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## PREPARATION AND RETENTION CHARACTERISTICS OF DIFFERENT PHENYLPOLYSILOXANE PHASES FOR REVERSED-PHASE LIQUID CHROMATOGRAPHY

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### SUMMARY

Reversed-phase silicas prepared by treating silica with three different phenylpolysiloxanes were compared with monomeric phenyl silica, by determining the specific surface area,  $S_{\text{BET}}$ , carbon content and also their properties in liquid chromatography using methanol–water mixtures as the eluents. Relative to the monomeric phenyl silica, the phenylpolysiloxane modified silicas show no marked differences in the surface concentration of the organic groups, but their hydrophobic characteristic is significantly higher. This results in a different chromatographic behaviour for solutes with different polarities.

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### INTRODUCTION

In reversed-phase liquid chromatography, hydrophobic packing materials, produced by surface reaction of silica, are most often used. The chromatographic properties of a reversed-phase sorbent are dependent on the synthesis conditions of the bonded phase. The preparation and study of bonded phase materials have received considerable attention. Modifications can be accomplished with mono-, di- or trichlorosilane or alkoxyasilane<sup>1</sup>. The choice of reagent together with the variation in type of silica (structure, pore volume and surface area) will result in packing materials having widely differing chromatographic properties. This has been well documented<sup>2–6</sup>. Much of this work has been concerned with monomeric bonded phases and has been reviewed<sup>7</sup>.

Although much research has been performed on monomeric phases, relatively little effort has been expended in the study of polymeric phases. The synthesis and characterization of silicone polymers varying in structure and polarity were surveyed by Aue *et al.*<sup>8</sup>, Novotny and Grushka<sup>9</sup> and Stewart and Perry<sup>10</sup>. Schmidt *et al.*<sup>11</sup> introduced a pellicular-type material, namely Zipax coated and bonded with 1% (w/w) of an high-molecular-weight polymer called ODS Permaphase. Majors and

Hopper<sup>12</sup> studied in detail the reaction between silica and various polar and non-polar organochlorosilanes and alkoxysilanes. Direct polymerization was achieved by treating the silica with a di- or trifunctional organochlorosilane in the presence of water vapour. Kirkland and Yates<sup>13,14</sup> patented a procedure in which a pre-polymerized material representing an organofunctional siloxane was deposited on the silica support. The reluctance of researchers to accept polymeric phases is probably the result of difficulties reported with early pellicular phases. Problems have included low column efficiency due to mass transfer limitations<sup>15,16</sup>, poor peak shape<sup>17</sup> and difficulties with the reproducibility of syntheses<sup>18</sup>. Recently, some researchers<sup>19–22</sup> synthesized and studied series of C<sub>18</sub> polymeric phases on totally porous silica for separation of polycyclic aromatic hydrocarbons. They concluded that significant differences existed in the chromatographic properties of C<sub>18</sub> bonded phases prepared in different ways. In general, the column selectivity was directly related to the bonded phase surface coverage, while the absolute retention was more closely related to the amount of carbon contained within the column (the phase ratio). Other kinds of polymeric phases have also been produced for use in size exclusion chromatography<sup>23,24</sup> and ligand exchange chromatography<sup>25</sup>.

In comparison with the relatively extensive literature on the preparation of C<sub>18</sub> polymer phases, only a limited number of papers have dealt with surface modification with phenylpolysiloxanes. Attempts to bind phenylpolysiloxane to the surface were made for capillary gas chromatography<sup>26,27</sup>.

In our work, we intended to modify silica gels with three different phenylpolysiloxane. Namely, fully hydroxylated porous silica was treated with phenylmethylpolysiloxane, phenylpropylpolysiloxane and diphenylpolysiloxane. The retention behaviours of solutes on columns packed with these types of phenyl phases were examined and compared with those of monomeric phenylmethyl silica gel in reversed-phase liquid chromatography. The polar characters of the different phases were studied so that we could show the effects of the modifiers bonded to the surface.

## EXPERIMENTAL

### *Equipment*

Chromatographic separations were carried out with a Varian 8500 solvent delivery system, a Model 7125 sample injector (Rheodyne, Berkely, CA, U.S.A.) and a Varian Model 635 UV–VIS monitor. The columns were packed in 250 mm × 4.0 mm I.D. stainless-steel tubes (Bio-Separation Technologies, Budapest, Hungary). The thermal studies were performed with a Derivatograph-3427 (MOM, Budapest, Hungary). The BET surface area of silicas was determined by a sorptometer made at the Department for Physical Chemistry of the Technical University of Budapest (Hungary).

