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On-Line Particle Concentrator with Upstream Ultrafiltration in Continuous SPLITT Fractionation

Myeong Hee Moon,*,† Dukjin Kang,† Dai Woon Lee,‡ and Yoon-Seok Chang§

Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Pusan 609-735, Korea, Department of Chemistry, Yonsei University, Seoul 120-749, Korea, and School of Environmental Engineering, Pohang University of Science & Technology, Pohang 790-784, Korea

An upstream ultrafiltration (UU) method is employed for the on-line concentration of collected particle fraction and for the convenient regulation of flow rates in split-flow thin (SPLITT) fractionation. Concentration of the collected particle fraction is necessary to fractionate particles by smaller cutoff diameters in SPLITT fractionation. By introducing a simple device utilizing upstream ultrafiltration with tangential flow, particle solution collected at each SPLITT outlet can be simultaneously concentrated within the device during the run without the need of a separate centrifugation. Since a needle valve can be implemented at the outlet of the particle concentrator using upstream ultrafiltration (PCUU), it provides a great convenience with an accuracy in adjusting outlet flow rates of the SPLITT channel, and it eventually brings accurate control of cutoff diameter in SPLITT fractionation of a micrometer-sized particle sample. Moreover, the volume of carrier solution required for SPLITT fractionation, especially for a high-speed SPLITT run, can be minimized by circulating the filtrate solution of PCUU into the carrier reservoir directly. The advantage of on-line particle concentration is demonstrated by utilizing a slow flow feed technique for the fractionation of an incinerator fly ash particle sample to obtain a highly efficient SPLITT separation.

Split-flow thin fractionation (SPLITT fractionation, or SF) has been developed into a useful tool for effectively and continuously separating colloid and particulate materials with rapid processing.[1−6] As with the field-flow fractionation (FFF) techniques, SF utilizes a thin ribbonlike rectangular channel and an external field applied to the normal direction to the axis of separation. However, SF channels differ slightly in their geometry from the FFF channel in that most SF channels have dual inlets and outlets each of which is divided by a splitter as shown in Figure 1. In SPLITT fractionation, suspended particles that are continuously fed into the thin channel through the upper inlet, a′, are pushed toward the upper wall of the channel by the high-speed flow from the bottom inlet, b′, and they migrate toward the end of the channel with differential field-induced transport rates.[5−8] Gravitational SF uses gravitational force to achieve transverse migration (or settling) of the particles. This is dependent on the differences in mass or particle size. Separation takes place across the channel and is normally achieved very quickly due to the thinness of the channel (100−500 μm). While particles are settling, they will be transported toward the end of the channel and the slower settling particles will emerge from the upper outlet, a, while the faster ones exit the lower outlet, b. Thus, collected particle fractions at both outlets are enriched or depleted in a certain range of particle sizes that are readily adjusted by controlling the two outlet flow rates.

The precise regulation of channel flow rates in SPLITT systems is important for the successful fractionation of the size of particles desired since the cutoff diameter, d_c, in gravitational SF is dependent on flow rates as shown in the following equation[2,6,8]

$$d_c = \sqrt{\frac{18\eta}{bLG\Delta\rho}\left(\dot{V}(\mathrm{a}) - \frac{1}{2}\dot{V}(\mathrm{a}')\right)} \qquad (1)$$

where η is the viscosity, b the breadth, L the channel length, G the gravitation, $\Delta\rho$ the density difference between the sample particle and the carrier liquid, and $\dot{V}$ the volumetric flow rate of a particular stream denoted by the term within parentheses. However, it is somewhat cumbersome to adjust, experimentally, since both of the outlet flow rates are calculated from a desired d_c. Since the direct use of a flow regulator at a SPLITT outlet cannot be easily done in the case of fractionating supramicrometer-sized particles, which are the typically targeted size range of a gravitational SF, the current method of flow adjustment relies mostly on the use of a proper standard tubing of different lengths and diameters.[3] Difficulties arise when narrow-bore tubing is used since it is difficult to generate enough pressure to allow for flow adjustment at the lengths needed. This often results in the

* To whom correspondence should be addressed: (e-mail) mhmoon@hyowon.pusan.ac.kr.

