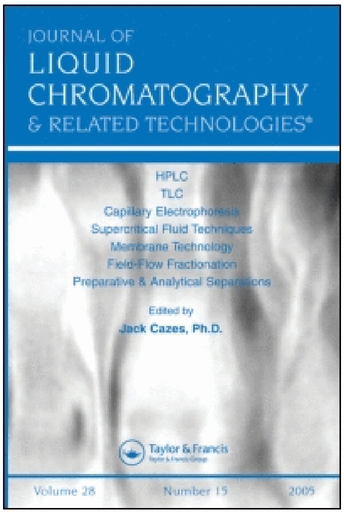

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Kim, Won-Suk , Park, Young Hun , Lee, Dai Woon and Lee, Seungho(2001) 'SAMPLE PREPARATION FOR SIZE ANALYSIS OF DIESEL SOOT PARTICLES USING FIELD-FLOW FRACTIONATION', Journal of Liquid Chromatography & Related Technologies, 24: 13, 1935 — 1951

To link to this Article: DOI: 10.1081/JLC-100104436

URL: http://dx.doi.org/10.1081/JLC-100104436

J. LIQ. CHROM. & REL. TECHNOL., 24(13), 1935–1951 (2001)

SAMPLE PREPARATION FOR SIZE ANALYSIS OF DIESEL SOOT PARTICLES USING FIELD-FLOW FRACTIONATION

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ABSTRACT

Sample treatment procedure, and the experimental parameters that need to be considered in size analysis of diesel soot particles using field-flow fractionation (FFF), are discussed. A probe-type sonication of 10 min in water containing 0.05% of Triton X-100 provides well-dispersed suspension of the soot particles. Sample treatment is found to be important for reduction in particle-particle interaction and, thus, for preparation of well-dispersed soot suspension.

FFF elution profile of untreated suspension has a long tailing that does not return to the baseline until the external field is removed. The scanning electron micrographs show that the untreated suspension contains aggregated particles. Extraction of chemicals is also found to be important for preparation of well-dispersed suspension. The suspensions prepared without the

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extraction step, have broader and larger size distributions than those prepared with the extraction step, due to the presence of soluble organic fractions (SOF) that cause particle-aggregation. FFF provides an excellent repeatability in size analysis of soot particles. The standard deviation of the mean diameter measured by FlFFF was 3.6%.

Both Flow FFF (FlFFF) and sedimentation FFF (SdFFF) are tested for size analysis of soot particles. SdFFF provides higher size-selectivity than FlFFF and is less problematic in terms of the particle-channel interaction. Unlike in SdFFF, FlFFF analysis does not require the density information and, thus, the fractogram can be directly transformed to the size distribution. But FlFFF provides lower size-selectivity and has narrower dynamic range than SdFFF.

INTRODUCTION

Size analysis of soot particles emitted from diesel engine is important for monitoring of their environmental impact as the particle size influences their physical and chemical characteristics during their transport processes.[1-3] Unfortunately, accurate size analysis of soot particles remains to be troublesome as the soot particles tend to interact with each other, resulting in aggregation of particles during soot collection, pre-treatment, and even during size-analysis.[4,5] Currently available sizing techniques for soot particles include electrical aerosol analyzer,[6-8] cascade impactor,[9] electron microscopy,[10] light scattering,[11,12] and field-flow fractionation (FFF).[4,13]

FFF is a family of techniques applicable to analysis of a broad range of polymers[14,15] and colloidal particles.[16,17] In FFF, a small volume of suspended particles is injected into a thin ribbon-like channel where separation takes place. Injected particles are swept down the channel by the channel flow, while an external field is applied in the direction perpendicular to the channel flow. The down-channel migration velocity of a particle depends on how strong the particle interacts with the external field. Particles having different characteristics interact differentially with the external field and, thus, migrate down the channel at different velocities, resulting in separation of particles. As the retention time is directly related with particle properties, FFF elution curves ("fractogram") can be transformed into distribution curves of the relevant properties, such as mass or size distributions. Various types of external field can be employed including centrifugal (sedimentation FFF), thermal gradient (thermal FFF), and cross-flow (flow FFF), etc. Among those, sedimentation FFF (SdFFF) and flow FFF (FlFFF) are the most widely used techniques for particle analysis.

