Journal of Chromatography, 477 (1989) 95–106
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 21 365

PERFORMANCE OF POROUS SILICA LAYERS IN OPEN-TUBULAR COLUMNS FOR LIQUID CHROMATOGRAPHY[a]

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SUMMARY

Progress has been made in the preparation of porous silica layers in fused-silica capillaries for open-tubular liquid chromatography. The porous silica layer is prepared by (i) static coating of the silica precursor, polyethoxysiloxane (PES), followed by (ii) converting the PES film into a porous silica layer with ammonia solution. The porous silica layer can be easily modified by silane reagents commonly used in packed column high-performance liquid chromatography. The performance of the silica layer with the different phase systems was tested with polyaromatic hydrocarbons and derivatized amino acids as samples.

INTRODUCTION

The search for greater resolving power in liquid chromatography is one of the major fields of activity in contemporary chromatographic research. Capillary chromatography [open-tubular liquid chromatography (OTLC)] is one of the possibilities for improving the resolving power significantly. This is the main reason why capillary liquid chromatography has been extensively examined both theoretically[1,2] and experimentally[3–14] in recent years.

From theoretical considerations[1,2], it has been found that the optimum capillary diameter is about 1–5 μm and that the external band broadening must be kept below 1 nl. It has been shown that these stringent requirements can be met in practice when applying on-column detection and split injection devices.

Despite these experimental improvements, a most difficult problem remains, namely that of the preparation of a stable and sufficiently thick stationary layer in columns with an inner diameter smaller than 10 μm. For a suitable phase ratio, the

[a] Part of this paper was presented at the *12th International Symposium on Column Liquid Chromatography, Washington, DC, June 19–24, 1988*. The majority of papers presented at this symposium have been published in *J. Chromatogr.*, Vols. 458, 459 and 460.

0021-9673/89/$03.50

stationary phase film thickness should be 0.3–2 μm in a 10-μm column, depending on the diffusion coefficient of the solute in the stationary phase[10]. The phase ratio should be high, first in order to be able to manipulate the retention and second, and possibly more important, in order to allow a sufficient loadability.

In capillary gas chromatography (GC), different stationary phases, such as cross-linked silicones and porous adsorbent layers, can be successfully coated in thin and thick films. The application methods include static coating[15], dynamic coating without[16] or with[17] a mercury plug and methods for depositing porous adsorbent layers, as reviewed by Ettre and Purcell[18] and de Zeeuw *et al.*[19]. Some of these stationary phases or coating techniques cannot be applied in OTLC. Recently, cross-linked silicones have been applied in 5- and 10-μm fused-silica capillaries by static[9,10], free-release[13] and "precipitation" coating[12]. The performances of these OTLC columns are in good agreement with theory. A disadvantage of the cross-linked silicone phases is that because of the low diffusion coefficient in the cross-linked phase[10] ($D_s = 7 \cdot 10^{-12}$ m^2/s), the film thickness should be small, which limits the mass loadability. The eluting concentration of the solute is proportional to the mass loadability, which implies that owing to the thin film in these columns detection problems may occur. The diffusion coefficient in porous materials is much larger (*ca.* $0.5 \cdot 10^{-9}$ m^2/s) and therefore the preparation of porous adsorbents layers in capillaries in principle offers better prospects.

In a previous paper[14], we described the preparation of a porous layer in 10–25-μm fused-silica columns by precipitation of porous silica from a dynamically coated film of polyethoxysiloxane (PES) with gaseous ammonia. Silica was chosen as the porous material because (i) the chemistry of silica, (ii) its use as a support or adsorbent in LC and (iii) the possibilities of modifying the silica surface are well documented. However, the thickness of the layer obtained by dynamic coating was too small and had to be increased. The deposition of a thicker film of PES can be achieved by repeated application of the dynamic coating procedure or by using static coating. The use of static instead of dynamic coating is advantageous because of (i) the possibility of coating thicker films in one step, (ii) easy control of the film thickness by varying the PES concentration in the coating solution and (iii) the possibility of using aqueous ammonia rather than gaseous ammonia in the conversion of PES into silica.