† Pusan National University.

‡ Yonsei University.

§ Pohang University of Science & Technology.

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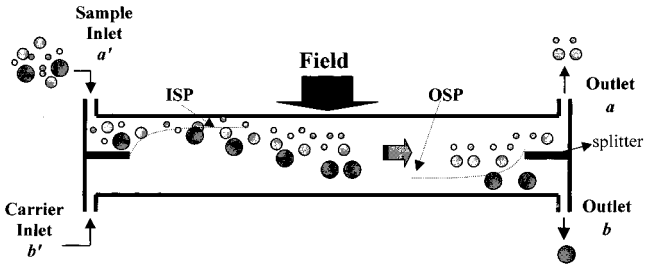

Figure 1. Side view of SPLITT cell. The two imaginary planes (ISP, inlet splitting plane; OSP, outlet splitting plane) are determined by the relative flow rates of inlet and outlet substreams.

blockage of tubing by large particles. It often causes a change in the flow rates and leads to a deterioration of separation resolution.

The separation resolution in SF is dependent on the efficient compression of an initial sample stream through inlet a′ into a thin laminar near the upper wall. This can be achieved by applying a sufficiently low feeding flow rate compared to that of a high-speed stream through inlet b′. However, a slow flow feed of the sample particles lowers the throughput of an SF experiment coupled with an increase of the separation time and causes an increase in volume of the collected particle solutions from the SPLITT channel outlets. In some cases, repetitive SPLITT runs at a fixed experimental condition somehow improve the separation efficiency. All of these cases result in an increase in concentrating collected particle solutions after each SPLITT run. The concentration is necessary to fractionate particles with smaller cutoff diameters or for the final retrieval of fractionated particles. A more serious situation may arise when an experiment is carried out to obtain a large cutoff diameter in SF since a relatively high flow rate is needed to transport larger particles toward the end of the SPLITT channel.

In this study, a particle concentrator using upstream ultrafiltration (PCUU) was developed. With this simple device, an accurate adjustment of outlet flow rates can be easily made using a flow regulator and the fractionated particles can be simultaneously concentrated during a SPLITT run. Since PCUU utilizes an upstream ultrafiltration method with tangential flow as shown in Figure 2a, fractionated particles at each outlet of a SPLITT channel can be concentrated within the PCUU during a run when they are connected as illustrated in Figure 2b. Since particulate materials of supramicrometer size quickly settle under the gravitational force, upstream ultrafiltration with stirring can prevent the buildup of a filter cake beneath the surface of a membrane and it will reduce the blockage of membrane pores that is often considered a serious problem in a typical downstream filtration system. By entrapping particles within the PCUU, an advantage is given to a SPLITT system by adopting a flow regulator at the upper outlet of PCUU for the convenient and accurate control of the flow rate. In addition, the total required volume of the carrier solution can be minimized by circulating the filtrate solution from both outlets of the PCUU into the carrier reservoir that in turn leads to carrier inlet b′. The volume of collected particle solution (normally from outlet a) can be very large when an experiment is attempting to obtain a large cutoff diameter or when a bulk amount of particle sample is to be fractionated. In both cases, on-line concentration is beneficial for a speedy operation without the need of a centrifuge to isolate particles with the retrieval of the carrier solution.

In this study, PCUU is employed in the SPLITT separation of fly ash particles. Its advantage is demonstrated by utilizing a slow flow feed technique of sample particles to obtain a highly efficient SPLITT separation.

