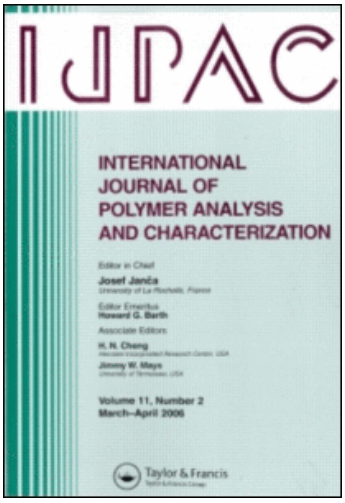

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Ultra-Micro-Thermal Field-Flow Fractionation

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Abstract: Micro-thermal field-flow fractionation, proposed conceptually and implemented experimentally several years ago, has developed rapidly in terms of theory, instrumentation, and numerous applications for the analysis and characterization of polymers and particles of synthetic, natural, and biological origin. Although the advances have been important, achieving the ultimate limits of miniaturization imposed by the physics as well as by recent technologies represents a challenge that was explored. The result of the reported experimental study is a new separation channel for ultra-micro-thermal field-flow fractionation, which was compared, in terms of performance, with the existing compact micro-thermal field-flow fractionation unit. The limits of the miniaturization are experimentally demonstrated with the use of suspensions of colloidal particles, which represent a more difficult case of separation than polymers in solution.

Keywords: Channel width and aspect ratio optimization; Colloidal particles; Particle size distribution; Polystyrene latex; Ultra-micro-thermal field-flow fractionation

INTRODUCTION

Micro-thermal field-flow fractionation (micro-TFFF) was proposed, the micro-channel constructed, and the method applied for the separation of

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polymers and colloidal particles several years ago.[1] Some applications of micro-TFFF were reviewed recently.[2] An important theoretical finding, confirmed experimentally, was that an increase in resolution can be achieved more efficiently by increasing the temperature drop across the channel than by a decrease in channel thickness.[1] The main conclusion resulting from the other theoretical and experimental analysis[3] is that a decrease in linear velocity $<v>$ of the carrier liquid has less important impact on the efficiency than a decrease in retention ratio R, both resulting in the same prolongation of the separation time. Retention ratio $R = V_0/V_R$ is available from the experimental retention volume of the unretained marker molecules, V_0, and the retention volume of the retained species, V_R.

The result of extensive theoretical and experimental research was the construction of the optimized, compact, and versatile micro-TFFF unit, including the channel equipped with inlet and outlet hydrodynamic splitting options.[4] The hydrodynamic inlet splitting allowed a decrease of aspect ratio of the channel and thus the elimination of edge effects. Aspect ratio, $a = b/w$, is defined as the ratio of the breadth b to the width w of the channel, as demonstrated in Figure 1. Although no systematic experimental study concerning standard-size FFF channels has been published, it is generally accepted that the aspect ratio should be approximately $a = 100$ or higher. The most used width of the micro-thermal FFF channel with hydrodynamic inlet splitting is 100 μm, and thus the reduced aspect ratio is $a = 32$. However, an optimization of a has not yet been studied for the micro-thermal FFF channel equipped with the hydrodynamic splitting option. Since diffusion coefficients of the retained macromolecular and particulate species are low, their diffusion to the edge layers of the carrier liquid inside the channel should not result in an increase of the zone broadening even for a lower than 32. Consequently, the aim of this study was the optimization of aspect ratio a and, simultaneously, the testing of a newly developed cooler based on Peltier elements. Such an experimental setup does not need the more expensive circulating and refrigerating thermostat.

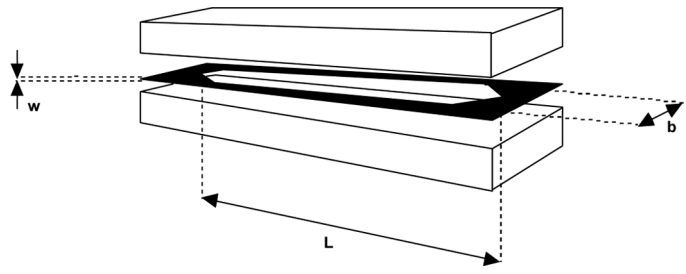

Figure 1. Schematic representation of the separation channel.