In this paper, the preparation and chemical modification of the porous silica layer is described. A number of different phase systems have been tested for various solutes.

THEORY

The plate height in OTLC is described by the extended Golay equation[20]:

$$H = \frac{2D_m}{u} + \frac{d_c^2 u}{96D_m} f_1(k') + \frac{2d_f^2 u}{3D_s} f_2(k') \tag{1}$$

where

$$f_1(k') = \frac{(1 + 6k' + 11k'^2)}{(1 + k')^2} \tag{2}$$

$$f_2(k') = \frac{k'}{(1 + k')^2} \tag{3}$$

D_m is the diffusion coefficient in the mobile phase, D_s is the diffusion coefficient in the stationary phase, k' is the capacity factor {zone capacity factor[21] when adsorption [reversed phase (RP), straight phase (SP)] is used}, u is the linear velocity of the mobile phase, H is the plate height, d_c is the inner diameter of the capillary and d_f is the thickness of the stationary layer.

Maximum film thickness

The desired film thickness, $d_{f,max}$, is limited by the decrease in efficiency caused by the third term in eqn. 1. As a more or less arbitrary, but reasonable, upper limit to the magnitude of this term, one can take 20% of the second term (the first can usually be neglected). On doing so, the following relationship for $k' = 3$ results:

$$d_{f,max} < \sqrt{0.12 D_s/D_m} \cdot d_c \tag{4}$$

Eluting concentration

To avoid external band broadening in OTLC with column diameters of 1–10 μm, the detection and injection volumes must be in the range 1–100 pl. To mitigate detection problems, the eluting concentration should be as high as possible. The eluting concentration is proportional to the sample load and is given by

$$C_m = \frac{M_{inj}}{V_{mp}\sqrt{2\pi N}} \frac{1}{(1 + k')} \frac{1}{MW} \tag{5}$$

where C_m is the outlet concentration (mol/m^3), V_{mp} is the volume of mobile phase in one plate, N is the plate number, M_{inj} is the amount injected in grams and MW is the molecular weight of the solute.

Increasing M_{inj} will eventually lead to mass overload. Both theoretically[22] and experimentally[23] it has been found that the relative peak broadening is a function of a dimensionless quantity m, in which the amount injected is normalized on the amount M_{pl} that can be sorbed into the stationary phase present in one plate. This normalization has the exact form

$$m = \frac{M_{inj}}{M_{pl}} \frac{k_\infty^2}{(1 + k_\infty)^2} \tag{6}$$

where k_∞ is the capacity factor at infinite dilution.

For Langmuir-type adsorption systems, M_{pl} is equal to the amount that saturates the surface in one plate. For liquid–liquid systems it is more difficult to estimate M_{pl}; however, it will be proportional to and of the same order as the amount of stationary phase in one plate, equal to $V_{sp}\rho_{sp}$[24]. In the above-mentioned studies, it was found that with $m = 2$ a 30% increase in the observed plate height is found. Defining m_{30} as the exact value of m at that point (it may have a different value for different solute–phase system combinations) it follows that

$$C_m^{max} = \frac{m_{30} V_{sp} \rho_{sp}}{V_{mp} \sqrt{2\pi N}} \frac{(k_\infty + 1)}{k_\infty^2} \frac{1}{MW} \quad (7)$$

$$= \frac{m_{30} \rho_{sp} V_s}{\sqrt{2\pi N} \cdot V_m} \frac{(k_\infty + 1)}{k_\infty^2} \frac{1}{MW} \quad (8)$$

where V_{sp} is the volume of stationary phase in one plate, V_s is the volume of the stationary phase, V_m is the volume of the mobile phase and ρ_{sp} is the density of the stationary phase. Eqn. 8 clearly indicates the importance of having a high phase ratio, which is limited, however, by eqn. 4.