EXPERIMENTAL SECTION

An in-house-built SPLITT channel is used in this study, and the channel has a thickness, w, of 360 μm, which is defined by the total thickness of two 130-μm-thick Mylar spacers and one 100-μm-thick stainless steel sheet splitter. The channel has a length, L, of 15.0 cm and a breadth, b, of 3.0 cm. The spacer layers, including the splitter, are inserted between two plexiglass blocks and bolted to each other as the plexiglass surfaces are used as the channel walls. Compared to a conventional SPLITT channel design, glass plates are not used for channel walls since the channel blocks need to be tighter in order to prevent leaking of the carrier solution from the pressure built by the PCUU. The two sets of PCUU are built with plexiglass as shown in Figure 2a (both blocks of a PCUU are tightened by four bolts), and the geometrical volume under the membrane surface is ~100 cm^3. The stainless steel screen inserted into a PCUU plays an important role in supporting the membrane during the upstream flow penetration. The membrane material used in a PCUU is cellulose (47 mm in diameter) having a pore size of 1.2 μm. During upstream ultrafiltration, magnetic stirring is applied to provide the tangential flow that is helpful in keeping the membrane pores from being blocked. After each use, the membrane surface is cleaned by sonication using a horn (CP130 model) from Cole Palmer Instruments (Vernon Hills, IL) at 70 Hz for 3 min to remove any absorbed particles. The two PCUUs are connected after each outlet as shown in Figure 2b, and each filtrate solution is forwarded to the carrier reservoir for circulation. To control flow rates, a Whitey SS-22RS2 fine metering needle valve from Crawford Fitting Co. (Solon, OH) is placed after the PCUU from outlet b.

A Minipulse3 peristaltic pump from Gilson (Villiers-le-Vel, France) and an FMI QDRH Lab pump from Fluid Metering, Inc. (Oysterbay, NY) are used for the continuous delivery of sample suspension through inlet a′ and for the high-speed flow stream through inlet b′, respectively. The carrier solution is prepared from purified (by reverse osmosis) and deionized water mixed with 0.02% NaN_3 as bactericide. Collected particle fractions are examined by an optical microscope, a CSB-HP3 from Samwon Scientific Ind. Co. (Seoul, Korea).

The raw fly ash sample collected from a municipal incinerator in Korea is initially treated with a 270-mesh sieve (~53 μm in pores) in wet condition and the fraction <53 μm is used for SF. The density of the fly ash particle sample is 2.5 g/cm^3, which has been determined by density fractionation work.[9] Concentrations of suspended fly ash particles used for the SPLITT are 0.1, 0.5, and 2% solid (w/v) in the carrier solution and the prepared particle samples are sonicated for 1 h prior to use.

RESULTS AND DISCUSSION

The particle concentrator, by utilizing upstream ultrafiltration (PCUU), is employed for the SPLITT fractionation of fly ash particles using a slow flow feed of sample particles to obtain a

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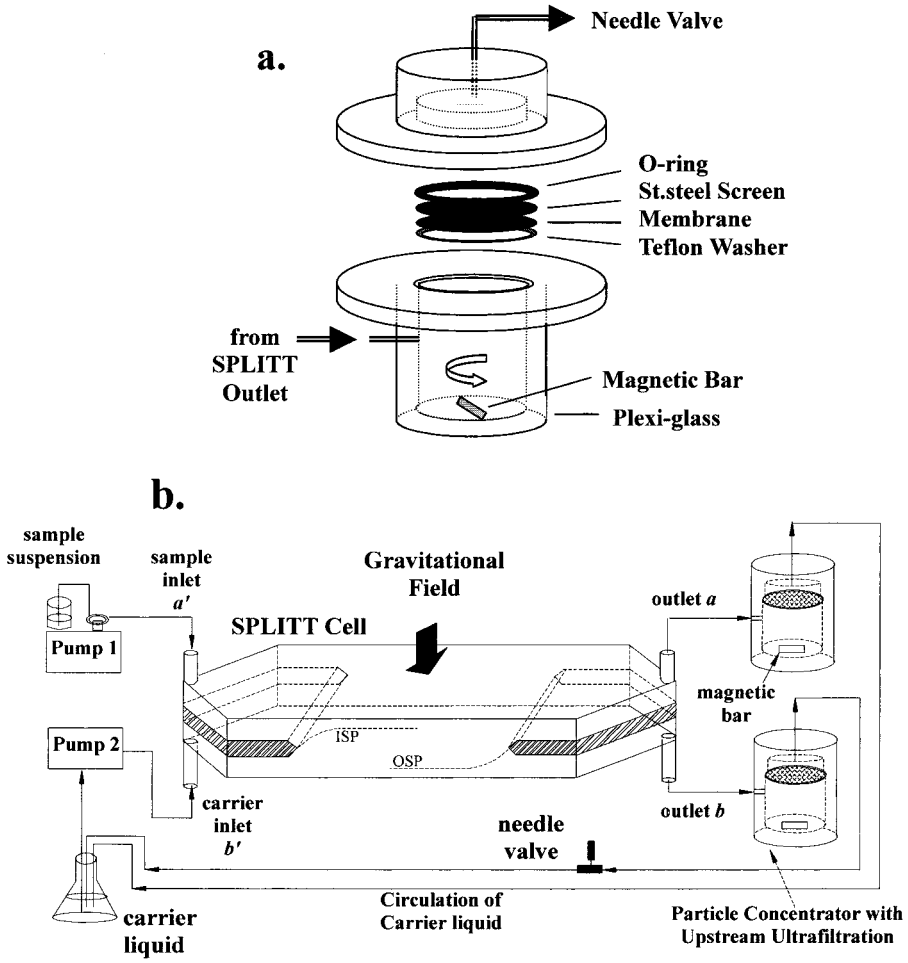