### *Chemicals and reagents*

Separon SGX Si-100 5- $\mu$ m was obtained from Laboratorní Přístroje (Prague, Czechoslovakia). Phenylmethyldichlorosilane, phenylmethylpolysiloxane (REN 50, molecular weight about 1500 g/mol), phenylpropylpolysiloxane (SY 308, molecular weight 1500 g/mol), diphenylpolysiloxane (SY 430, molecular weight about 1700 g/mol) (Wacker, München, F.R.G.) and trimethylchlorosilane (Merck, Darmstadt,

F.R.G.) were used as received. All other chemicals obtained from commercial sources were used without purification. The test solutes were dissolved in methanol at a concentration of 0.1 mg/ml by weight. Typically 10  $\mu$ l were injected. The flow-rates were 1 ml/min as usual. Sample peaks were detected at 254 nm.

#### *Preparation of phenylmethyl phase packing*

The preparation of the phenylmethyl packing material was based on Unger's procedure<sup>28</sup>. A 10-g amount of dried silica gel was mixed with 5% phenylmethyldichlorosilane in anhydrous toluene and refluxed in a sealed flask. The reaction was completed within 8 h. The phenyl silica gel was filtered off and washed with toluene, methanol, water and methanol, respectively. The solid phase was then kept at 353 K for several hours under vacuum. Residual hydroxyl groups were deactivated by treating the solid material with a 10% solution of trimethylchlorosilane in toluene. This deactivated phenyl-bonded silica gel was high-pressure slurry packed into a 250 mm  $\times$  4.0 mm I.D. column by Bio-Separation Tech.

#### *Preparation of phenylpolysiloxane phase packing*

The preparation of phenylpolysiloxane packings was based on the procedure of Kirkland and Yates<sup>13</sup>. A 10-g amount of dried silica gel was mixed with 1% phenylpolysiloxane in toluene and refluxed gently under a condenser for 2 h. The volatile solvent was removed while stirring the mixture under vacuum. The resulting dry powder was then heated at 473 K for 2 h. After heating, the silica gel was washed with toluene, dioxane, methanol, water and methanol, respectively. The solid phase was then kept at 353 K for 4 h under vacuum. Residual hydroxyl groups were deactivated by treating the silica gel with a 10% solution of trimethylchlorosilane in toluene. These phenylpolysiloxane-bonded silica gels were high-pressure slurry packed into 250 mm  $\times$  4.0 mm I.D. columns by Bio-Separation Tech.

#### *Analysis of stationary phase*

The amount of organic moiety bound to the silica supports was determined from the thermogravimetric curves of the modified silica gels<sup>29</sup>. The specific surface areas of the gels,  $S_{\text{BET}}$ , were obtained from sorption measurements at 77 K.

### RESULTS AND DISCUSSION

#### *Analysis of stationary phase*

The specific surface area,  $S_{\text{BET}}$ , was obtained from nitrogen sorption measurement at 77 K. It was assumed that the starting silica support had a surface area of 535 m<sup>2</sup>/g (Laboratori Pristroje). These measurements (see Table I) demonstrate a considerable reduction in  $S_{\text{BET}}$ . The decrease in  $S_{\text{BET}}$  values on different phenyl phases is about 25–40% of that of the starting silica gel. The amounts of organic moiety bound to the silica supports were determined from the weight losses of the modified gels and are given in Table I. It is seen that the carbon content of different phenyl phase silica gels is about the same.

