFF calibration curve showed a good linearity with R^2 value of 0.9983, and results showed an excellent capability of Sd/StFFF for a size-based separation of micron-sized particles.The optical microscopy (OM) was also used to study the size and the shape of the dust particles. The size distributions of the samples collected during a thick dust period were shifted towards larger sizes than those of the samples collected during thin dust periods. It was also observed that size distribution of the sample collected during dry period shifts further towards larger sizes than that of the samples collected during raining period, suggesting the sizes of the dust particle decrease during raining periods as the components adsorbed on the surface of the dust particles were removed by the rain water. Results show Sd/StFFFis a useful tool for size characterization of environmental particles such as the Asian dust.

요 약: 황사입자들은 수 나노미터에서 수 마이크론 사이의 크기를 가지는 것으로 알려져 있다. 황사가 환경 및 인체 건강에 미치는 영향은 황사 입자의 크기에 의존한다. 입자가 작을수록 멀리까지 이동하며, 인체의 호흡기관 깊숙이 침투한다. 침강장-흐름 분획법(sedimentation field-flow fractionation, SdFFF)은 채널 내 포물선형태의 흐름(parabolic flow profile)과 외부에서 가해지는 원심력의 상호작용을 이용하여 나

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노 및 마이크론 크기의 입자들의 분리를 제공한다. 본 연구에서는 황사입자의 크기별 분리와 특성분석을 위한 steric 모드 침강장-흐름 분획법(Sd/StFFF)의 응용 가능성을 테스트하였다. 이를 위하여 다양한 Sd/StFFF 파라미터들을(유속, stop-flow time, 원심력의 세기, 등) 최적화 하였다. Sd/StFFF 보정곡선의 R^2값은 0.9983으로 높은 직선성을 보였으며, 실험결과는 Sd/StFFF가 마이크론 입자의 크기별 분리에 우수함을 보여주었다. 광학현미경(optical microscopy, OM)을 이용하여 황사입자들의 크기와 모양을 조사하였다. 황사가 진할 때에는 약할 때보다 입자크기가 증가함을 보여주었다. 또한 비가 올 때에는 건조할 때보다 입자크기가 감소하였는데, 이는 입자 표면에 흡착되어 있는 성분들이 빗물에 의해 제거되었기 때문인 것으로 보여진다. 본 연구의 결과는 Sd/StFFF가 황사와 같이 환경입자의 크기특성분석에 유용함을 보여준다.

Key words: asian dust, particle size distribution, sedimentation/steric field-flow fractionation (Sd/StFFF)

1. Introduction

Asian dust is transported during spring in East Asia, and causes environmental and health problems as they carry various toxic compounds. Asian dust is a serious and growing environmental concern in East Asia as well as in the west Pacific Ocean. Central Asia is one of the world's largest dust sources. The world map shows a belt of arid and semiarid areas from Central Eurasia to the Far East, including Kazakhstan, Mongolia and Northern China, where the Asian dust is produced frequently.[1]

Asian dust carries some chemical species along with its original soil components. The Asian dust particles may react with SOx and NOx, resulting in transport of modified Asian dust to East Asia, with sulfate and nitrate deposition and with elevated levels of minerals.[2-4] As the mineral dust reacts in the air, the physicochemical properties of the particles change, as does their effectiveness to serve as the cloud condensation nuclei.[5,6] Furthermore, the chemistry of the Earth's atmosphere is influenced by reducing photolysis rates of important atmospheric gasphase species through the heterogeneous chemical reaction of mineral dust particles,[7,8] hence, increasing attention has been devoted to the study of modification of the physicochemical properties of Asian dust particles during long-range transport.[4,9,10]

The occurrence and intensity of Asian dust have gradually increased in Korea recently. The most efficient way to prevent the damages from Asian dust is, of course, the restraint of the occurrence of the Asian dust. Unfortunately, there is no short term solution to manage the Asian dust, a natural phenomenon. The first step towards minimization of the damages from Asian dust is establishing basic data, so that one could better understand the harmfulness of the Asian dust, and to trace the source area of Asian dust. Rare earth element analysis was performed to find the source of the Asian dust in Daejeon, Korea,[11] and results suggested Asian dust in the Daejeon area might be derived from the south-eastern part of Ordos desert. Also the Sr-Nd isotopic ratio analysis, which is one of the most common method to trace the source of geological materials, indicated that Asian dust was originated from Central Loess Plateauand/or Ordos desert in spring, 2007.[12]