Figure 2. Schematic diagram of (a) PCUU and (b) the system configuration of the SPLITT channel with PCUU.

high percent recovery of particles at a desired cutoff diameter. For the fly ash sample used in this work, several cutoff diameters were originally selected to study the characteristics of pollutants contained in particles of various diameter intervals. In this report, the only size ranges smaller than 18.1 μm in diameter are used to demonstrate the improved performance a PCUU produces when it is applied to a SPLITT system. The preliminary fractionation of the sieved fly ash particles has been carried out by using a SPLITT channel (2 × 10 cm) for a cutoff diameter of 18.1 μm obtained at flow rates of $\dot{V}(a') = \dot{V}(b) = 4.0$ mL/min and $\dot{V}(b') = \dot{V}(a) = 34.0$ mL/min. This is done by a conventional method using tubing control and centrifuge work. The fraction smaller than 18.1 μm in diameter is examined microscopically, and the percent recovery smaller than the cutoff diameter shows ~95% in number measurements of several micrographs. The fraction a is smaller than 18.1 μm and is eluted at outlet a. Fraction b should be larger than the cutoff diameter and is collected at outlet b. While fraction a is recovered at a relatively high rate, the percent of fraction b recovered did not increase above ~70% despite two repetitions of the operation being done on the sample. The main reason for this low recovery at outlet b is attributed to the coelution of undersized particles, mostly smaller than 4 μm. This is in part caused by the use of a relatively high concentration of particle suspension (2% (w/v) solid) since good resolution occurs at a much lower concentration as expected from other studies.[3,6] During each run, the volume of collected solution at the upper outlet a is ~420 mL/g of sample particles (calculated from 4.0 mL/min feed rate for 2% (w/v) particle suspension) fed into the SPLITT channel. If repeat runs at the same flow rate are made, the solution volume to concentrate would be increased as much. In this case, the total volume of particle solution becomes nearly 10 times that of the feed volume after each SPLITT run. When a more dilute sample suspension is used, the volume will be increased in proportion to the amount it is diluted.

Since fraction a appears to contain most of the particles that are smaller than the cutoff diameter (18.1 μm), it is used for the adaptability test of PCUU. The micrograph of the fraction a is shown at the top of Figure 3. The PCUU is applied to the SPLITT system with further fractionation of fraction a at a cutoff diameter, d_c, of 9.5 μm. The system configuration is illustrated in Figure 2. The channel used hereafter has the dimensions of 3 × 15 cm, and the flow rate condition used for obtaining the specified cutoff is $\dot{V}(a') = \dot{V}(b) = 4.0$ mL/min and $\dot{V}(b') = \dot{V}(a) = 22.0$ mL/min. As shown in the micrographs of fraction 1a and 1b in Figure 3, fraction 1a shows particles mostly smaller than the cutoff diameter; however, fraction 1b contains larger ones ($> d_c$) including a number of small particles. Fractions 1a and 1b appear to contain 95% of the particles that are smaller than the cutoff diameter, d_c, of 9.5 μm and 23% that are larger than d_c, respectively. The data are listed in Table 1 for a series of fractionations of the fly ash sample. About 43% of the small particles appearing in fraction 1b are smaller than 4 μm. The low recovery rate is most likely caused

