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Self-adjustable channel for split-flow lateral-transport thin separation of micrometer size particles

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ABSTRACT

A new construction of split-flow transport-thin fractionation (SPLITT) channel has been developed. The channel is designed to work in full-feed depletion mode. Through the use of fixed and different diameters of outlets, the channel has ability to self-adjust the velocity of sample flow at the outlets. Thus the entire fractionation is achieved with one adjustable parameter, namely the flow rate at the inlet to the channel simple to set by low pulsation pump. Moreover, only one splitter at the end of separation cell was applied to enhance the sample throughput. The system performance was tested with silica particles suspension during both short and long term fractionations. Additionally, natural zeolite was used to check the feasibility of channel to separate other materials. The particle size distribution in obtained fractions and initial suspensions were measured with laser diffraction particle sizer. The results confirm a good resolution of the separation during an hour of permanent use. After 48 h the separation still occurs, however, the resolution is significantly decreasing. Intersection of particle size distribution curves of separated fractions obtained from particle sizer can be used to check an agreement between theoretical and practical value of cut-off diameter.

1. Introduction

Fractionation of micrometer size particles becomes an important issue of modern analytics and bioanalysis. Monodisperse particles are becoming very valuable in terms of their specific, unique properties, e.g. strictly defined size of silica is desirable as high performance separation packing materials [1], whereas the clean cultures of bacteria are important due to their healing ability or as indicators of diseases [2]. The size based distribution of pollutants (so called physical speciation) is also recognized as the key factor in determination of their bioavailability [3].

Filtration, ultracentrifugation or reverse osmosis are becoming therefore more and more important steps of purification process. Those techniques have several disadvantages, with the major one which is the change of original sample composition. There are, however, techniques able to separate the sample components in soft fractionation with only minor or even neglectable changes in composition of sample [4]. Those techniques belongs to the family of field-flow fractionation (FFF) methods supplemented with Split-Flow Lateral-transport thin fractionation (SPLITT). FFF and SPLITT encompasses a large variety of methods enabling the separation of macromolecules, colloids, particles, cells according to their size. The general concept of FFF and SPLITT was invented by Giddings [5,6]. Separation effect is reached by a combined action of the laminar flow of a carrier liquid along the separation channel and transverse physical field applied perpendicularly to this carrier. Apart of FFF, SPLITT is semipreparative method with ability to separate relatively large quantities of sample (milligrams or even grams of dry particles) in reasonable time. The fractionation channel consists two inlets and two outlets (Fig. 1). Separation is based on the settlement of particles forced by gravity during their transportation along the channel with the carrier liquid at constant flowrate. Two fractions differing with particle sizes are collected at the end of channel simultaneously at upper and lower outlets. In the classical separation (CS) mode, all inlets and outlets of SPLITT channel are used with controlled flow rates separated by physical stream splitters (Fig. 1). The sample is introduced continuously into the SPLITT channel through the inlet a′ with a flow rate of $V(a')$. Sample-free carrier liquid is introduced into the channel through the inlet b′ with a flow rate of $V(b')$. The flow rates are usually adjusted in such a way that $V(b')$ is much greater than $V(a')$, so that the sample particles are driven (compressed) to the thin region above the inlet splitting plane (ISP) as the two inlet flow streams merge at the edge of the inlet splitter. The difference in velocity for particles of a certain size is the driving force for separation. If this velocity is high enough, particles are crossing the outlet splitting plane (OSP) and exiting the channel by outlet b. Smaller particles which cannot pass the OSP are collected at the

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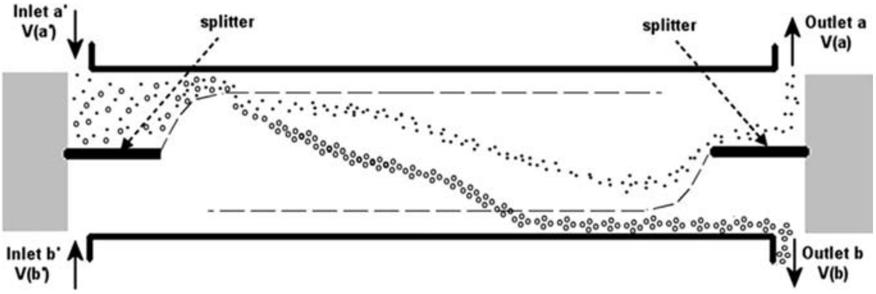

Fig. 1. Cross-section of SPLITT channel and illustration of separation process.

outlet a. ISP and OSP positions are determined by the relative flow rates of the two inlet and two outlet sub-streams.

