Resistance to mass transfer on pseudomorphic reversed stationary phases for HPLC columns

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Introduction

The "Laboratoire de matériaux" of Montpellier has developed a new process of stationary phase synthesis for a liquid chromatography filled column. These phases come from the dissolution of a commercial stationary phase (Nucleosil 100 for example) in basic medium, which is then restructured around micelles of surfactant. The aim of this study was to maintain the same particle size as the commercial phase, so as to improve the homogeneity of the granulometry and increase the porous volume. Thus, a better efficiency could be reached in a high flow rate HPLC analysis. With these conditions, the efficiency depends on the resistance to mass transfer of particles within the column. 4 phases have been studied in high flow rate: A commercial phase, a MCM-41(1 day) phase, a MCM-41(4 day) ("1 day" and "4 days" are restructuring times of these phases and MCM is an for Micellar Condensed Materials) and a MTS (Micelle Templated Silica) phase which uses swelling agents (trimethylbenzene, TMB) allowing for the surfactants to settle and form bigger pores. These phases are all grafted C8 reversed phases.

Experimental methods

Before each analysis, a 4.8cm x 4mm column was filled with stationary phase. 0.7g of commercial phase was added to 2.5mL of a CCl4/heptane 80/20 solution, homogenized in an ultrasonic bath and filled into the guard tube, placed before the analysis column. 100mL of 99% methanol, then 70mL of a water/methanol 35/65 solution were used to push the stationary phase in the column at 550 bars. Once the filling was finished, the column was washed with acetonitrile.

The assembly used to wash and analyze included: a pump, a dynamic stirrer, a primary column to absorb pressure pulses, a manual injector, the prepared column and a detector. After validating assembly caused dispersion was weak, the experiment was performed.

The detector wavelength was fixed at 220nm and a mixture composed of toluene, propylbenzene and butylbenzene were injected. The retention factors (1.5 for toluene, 3 for propylbenzene) were kept constant during the experiment; the mobile phase, composed of water and acetonitrile, was adapted each time.

After each injection, the flow rate varied from 0.5 to 8mL/min, and the efficiency N of each elution peak was measured. Then the height equivalent of the theoretical plate H was calculated, to draw a Van Deemter curve H=f(u) (u=mobile phase swiftness). Finally the tendency curve was calculated and its equation was determined in the area of the resistance to mass transfers. The equation's type was y = Cx + B, where C was the resistance to mass transfer factor. Our results were reported in figure 1.The weaker the C factor, the lower the loss of efficiency, when the flow rate was increased. This caluculation allowed us to work with the same efficiency, but in a shorter analysis time. Our results for the C factor are presented in figure 1.

	Factor C Toluene	Factor C Propylbenzene	Factor C Butylbenzne
commercial	26	19	16
MCM 41 (1 day)	24	19	15
MCM 41 (4 day)	41	31	24
MTS large pores	27	19	18
Lissage phase par phase	Factor C Toluene	Factor C Propylbenzene	Factor C Butylbenzne
commercial	25	22	20
MCM 41 (1 day)	27	24	15
MCM 41 (4 day)	41	24	23
MTS large pores	25	22	19
Lissage colonne par colonne	Factor C Toluene	Factor C Propylbenzene	Factor C Butylbenzne
commercial	25	22	20
MCM 41 (1 day)	26	22	16
MCM 41 (4 day)	42	28	27
MTS large pores	28	22	19

Figure 1. C factor's results for each stationary phase with smoothed and unsmoothed curves.

However the MCM-41 phase was very interesting because the resistance to mass transfer was less important in comparison to the other phase, when the retention factor increased. Hence, it can be used for solute analysis. With an important retention factor, or in high flow, under these conditions, a good efficiency should be reached with a short analysis time.

Conclusion

The resistance to mass transfer seems to be equivalent for the MCM-41 (1 day) and the classical phase, whereas it is higher for MTS phases and the MCM-41 (4 day phase). Nevertheless, the MCM-41 (1 day) presented a weaker C factor than the other, phases when the retention factor was important. Smoothing the curves confirmed the first results. The MCM-41 (4 day) phase and the MTS phase provided no advantage compared to the commercial phase.

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