Unlike chromatography, there is no stationary phase to interact with the sample in FFF. The openness of the FFF channel minimizes shear degradation or adsorption of the sample. FFF is, thus, useful for analysis of large molecules and highly interactive particles such as soot particles. The potential and the capability of FFF for size analysis of soot particles have been shown.[4,5,18-20] As the soot particles tend to interact with each other, which could cause particle-aggregation, FFF-analysis requires a pre-treatment of the soot particles to prepare a well-dispersed suspension of the soot particles. The pre-treatment procedure includes

(1) recovering the soot particles from membrane filters (filters are used to collect the soot particles),

(2) extracting chemicals adsorbed at the surface of the soot particles, and

(3) dispersing the soot particles in an appropriate liquid. The extraction step is necessary for qualitative and quantitative analysis of chemicals and also for reducing the surface-activity of the soot particles.[5]

We have developed a pre-treatment procedure for FFF analysis of soot particles.[4] First, the soot particles are collected using membrane filter(s) placed in the engine exhaust line. Then, the filter is bath-sonicated in ethanol for recovery of soot particles from the filter. Recovered particles are treated in two steps. First the chemicals adsorbed at the surface of the soot particles are removed by liquid-extraction, for which two procedures, named "focusing method" and "hexane-decantation method," were proposed.

In the focusing method, the mixture of ethanol and soot particles obtained in the recovery step is mixed with n-hexane and water containing 0.05% of Triton X-100, a nonionic surfactant. This results in concentration (focusing) of soot particles at the boundary between the aqueous and the organic phase (n-hexane), allowing extraction of both polar and nonpolar species at the same time. After the removal of ethanol and n-hexane, the particle-containing aqueous phase is heated at 60°C for complete removal of remaining n-hexane and ethanol. In the hexane-decantation method, the same mixture of ethanol and soot particles is heated at 70°C until about 5 mL of ethanol remains. Then, 20mL of n-hexane is added, and heated for extraction of organic compounds.

After the liquid-extraction, 2-3 mL of dispersing liquid (water containing 0.05% of Triton X-100 and 0.02% of NaN_3) is added, and sonicated in a probe-type sonicator to prepare a suspension of soot particles for FFF analysis. In the hexane-decantation method, the suspension is heated again for complete removal of n-hexane.

In this paper, we present the results obtained during optimization of the sample-treatment procedure and we discuss the experimental parameters that need to be taken into consideration for FFF analysis of soot particles.

THEORY

Both SdFFF and FlFFF separate particles based on their size and, thus, can be used for size determination of particles. In the normal mode of SdFFF, particle diameter d is related with the retention time t_r by:[13]

$$d = \left[\frac{36kT}{\pi\, G w t^{0} \Delta\rho} \, t_r \right]^{1/3} \tag{1}$$

where k is the Boltzmann constant, T the temperature, G the centrifugal acceleration, w the channel thickness, t^o the channel void time (elution time of unretained solute), and $\Delta\rho$ the density difference between the particle and carrier. The size based-selectivity, S_d, is defined by:[21]

$$S_d = \left| \frac{d \ln t_r}{d \ln d} \right| \tag{2}$$

According to eq 1, the retention time t_r is proportional to d^3 and, thus, the size-based selectivity S_d is 3 in SdFFF. Using eq 1, particle diameter can be determined by measuring retention time t_r if the density of particle (thus, $\Delta\rho$) is known.

In the normal mode of FlFFF, particle diameter d is related to the retention time t_r by:[13]

$$d = \frac{2kTV^{o}}{t^{o} w^{2} \pi \eta V_c} t_r \tag{3}$$

where V^o is the channel volume, η viscosity of the carrier liquid, and V_c the cross flow rate. As in SdFFF, retention time increases with diameter in FlFFF. This time t_r is proportional to d (not d^3) and the size-based selectivity is 1, one-third of that in SdFFF. In FlFFF, particle diameter can be determined by measuring the retention time t_r using eq 3.

EXPERIMENTAL

The SdFFF system is the model S101 colloid/particle fractionator purchased from FFFractionation, LLC (Salt Lake City, Utah, USA). The FlFFF system is assembled in our laboratory, and is similar to the Universal Fractionator model F-1000 of FFFractionation, LLC. The membrane used for the accumulation wall of the FlFFF system is YM-10, a regenerated cellulose having the cut-off-molecular weight of 10,000, purchased from Amicon (Beverly, Maine, USA).

The carrier liquid for both SdFFF and FlFFF is doubly distilled, and deionized water containing 0.05% (w/v) Triton X-100 and 0.02% (w/v) NaN_3. NaN_3 is added as a source of a salt, as well as, a bactericide. Triton X-100, a nonionic surfactant, is added as a dispersing agent for the soot particles. The pH and ionic strength are important parameters that influence the degree of particle-particle and particle-channel wall interaction.

For FFF analysis of diesel soot particles, the optimum pH and ionic strength of the carrier liquid are found to be 8.0 ~ 9.0 and 0.0041 M, respectively, based on our preliminary study.[22] The pH of the carrier was adjusted by adding an appropriate amount of 0.1N NaOH. Polystyrene latex standards are purchased from Duke Scientific (Palo Alto, CA, USA).

