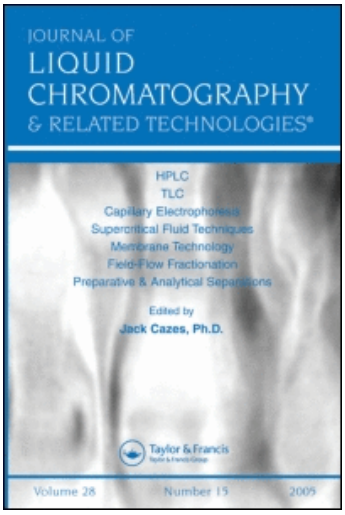

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PHENYLVINYLMETHYLPOLYSILOXANE ENCAPSULATED STATIONARY PHASE FOR REVERSED-PHASE LIQUID CHROMATOGRAPHY

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ABSTRACT

Silica beads of 6μm average diameter were silanized with methylvinyldiethoxysilane and then coated with phenylvinylmethylpolysiloxane. The chromatography (RP-HPLC) with the prepared material has superior ability for the separation of polar, non-polar and basic compounds. The chromatographic peaks are symmetric. Its stability has been studied. After continuous use for four months, the carbon content and chromatographic behavior of the phase were unchanged.

INTRODUCTION

Reversed-phase (RP) packings are the stationary phases most widely used in HPLC. Although silanized bonded reversed phases usually have fine chromatographic behaviour and selectivity, the many residual silanol groups which usually cause irreversible adsorption of solutes, especially basic solutes,

lead to tailing and even disappearance of chromatographic peaks. The application of RP packings is also limited by the narrow pH range in which they can be used, they are very unstable in basic media.

Coated reversed-phase packings have recently been developed to overcome these shortcomings.[1-7] They are prepared by coating lipophilic polymer on to the silica surface to give an uniform organic film. Column packings prepared in this way has both good chromatographic behavior and superior selectivity. Because contact of the silica matrix with the mobile phase is avoided, the alkali-resisting ability of the stationary phase is increased. The non-specific adsorption of alkaline solutes on to the silica surface is also avoided because of the complete coverage of surface silanol groups. Reports of stationary phases encapsulated with polystyrene,[4,6,7] polybutadiene[1] and coated with octadecylsiloxane polymers have recently appeared in the literature 3.

In this paper we report the encapsulation of phenyl-vinylmethylpolysiloxane (SE-54) on to a silica matrix previously modified with methylvinyldiethoxysilane. The resulting phase has superior reversed-phase performance in reverse phase HPLC separation.

EXPERIMENTAL

Reagents

Phenylvinylmethylpolysiloxane with a phenyl content of 5% and a vinyl content of 1% was obtained from Silar Labs, USA. Methylvinyldiethoxysilane was obtained from the Sichuan Chen Guang Chemical Plant, China. Micro silica beads 6 ± 1μm, specific surface area $100m^2g^{-1}$, mean pore size 6.7nm, were prepared in our laboratory.

Preparation of the Stationary Phase

To increase the strength of bonding of phenylvinylmethylpolysiloxane encapsulated on the silica surface and thus enhance the stability of the stationary phase, the silica matrix was modified with methylvinyldiethoxysilane firstly to yield a vinyl derivative, the silica beads derived with methylvinyl groups were then encapsulated with the polysiloxane.

Modification of the Silica Beads

The micro silica beads were pretreated according to literature 4 and 5. The pretreated beads were then put into a toluene solution of methylvinyldiethoxysilane and refluxed for 6h. The mixture was centrifugalized and the beads were washed with toluene and acetone consecutively to remove the unreacted silane and then dried. The carbon content of the bonded silica was 1.9 ≃ 2.2%

Encapsulation of the Polymer

The modified beads were added to a solution of phenylvinyl-methylpolysiloxane in acetone and the mixture was stirred to evaporate the solvent gradually. The encapsulation stationary phases of 3.58, 4.92, 7.35, 9.57, and 12.80% carbon content were prepared.

Chromatography

HPLC was performed with a Varian 5000 high-performance liquid chromatograph fitted with a 150 X 4.6mm i.d. stainless-steel column which was slurry-packed with stationary phase at 37MPa. Ultraviolet detection was performed at 254nm. Data were recorded and analyzed with a Shimadzu (Japan) C-R2AX data processor.