#### *Retention of test solutes*

Retention data for the test solutes were obtained on three different phenyl-

TABLE I  
CHARACTERISTICS OF SILICA GELS PREPARED

Material	Particle size ( $\mu\text{m}$ )	Functional group bonded	Specific surface area $S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Carbon content (%)	Surface concentration ( $\mu\text{mol}/\text{m}^2$ )
A	5	Phenylmethylhydroxysilyl	397	13.0	2.92
B	5	Phenylmethylpolysiloxane	327	10.7	2.41
C	5	Phenylpropylpolysiloxane	325	12.7	2.23
D	5	Diphenylpolysiloxane	368	12.8	1.68

polysiloxane phases and on a monomeric phenylmethyl phase, using mixtures of methanol–water (60:40) as the mobile phase. Fig. 1 shows the separation of the test solutes on different phenyl stationary phases. The retention characteristics of the chromatographed substances are expressed in terms of their capacity factor,  $k'$ , and their selectivity factor,  $\alpha$ . In order to eliminate the influence of the specific surface area of the sorbents investigated, we used the  $k'/S_{\text{BET}}$  values. These data are in Table II. It is apparent that the value of  $k'$  for the highly hydrophobic substances (toluene, bromobenzene, *p*-xylene, propylbenzene) are higher on any polysiloxane phase; in contrast the value of  $k'$  increases for phenol, cresol acetophenone, anisole and methyl benzoate, more polar species, on the monomeric phenyl phase.

Again, the elution order is the same on every phenyl packing. After comparing the  $k'/S_{\text{BET}}$  values of test solutes on phases A–D, it is evident that any phenylpolysiloxane support is less polar than the monomeric phenyl phase. The polarity of phenylpolysiloxane silica gels increase in the sequence phenylmethyl-, phenylpropyl-, diphenylpolysiloxane. Polymeric phenyl-modified silica gels seem to be better stationary phases for non-polar aromatics than monomeric phenyl phases.

#### *Comparison of monomeric and polymeric phenylmethyl phases*

Monomeric and polymeric modified packings having the same functional group (phenylmethyl) were prepared. In this section, only a brief discussion will be given of the packing properties that influence the retention behaviour of solutes in reversed-phase chromatography. According to the generally accepted rules, the elution volumes of chromatographed substances on reversed-phase columns are mainly due to non-specific interactions between the solute molecules and the stationary phase. The character of this type of interactions may be evaluated by the relationship  $\log k'$  vs.  $n_c$  where  $n_c$  represents the number of carbon atoms in the solute molecule<sup>30,31</sup>. This relationship is linear for solutes belonging to an homologous series<sup>31</sup>. In order to eliminate the influence of  $S_{\text{BET}}$  of the sorbents investigated, we used the  $\log (k'/S_{\text{BET}})$  values, instead of  $\log k'$ . For these investigations the same mobile phase composition (methanol–water, 70:30) was used. The appropriate retention data are shown in Table III. Fig. 2 presents plots of  $\log (k'/S_{\text{BET}})$  vs.  $n_c$  for the stationary phases investigated by us. It appears that the highest of  $k'$  were obtained for the polymeric phase. Also that the plots are not parallel for both packing materials, the slope of the plot for the monomeric phase being smaller. According to Colin and Guiochon<sup>31</sup>, the slope of such plots increases with the degree of coverage of the support surface, but the surface coverage of both silica gels is the same (see Table I). The different slopes of the plots