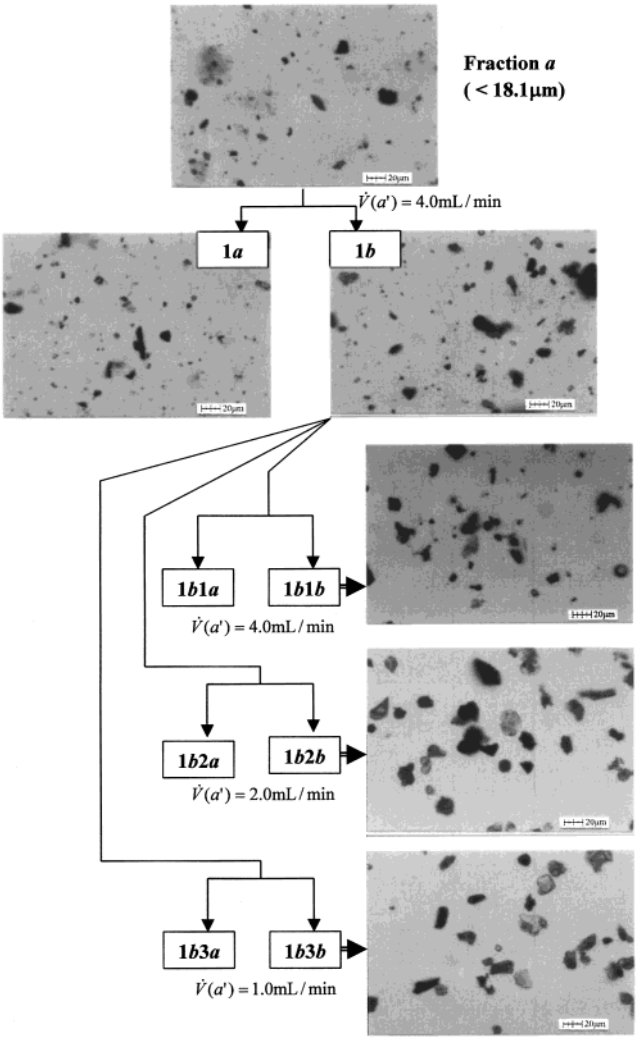

Figure 3. Scheme of SPLITT cell separation of the fly ash particle sample with optical micrographs of the collected fractions.

Table 1. Number Percentage of Particles That Are Collected at Each Outlet of the SPLITT Channel[a]

	volumetric flow rate (mL/min)				d_c (μm)	number %	
fractions	a′	b′	a	b		$<d_c$	$>d_c$
1a	4	22	22	4	9.5	95	5
1b						77	23
1b1a	4	22	22	4	9.5	94	6
1b1b						63	37
1b2a	2	22	22	2	9.7	93	7
1b2b						18.4	81.6
1b3a	1	22	22	1	9.9	97	3
1b3b						8.9	91.1

[a] About 400−500 particles are counted for each fraction.

by the use of a relatively high concentration (∼2%) of sample suspension as has been explained. A run at a much lower concentration is expected to provide a significant increase in recovery and this will be discussed later.

To check the difference in the separation efficiencies between a repetitive fractionation under the same run condition and a reduced feed flow rate, fraction 1b is divided into three parts and each third is subject to SPLITT fractionation by varying the feed rate of the sample suspension from 4.0 to 1.0 mL/min. However,