Five diesel soot samples (soot #1~5) are collected and analyzed in this study (Table 1). The soot #1~3 are collected from a heavy-duty (urban bus), and the soot #4 and 5 are collected from a light-duty diesel engine (jeep-style all terrain vehicle). The soot #1 was collected from an engine running in D-13 mode. The D-13 mode is an exhaust gas restriction mode for heavy-duty diesel engines, which consists of thirteen steps of various combinations of engine speed, load rate, and the driving time.[23] The soot #2~5 are collected from an engine running at a fixed rpm and the load rate (Table 1).

The bath-sonicator used for recovery of soot particles from a membrane filter is the Solid State/Ultrasonic FS-28 (Fisher Scientific Co., Pittsburgh, PA, USA).

For dispersing of soot particles after extraction of chemicals, a probe-type sonicator (50W, Fisher Scientific Co., Pittsburgh, PA, USA) is used. A JEOL model JSEM-5410LV (Tokyo, Japan), a high resolution scanning electron microscope (SEM), is used for electron microscopy of soot particles.

Table 1. Diesel Soots Collected for This Study

Soot No.	Filter Type	Operating Mode	Engine Type	Source
1	Quartz membrane	D-13	Heavy-duty[a]	MVERL[b]
2	Quartz membrane	1300 rpm 100% load rate	Heavy-duty	MVERL
3	Quartz membrane	1400 rpm 100% load rate	Heavy-duty	MVERL
4	Horiba filter	Constant rpm between 3000 ~5000	Light-duty	HMC[c]
5	Horiba filter	Constant rpm between 3000 ~5000	Light-duty	HMC

[a]Natural aspirator-type heavy-duty diesel engine, [b]Motor Vehicle Emission Research Laboratory, [c]Hyundai Motor Corporation.

RESULTS AND DISCUSSION

Focusing vs. Decantation Method

To compare the effectiveness of two extraction methods (focusing and hexane-decantation method), two suspensions are prepared from the soot #4 using the same procedure except for the extraction step, one by the focusing method and the other by the hexane-decantation method. For both, final suspensions are prepared by 10-min probe-type sonication. Figure 1 shows SdFFF fractograms of the two suspensions. The fractogram of the suspension prepared by the decantation method, is broader and extends further toward higher elution time

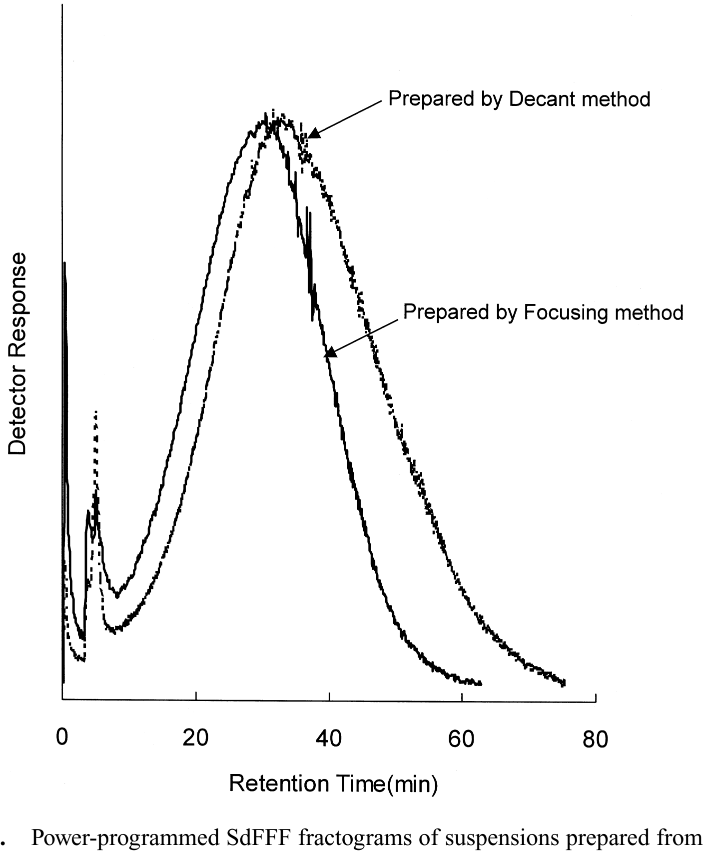

Figure 1. Power-programmed SdFFF fractograms of suspensions prepared from soot #4 using focusing and decantation method. Programming parameters: initial field-strength = 1680 rpm, t_1 = 4.5 min. The stop flow time is 10 min and the flow rate 1.04 mL/min.

than that of the suspension prepared by the focusing method. It means the decantation method yields a suspension whose size distribution is broader and larger. This difference is probably due to repeated heating in the decantation method that could promote particle-aggregation.[5] This result suggests the focusing method is more effective in extracting chemicals and in dis-aggregating the particles than the decantation method and, thus, is chosen in this study. After a number of tests, a mixture of ethanol, n-hexane, and water with the volume-ratio of 1:1:0.5 is selected as the extracting solvent for the focusing method.