Testing

The residual silanols or hydroxyl groups on the surface of stationary phase may cause problems for basic solutes or basic group-containing compounds. Characterization and quantification of residual silanols by various methods had been reported, but the titration method presented by Khurana and Ho is simple and quantitative[8]. The titration with 0.01N NaOH were carried out by suspending 0.5g stationary phase in 10 mL 10% solution of NaCl containing 3mL isopropanol. The titration ended at pH9. pH was measured with a glass electrode and a calomel reference electrode. The process can not be easily performed in aqueous suspension, but addition of 10% salt increases their ionization sufficiently so that titration with dilute alkali is probable. Elemental analysis of the encapsulated phase was performed with a Vario EL Elemental Analyzer (Germany).

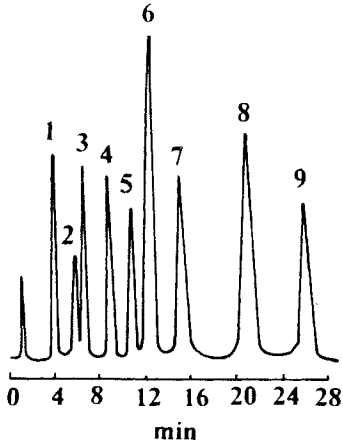


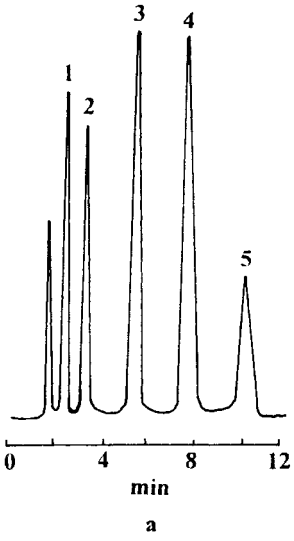
Figure 1. Separation of polynuclear aromatic hydrocarbons. Carbon content of stationary phase 7.35%; mobile phase, MeOH-H_2O, 60 : 40 (v/v); Flow-rate 1.0 mL/min^{-1};detention UV 254nm Peaks: 1=benzene; 2=toluene; 3=naphthalene; 4=dimethylbenzene; 5=diphenyl; 6=anthracene; 7=pyrene; 8=chrysene; 9=benzanthracene.

RESULTS AND DISCUSSION

Separation of Polynuclear Aromatic Hydrocarbons

The separation of polynuclear aromatic hydrocarbons is one characteristic application of RP-HPLC. By use of the encapsulated phenylvinylmethyl-polysiloxane column, superior separation of polynuclear

Figure 2 (right). Separation of polar compounds. a) Conditions: Carbon content of stationary phase, 7.35%; mobile phase, MeOH-H_2O, 55:45 (v/v); Flow rate, 1.0mL/min. Peaks: 1=benzyl alcohol; 2=benzaldehyde; 3=methylphenoxide; 4=benzophenone; 5=triphenylcarbinol. b) Conditions: Carbon content of stationary phase, 7.35%; mobile phase, MeOH-H_2O, 70:30 (v/v); Flow rate, 1.0mL/min. Peaks: 1=iodobenzene; 2=benzyl chloride; 3=chlorobenzene; 4=bromobenzene; 5=m-dibromobenzene; 6=trichlorobenzene; 7=tribromo- benzene. c) Conditions: Carbon content of stationary phase, 7.35%; mobile phase, MeOH-H_2O, 55:45 (v/v); Flow rate, 1.0mL/min. Peaks: 1=p-hydroxy phenol; 2=phenol; 3=naphthol; 4=phenoxide; 5=anthraquinone; 6=anthrone; 7=2-ethylanthraquinone. d) Conditions: Carbon content of stationary phase, 7.35%; mobile phase, MeOH-H_2O, 40:60 (v/v); Flow rate, 1.0mL/min. Peaks: 1=m-chlorophenol; 2=p-chlorophenol; 3=o-chlorophenol.



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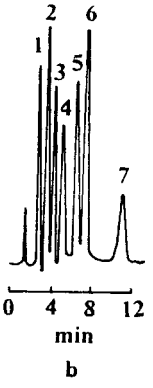

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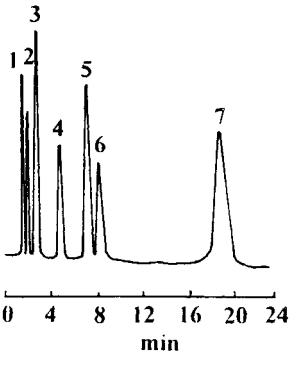