Field-flow fractionation (FFF) is an elution technique that is useful for high-resolution separation and characterization of a broad range of colloidal particles, polymers, and biological macromolecules. FFF uses a thin (usually 50-500 μm thick) ribbon-like flow channel that provides a well-defined parabolic (laminar) flow profile. An external field is applied perpendicularly to the flow axis and forces the sample particles (or molecules)to migrate toward the accumulation wall of the channel.[13]

The steric mode of sedimentation FFF (Sd/StFFF) is particularly usefulseparation and characterization technique of colloidal particles larger than about 1ìm in diameters.[14] For spherical particles of uniform density, Sd/StFFF provides size-based separation, and allows direct conversion of the Sd/StFFF elution profile (fractogram) to the size distribution. The combination of high resolution and high speed with system flexibility has made Sd/StFFF an attractive tool for the analysis of various particulate materials, including biological cells,[15] chromatographic supports,[16] and industrial materials.[17]

The size and size distribution of Asian dust are of interest, because they influence the transport pathway of pollutants and the degree of penetration of the particles into the human respiratory system. The effect of particle size on the adsorption characteristics of toxic chemicals has been studied for Asian dust, in which the formation mechanism and the relationship of the particle size with the amount of toxic inorganic species, such as heavy metals, have been investigated.[17] It has been reported that the density and size of the Asian dust are typically around 2.0 g/cm^3 and in the rage of 2-20 μm in diameters, respectively. Particles larger than about 20 μm are not transported long distances. It has been also reported that these fine particles often include microorganisms.[1] In this study, Asian dust samples were collected, and analyzed for more accurate determination of size distribution using Sd/StFFF.

2. Theory

2.1. Principle of SdFFF

In SdFFF, separation is brought about by introducing centrifugal field force on the suspended particles. The centrifugal force causes sedimentation of the sample components.

Particles are distributed between different axial flow vectors according to the balance between the applied centrifugal field and diffusion of the particles.

In the steric mode of SdFFF (Sd/StFFF), the retention time (t_r) of particles having diameter d is given by[18]

$$t_r = \frac{wt}{3\gamma d} \tag{1}$$

where w is the channel thickness, t^0 the channel void time, and γ a dimensionless "steric correction factor".

As can be seen in Eq. (1), if γ is a constant, t_r is inversely proportional to d. Thus Sd/StFFF can provide size-based separations with larger particles eluting earlier than smaller ones.

Due to the uncertainty in γ, the size-analysis by Sd/StFFF requires a calibration. The Sd/StFFF calibration curve (log t_r vs. log d) is usually linear, and is expressed by[19]

$$\log t_r = -S_d \log d + \log A \tag{2}$$

A is a constant equal to the extrapolated value of the retention time t_r for a particle of unit diameter. The slope of the calibration curve is defined as the size-based selectivity, S_d. Assuming the band broadening is negligible, Sd/StFFF fractogram can then be transformed into size distribution by[19]

$$m(d) = c(t_r)\dot{V}S_d A\left(\frac{t_r}{A}\right)^{\frac{Sd+1}{Sd}} \tag{3}$$

where $m(d)$ is the mass-based size distribution, $c(t_r)$ the fractogram signal (detector response), and $\dot{V}$ the volumetric flow rate.[19]

In Sd/StFFF, retention depends on the density as well as the size.[20] Thus, for pure size-based separation, both the calibration standards and the sample need to have the same density as that of the sample. If the density of the calibration standard is different from that of the sample, the density of the sample needs to be known. Then a density-compensation can be used in which thefield strength (channel rotation rate) is adjusted for the sample to compensate the density difference between the standards and the sample. The adjusted channel rotation rate for the sample, $(rpm)_{sample}$, can be calculated by[21]

$$(rpm)_{sample} = \sqrt{\frac{\Delta\rho_{std}}{\Delta\rho_{sample}}}(rpm)_{std} \tag{4}$$

where $(rpm)_{std}$ is the rotation rate for the standard runs, $\Delta\rho_{std}$ is the density difference between the standard and the carrier, and $\Delta\rho_{sample}$ is the density difference between the sample and the carrier. With the density compensation, the particles having the same size are subjected to the same centrifugal force irrespective of density, and thus, they elute at the same time. With the density compensation, a calibration based on standards having a different density from that of the sample can be used for size determination of the sample.[17]

3. Experimental

3.1. Materials and samples

Polystyrene latex beads obtained from Duke Scientific (Palo Alto, CA) were used as particle-size standards.

