ELSEVIER

Journal of Chromatography A, 773 (1997) 53–63

JOURNAL OF CHROMATOGRAPHY A

Retention characteristics and selected applications of cyclic siloxane-based octadecylsilyl bonded phases in reversed-phase high-performance liquid chromatography

S.O. Akapo[a,*], M.T. Matyska[b], J.J. Pesek[b]

[a]*SETI Institute, NASA-Ames Research Center, Exobiology Branch, Mail Stop 239-12, Moffett Field, CA 94035, USA*

[b]*Department of Chemistry, San Jose State University, 1 Washington Square, San Jose, CA 95192, USA*

Received 10 December 1996; revised 18 February 1997; accepted 25 February 1997

Abstract

Hexamethylcyclotrisiloxane- and octaphenylcyclotetrasiloxane-based octadecyl bonded phases are prepared and evaluated for liquid chromatographic separation of various compounds. As revealed by the retention data of the selected solutes, the hexamethylcyclotrisiloxane–octadecyl phase exhibits better chromatographic performance than octaphenylcyclotetrasiloxane–octadecyl phase presumably due to greater accessibility of the bonded alkyl groups on the siloxane skeleton for interactions. The peak asymmetry values showed that solute retention on the hexamethylcyclotrisiloxane–octadecyl phase is essentially controlled by dispersive interactions. The retention characteristics of the cyclicsiloxane-based phases were compared to those obtained on a commercial C_{18} column and an octadecyl phase synthesized through a silanization–hydrosilation addition process. While the two phases gave baseline separation of polycyclic aromatic hydrocarbons and barbiturates, the hexamethylcyclotrisiloxane–octadecyl phase allowed fast and efficient separation of a four-component standard mixture of tricyclic antidepressants.

Keywords: Stationary phases, LC; Polynuclear aromatic hydrocarbons; Barbiturates; Antidepressants, tricyclic

1. Introduction

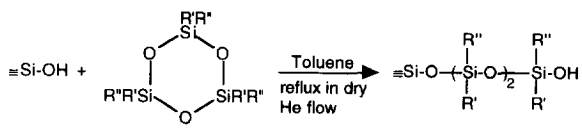
Chemically bonded stationary phases have found widespread applications in a variety of chromatographic techniques since their introduction by Halász and Sebastian [1] and Kirkland and DeStefano [2] many years ago. Among the available packing materials today, alkyl bonded silicas have enjoyed tremendous patronage due to their high mechanical and hydrolytic stability and, more importantly, the ready availability of the silica support as porous and non-porous micron and sub-micron particles. Also, the physical characteristics of silica such as surface area, mean pore diameter and pore volume can easily be altered to achieve the desired chromatographic separations [3]. Consequently, several approaches and techniques have been reported in the literature for the preparation of these type of bonded phases with the aim of improving their reproducibility, stability and selectivity [4–16]. In addition, the effect of alkyl chain length, nature of the silica substrate, type and structure of silanizing agents and surface coverage of the bonded ligands on retention characteristics in reversed-phase liquid chromatography have been investigated by many authors [17–24].

Following our earlier work on the application of

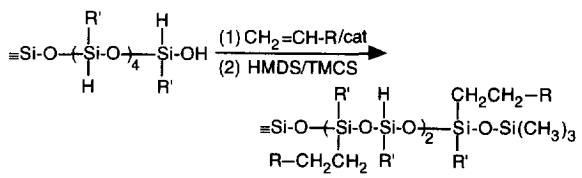
*Corresponding author.

PII S0021-9673(97)00241-0

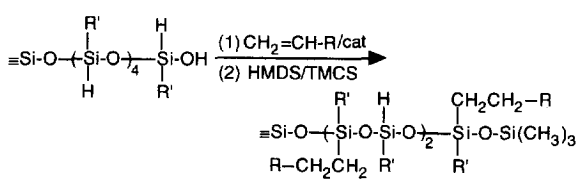
cyclic siloxane bonded phases for the separation of lower hydrocarbons by gas chromatography [25], we recently reported the retention characteristics of cyclic siloxane-based *n*-alkyl bonded phases [26]. These packings were designed to enhance the surface coverage and hence the selectivity of cyclic siloxane bonded phases for light hydrocarbons by incorporating octyl or octadecyl groups on the siloxane skeleton. The synthetic process involved (i) deactivation of the silica support with a cyclic siloxane, e.g. hexamethylcyclotrisiloxane:



where $R'=R''=CH_3$ and (ii) silanization of the silanol-terminated end of the opened siloxane chains with a reactive silane:



where X=Cl and R=$CH_3(CH_2)_{15}$- or $CH_3(CH_2)_5$-. For silica deactivated with pentamethylcyclopentasiloxane, the final product was formed by olefin hydrosilation of the hydride groups on the anchored siloxane chains in the presence of a transition metal catalyst followed by endcapping with a mixture of hexamethyldisilazane–trimethylchlorosilane (1:1 molar ratio) to remove the terminal hydroxyl groups and possibly the residual silanols on the bonded silica surface:



Beside exhibiting greater selectivity for the test solutes, the overall gas chromatographic properties of the cyclic siloxane–octadecylsilyl (or octylsilyl) bonded phases are somewhat better than that of the conventional octadecyl column despite the high surface coverage of the latter. The improved chromatographic performance of the bonded phases was attributed to the possibility of having the attached hydrocarbon chains well positioned so that they are more readily available for interactions with the analytes [26]. While the residual silanols are possibly shielded by the methyl side groups, their concentrations on the bonded silicas are also reduced by the initial deactivation of the silica surface with cyclic siloxanes prior to the silanization or hydrosilation reaction, leading to sharp and symmetrical peaks. The intended surface structure of the bonded phase is schematically shown in Fig. 1 where the alkyl groups are attached to the open end of the anchored siloxane chains. Diffuse reflectance infrared Fourier transform (DRIFT) and solid state NMR spectroscopic studies have successfully been used to confirm the presence of the octadecyl groups on similar bonded phases in previous studies [25,26].