Usually strategy to remove particles equal or bigger to specific diameter (cut-off—d_c) by outlet b is applied. Cut-off diameter is related to the velocity of transport region and can be described by a simple equation:

$$V(t)=\frac{bLGd_c^2|\Delta\rho}{18\eta_o} \tag{1}$$

where: $V(t)$ is the velocity of transport region, b and L are the dimensions of the SPLITT channel, G is the gravitational constant, $\Delta\rho$ is the difference in density between the particle and the carrier, η is the carrier viscosity. In CS mode, $V(t)$ is equal to the difference between velocity in the upper outlet $V(\mathrm{a})$ and the upper inlet $V(\mathrm{a}')$. In theory, there are infinite numbers of pairs of $V(\mathrm{a})$ and $V(\mathrm{a}')$ for a given $V(t)$. In practice, however, the appropriate ratio of $V(\mathrm{a}')$ to $V(\mathrm{a})$ has to be optimized to compromise the appropriate resolution and in the same time the throughput of sample.

Fractionation in SPLITT can also be achieved in so called full-feed depletion mode (FFD) where only one inlet a′ with sample flow is used [7–11]. Such operational mode avoids the dilution of sample but mechanism of separation remains nearly the same as in conventional CS with two inlets. In FFD however, velocity of carrier in transport region $V(t)$ is given by following equation:

$$V(t)=V(\mathrm{a}')-0.5V(\mathrm{b}) \tag{2}$$

The major difference between FFD and CS is the absence of ISP. That results in the fact that particles are not compressed towards the top wall of channel and it can lead to deterioration in resolution of the separation [12].

The unique properties of SPLITT fractionation are widely adopted in environmental studies [8,11], bioanalitycs [14,15] and material science [10] with several modifications and improvements of channel construction and system setup. Jiang et al. [12] and Hoyos et al. [15] used additional magnetic field to fractionate the magnetic particles. Kinde and Dutta [14] applied the electrical field to purify *N*-(2-triethoxysilylpropyl) formamide while Merugu et al. [13] used so called diffusion-SPLITT to fractionate peptides according to their different diffusivity. Splitter-less SPLITT channel was constructed by Lee et al. [11] to fast fractionation of large amount of sea sediment particles. In the current study we propose the new construction of SPLITT channel described in next section. The objectives of this work were (i) construction a self-adjustable channel designed to fractionate specific material with a desired cut-off value, and (ii) testing the performance of this channel.

2. Materials and methods

The separation tests were carried out in a prototype of the channel with following size of separation cell: 22 × 108 × 0.54 mm (Fig. 2). The channel is characterized by an asymmetric construction of the separation cell, with one splitter located at the end of channel. Separation performance was comparable with classical channel, which has been tested together. Asymmetric construction has been chosen as the most suitable to operate in the FFD-SF full depletion system due to the compromise between simplicity and performance. The module was equipped with only one inlet and two outlets. One of the major goals of this study was the development of an easy-to-use system, in which there is no need to adjust flow velocities at the outlets of the tested channel. Self adjusting of flow velocities was obtained by applying different outlet diameters. The entire fractionation process is achieved with one adjustable parameter only, namely the flow rate provided by the peristaltic pump at inlet to the channel.

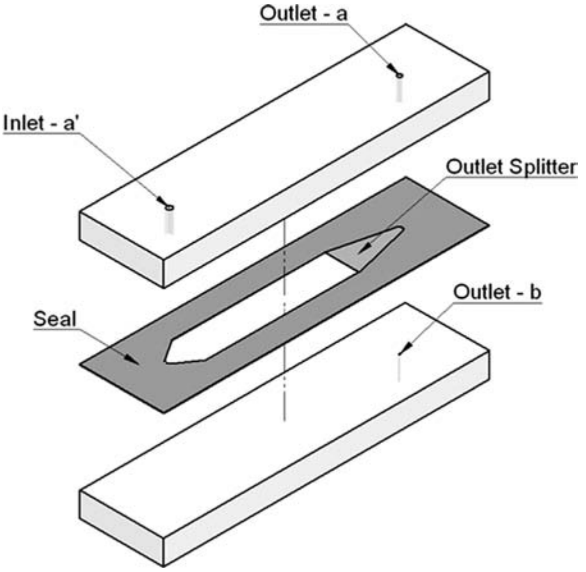

Fig. 2. The schematic picture of prototype of asymmetrical self-adjustable channel.

The prototype was manufactured of readily available materials. The housing claddings were made on a CNC milling machine, while the separator and gaskets were cut off on a cutting plotter. The materials applied to the manufactured modules' claddings are the commercially available methyl (poli)metacrylane PMMA, 20 mm thick. The splitter was made of polyester foil, whereas the gaskets of adhesive polyamide foil.