With eqns. 4–8, some theoretical values have been calculated for three different phase systems, which in our opinion can be applied in OTLC. The results are given in Table I. The phase systems are (i) polymers (cross-linked silicones), (ii) porous layers used as an adsorbent (possibly modified) and (iii) porous layers used as a support for a stationary liquid (preferably with complete pore filling). The phase ratio of the porous adsorbent phase system was calculated assuming that the specific surface area of the porous silica layer is 300 m^2/g. From Table I it can be seen that from the point of view of mass loadability, porous layer columns are preferable to the polymer columns.

TABLE I

CALCULATED VALUES FOR THREE DIFFERENT PHASE SYSTEMS

d_c = 10 μm; N = 100 000; k' = 3; $D_m = 1 \cdot 10^{-9}$ m^2/s; H = 10 μm; MW = 200; ρ_{sp} = 1 g/ml.

Parameter	*Phase system*		
	Polymers	*Porous adsorbent*	*Liquid with porous support*
$d_{f,max}$ (μm)	0.30	2.5	2.5
C_m^{max} (mmol/l)	0.7	1.7	7.0
D_s (m^2/s)	$7 \cdot 10^{-12}$	$0.5 \cdot 10^{-9}$	$0.5 \cdot 10^{-9}$
M_{pl} (pmol)	≈0.5	≈1.0	≈5.0
Phase ratio (max.)	0.12	$3.7 \cdot 10^8$ m^{-1}[a]	1.25

[a] Equivalent to $m^2/l \cdot 10^{-3}$.

EXPERIMENTAL

Chemicals and materials

The solvents used were analytical reagent grade cyclohexane, methanol and ethanol (Merck, Darmstadt, F.R.G.), acetonitrile (Rathburn, Walkerburn, U.K.), methylene chloride, pentane, hexane, γ-butyrolactone (Janssen, Beerse, Belgium) and monochloroethane (Aldrich, Brussels, Belgium). Distilled water was first deionized through a PSC filter assembly (Barnstead, Boston, MA, U.S.A.). Prior to use, all solvents were filtered by vacuum suction over 0.5-μm filters (Type FH; Millipore, Bedford, MA, U.S.A.).

The polycyclic aromatics used as test compounds were obtained from Janssen and Aldrich. Stock solutions of the test compounds were prepared in the mobile phase.

Polyethoxysiloxane (PES) was prepared by hydrolytic polycondensation of tetraethoxysiloxane (Janssen). Monochlorodimethyloctadecylsilane (ODS) was obtained from Aldrich. The derivatization reagents *o*-phthaldialdehyde (OPA) and 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl) were obtained from Merck and Aldrich, respectively.

The 10-μm fused-silica capillaries were obtained from Polymicro Technology (Phoenix, AZ, U.S.A.).

Apparatus

Fig. 1 shows schematically the experimental set-up for the OTLC system. It consisted of a thermostated solvent reservoir (volume 400 ml), which could be pressurized with helium and served as a constant pressure pump, and a 0.5-μl injection valve (Model 7520; Rheodyne, Berkely, CA, U.S.A.) equipped with a splitting device. The columns were fitted in a laboratory-made thermostated jacket connected to a circulating liquid thermostat (Type F; Haake, Berlin, F.R.G.). A helium–cadmium laser, λ = 325 nm (Model 356 XM; Omnichrome, Chino, CA, U.S.A.) was used as a light source for on-column fluorescence detection. The laser beam passed a 325-nm bandpass filter (Oriel, Stratford, CT, U.S.A.) and was focused with a quartz lens (f = 50 mm) (Melles Griot, Zevenaar, The Netherlands). The emitted light was collected at a 90° angle by a Fresnel lens (f = 16 mm), then passed a 380-nm cut-off filter (Oriel). With NBD-Cl, a helium–cadmium laser, λ = 442 nm (Model 4207 NB; Liconix, Sunnyvale, CA, U.S.A.) was used, in combination with a 442-nm bandpass filter (Oriel) and a 500-nm cut-off filter (Oriel). The intensity was measured with a photomultiplier tube (Type 6225 S; EMI, Hayes, U.K.) and the resulting current was converted into a voltage by means of an amplifier (Diomod 72-W; Knick, Berlin, F.R.G.). The protective layer was burned off at the end of the capillary over a length of 1 cm. The signal was recorded with a potentiometric recorder (Kompensograph; Siemens, Karlsruhe, F.R.G.).