The Asian dust samples were collected four times during which the Asian dust-watch was issued by the Korean meteorological administration (KMA) in a two month-period, March and April of 2007. They were named "sample-a, b, c, and d", respectively. Sampling was made at the top of a building in the Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon, Korea to prevent contamination of the sample by vehicle exhaust or road sediments. Samples were collected using an Anderson type high volume air sampler (Sibata Ltd, Saitama, Japan) equipped with a quartz fiber filter (QR-100, 12"×20") for 24 hrs at the rate of 1,000 L/min.

The sample-a was collected during a thick dust period (PM10 concentrations higher than 200 μg/m^3) and sample-b when it was raining in a thick dust period. Sample-c was collected during a thin dust period (PM10 concentrations lower than 200 μg/m^3) and sample-d when it was raining in a thin dust period.

All Asian dust sampleswere dispersed in water containing 0.1% FL-70at the concentrations of 0.5 g in 5 mL liquid, and then passed through a 270-mesh (having pores of ~53 μm) to remove particles larger than about 50 μm before they were injected into FFF channel to prevent plugging of the channel.

3.2. Sedimentation Field-Flow fractionation

The SdFFF channel used in this study is 0.02 cm thick, 89.5 cm long and 1cm wide. The radius of the channel rotor is 15.1 cm. The channel void volume was measured from the elution volume of bromo phenol blue (BPB) to be 2.2 mL. The carrier solution was pumped by a M930 HPLC pump (Young-Lin Scientific Co., Anyang, Korea). The eluted particles were monitored by a UV-106 UV/VIS detector (Linear Instruments, Reno, USA) operating at the fixed wavelength of 254 nm. The control of SdFFF operation and data collection/processing was performed by a personal computer loaded with the software provided by Postnova USA (Salt Lake City, Utah, USA). The injection volume was between 20 and 40 μL, depending on the sample concentration. All samples were directly injected through a septum into the channel. All experiments were performed at room temperature (23~24 ^{o}C).

4. Results and discussion

Fig. 1(a) shows Sd/StFFF fractograms of 3, 8, 12, 20, and 40 μm polystyrene latexbeads obtained at the channel rotation rate of 1000 rpm and flow rate of 5 mL/min. The stop-flow time was 1 min. As predicted from theory, smaller particles were eluted

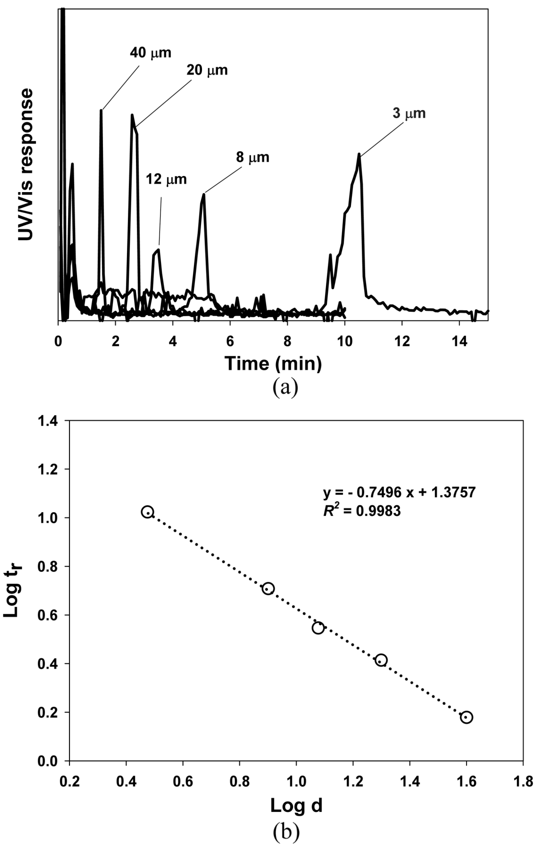


Fig. 1. Sd/StFFFfractograms of 3, 8, 12, 20 and 40 mm polystyrene latex beads (a) and calibration plot (b). The channel rotation rate was 1000 rpm, and the flow rate was 5 mL/min