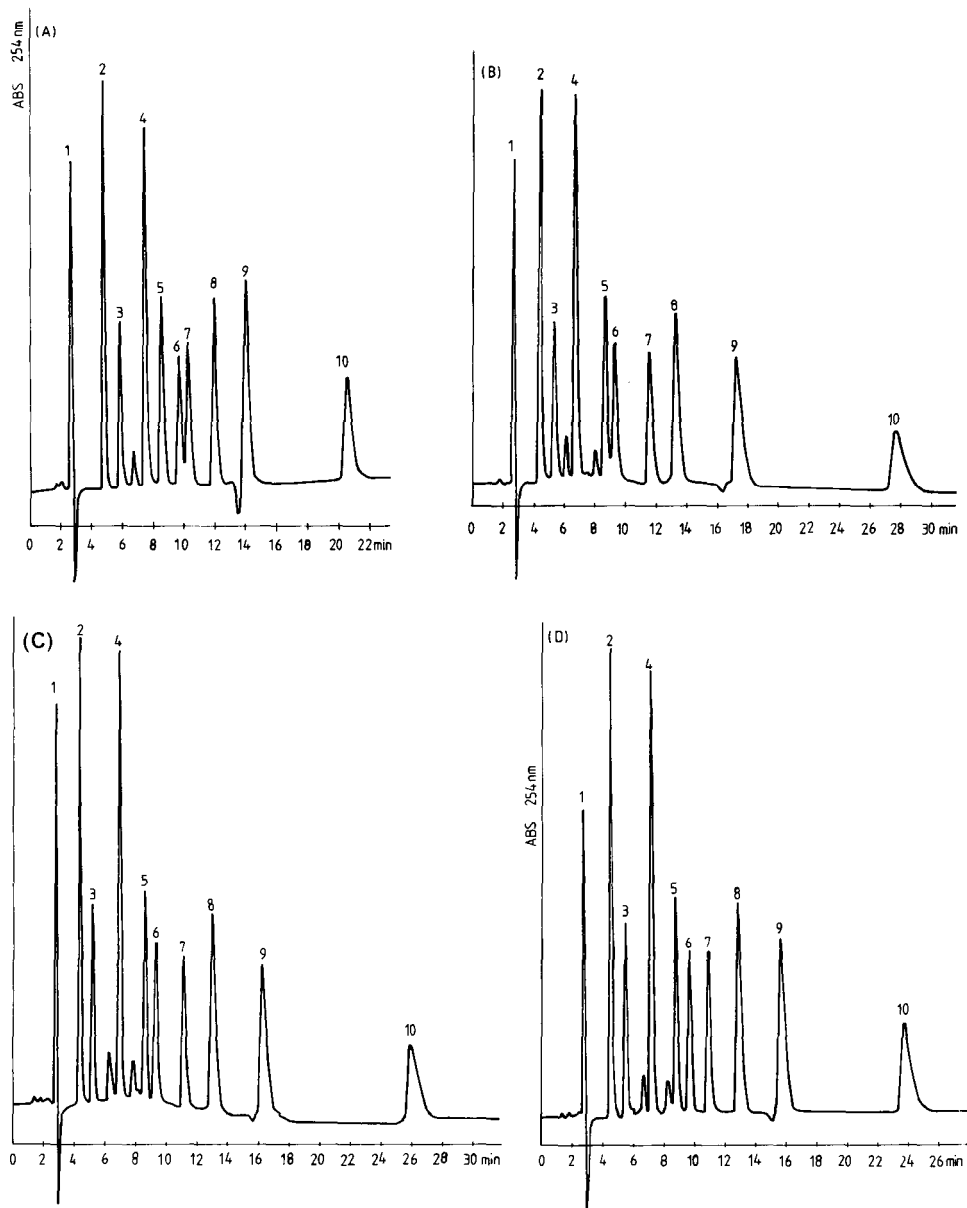


Fig. 1. Separation of test solutes on phenylmethyl (A), phenylmethylpolysiloxane (B), phenylpropylpolysiloxane (C) and diphenylpolysiloxane (D). Peak identities: 1 = methanol; 2 = phenol; 3 = *o*-cresol; 4 = acetophenone; 5 = anisole; 6 = methyl benzoate; 7 = toluene; 8 = bromobenzene; 9 = *p*-xylene; 10 = propylbenzene. Mobile phase: methanol-water (60:40). Flow-rate: 1 ml/min. Detection: UV absorbance (ABS) at 254 nm. Temperature ambient.

TABLE II

## CAPACITY AND SELECTIVITY FACTORS OF TEST SOLUTES ON DIFFERENT PHENYL PHASES

Eluent: methanol–water (60:40, v/v) Temperature: ambient. Columns: A, bonded group, phenylmethylsilyl; B, phenylmethylpolysiloxane; C, phenylpropylpolysiloxane; D, diphenylpolysiloxane.

Sample	Column A			Column B			Column C			Column D		
	$k'$	$k'/S_{\text{BET}} \cdot 10^3$	$\alpha$	$k'$	$k'/S_{\text{BET}} \cdot 10^3$	$\alpha$	$k'$	$k'/S_{\text{BET}} \cdot 10^3$	$\alpha$	$k'$	$k'/S_{\text{BET}} \cdot 10^3$	$\alpha$
Phenol	0.85	2.141		0.57	1.743		0.57	1.753		0.57	1.548	
<i>o</i> -Cresol	1.27	3.190	1.49	0.89	2.721	1.56	0.85	2.615	1.49	0.92	2.500	1.61
Acetophenone	1.88	4.735	1.48	1.39	4.250	1.56	1.50	4.615	1.76	1.57	4.266	1.71
Anisole	2.30	5.793	1.23	2.07	6.331	1.48	2.07	6.369	1.38	2.14	5.815	1.36
Methyl benzoate	2.71	6.826	1.18	2.32	7.094	1.12	2.35	7.230	1.12	2.42	6.576	1.13
Toluene	2.96	7.455	1.09	3.14	9.602	1.35	3.00	9.231	1.27	2.89	7.053	1.19
Bromobenzene	3.62	9.110	1.23	3.71	11.345	1.18	3.64	11.200	1.21	3.57	9.701	1.23
<i>p</i> -Xylene	4.42	11.135	1.22	5.14	15.718	1.30	4.82	14.830	1.32	4.57	12.418	1.28
Propylbenzene	6.92	17.431	1.56	8.05	27.060	1.72	8.20	25.476	1.71	7.50	20.380	1.64