The whole set was bolted together with bolts and nuts of stainless steel. A peristaltic pump (REGLO Digital MS-4/8, Glattbrugg, Switzerland) was utilized for feeding the module with the solution. During the fractionation the silica suspension was stirred continuously with the magnetic stirrer (Big Squid, Ika, Germany) at 500 rpm to avoid particle sedimentation. The size distribution of the obtained fractions, as well as of initial mixtures of particles, were measured by the laser diffraction instrument (Mastersizer MS2000, Malvern, Malvern, United Kingdom). All samples were measured with three repetitions. Colloidal silica of nominal diameters 3.5, 7.0 and 10 μm (Lichrosorb Si 100, Merck, Germany) was utilized as the model material for separation. The particle density was assumed as 1.52 g cm^{-3} and the viscosity of the carrier liquid as 0.008905 g cm^{-1} s^{-1}. Optical parameters to measure particle size distribution of silica were as follows: RI of dispersant: 1.330, RI of particles: 1.544, absorption of light: 0.1.

3. Results and discussion

The research study was conducted in three steps. Within the first one, three repetitions (day by day) of 250 mL deionized water containing 250 mg of each (3.5 and 7.0 μm) silica particles (Fig. 3a). The separation was setup to operate with cut off diameter equal to 5 μm. Thus, the flow rates through the SPLITT channel at 1.3; 0.95 and 0.35 mL min^{-1}, for *V*(a′), *V*(a) and *V*(b), respectively.

After each fractionation, taking place about 1 h, the channel and tubes were cleaned from the residues. For each repetition the flow rate was adjusted separately. In this step, apart from the separation performance, the repeatability of the fractionation was measured.

During the second step the same mixture of silica particles was separated with the same flow rates through the SPLITT channel, but outlet tubes from channel carrying both fractions were placed into the bottle containing silica mixture (see Fig. 3b). The fractionation was carried out continuously for 48 h and after that both fractions were collected and then the particle sizes were measured. Within the second step the long term performance of channel was tested.

In the third step 10 μm silica was fractionated in the same manner as in the first step. This time the separation was setup to operate with cut off diameter equal to 10 μm. Thus, the flow rates through the SPLITT channel at 5.2; 3.7 and 1.5 mL min^{-1}, for *V*(a′), *V*(a) and *V*(b), respectively. *V*(a) to *V*(b) ratio is about 10% smaller than in previous experiment. This fact is caused by the change of liquid pressure in the channel directly connected with the pressure of liquid at the pump.

The aim of the first step of the experiment was to provide the data to validate the quality of fractionations. The results have been

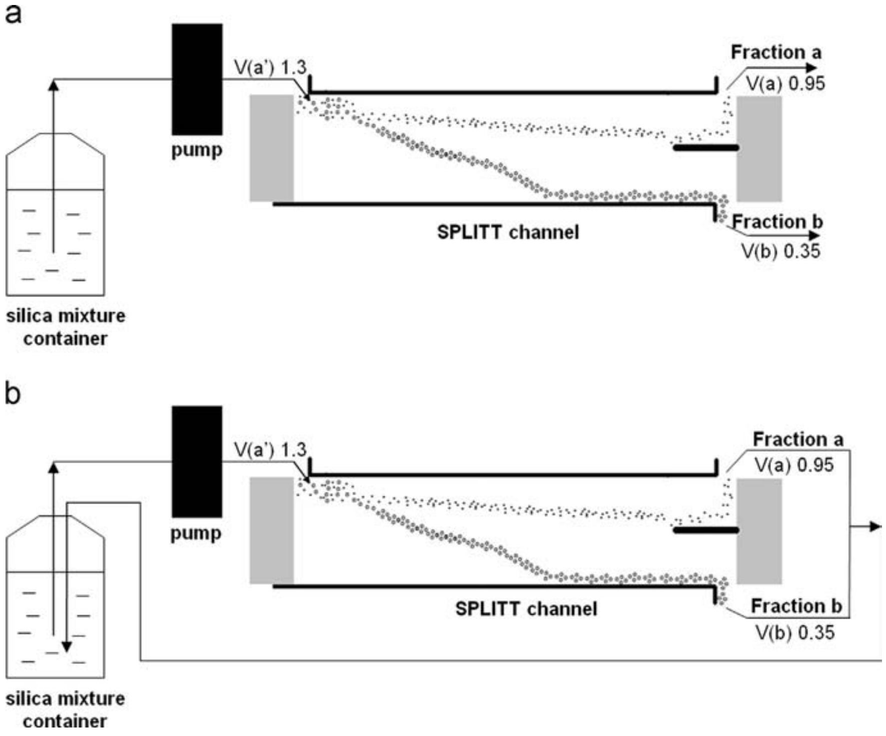

Fig. 3. Experimental setup: (a) short, and (b) long, term fractionation.