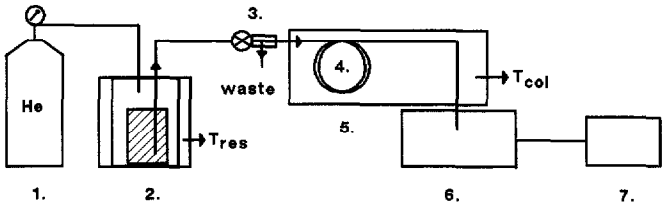

Fig. 1. Experimental set-up. 1, Helium bomb; 2, pressurized solvent reservoir; 3, injection valve with split injection; 4, capillary column; 5, thermostated jacket; 6, laser-induced fluorescence detector; 7, recorder.

Procedures

Preparation of a porous silica layer from PES. The deposition of a stable porous silica layer on the inner wall of fused-silica capillaries was performed by precipitation of silica from a solution of polyethoxysiloxane (PES). PES was prepared by hydrolytic polycondensation of tetraethoxysilane (TES) according to Unger and co-workers[25–27]. To 50 ml (0.22 mol) of TES dissolved in 30 ml of dry ethanol, 6.5 ml (0.36 mol) of water containing 70 μmol hydrochloric acid was added. This solution was

stirred vigorously for 1 h and refluxed for 6 h, then ethanol and hydrochloric acid were evaporated *in vacuo*.

The capillaries were treated with 1 *M* potassium hydroxide at room temperature for 2 h, then with 0.01 *M* hydrochloric acid at room temperature for 30 min, rinsed with water and finally dried for at least 2 h at 200–250°C whilst purging with dry helium (Fig. 2). Next the capillaries were filled with freshly prepared and degassed PES coating solution with pentane–monochloroethane or hexane–dichloromethane. The PES solution was prepared by dissolving PES in a polar solvent (dichloromethane or monochloroethane). Next, a non-polar solvent (hexane or pentane) was added until PES started to precipitate from the solution. Finally, PES was dissolved by adding a few drops more of the polar solvent. The solvent composition and the PES concentration were measured by weighing the amount of solvent added. The solvent was removed by evaporation under reduced pressure in a vacuum desiccator at one end of the capillary; the other end was closed with a septum. PES remained on the wall and was converted into silica by treatment with ammonia solution (pH 8–11) for 1 h, followed by rinsing with water for 2 h. The capillaries were dried by flushing with helium and could (i) be coated with PES again or (ii) be treated with a chemical modifier or (iii) be used as such in normal-phase chromatography.

Column diameters were determined as described previously[14].

Chemical modification. The dried capillary was flushed with a 5% (w/v) solution of ODS in toluene and heated at 140°C for 6 h. The capillary ends in a bottle of toluene to prevent blockage of the end of the capillary by precipitation of the silane reagent. Next the capillary was rinsed with toluene, acetonitrile or methanol before use. The liquid–liquid system was used as described previously[14].

Chemical derivatization of amino acids. The derivatization of amino acids with OPA was carried out according to Jones and Gilligan[28] and derivatization with NBD-Cl according to Ahnoff *et al.*[29].

RESULTS AND DISCUSSION

Static coating of polyethoxysiloxane (PES)

In a previous paper, the deposition of a porous silica layer was described[14]. The porous silica layer was prepared by dynamic coating of the silica precursor PES, which was converted into porous silica with gaseous ammonia. The main conclusion drawn was that this method is an elegant way to prepare a stationary layer, but resulted in a small phase ratio. The use of dynamic coating puts limits on the thickness of the silica layer and therefore static coating was suggested. In GC, static coating is used for preparing wall-coated open-tubular columns, with highly viscous non-polar polymers[30]. With static coating, the column is filled with a solution of the polymer in a volatile solvent. The solvent evaporates under reduced pressure and the polymer remains on the capillary wall. The polymers must be viscous, otherwise droplet formation and plugging, possibly caused by Rayleigh instability, will occur[30]. In our case we have to apply the same technique to coat PES, which is prepared by polycondensation from tetraethoxysilane (TES) and water. The kinematic viscosity can be adjusted in the range 10–20 000 cSt by varying the water-to-TES molar ratio from 1 to 1.5 (ref. 26). Adding more water to TES will result in the premature formation of silica gel, which cannot be used. Therefore, an even higher viscosity of the PES, which would be desirable, cannot be obtained.