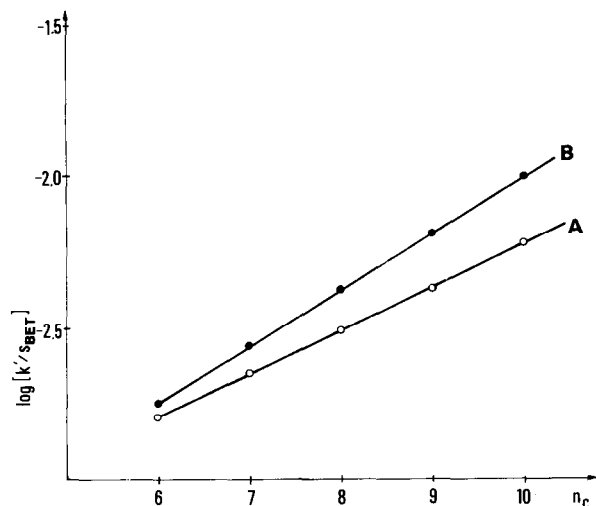


Fig. 2. Plots of  $\log(k'/S_{\text{BET}})$  vs. number of carbon atoms,  $n_c$ , for monomeric phenylmethyl silica gel (A) and polymeric phenylmethyl silica gel (B). Mobile phase: methanol-water (70:30).

for the two silica gels probably result from the different types of interaction between the solute molecules and the bonded film. It is not clear, when the surface coverage of these two silica gels is the same, whether this is caused by an additional hydrophobic interaction on the polymeric modified packing of the new surface site (siloxane bridges) with the solutes. Young<sup>32</sup> reported that siloxane bridges on the silica surface are essentially hydrophobic.

#### Separation of non-polar aromatics

Polymeric phenyl phases were supposed to be better stationary phases for non-polar solutes than monomeric phenyl packings. So we decided to examine the chromatographic behaviours of some polycyclic aromatic hydrocarbons on monomeric

TABLE III

CAPACITY AND SELECTIVITY FACTORS OF AROMATIC HOMOLOGOUS SOLUTES ON COLUMNS PACKED WITH MONOMERIC AND POLYMERIC PHENYLPROPYL MODIFIED SILICA

Columns: A, monomeric phenylmethyl silica gel; B, polymeric phenylmethyl silica gel. Eluent: methanol-water (70:30, v/v).

Sample	Column A			Column B		
	$k'$	$k'/S_{\text{BET}} \cdot 10^3$	$\alpha$	$k'$	$k'/S_{\text{BET}} \cdot 10^3$	$\alpha$
Benzene	0.63	1.62	1.36	0.58	1.77	1.55
Toluene	0.86	2.21	1.38	0.90	2.75	1.52
Ethylbenzene	1.19	3.05	1.37	1.37	4.19	1.53
Propylbenzene	1.63	4.18	1.41	2.10	6.42	1.53
Butylbenzene	2.31	5.92		3.22	9.85	

TABLE IV

## CAPACITY AND SELECTIVITY FACTORS OF AROMATIC HYDROCARBONS ON COLUMNS PACKED WITH MONOMERIC AND POLYMERIC PHENYL MODIFIED SILICA GELS

Eluent: methanol–water (70:30, v/v) Temperature: ambient. Columns: A, phenylmethylsilyl; B, phenylmethylpolysiloxane; C, phenylpropylpolysiloxane; D, diphenylpolysiloxane.