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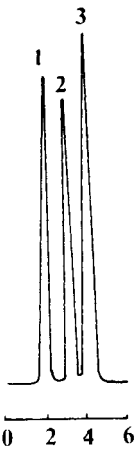

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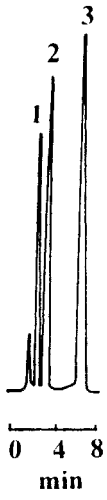

Figure 3. Separation of amine mixture. Conditions: Carbon content of stationary phase, 9.57%; mobile phase, MeOH-H_2O, 55:45 (v/v); Flow rate 1.0mL/min. Peaks: 1=aniline; 2=benzyl amine; 3=N,N-dimethylaniline.

aromatic hydrocarbons can be achieved; the order of elution is the same as that from an ODS column (Figure 1), which indicates that the two stationary phases have similar selectivity. When the methanol content of the mobile phase is increased, the retention of all solutes is reduced but the order of elution does not change.

So, it can be concluded that the mechanism of retention of the encapsulated phase is that of reversed-phase chromatography.

Separation of Polar Compounds

The separation of some groups of compounds with the encapsulated phase is shown in Figure 2. It can be seen from Figure 2a that the encapsulated phase gives good separation of oxygen-containing compounds of same carbon number but of different structure, e.g. benzaldehyde, benzyl alcohol, and anisole. Figure 2b shows that the order of the retention in the separation of halobenzenes is iodobenzene < benzyl chloride < chlorobenzene < bromobenzene.

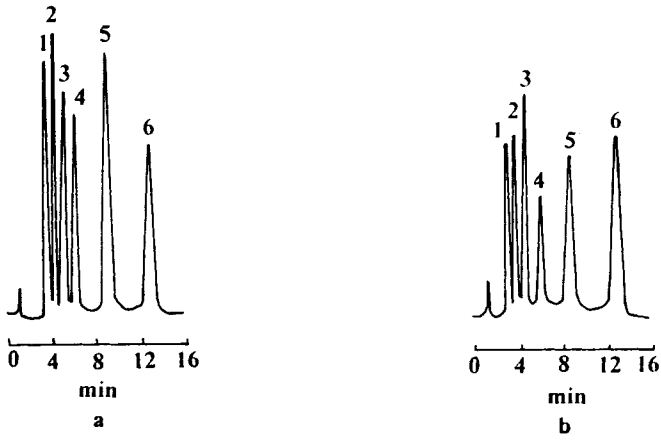

Figure 4. Separation of ferrocene derivatives. Conditions: Carbon content of stationary phase, 4.92%; Mobile phase, MeOH-H_2O, 60:40 (v/v); Flow rate 1.0mL/min. (a) Peaks: 1=n-pentyl-α-ferrocenyl acetamide; 2=n-heptyl ferrocenyl formamide; 3=n-hexyl-β-ferrocenyl propanamide; 4=n-heptyl-α-ferrocenyl acetamide; 5=n-octyl-α-ferrocenyl acetamide; 6=n-octyl-γ-ferrocenyl butanamide. (b) Peaks: 1=n-butyl-β-ferrocenyl propanamide; 2=n-butyl-γ-ferrocenyl butanamide; 3=n-pentyl-γ-ferrocenyl butanamide; 4=n-heptyl-α-ferrocenyl acetamide; 5=n-heptyl-γ-ferrocenyl butanamide; 6=n-octyl-γ-ferrocenyl butanamide.

If benzene is substituted by the same halogen the retention order is monohalobenzene < dihalobenzene < trihalobenzene. Figure 2c shows the separation of compounds of heavy polar character. Figure 2d illustrates the separation of position isomer of chlorophenol, the retention order is m-chlorophenol < p-chlorophenol < o-chlorophenol. It can be seen that this phase can be used for the separation of position isomer.

Separation of Amines

Figure 3 shows the separation of some aromatic amines. Baseline separation is achieved in the solution of methanol-water and the peaks are symmetric.

It is obvious that the residual silanol groups of the silane bonded phase are encapsulated with polymer layer, the peak tailing arose from nonspecific adsorption between solute and silanol group is greatly reduced.