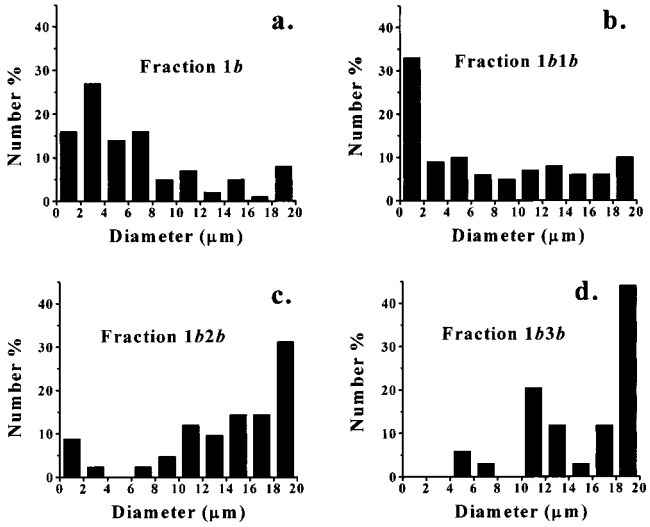

Figure 4. Particle size distribution of fractions (a) 1b, (b) 1b1b, (c) 1b2b, and (d) 1b3b. The cutoff diameters varies slightly from 9.5 μm for plots a and b, 9.7 μm for plot c, and 9.9 μm for plot d.

the flow rates through inlet b′ and outlet a for the following three runs are fixed at 22.0 mL/min and this run condition provides the same d_{bs}, which is the diameter of smallest particles at fraction b,[10] 10.0 μm for the fraction collected at outlet b. Since the feed flow rate varies, the cutoff diameter varies slightly as listed in Table 1. The optical micrographs of the collected particles of each run are shown in Figure 3, and the measured data are listed in Table 1. SPLITT fractionation of one-third of fraction 1b is made at the same feed flow rate, 4.0 mL/min, and the other two runs are made at feed flow rates of 2.0 and 1.0 mL/min, respectively. The micrograph of the fraction 1b1b shows that a repetition gives an improved separation compared to that of the fraction 1b, but the percentage of particles larger than the cutoff diameter increases to 37% in fraction 1b1b. It seems that a large number of small particles still coexist in fraction 1b1b. However, the number percentage greatly increases to 81.6% for fraction 1b2b when the sample feed is made at a rate of 2.0 mL/min. Furthermore, it reaches 91.1% for fraction 1b3b obtained at a feed rate of 1.0 mL/min. The particle size distributions of the four fractions (1b, 1b1b, 1b2b, and 1b3b) are shown in Figure 4, obtained by measuring particle sizes from micrographs. Particle size measurements are done with about 300−400 counts for each fraction. It is demonstrated that the slow flow feeding of sample particles is much more efficient to increase the percent recovery than that of a repeat run and it could be useful for a concentrated particle suspension.

The effect of particle feed concentration on the percent recovery is examined by fractionating fraction a (<18.1 μm) at two reduced concentrations: 0.5 and 0.1% (w/v). Runs are made with the particles of fraction a under a feed rate of 2.0 mL/min and a carrier flow rate of 22.0 mL/min. As shown in the micrographs of collected fractions in Figure 5, the efficiency is greatly improved at reduced feed concentrations compared to fractions 1a and 1b shown in Figure 4. The calculated number percentage of the fraction larger than d_c (=9.7 μm) increases to 55% for the micrograph of fraction 1b-1 at a feed concentration of

(10) *Instrument Manual for Series SF1000 SPLITT Particle Separator*, Version 1; FFFractionation, Salt Lake City, UT, 1997.