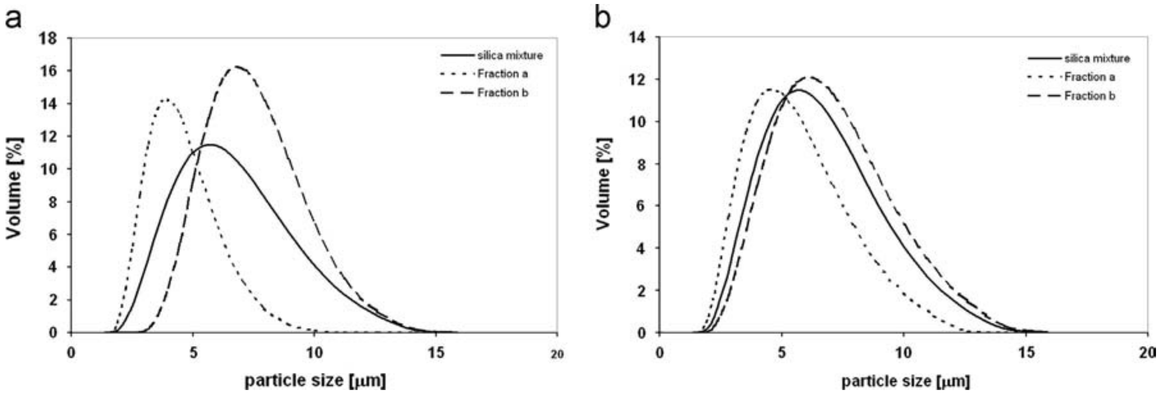

Fig. 4. Results of fractionation of colloidal silica mixture (d_c=5 μm); left graph: an average PSDs of short separations; right graph: long term separation.

presented as an averaged particle size distributions (PSDs) (calculated from three repetitions) of three samples: silica mixture before fractionations and fractions ‘a’ and ‘b’ collected from channel’s outlet a and b (see Fig. 4). The relative standard deviations (RSD) of mass median diameter —$d(v, 0.5)$, calculated for three repetitions, were smaller than 3% for both fractions ‘a’ and ‘b’, and that indicates very good repeatability of the fractionation.

From the SPLITT theory, cut-off diameter (d_c) is the diameter of particles that exit the channel through the outlets a and b in the same proportions [2]. d_c defined in such a way can also be derived from the particle size diagrams (Fig. 4a) as the intersection point of PSDs of fractions a and b, and it indicates the size of silica which leave SPLITT channel in the same volumic concentration via both outlets. In that sense, the achieved fractionation is consistent with theory, as the intersection point lays at 5.1 μm. Usually, for size determination the optical microscopy (OM) with high resolution CCD camera was used [11]. Possibility to observe the shape and morphology of particles is the major advantage of OM. However, OM observes the number of objects limited by the magnification and software used while the laser diffraction instrument calculate the size of particles constantly flowing through the detection cell. In that sense laser diffraction measurements are more representative for large volume of heterogeneous fractions.

The third important parameter related to the quality of fractionation is the range of particle sizes in fractions a and b. Table 1 provides $d(0.1)$, $d(0.5)$, and $d(0.9)$ which stand for volumic particle diameter in 10%, 50% and 90% of cumulative volume of PSD.

Fraction ‘a’ contains meager percentage of particles greater than desired d_c, while fraction ‘b’ the share contribution of silica smaller than 5 μm is also small. The resolution of FFD mode is usually lower than in classical system but the obtained results clearly indicate a good separation during the first 60 min of the process.

In the second step, long term separation performance was tested. Fig. 4b depicts the obtained PSDs. Silica particles in the mixture prior to fractionation have almost the same size distribution as in previous experiment. The differences in PSD were much more visible after separation for both fractions. First of all, the intensity of PSD was considerably lower, reaching nearly 12%. Second, the range of silica sizes was more wide for both fractions (Table 1). These two facts indicate that during the long term fractionation the channel is losing its performance. The decrease of PSD peak intensity is due to the sedimentation of silica observed in the tubes and the reservoir and reported before [15]. Broadening of PSDs is connected with sedimentation of particles at bottom wall of the channel. However, one should note that the intersection point is located at 5.6 μm and still remains close to the theoretical cut-off value. The suggested channel construction, with one splitter located near the outlets, improves the sample throughput and that was also suggested by some other authors [10].