Importance of Sample Pre-treatment

To study the importance of the sample pre-treatment, two suspensions are prepared from soot #1, with and without the pre-treatment procedure. FlFFF fractograms of the two suspensions are shown in figure 2. The treated suspension (dotted line) eluted well within about 20 min. The SEM picture confirms the particles are well dispersed. At the same FlFFF condition, the untreated suspension did not elute well. The elution profile shows a long tailing, and does not return to the baseline until the external field is removed by stopping the cross-flow. The SEM picture of the untreated sample shows particles are seriously aggregated. This result shows the sample pre-treatment is very important for reduction in particle-particle interaction and, thus, for preparation of well-dispersed soot suspension.

To see the effect of extraction, two suspensions are prepared from the soot #2 and 3, with and without the extraction step. To prepare a suspension without extraction, particles recovered in ethanol-bath sonicator are directly dispersed in the dispersing liquid (water containing 0.05% Triton X-100 and 0.02% NaN_3) after removal of ethanol by N_2 gas. Figure 3 shows FlFFF fractograms of the suspensions obtained at the same condition as in figure 2. For both soot #2 and 3, fractograms of suspensions prepared without the extraction step are broader, and extend further toward higher retention time, than those prepared with the extraction step. This indicates the suspensions prepared without the extraction step have broader and larger size distributions than those prepared with extraction.

The difference in size distribution is probably due to the presence of chemicals such as SOF (soluble organic fraction) on the surface of particles prepared without the extraction step, which are known to cause particle-aggregation.[23] This result shows the extraction step is also necessary to prepare well-dispersed soot suspensions.

It is also noted, that two fractograms of suspensions prepared with the extraction step look similar, while those of samples prepared without the extraction step look quite different. This indicates the extraction step is necessary not

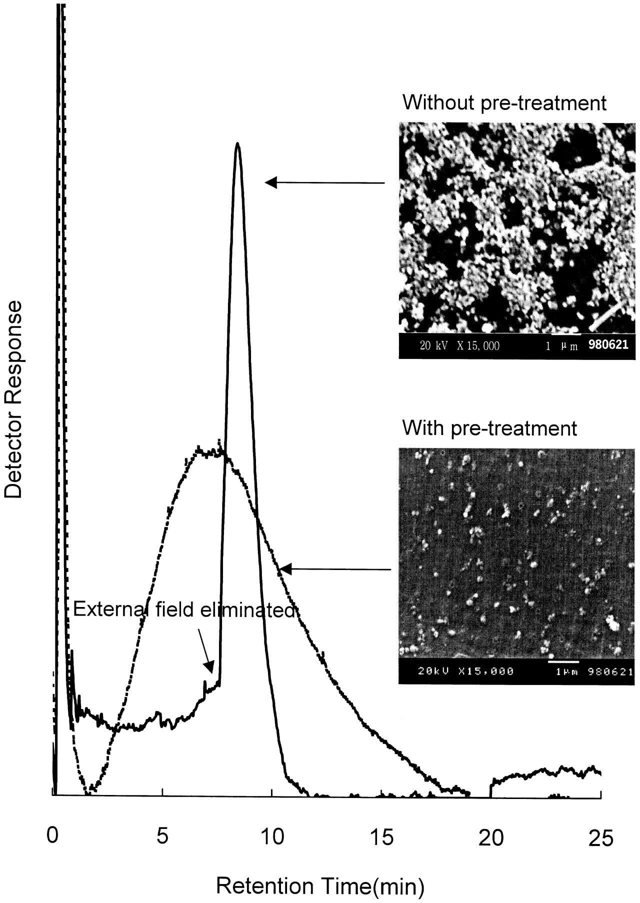

Figure 2. FlFFF fractograms and scanning electron micrographs of two suspensions prepared from soot #1 with and without pre-treatment. Experimental conditions: channel flow rate = 4.63 mL/min, cross flow rate = 0.60 mL/min, stop-flow time = 1.5 min.

only for the preparation of well-dispersed suspensions, but also for better reproducibility in size measurements.

Reproducibility of FFF Analysis

Four suspensions are prepared from the same soot#1 and then analyzed separately using FlFFF. As seen in Table 2, the average value of the mean diame-