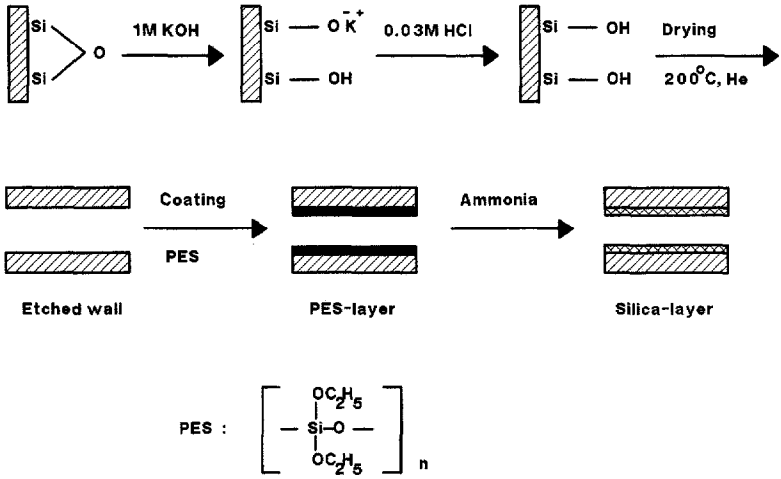

Fig. 2. Procedure for preparing porous silica layer.

The composition of the static coating solvent appeared to be critical. The solubility of PES in the solvent mixture should be carefully chosen. If the solubility of PES is good, then plugging of the solvent front during evaporation will occur. The concentration of PES in the solvent front will increase to such an extent that evaporation of the solvent will stop and the column becomes plugged. The solubility of PES should be lower, so that during evaporation PES precipitates on the wall and the coating process will proceed.

The choice of the solvent mixture was based on two factors: (i) the boiling temperature of the solvents should be around ambient, otherwise the coating process takes too long, and (ii) the polar solvent should preferably be more volatile than the non-polar solvent, in order to promote precipitation of PES at the outset of evaporation. The evaporation under reduced pressure was done from one end of the capillary, because static coating from both open ends of the capillary did not work. In this instance it appeared that the solvent plug moves to one end and out of the capillary. The static coating procedure, with dichloromethane–hexane as solvent mixture, takes about 2–3 days at room temperature, but often the capillary became plugged. With the monochloroethane–pentane mixture it was very laborious and difficult to make a good mixture, especially because the boiling temperature of monochloroethane is 12.3°C.

The PES concentration used was about 2% (v/v), which could give a layer thickness of 50 nm in a 10-μm tube. This choice was a compromise; higher concentrations were desirable because of the layer thicknesses that we were aiming for. However, the experimental problems in the coating process, which are negligible at concentrations below 1%, become insurmountable at concentrations above 2%. An alternative would be to obtain thick layers by repeating the coating. Although this has been applied successfully, it is a laborious approach.

