Optimization of a monolithic stationary phase for microchip electrochromatography

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Introduction

Analytical chemistry is an area in demand for methods allowing faster analysis and lower consumption of solvent. In this context "labs on a chip" were developed, which can combine all the analytical processes (sample preparation, separation, and detection) in a single device. Electrochromatograhy, a technique that can separate both ionic and neutral compounds requires the synthesis of a stationary phase directly in the microchannel of the analytical chip. The "Laboratoire des Sciences Analytiques" in Lyon works on the in-situ synthesis of monolithic stationary phases. The use of plastic material to manufacture the microchip requires a new methacrylate monolithic stationary phase. The aim of this work was to find an adequate monolithic formulation and to test it to provide an efficient electrochromatography technique in microchips.

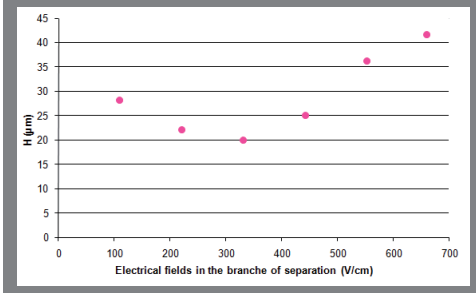
Experimental methods

Monoliths were prepared from polymerization mixtures obtained by weighing proper amounts of ethylene dimethacrylate (EDMA), lauryl methacrylate (LMA) (LMA/EDMA 60:40 wt%), 2- Acrylamino – 2 methyl-propanesulfonic (AMPS – 0.5 wt% with respect to the monomers) and a binary pore-forming solvent composed of 1,4 butanediol and 1 – propanol combined at several ratios. Benzoin methyl ether (1 wt% with respect to the monomers) was added as an initiator. After mixing these compounds, polymerization mixtures were introduced either in capillaries or in microchips and exposed to 9.UV at 365 nm at 6J/cm².
The resulting monolithic columns were flushed with methanol either with an HPLC pump for capillaries or using electroosmotic flow for microchips in order to remove pore – forming solvents and possible unreacted monomers or oligomers. Lastly, they were tested as electrochromatography columns using UV detection for capillaries and using Fluorescence detection for microchip with a mobile phase (acetonitrile –phosphate buffer at different ratios).

Results

Two main characteristics of the monolith were studied: the repeatability of retention factor and the efficiency. Various synthesis formulations were tested using neutral PAH (polycyclic aromatic hydrocarbons) solutes.
In a first step, the stationary phase was studied in capillary format. It proved that the best monolith could generate an electroosmotic flow useable in a " lab on a chip" (1.2 . 10-4 cm²/V.s). Efficiencies on anthracene peak were found to be Hmin = 14 µm at [90:10] and Hmin = 35 µm at [80:20], with a good repeatability.
In a second part, the optimal stationary phase was transferred to the microchip. The analysis of a mixture containing four PAH was carried out and a very good separation was observed (Figure 2).The characteristics of monolith were well transposed from the capillary to the microscale format. Indeed, a repeatability of 0.86% was obtained (same conditions as in figure 2). The Van Deemter Curve shows a minimum plate height equal to 20 µm (RSD = 11%) (Figure 1).

Fig.1 : Van Deemter Curve of Antracene (Variable separation – Mobile phase: acetonitrile/ phosphate buffer [85:15]).



1: Anthracene
2: Fluoranthene
3: Pyrene
4: benzo[a]anthracène

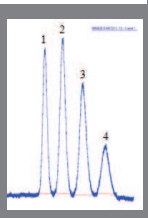


Fig.2 : Separation of mixture contained 4 PAH (Separation: 2 kV with 1.75 kV of receding – Mobile phase: acetonitrile / phosphate buffer [85:15]).

All analyses were carried out using:
Detection at 2.5 cm - Injection: 2 kV with 1.5 and 4 kV of pinching voltage during 60 sec – Expansion: 0.8 kV during 2 sec.

Conclusion

To conclude, a new formulation of methacrylate monolith was optimized in both capillary and microchip format. Even if a complete study of its electrochromatographic behavior needs to be carried out, the first results showed very promising performance, allowing the electrochromatography separation of a range of neutral solutes in a short time (10 min) with a low solvent consumption.

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