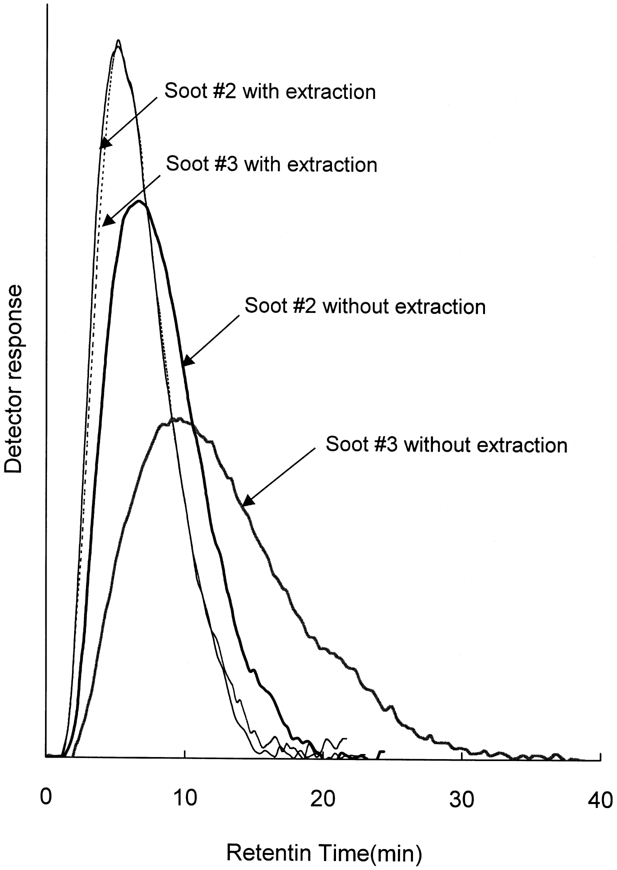

Figure 3. FlFFF fractograms of suspensions prepared from soot # 2 and 3 with and without extraction step. Experimental conditions are the same as those in Figure 2.

Table 2. Mean Diameters Measured by FlFFF for Four Suspensions Prepared from Soot #1

Experiment No.	Mean Diameter (nm)
1	85.0
2	79.0
3	85.5
4	83.5
Average (standard deviation)	83.3 (2.96)

ters measured for four suspensions is 83.3 nm with the standard deviation of 2.96 nm (3.6%), showing an excellent reproducibility. It is noted, that the reproducibility is better than 3.6%, as other errors, such as instrumental error, also contribute to the total standard deviation of 3.6%. In Table 2, the mean diameters are determined from the first moment of the FlFFF fractograms.

Dispersing Agent

The soot particles need to be dispersed well in water for accurate FFF analysis. A dispersing agent must be carefully chosen, as it influences the degree of interactions between the particle and channel wall (causing adsorption of particles on the channel wall), as well as, between particles themselves (causing particle-aggregation). Triton X-100, a nonionic surfactant, is found to be most effective in dispersing the soot particles among more than 10 surfactants tested.[22] The tested surfactants include Triton X-100, Aerosol OT (anionic), FL-70 (anionic and nonionic), Tergitol NP-10, and Tween 20 (nonionic), etc.

Dispersing Method

As for the dispersing method, a probe-type sonication is chosen among various methods tested, as it provides higher dispersing efficiency and output-per-time.[22] Tested methods include bath-type sonication, micro-fluidizing, and shear-mix homogenizing. Although the shear-mix homogenizing was found to be as effective as the probe-type sonication in dispersing the soot particles, it is not chosen because it may subject the particles under excessive mechanical shear force. The probe-type sonication is applied intermittently for the duration of 1 min at a time to prevent excessive heating.

To find the optimum period of sonication for dispersing the soot particles, suspensions are prepared from the soot #1 by varying the sonication time, and then analyzed by SdFFF at the same condition as in figure 1. With the total sonication time of 3 min, the SdFFF signal intensity is very low and the elution profile shows severe tailing, indicating particles are not well dispersed. The signal intensity and the elution profile gradually improve as the sonication time increases, and when it reaches 10 min, the profile becomes almost a gaussian. Figure 4 is a plot of the mean diameter measured by SdFFF as a function of sonication time.

Each run is repeated 3 times and the error bar is ±0.01 standard deviation. The mean diameter gradually decreases as the total sonication time increases, and after about 10 min, the mean diameter levels off. Figure 5 shows SdFFF fractograms of samples prepared by the focusing method from soot #4, with the total