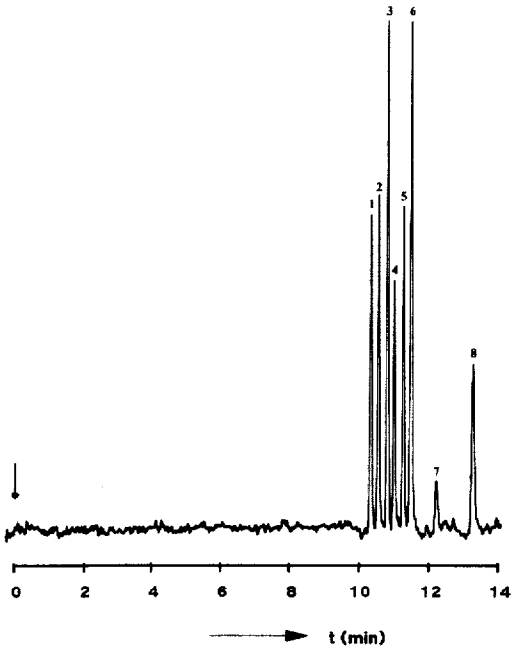

Fig. 3. LLC chromatogram of a capillary with a porous silica layer. Column, 1.55 m × 10.7 μm I.D.; mobile phase, cyclohexane saturated with γ-butyrolactone; stationary phase, γ-butyrolactone; linear velocity of mobile phase, 2.7 mm/s; inlet pressure, 0.9 MPa; T_{res} = 19.9°C; T_{col} = 20.0°C; V_{inj} = 23 pl; phase ratio, 0.019. Peaks: 1 = 9,10 diphenylanthracene; 2 = 9-phenylanthracene; 3 = 9-methylanthracene; 4 = anthracene; 5 = pyrene; 6 = fluoranthene; 7 = 1,2-benzanthracene; 8 = 9-anthracenecarbonitrile.

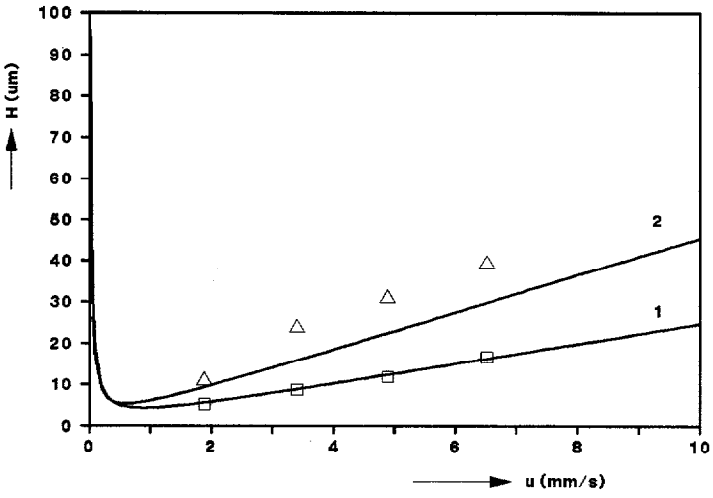

Fig. 4. *H versus u* curve for LLC capillary with porous silica layer. Column, 2 m × 10 μm I.D.; phase ratio, 0.038. 1, Theoretical curve for anthracene; 2, theoretical curve for benzo[*a*]pyrene; □, anthracene (k' = 0.26); △, benzo[*a*]pyrene (k' = 0.58).

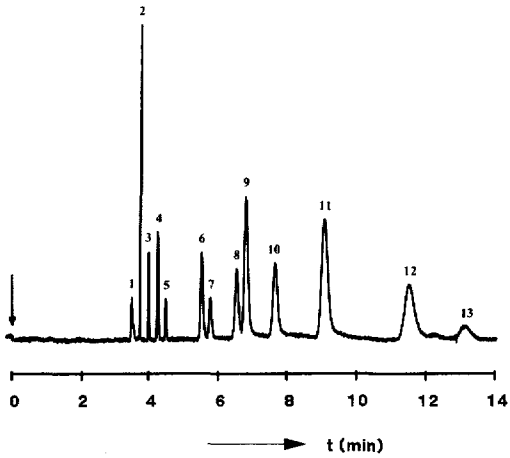

Fig. 5. Reversed-phase chromatogram for a capillary with an ODS-modified porous silica layer. Column, 1.34 m × 11.48 μm I.D.; mobile phase, acetonitrile–water (2:3); linear velocity of mobile phase, 6.4 mm/s; inlet pressure, 2 MPa; V_{inj} = 39 pl. Peaks: 1 = unretained; 2 = unknown; 3 = naphthoquinone; 4 = 9-anthracenemethanol; 5 = anthrone; 6 = 9-anthracenecarbonitrile; 7 = anthracene; 8 = fluoranthene; 9 = pyrene; 10 = 9-vinylanthracene; 11 = 1,2-benzanthracene; 12 = 9-phenylanthracene; 13 = benzo-[*a*]pyrene.