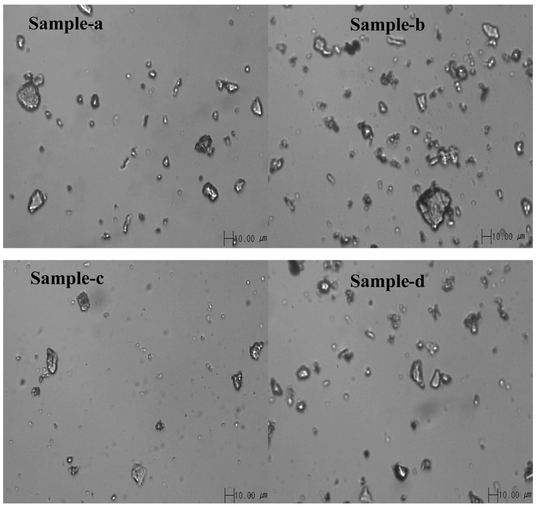


Fig 2. Optical micrographs of four Asian dust samples.

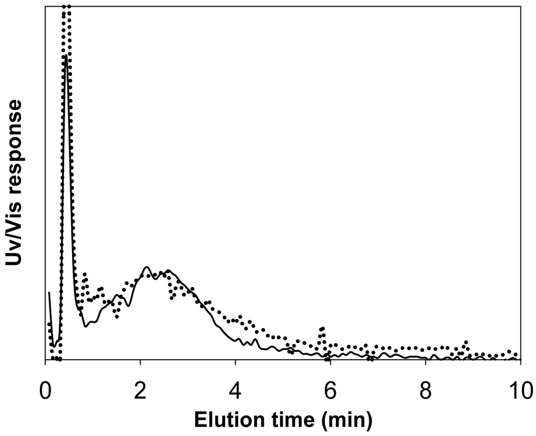


Fig. 3. Repeated SdFFF fractograms of sample-*a*. The channel rotation rate was 150 rpm, and the flow rate was 5 mL/min.

later than larger ones. *Fig.* 1(b) is the calibration curve obtained from the retention times of the polystyrene beads shown in *Fig.* 1(a). The calibration curve shows an excellent linearity with R^2 value of 0.9983. *Fig.* 1(a) and (b) clearly shows the capability of Sd/StFFF for a size-based separation of micron-sized particles.

Fig. 2 shows optical micrographs of four Asian dust samples. For each sample, about 0.5 g of the dust was dispersed in 5 mL of the SdFFF carrier liquid (water containing 0.1% FL-70) by sonication. It can be seen that the sample-*a*, collected in a dry (no rain) thick dust period, contains more of the particles than the sample-*c*, collected in a dry thin dust period, as expected. And more particles are present when they were collected in raining period as shown in the sample-*b* and *d* than in the samples-a and b, which were collected during dry period. It is difficult to determine the particle size and its distribution of the dust particles from optical microscopy (OM) images. However, the differences in particle populations between samples collected during dry and wet period observed in *Fig.* 2 suggest that the average particle sizes may be smaller in samples collected during wet period than those in samples collected during dry period (there are higher populations of particles in samples collected during wet period than in those collected during dry period for the same total mass of the particles).

As mentioned earlier, the calibration curve shown in *Fig.* 1-(b) cannot be used for size calculations of the Asian dust particles, because the density of Asian dust is different from that of the polystyrene standard. The density of the Asian dust (reported to be about 2 g/mL) is much higher than that of the polystyrene beads (1.05 g/mL). The density compensation was thus needed, and the adjusted channel-rotation rate for the Sd/StFFF analysis of the Asian dust wascalculated by Eq. (4) to be 147 rpm. In this study, the channel rotation rate of 150 rpm was used for all Sd/StFFF analysis of Asian dust samples.

Fig. 3 shows Sd/StFFF fractograms of the sample-a obtained by repeated runs. Thecarrier liquid was water containing 0.1%FL-70.The channel rotation speed was 150 rpm (G=11.64 g) and the flow rate was 5 mL/min. The stop-flow time was 1 min. Considering the complex nature of the sample, the repeatability was acceptable.