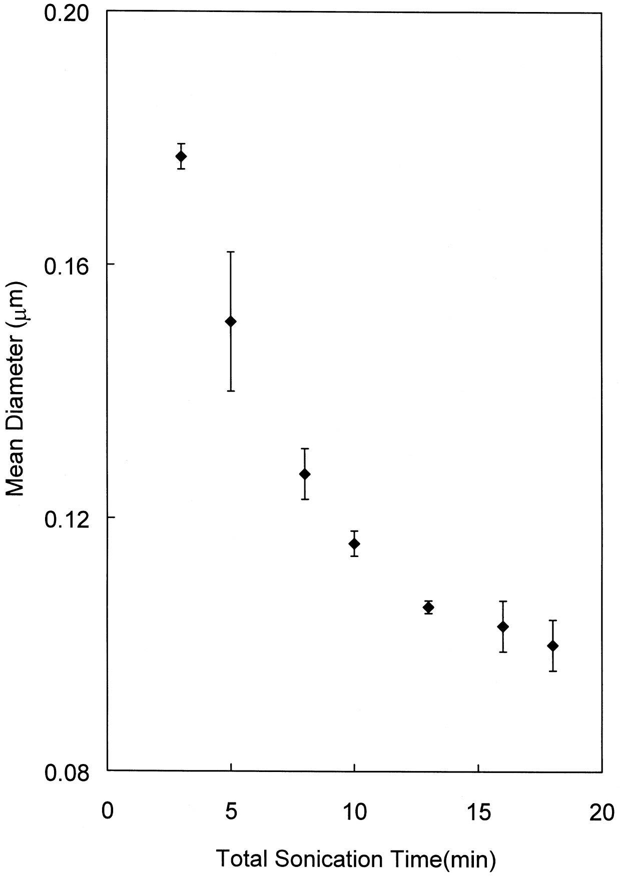

Figure 4. Effect of sonication time on mean diameter measured by SdFFF for soot #1. SdFFF conditions are the same as in Figure 1.

sonication time of 5 and 10 min. The sample prepared with the total sonication time of 10 min has the size distribution narrower and smaller than that of the suspension prepared with 5-min sonication. Based on this result, sonication time of 10 min is chosen.

SdFFF vs. FlFFF

Care needs to be taken in FlFFF, as the FlFFF channel has a membrane that may adsorb the soot particles. Based on our experience, adsorption of particles

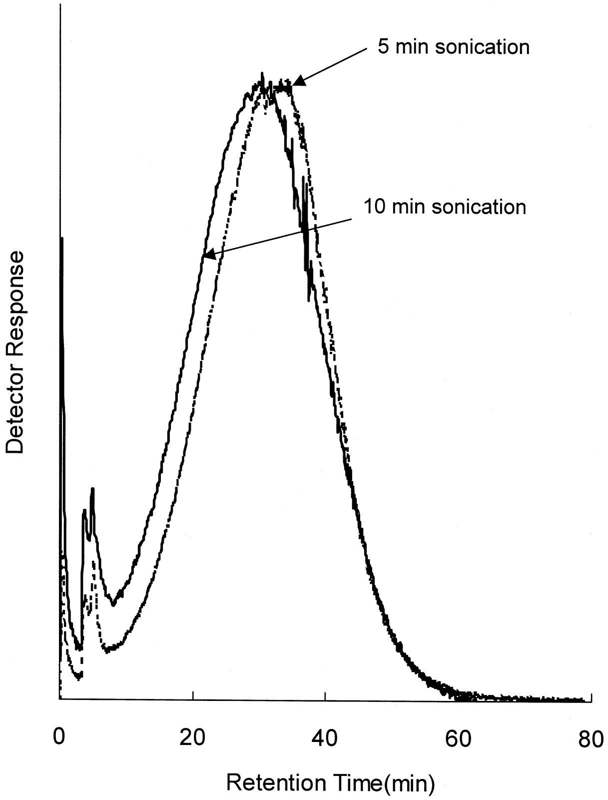

Figure 5. Power-programmed SdFFF fractograms of suspensions prepared by focusing method with the sonication time of 5 and 10 min from soot #4. Experimental conditions are the same as those in Figure 1.

onto the FlFFF membrane is not completely avoidable, especially in repeated experiments with surface-active particles such as soot particles. The FlFFF channel is back-flushed with the carrier after each experiment. It was found that periodically opening the channel and washing the membrane with high-speed water is helpful.

To compare the capability of SdFFF and FlFFF for size analysis of soot particles, the same sample is analyzed using SdFFF and FlFFF. The sample is a suspension prepared from the soot #5 using the decantation method, which contains some aggregated particles. Figure 6 shows SdFFF (A) and FlFFF (B) fractograms of the suspension. FlFFF fractogram (figure 6-B) shows a small peak (circled) at the retention time of around 13 min followed by a rapid return to the baseline, a characteristic "signature" of the steric transition.[24] SEM pictures of