EXPERIMENTAL SECTION

The apparatus for ultra-micro-TFFF consisted of a syringe pump, model IPC 2050 (Linet Compact, Czech Republic), equipped with a special stainless-steel syringe (Institute of Scientific Instruments, Academy of Sciences of the Czech Republic), a commercial micro-TFFF channel unit (MicroFrac Laboratory, microfrac@atlas.cz and www.watrex.cz, Czech Republic), equipped with an electronic device (MicroFrac Laboratory, Czech Republic) regulating the electric power for the heating cartridge and controlling the temperature of the hot wall. The cooling of the cold wall of the channel was realized by a special Peltier elements unit (constructed in the MicroFrac Laboratory), which was attached to the cold wall of the channel. Since the compact ultra-micro-TFFF channel is very versatile, the Peltier elements unit is easily removable and can be replaced by a standard cooling element connected to a circulating liquid refrigerated by a thermostat. The dimensions of the versatile ultra-micro-TFFF channel used in this work were $0.023–0.250 \times 1.5–3.2 \times 76$ mm. The compact ultra-micro-TFFF unit was further equipped with an injection valve, model 7410 (Rheodyne, USA) with a 1 μL loop and with a system of a graduated micro-splitter valve, model P 470, and a micro-metering valve, model P 446 (Upchurch Scientific, USA), allowing the splitting of the carrier liquid flow into two separate entries of the channel and also the casual splitting of the outgoing liquid between the detector and the waste.[4] The ultra-micro-TFFF unit is shown in Figure 2.

A variable wavelength detector (Jasco UV-975, Japan) equipped with a 1 μL measuring cell and a recorder-integrator (Hewlett-Packard 3395,

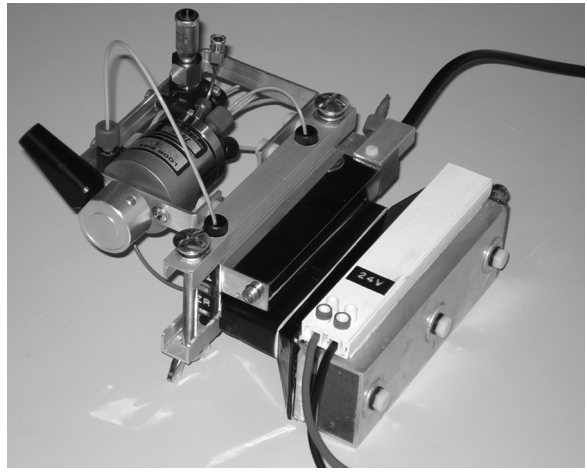

Figure 2. Compact and versatile ultra-micro-thermal field-flow fractionation unit.

USA) were used to record the fractograms. The temperatures at very close proximities of the cold and hot walls were also measured independently by a digital thermometer (Hanna Instruments, Portugal) equipped with two thermocouples.

An aqueous solution of 0.1% detergent Brij 78 (Fluka, Germany) and 3 mM/L NaCl was used as a carrier liquid. The experimental conditions of micro- and ultra-micro-TFFF experiments, such as the linear velocity of the carrier liquid and temperature drop across the channel, varied from experiment to experiment and are given for each particular case with the graphical representation of the result.

Spherical polystyrene latex (PSL) particles (Polymer Laboratories, UK) of narrow particle size distribution (PSD) and with the nominal mean particle diameter of 108 nm (PSL 108) and 155 nm (PSL 155) and pure acetone (non-retained marker molecules) were used in this study. The particle sizes of the PSL samples provided by the manufacturer were confirmed by dynamic light scattering measurement.

RESULTS AND DISCUSSION

Our previous experimental study confirmed the theoretical conclusion concerning the effect of channel width on the retention of the colloidal particles.[5] Some experimental data from the study[5] are presented in

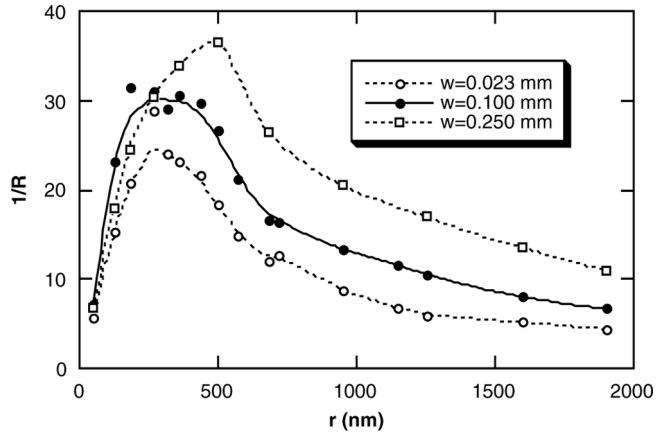

Figure 3. Experimental dependence of the inversed value of retention ratio R on the radius r of the retained PSL particles, obtained for three different widths w of the separation channel. Temperature drop was in all cases $\Delta T = 40$ K and average linear velocity of the carrier liquid $\langle v \rangle = 0.4$ cm/s.[5]