Fig. 4 shows Sd/StFFF fractograms of the sample-a obtained with various sample injection volumes. With 40 μL injection, a better elution profile was obtained with strong enough signal and a reasonable separation from the void peak. The signals were too weak with the sample injection volume of 20 and 30 μL. The sample injection volume of higher than 40 μL does not seem to be necessary in terms of the

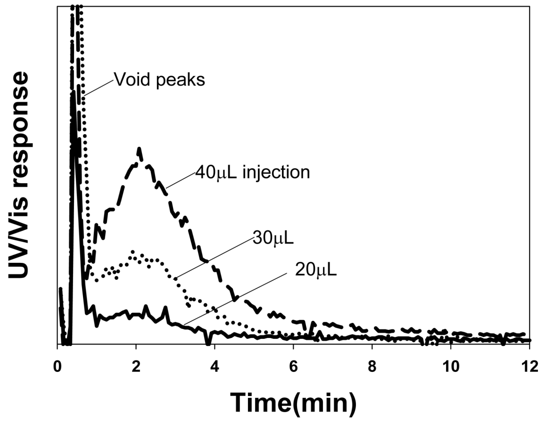
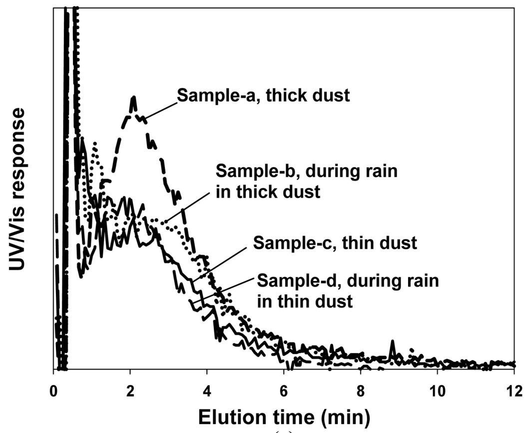


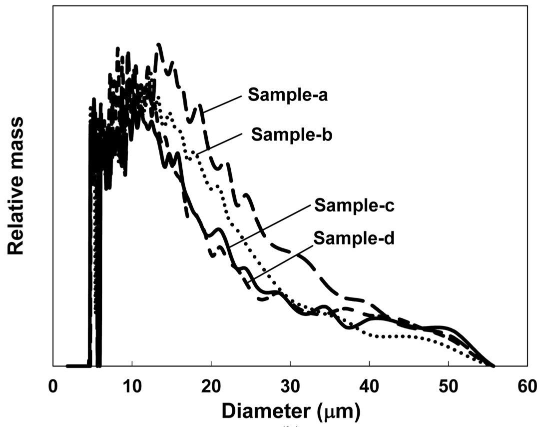
Fig. 4. Sd/StFFF fractograms of Asian dust sample-*a* obtained with various injection volumes. All other experimental conditions were the same as those in Fig. 3.

signal intensity, and may cause over-loading, which needs to be avoided in all FFF analysis. Based on the results shown in *Fig.* 4, the injection volume of 40 μL was chosen in this study.

Fig. 5(a) shows Sd/StFFF fractograms of all four Asian dust samples. The experimental conditions were again the same as those in *Fig.* 3. The fractograms were converted to size distributions using Eq. (3) after removing the void peak. The size distributions were area-normalized for comparison, and were plotted in *Fig.* 5(b). It can be seen that the size distributions of the samples-a and b, collected during a thick dust period, were shifted towards larger sizes than those of the samples-c and d, which were collected during thin dust periods. It is also noted that the size distribution of sample-a, collected during dry thick dust period, was shifted further towards larger sizes than the sample-b, which was collected during wet thick dust period. This is in accordance with the expectation discussed in *Fig.* 2. Possible explanation for this phenomenon is that the sizes of the dust particle decrease during raining periods as the water-soluble components adsorbed on the surface of the dust particles were removed by the rain water. The difference in size distributions of the sample-c and d was not significant, probably because the dust concentrations were not high enough to yield significant difference in particle size by the rain water. More detailed investigation is needed for more accurate explanation on this reduction in particle size during raining period.



(a)



(b)

Fig 5. Sd/StFFF fractograms (a) and normalized size distributions of Asian dust samples. All experimental conditions were the same as those in Fig. 3.

5. Conclusions

The applicability of Sd/StFFF for size analysis of Asian dust particles was investigated. Results indicate that Sd/StFFF is a useful tool for size-characterization of various types of micron-sized environmental particles such as Asian dusthaving complex chemical compositions and broad size distributions.Being an elution technique, Sd/StFFF provides size-based separation of those particles, allowing direct conversion of the fractogram to the size distributions. Sd/StFFF also allows size-fractions to be collected for further analysis such as Inductively Coupled Plasma/Mass spectrophotometer (ICP/MS) for compositional analysis of the particles in different size ranges.

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