Chromatography

Solvent-generated liquid–liquid column (LLC) system. It was shown previously[14] that a non-viscous polar liquid, γ-butyrolactone, can be generated dynamically in the pores of a porous silica layer by pumping through cyclohexane saturated with γ-butyrolactone. It appeared possible to retain polycyclic aromatics on this phase system. Fig. 3 shows a chromatogram of eight polycyclic aromatics obtained on a 10.7-μm liquid–liquid column with a phase ratio of 0.019. For another capillary

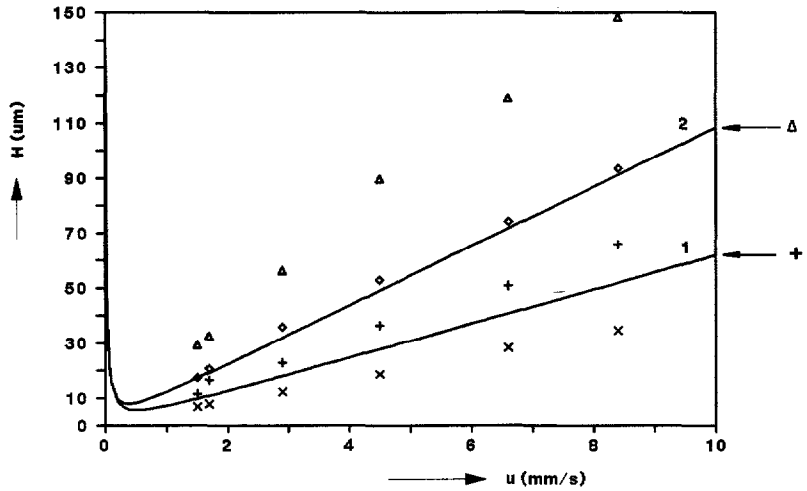

Fig. 6. *H versus u* curve for a capillary with an ODS-modified porous silica layer. 1, Theoretical curve for anthracene; 2, theoretical curve for 1,2-benzanthracene; ×, 9-anthracenecarbonitrile; +, anthracene; ◇, fluoranthene; △, 1,2-benzanthracene. Other details as in Fig. 5.

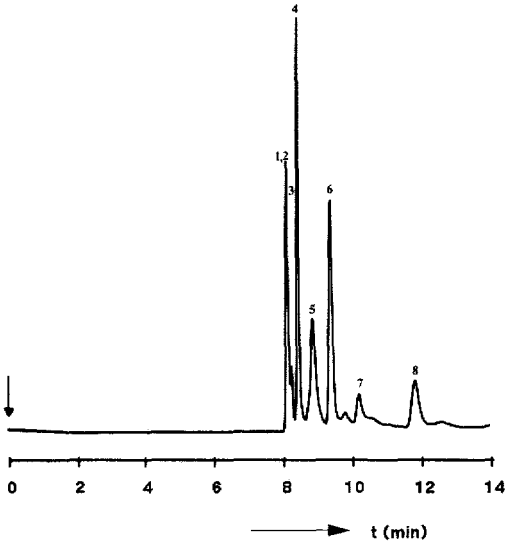

Fig. 7. Separation of some OPA-amino acids by reversed-phase OTLC. Column, 1.34 m × 11.48 μm I.D.; mobile phase, methanol–phosphate buffer (pH 7) (3:7); linear velocity of mobile phase, 2.7 mm/s. Peaks: 1 = glutamate; 2 = asparagine; 3 = threonine; 4 = alanine; 5 = histidine; 6 = valine; 7 = phenylalanine; 8 = leucine. Other details as in Fig. 5.