Figure 3, which demonstrates the dependence of the inverse value of the retention ratio R on the radius of the retained particles. All three curves in Figure 3 exhibit a maximum, or inversion point, at which the polarization mechanism of separation, effective in the range of small size particles, is inverted to the focusing mechanism. Thus, the ascending part of the curves indicates the dominant action of the polarization mechanism, and the descending part corresponds to the focusing mechanism. It has to be stressed that the so-called steric mechanism of separation is practically never effective. The consequence of the inversion of one dominant mechanism to the other one is that the order of the elution with respect to the size of the particles is reversed.

The maximum of the $1/R = f(r)$ dependence in Figure 3 is progressively shifted to larger particle size with increasing width w of the channel. This shift is predicted by the theory.[5] Although this fact can be seen as an advantage because the size range of the particles undergoing separation by the action of the dominant polarization mechanism is enlarged, the disadvantage is that the efficiency, characterized by plate height, decreases with increasing w, and the time of the stop-flow for the relaxation after the injection of the sample must be substantially longer. The decrease of the efficiency and the necessary prolongation of the stop-flow time can be compensated for by an increase in ΔT. Nevertheless, whenever the focusing mechanism dominates the separation, the resolution is higher, and thus it is preferable that the size limit of the species retained by the polarization mechanism is as low as possible. Consequently, a channel thinner than $w = 250\,\mu m$ should be preferred. At the other extreme, when decreasing the width w of the channel, an important decrease in selectivity, $d(1/R)/dr$, is predicted by the theory and confirmed by the experiment for the largest particles. This is especially true for $w = 23\,\mu m$ in Figure 3, where a decrease of the slope of the descending extreme part of the curve is obvious. As a result, the optimal width of the channel universally applicable for the separation of the macromolecules in solution and particles within a wide range of sizes seems to be $w = 100\,\mu m$.

The crucial point studied in this work concerned the ultimate limit of aspect ratio a that can be exploited without losing the resolution when using the channel equipped with the hydrodynamic splitting option. Comparison of the fractograms of PSL particles obtained under similar experimental conditions on the micro-TFFF channel whose $a = 32$ and on the ultra-micro-TFFF channel with $a = 22$ and $a = 12$ is in Figure 4. Although the experiment with the use of the ultra-micro-TFFF channel with $a = 22$ was performed at higher average linear velocity of the carrier liquid than the experiment with the separation of two PSL particles on the micro-TFFF channel with $a = 32$, the retained sample PSL 108 exhibits an even slightly narrower fractogram on the ultra-micro-TFFF

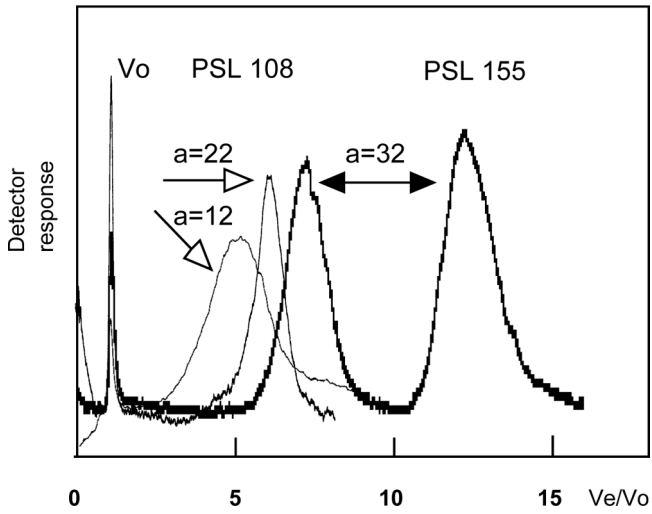

Figure 4. Fractograms of the PSL particles obtained with micro-TFFF channel: $w = 100\,\mu m$, $a = 32$ at $\Delta T = 35\,K$, and $\langle v \rangle = 0.009\,cm/s$; and with ultra-micro-TFFF channel: $w = 100\,\mu m$, $a = 22$ at $\Delta T = 32\,K$, and $\langle v \rangle = 0.025\,cm/s$ or $w = 125\,\mu m$, $a = 12$ at $\Delta T = 35\,K$, and $\langle v \rangle = 0.029\,cm/s$.

channel. On the other hand, retention is slightly lower than that obtained in the micro-TFFF channel with $a = 32$.