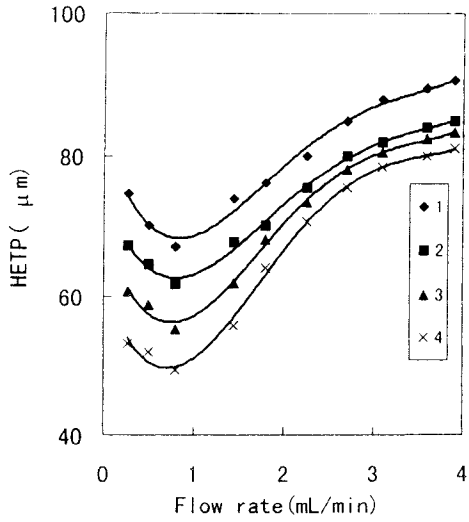

Figure 5. H-u plots. 1=methylbenzoate; 2=ethylbenzoate; 3=propylbenzoate; 4=naphthalene. Chromatographic conditions: Same as in Fig. 2b.

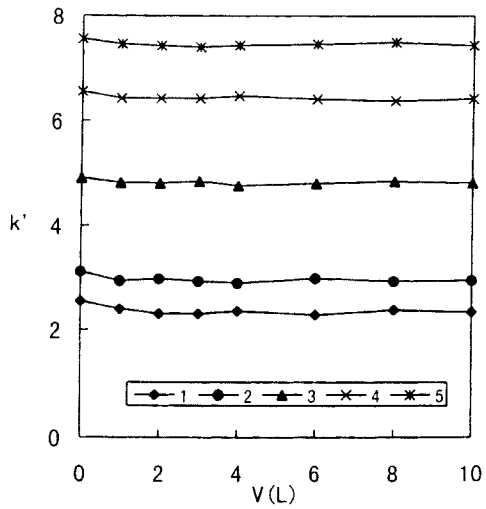

Figure 6. Stability Test. Conditions: Carbon content of stationary phase, 7.35%; Mobile phase, MeOH-H_2O, 55:45 (v/v), pH=10.0 1=pyridine; 2=benzaldehyde; 3=methylbenzoate; 4=dimethylaniline; 5=ethylbenzoate.

Table 1

Titration Results for Residual Silanols

Sample	Starting Silica	LC-1	LC-2	LC-3
Residual Silanol	2.5	0.015	0.009	0.0054

Table 2

Elemental Analysis of the Stationary Phase

	C (%)	H (%)
Before Use	7.35	1.35
After 4 Months Service	7.29	1.30

* Standard deviation 3%.

Separation of Ferrocene

Due to the specific sandwich structure and aromaticity, ferrence and its derivates are of great use in the process of catalytic reaction and they can be used for adjusting combustion rate, moreover, they can be used in the pharmacology for their physiological activity. So their separation study is of interest. On the prepared stationary phase, the separation of amide derivatives of ferrocene is tested, and good results have been obtained (Figure 4).

Column Efficiency

Figure 5 is the H-u plot of some aromatic compounds. It can be seen that the H value does not change much along with the increasing of the flow rate.

Residual Silanols

Table 1 shows the results of the titration for the residual silanols. The data indicate that 97 $\simeq$ 99% silanols on the initial silica surface were shielded by phenylvinylmethylpolysiloxane film.

Stability

The elemental analysis of stationary phase are tested before and after 4 months use (passage of 45L of 55:45 (v/v) methanol-water and 10L of 55:45 (v/v) methanol-water of pH=10.0). The results are shown in Table 2, the standard deviation was 3%. It is clear that there was no fundamental difference between C and H content before and after four months service, i.e. the encapsulated SE-54 was not washed off by the alkali solvent. As is apparent from Figure 6 the retention of solutes remained constant during operation, demonstrating the high stability of the encapsulated phase.

REFERENCES

1. M. Hanson, B. Eray, K. Unger, A. V. Neimark, J. Schmid, K. Albert, E. Bayer, Chromatographia, **35**, 403 (1993).

2. R. Ohmacht, M. Kele, Z. Matus, Chromatographia, **28**, 19 (1989).

3. T. A. Anazawa, I. C. S. Jardim, J. Liq. Chromatogr., **17(6)**, 1265 (1994).

4. N. Song, L. R. Chen, Chin. J. Chromatogr., **12(6)**, 398 (1994).

5. X. J. Zuo, L. R. Chen, Q. Wang, J. Instrum. Anal., **13(3)**, 86 (1994).

6. A. Kurganov, O. Kuzmenko, V. A. Davankov, J. Chromatogr., **506**, 391 (1990).

7. Y. M. Zuo, B. R. Zhu, Y. Liao, M. D. Gui, Z. L. Pang, J. X. Qi, Chromatographia, **38**, 756 (1994).

8. A. L. Khurana, C. T. Ho, J. Liq. Chromatogr., **11**, 3205 (1988).

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