Within the third step the channel versatility to separate silica with different cut-off diameters has been tested. The increase of $V(a')$ is causing proportional increase of carrier flow at the outlets $V(a)$ and $V(b)$, however the $V(a)$ to $V(b)$ ratio is constant and it is controlled by the outlet diameters. Thus the self-adjustable channel should also be able separate the particles with other d_c and this value is only limited by maximum flow rate directly related to dimensions of channel. Second limitation is related to the resolution of fractionation. The $V(a')$ to $V(b)$ ratio has to be between 0.25 and 0.33 to obtain good both resolution and throughput. Fig. 5 depicts the PSDs obtained for 10 μm silica and both fractions after the separation. The experimental d_c (intersection of PSDs obtained for both fractions) is equal to the theoretical.

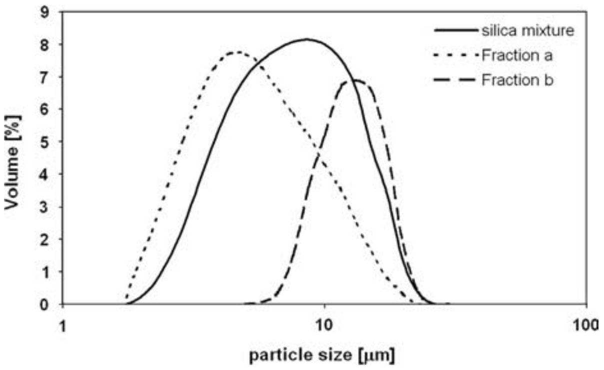

Fig. 5. Results of fractionation of colloidal silica mixture ($d_c = 10$ μm).

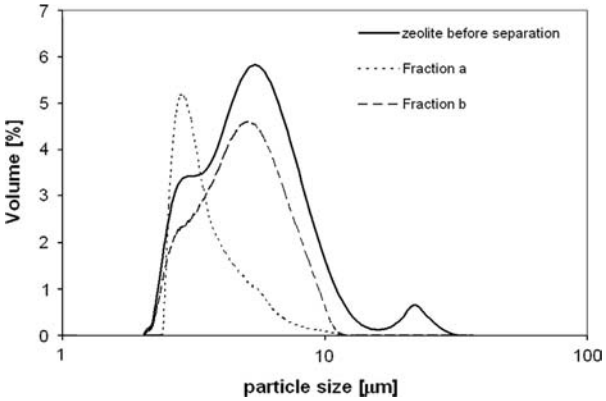

Fig. 6. Results of fractionation of zeolite particles ($d_c = 10$ μm).

Table 1
An averaged range of particle size of silica separated by self adjustable SPLITT channel during short and long term fractionations.

Short term fractionation	d (0.1)	d (0.5)	d (0.9)	Long term fractionation	d (0.1)	d (0.5)	d (0.9)
Silica mixture	3.166	5.262	8.492	Silica mixture	3.172	5.246	8.502
Fraction a	2.546	3.762	5.678	Fraction a	2.727	4.409	7.245
Fraction b	4.506	6.428	9.116	Fraction b	3.483	5.663	8.929

Additionally, natural zeolite material: clinoptilolite rock from Sokyrnytsya deposit (the Transcarpathian region, Ukraine) with density 1.89 g cm^{-3} has been also fractionated with the self-adjustable channel to check ability to separate other materials (RI of particles: 1.475, absorption of light: 0.1). Zeolite was grounded with porcelain mortar. Particles larger than 10 μm was sedimented in glass burette. Smaller particles were used to perform SPLITT fractionation. Fig. 6 depicts achieved PSDs for initial mixture and two fractions. The shift between experimental cut-off (3.5 μm) and theoretical value (5 μm) is due to the fact that shape of clinoptilolite is not spherical as is assumed by Eq. (1) and SPLITT theory.

4. Concluding remarks

The performed tests of silica and zeolite fractionation confirms the correctness of the concept of self-adjusting SPLITT channels with one splitter designed to work in FFD-SF mode. The difference in outflow velocities, enforced with the appropriate selection of the outlet openings’ diameters, obtained by mathematical calculation, confirms the compliance between experiment results achieved and the theoretical assumptions made. Such a conception (i) can be easily adopted to other materials which differ in density and size, and (ii) provides an easy to use SPLITT module to fractionate small volumes of suspensions with good resolution on very simple system (no bubble trap commonly used). Repeating of the separation can be also applied to enhance the purity of fractions.

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