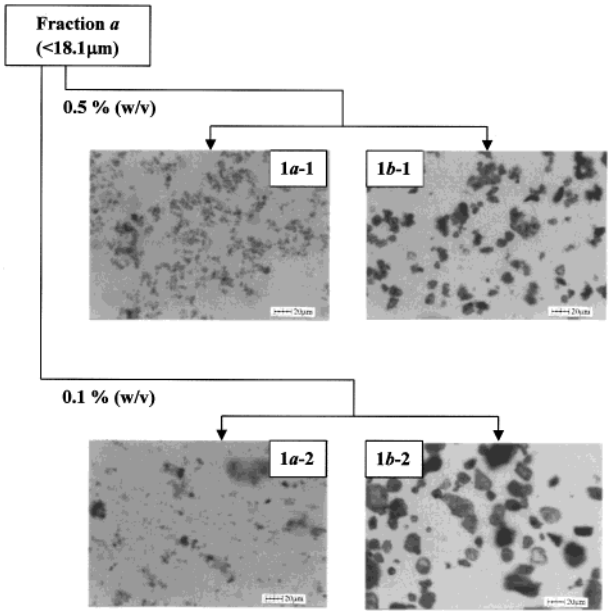

Figure 5. Optical micrographs of fractions of fly ash particles at two different feed concentrations: 0.5 and 0.1% (w/v). Flow rates are $\dot{V}(a') = \dot{V}(b) = 1.0$ mL/min and $\dot{V}(b') = \dot{V}(a) = 22.0$ mL/min. The cutoff diameter $d_c = 9.7$ μm.

0.5% (w/v) and it greatly increases to 90.5% for fraction 1b-2 at 0.1% (w/v). Fractions 1a-1 and 1a-2 are nearly 99%. The resolution improvement at a much lower concentration indicates the same trend for the work reported in the literature.[3] The recovery at 0.1% feed concentration is similar to the result obtained for fraction 1b3b, which is done at a reduced feed flow rate. However, operation at a lower concentration requires a longer feed time and this yields a significant amount of solution collected from SPLITT outlets to be centrifuged. This will increase the total process time when a large amount of sample is to be fractionated. For this case, it would be desired to first fractionate the particle sample at a relatively high feed concentration. Once the majority of the smaller particles (smaller than the cutoff diameter) are removed by the first cut, then the same run can be repeated at an optimized low feed concentration for the collected fraction, which amount is already reduced, or repeated at a slow flow feed. In any of the cases, it is necessary to have a fast and reasonable method to retrieve particles from bulk suspension after the SPLITT run. With PCUU, concentration of the collected particle suspension is made simultaneously with the SPLITT run.

When the two PCUUs are employed at the last three SPLITT runs in Figure 4, the membrane filters used for each PCUU are sonicated from the backside of a filter by a horn for ~3 min to remove any particles adsorbed at the membrane surface. Sonicated membrane filters are then dried at 105 °C for 1 h, and then the change in the membrane weight after being dried is recorded before and after it is used. To exclude any moisture absorbed by the membrane, the drying loss is measured separately and is subtracted for the calculation. The change in the weight of the membrane is observed with an average of 0.1% for each SPLITT process of 1 g of sample particles. The particle loss by adsorption to a membrane filter does not seem to be significant. However, it is serious when the retentate solution in a PCUU is not rotated during a run while the size range of collected particles is similar to the membrane pore size. The maximum efficiency is achieved in the case of feeding sample particles at 1.0 mL/min with a substantial increase of feed time. Even though it lengthens the separation time, the total process will be shortened due to bypassing the centrifuge. For each gram of fly ash particles fractionated by a SPLITT channel, it will require 50 min to feed a 2% (w/v) sample suspension at $\dot{V}(a') = \dot{V}(b) = 1.0$ mL/min and $\dot{V}(b') = \dot{V}(a) = 22.0$ mL/min, and this will end up with 1.1 L of solution to be centrifuged (the total solution volume is increased more than 20 times the feed volume after each SF run). If it is done with a lower sample concentration (0.1%) at 2.0 mL/min feed rate, it will require a 10 times larger volume of solution to be concentrated with that much longer operation. This is a significant quantity of solution volume generated after an SF run, and the centrifuge work will govern the speed of the entire process if a bulk amount of particles are to be fractionated or an SF run for a large cutoff diameter is needed.

By utilizing the device, the volume of carrier solution needed for the entire run can be significantly reduced with the removal of centrifuging work. Therefore, the on-line use of PCUU on a SPLITT system will be useful in providing a simultaneous concentration of particle solutions collected at both outlets during SPLITT runs and a flexibility in the potential use of a slow flow feed for improved resolution. In terms of system operation, the PCUU brings an operational convenience by introducing a needle valve to the SPLITT system to accurately control both outlet flow rates and simultaneously leads to an accurate fractionation.

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