EXTENDING THE FUNCTIONALITIES OF SHEAR-DRIVEN CHROMATOGRAPHY NANO-CHANNELS USING HIGH ASPECT RATIO ETCHING

W. De Malsche 1,2, D. Clicq 1, H. Eghbali 1, N. Vervoort 1, H. Gardeniers 2, A. van den Berg 2 and G. Desmet 1

1Department of Chemical Engineering, Vrije Universiteit Brussel, Belgium
2MESA+ Research Institute, University of Twente, The Netherlands

ABSTRACT

An new injection system is presented for shear-driven chromatography. The device has been fabricated by high aspect ratio etching of silicon. The performance of the injection slit is studied through the aid of computational fluid dynamics, and the first experimental results are presented.

Keywords: Shear-driven chromatography, injection system, high aspect ratio etching, computational fluid dynamics, nano-channels

1. INTRODUCTION

In recent work [1,2], we reported on the possibility to separate 4-component coumarin dye mixtures in less than 0.1 seconds using shear-driven flows in 1-dimensional nano-channels (Fig. 1). The combination of high velocities and ultra-thin liquid layers is very beneficial to conduct separations and reactions requiring rapid mass transfer between different phases, as is the case for liquid chromatography.

Although we demonstrated the powerful chromatographic separation performances of the system, the shear-driven chromatography (SDC) channel systems we are using still lack a number of critical functionalities (gradient elution, parallel array operation, coupling to MS,…) so as to be competitive with existing chromatographic instruments.

In the present study, we are exploring the possibilities of using wet and dry etching techniques to integrate the SDC channels with minimal volume connections to i) an array of injection wells connecting directly to one member of a parallel SDC channel array through a narrow rectangular injection slit, ii) an array of accurately positioned buffer wells to perform on-column gradient mixing.

2. EXPERIMENTAL

The injection slits were machined by backside KOH etching of a silicon substrate until a membrane of 50 microns was obtained. The through hole was subsequently generated by deep reactive ion etching from the front side. The channel was formed between two polished substrates, one relatively short silicon substrate (10 mm long) containing an array of RIE etched spacers in a silicon nitride layer with a height which can vary between 100 nm and a few μm and held within a stationary frame, and one relatively large glass
substrate (50 mm long) which is completely flat and held in a translation stage-driven moving frame. Moving the larger substrae past the shorter, any type of liquid can be dragged (i.e., is shear-driven) through the nano-channel space formed between both gaps at velocities up to centimetres per second and independently of the channel depth.

![Image](image_url)

**Figure 1.** CCD-camera images (stopped-flow image) of the separation of a mixture of 4 coumarin dyes (C440, C450, C460 and C480) in a channel with d=280nm (sample concentration=1 mM) and coated with a monolayer of C8 (separation time = 1.44 s).

### 3. RESULTS AND DISCUSSION

Since flow hydrodynamics play an important role in the performance of the injection and outlet slits, all designs have been supported using extensive computational fluid dynamics (CFD) simulation studies. Fig. 3 shows a CFD generated image of the injection plugs which can be created using the injection slit shown in Fig. 2. This figure shows a WYKO (optical profilometry) scan of one of the injection slits coupling the channel with a sample well machined at the back of the channel substrate. CFD revealed a linear relationship between the injection time and the width of the injected peak. This allows a controlled injection of a well defined plug.

With this injection system experiments were carried out according to the procedure in Fig. 3. Fig. 4 depicts a plug of a dye which was introduced in the channel. At time 0, the filled reservoir with dye was moved by 0.1 mm, after which the reservoir was replenished by buffer and the shear driven principle was performed at 2 mm/s. Theoretically this should lead to a 0.05 mm wide plug which is confirmed by the experiment, see Fig. 4.

![Image](image_url)

**Figure 2.** Wyko scan of injection slit.
Figure 3. CFD simulation of the different steps during injection: a) Sample loaded into injection slit; b) sample is injected into the channel (by displacement of the moving wall); c) Sample in the injection slit is replaced by buffer; d) Injected plug is moved through the channel by restarting the motion of the movable wall.

Figure 4. Injection of coumarin 440 dissolved in methanol (0.5 mM) in a channel with a depth of 400 nm.

4. CONCLUSIONS

A new injection system for shear-driven chromatography has been evaluated by CFD and the device has been fabricated and tested. This paves the way for injecting well-defined plugs for future chromatographic separations. Experimental work is under way to evaluate the performance of all fabricated structures.

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REFERENCES