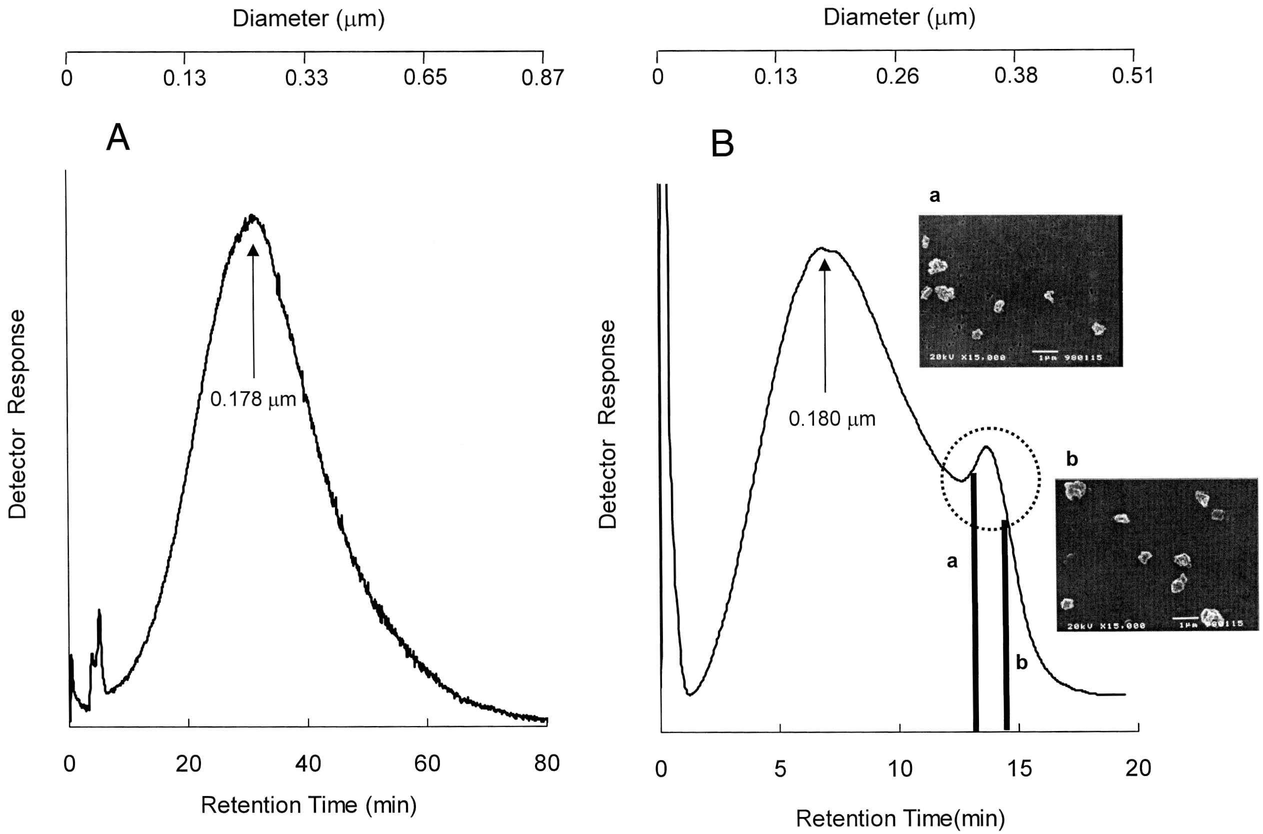

Figure 6. SdFFF (A) and FlFFF (B) fractograms of the same suspension prepared from soot #5. SdFFF and FlFFF conditions are the same as those in Figures 1 and 2, respectively.

the fractions collected right before and after the small peak, show the fractions contain particles having a diameter larger than about 0.4 μm.

In contrast, SdFFF fractogram (figure 6-A) does not show the "signature," indicating the normal mode operation extends further to the larger size in SdFFF than in FlFFF. In figure 6-A and B, the diameters corresponding to the peak maximum are 0.178 and 0.18 μm, respectively, showing good agreement between size data from SdFFF and FlFFF. However, the size distribution obtained from FlFFF is not expected to be accurate due to the steric transition phenomenon.

To confirm the steric transition truly occurs in FlFFF, twelve polystyrene latex standards having diameters ranging from 0.064 to 5.01 μm are run in FlFFF at the same condition as in figure 6. Figure 7 shows a log-log plot of the retention time vs. nominal diameter measured for the standards. According to eq 3, the plot is expected to be linear with the slope of unity in the normal mode (the slope of the plot is the size-based selectivity, S_d, as seen in equation 2). As shown in figure 7, the retention time increases with the diameter (Normal mode) and then decreases (steric mode).

The first order least-square fit of the data is also shown for each mode. Only the first five and the last five data are used for the least square fitting for the

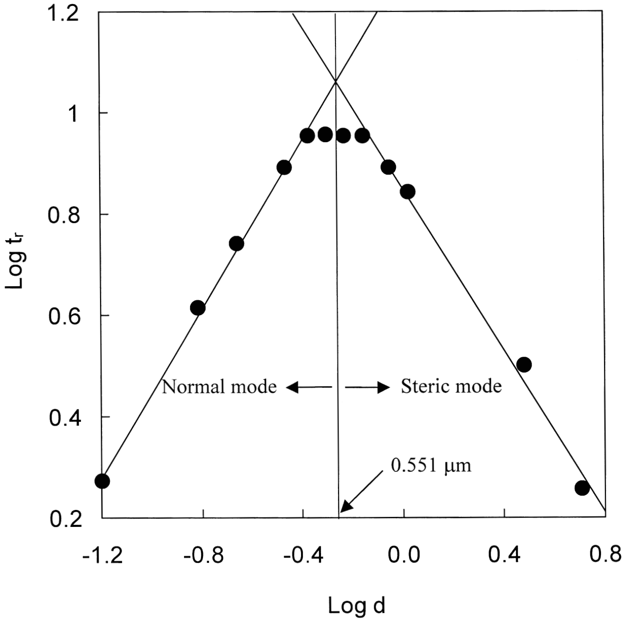

Figure 7. FlFFF retention time as a function of diameter for polystyrene latex standards. FlFFF conditions are the same as those in Figure 6.

normal and the steric mode, respectively. Figure 7 shows the steric transition occurs at the diameter of 0.551 μm. The plot is linear as expected, with the size-based selectivity of 0.83 in the normal mode. The plot is also linear with the size-based selectivity of 0.8 in the steric mode. Correlation coefficients are above 0.99 for both normal and steric modes.