The further decrease of aspect ratio to $a = 12$ resulted in further decrease in retention and in the substantial broadening of the fractogram. The application of stop-flow time after the injection could change neither the shape nor the position nor the width of the fractogram. Consequently, the casual incomplete primary relaxation after the injection of the sample is not the main cause of the excessive broadening. A partial explanation of the important increase of the zone broadening obtained with the ultra-micro-TFFF channel with $a = 12$ is because of a slightly higher linear velocity of the carrier liquid. An increase in average linear velocity of the carrier liquid results in more pronounced effect of the secondary relaxations or, in other words, in more important deviation of the transverse concentration distribution of the retained particles from equilibrium. These far-from-equilibrium conditions also cause the shift of the retention volumes to lower values, as demonstrated in Figure 5 for the micro-TFFF and ultra-micro-TFFF channels as well. However, it is also probable that the micro-turbulence in the narrow edge layers inside the channel, caused by the imperfections of the cutting of the channel in the spacer, which are negligible for higher aspect ratios, comes to play an important role for extremely low a values.

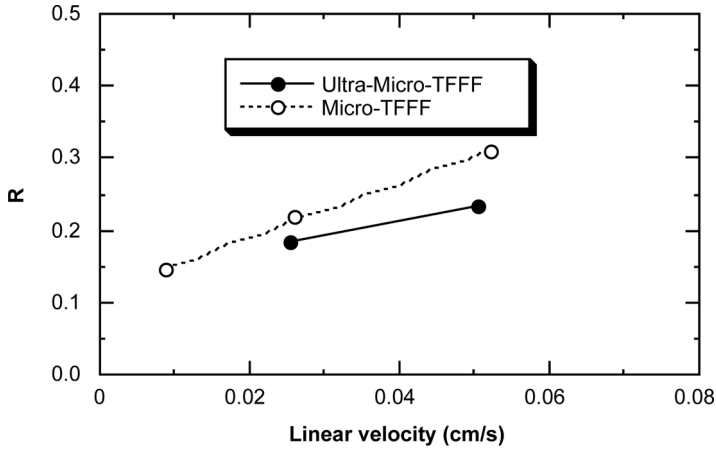

Figure 5. Dependence of retention ratio R on the average linear velocity of the carrier liquid $\langle v \rangle$ of PSL 108 particles obtained with micro-TFFF channel with $a = 32$ and with ultra-micro-TFFF channel with $a = 22$.

CONCLUSION

The experimental study presented in this article shows that an aspect ratio as low as approximately $a = 20$ can be applied in an ultra-micro-TFFF channel equipped with inlet hydrodynamic splitting option. The resulting reduced inner surface of the channel allowed further decrease in total heat flow across the channel and thus the use of Peltier elements for the cooling of the cold wall. It seems that further decrease of aspect ratio is difficult to realize without an important decrease of the performance of separation. The micro-turbulence in edge layers of the channel is practically inevitable due to the technical limits of the utilized manufacturing method of the channel spacer.

REFERENCES

[1] Janča, J. (2002). Micro-channel thermal field-flow fractionation: New challenge in analysis of macromolecules and particles. *J. Liq. Chromatogr. Relat. Technol.* **25**, 683.

[2] Janča, J. (2006). Micro-thermal field-flow fractionation in the analysis of polymers and particles: A review. *Int. J. Polym. Anal. Charact.* **11**, 57.

[3] Janča, J. (2007). Optimization of retention in micro-thermal field-flow fractionation for the determination of true particle size distribution. *Int. J. Polym. Anal. Charact.* **12**, 315.

[4] Janča, J. and J. Dupák. (2005). Elimination of edge effects in micro-thermal field-flow fractionation channel of low aspect ratio by splitting the carrier

liquid flow into the main central stream and the thin stream layers at the side channel walls. *J. Chromatogr. A* **1068**(2), 261–268.

[5] Janča, J., I. A. Ananieva, A. Yu. Menshikova, T. G. Evseeva, and J. Dupák. (2004). Effect of channel width on the retention of colloidal particles in polarization, steric, and focusing micro-thermal field-flow fractionation. *J. Chromatogr. A* **1046**(1), 167–173.