Sample	Column A			Column B			Column C			Column D		
	$k'$	$k'/S_{BET} \cdot 10^3$	$\alpha$	$k'$	$k'/S_{BET} \cdot 10^3$	$\alpha$	$k'$	$k'/S_{BET} \cdot 10^3$	$\alpha$	$k'$	$k'/S_{BET} \cdot 10^3$	$\alpha$
Benzene	0.63	1.58		0.58	1.77		0.82	2.52		0.67	1.82	
Naphthalene	1.23	3.09	1.95	1.51	4.62	2.61	1.62	4.95	1.96	1.54	4.18	2.29
Phenanthrene	2.20	5.74	1.85	3.21	9.82	2.12	3.01	9.26	1.07	3.11	8.45	2.02
Anthracene	2.35	5.92	1.03	3.52	10.76	1.09	3.23	9.94	1.07	3.40	9.24	1.09
Pyrene	2.88	7.25	1.22	4.72	14.43	1.34	4.05	12.46	1.25	4.52	12.28	1.33
Chrysene	4.43	11.16	1.53	7.31	22.35	1.55	5.65	17.38	1.39	6.33	17.20	1.40
Benz[ <i>a</i> ]anthracene	4.58	11.54	1.03	7.60	22.24	1.04	6.13	18.86	1.08	6.53	17.74	1.03
Benz[ <i>b</i> ]anthracene	4.92	12.39	1.07	8.74	26.74	1.15	6.70	20.62	1.09	7.01	19.05	1.07
Benzo[ <i>a</i> ]pyrene	5.81	14.63	1.18	11.27	34.46	1.29	8.35	25.69	1.24	6.64	18.04	0.94
Benzo[ <i>e</i> ]pyrene	6.27	15.79	1.07	9.80	29.97	0.87	7.73	23.78	0.92	8.88	24.13	1.34
Dibenz[ <i>a,c</i> ]anthracene	7.84	19.75	1.25	14.50	44.34	1.48	11.20	34.15	1.43	12.83	34.86	1.44
Dibenz[ <i>a,b</i> ]anthracene	8.74	22.02	1.11	14.09	45.56	1.03	11.79	36.27	1.06	13.32	36.19	1.04



phenyl silica gel and polymeric phenyl supports. Retention data for solutes were obtained on three different phenylpolysiloxane phases and monomeric phenyl silica gel, using methanol–water (70:30) as the mobile phase. The retention of the chromatographed substances is expressed in terms of their capacity factors  $k'$ . In order to eliminate the influence of the surface area of the sorbents investigated, we used the  $k'/S_{\text{BET}}$  values. In Table IV these data are presented. It is seen that the values obtained from  $k'$  and  $k'/S_{\text{BET}}$  decrease in the sequence phenylmethylpolysiloxane phenylpropylpolysiloxane- > diphenylpolysiloxane > phenylmethyl phase. This illustrates that, with the same mobile phase, the retention will be weakest on the monomeric phenylmethyl phase and strongest on the phenylmethylpolysiloxane phase. After comparing columns B–D, it is evident that the phenylmethylpolysiloxane silica gel is the most hydrophobic and the diphenylpolysiloxane packing is the least. This fact confirms the conclusion obtained from reversed-phase high-performance liquid chromatography<sup>33</sup>, namely that the hydrophobicity of monomeric phenyl phases increases in the sequence triphenyl < diphenyl < phenylmethyl.

It is easily seen from Table IV that the separation of the substances investigated is best on the phenylmethylpolysiloxane support (column B), but phenylpropylpolysiloxane (column C), diphenylpolysiloxane (column D) and phenylmethyl silica (column A) are well suited. The selectivity of the packings was observed for the chromatographic behaviour of benzantracenes, benzopyrenes and dibenzanthracenes. The elution order of the benzantracenes from all columns was benz[*a*]anthracene < benz[*b*]anthracene. The elution order of the dibenzanthracenes from all columns was dibenz[*a,c*]anthracene < dibenz[*a,h*]anthracene. The elution order of benzopyrenes from columns A and D was benzo[*a*]pyrene < benzo[*e*]pyrene and that from columns B and C was benzo[*e*]pyrene < benzo[*a*]pyrene, using methanol–water mixtures.

Stationary phases modified with different phenylpolysiloxane were shown to have some merit such as retentivity and different selectivity from the monomeric phenyl phase. They can be a good alternative for the monomeric type packings, and the complementary use of such stationary phases with the commercial phenyl silica gel will increase the capability of reversed-phase liquid chromatography.

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