Figure 8 shows FlFFF fractograms of the same sample as in figure 6, obtained at various combinations of the channel and cross flow rates. Although, the overall retention decreases as the ratio of the channel to cross flow rate decreases, the "signature" of the steric transition does not disappear. It can be concluded, that FlFFF application is limited to soot particles having diameter

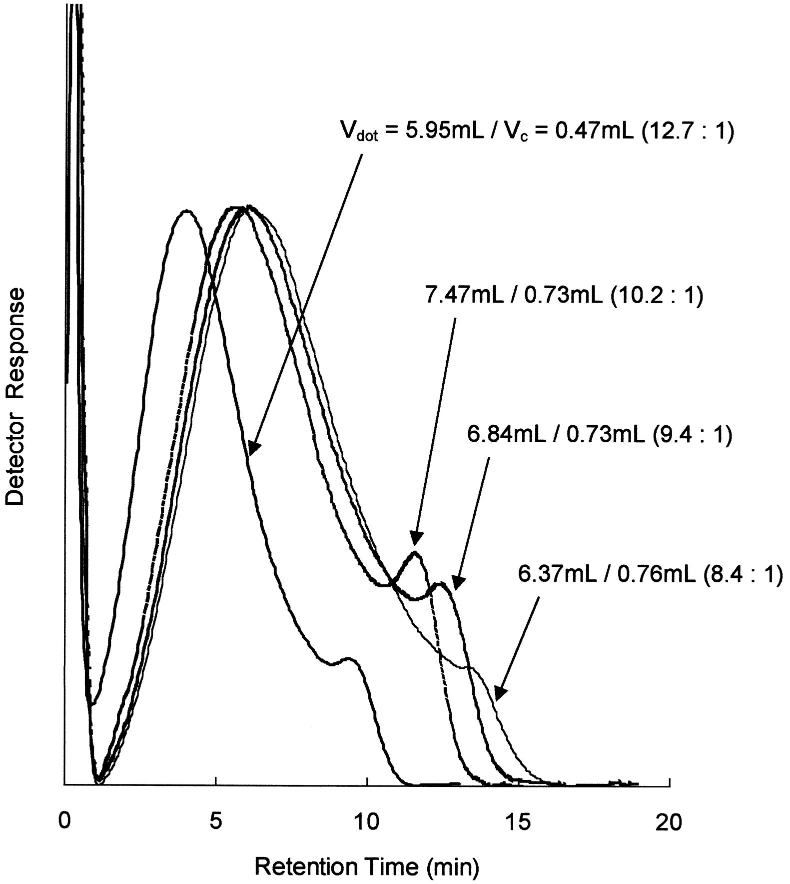

Figure 8. FlFFF fractograms of the same suspension as in Figure 6, obtained at various combinations of the channel and the cross flow rate.

smaller than about 0.5 μm in constant field operations of FlFFF. For samples containing particles larger than about 0.5 μm, use of a programmed field, where the field-strength (cross flow rate) is gradually decreased during a run,[25,26] may be useful for size analysis of soot particles using FlFFF.

CONCLUSION

Both FlFFF and SdFFF can be employed for size analysis of soot particles. In terms of the size-based selectivity, SdFFF is better than FlFFF in providing selectivity three times higher than FlFFF in theory. SdFFF does not used a membrane and, thus, is less problematic in terms of the particle-channel interaction.

One of problems in SdFFF analysis is it requires the density information of the sample. If the diesel soot contains particles of different densities, the use of the average density for size calculation will result in an error in the measured size.

One of major advantages of FlFFF over SdFFF is that it does not require the density information, and, thus, the fractogram can be directly transformed to the size distribution using equation 3. But FlFFF provides lower selectivity and has narrower dynamic range (due to steric transition) than SdFFF.

One must make a proper choice between two FFF techniques based on the availability of particle density information, size range of the sample, field-programming capability, and etc.

ACKNOWLEDGMENTS

This work was supported by the Center for Molecular Catalysis (KOSEF). The authors wish to thank the Motor Vehicle Emission Research Laboratory (MVERL) of Korea for collecting soot particles for this research.

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Received September 3, 2000
Accepted December 29, 2000
Manuscript 5386