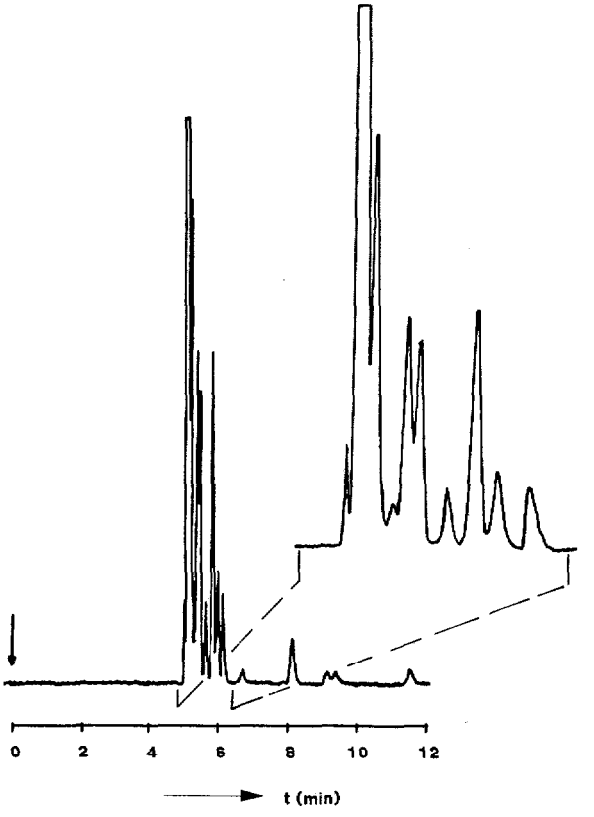

Fig. 8. Separation of some NBD-Cl amino acids by reversed-phase OTLC. Column, 2 m × 10 μm I.D.; mobile phase, acetonitrile–phosphate buffer (pH 7) (1:9); linear velocity of mobile phase, 7.0 mm/s. Other details as in Fig. 5.

a graph of *H versus u* was recorded (Fig. 4). Fig. 4 also shows theoretically calculated *H versus u* curves based on data obtained earlier for the diffusion coefficient[31]. The agreement is excellent for anthracene ($k' = 0.26$), whereas for benzo[*a*]pyrene ($k' = 0.58$) the agreement is within 30%. Although the phase ratio for these columns is still small, these results do illustrate the potential of liquid–liquid OTLC.

Reversed-phase chromatography. The applicability of phase systems with different kinds of chemistry in HPLC is well documented, and the reaction of silane reagents with silica can be simply carried out. For OTLC these silane reagents have hardly been used, but via the deposition of a porous silica layer in 10-μm capillaries this kind of chemistry can be applied in OTLC. Fig. 5 shows a chromatogram of polycyclic aromatics separated isocratically within 15 min on an 11.5-μm capillary with a chemically modified porous silica layer. The recorded *H versus u* curve (Fig. 6) shows fair agreement with the theory. The deviation at higher velocities can probably be explained by an incorrect value of the calculated diffusion coefficient by Wilke and Chang[32]. In Figs. 7 and 8 two chromatograms are shown with an isocratic separation of derivatized amino acids with OPA and NBD-Cl. From Figs. 5–8 it can be seen that reversed-phase OTLC in capillaries with a porous silica layer is possible. Other kinds of chemical modifications can probably also be used.

CONCLUSION

The preparation of porous silica layers in 10-μm open-tubular columns shows attractive features. The method described for depositing these layers is very elegant, because high-temperature treatments and other rigorous conditions are not necessary. However, in the static and dynamic coating steps serious experimental problems were encountered. The layer thickness, obtained by these coating procedures, is still too small.

The insufficient viscosity of PES is probably one of the drawbacks to static coating in 10-μm tubes. This problem was aggravated during our experiments because relatively high PES concentrations were used. This leads to even worse stability of the once formed PES layer, and also slows the evaporation. However, with the prepared porous silica layers excellent results in liquid–liquid and reversed-phase chromatography were obtained. It is expected that several other kinds of stationary phase modifications can be applied in these columns. Other routes for obtaining thick porous silica layers, using other silica precursors, are currently under consideration.

ACKNOWLEDGEMENTS

The authors thank Peter Schoenmakers, Philips Research Laboratories, for critical discussions and Dick Schoutsen for practical assistance. Support for this work was provided by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for Scientific Research (NWO) under grant 700-344-003.

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