In view of their successful application in gas chromatography, the present paper describes the retention characteristics of similar packing materials in reversed-phase high-performance liquid chromatography (RP–HPLC). For comparative purpose, the retention data of the selected compounds on Nova-Pak C_{18} and a laboratory-made C_{18} (denoted as TES-C_{18}) columns are also evaluated under identical

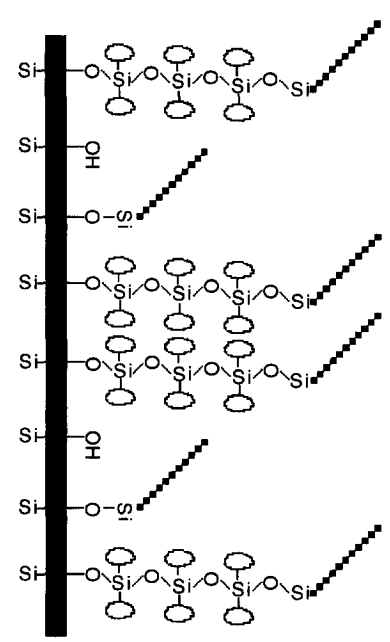


Fig. 1. Schematic representation of the surface structure of cyclic siloxane-based octadecyl bonded phases.

chromatographic conditions. The latter column, prepared by olefin hydrosilation of a silica hydride intermediate [9,10], was chosen because it has been shown to exhibit better chromatographic performance than the conventional octadecyl silica column [27]. The potential application of the phases in different analytical areas is demonstrated with the separation of polycyclic aromatic hydrocarbons (PAHs), barbiturates and tricyclic antidepressants.

2. Experimental

2.1. Materials

Octadecyldimethylchlorosilane, hexamethylcyclotrisiloxane (D_3^{Me}) and octaphenylcyclotetrasiloxane (D_4^{Ph}) were obtained from United Chemical Technologies (Bristol, PA, USA) and used as received. Analytical grade toluene, methylene chloride and methanol (Mallinckrodt, Paris, KY, USA) were used in the preparation of the bonded phases. Toluene was dried over 5A molecular sieves before use. The silica used was Vydac 101 TPB5 (The Separation Group, Hesperia, CA, USA) with specific surface area of 106 $m^2 g^{-1}$, particle diameter of 6.6 μm and mean pore diameter of 300 Å as supplied by the manufacturer. The Nova-Pak C_{18} column (150×3.9-mm I.D.) was obtained from Waters (Millipore, Waters Chromatography Division, Milford, MA, USA).

2.2. Bonded phase preparation

The synthesis of the bonded phases was according to the procedure given for Phase Type A in a previous report [26] and is briefly reiterated here for clarity: About 3 g of Vydac 100 TPB5 silica was suspended in a warm solution of 30 ml of dry toluene containing 10 ml of hexamethylcyclotrisiloxane (or 5 g of octaphenylcyclotetrasiloxane) and refluxed for 24 h at 110°C under gentle dry helium flow. The modified silica was washed as previously described [25,26] and then treated with 5 ml of octadecyldimethylchlorosilane dissolved in 30 ml of toluene for 4 h under the same reaction conditions as described above. The silylated particles were again washed in the usual manner, dried in a vacuum oven at 100°C overnight and stored in a dry bottle. The carbon content of the dried samples was determined by elemental analysis. For the sake of convenience, the columns are identified as D_3^{Me}–C_{18} and D_4^{Ph}–C_{18}, representing hexamethylcyclotrisiloxane and octaphenylcyclotetrasiloxane deactivated support, respectively.

2.3. Chromatography

The bonded phases were slurry-packed (10% w/v bonded silica in 9:1 v/v carbon tetrachloride/methanol) into 150×4.6 mm I.D. stainless steel tubes (Alltech, Deerfield, Il, USA) using a Haskel (Burbank, CA, USA) pneumatic pump at 40 MPa with methanol as the driving solvent. The columns were evaluated on a Hitachi (Tokyo, Japan) liquid chromatographic system consisting of a ternary gradient pump (Model L-6200 Intelligent Pump) and a variable wavelength UV detector (Model L-4000) operated at 254 nm. The chromatograms were recorded with a Spectra-Physics SP4400 integrator (San José, CA, USA). Solutes were injected into the columns using a Rheodyne 7125 valve fitted with a 10-μl loop.

HPLC-grade solvents were used for all the chromatographic measurements and deionized water was prepared with a Milli-Q (Millipore, Bedford, MA, USA) purification system. An LC Universal Test Mix (known as 'Perkin-Elmer Mix') and a standard mixture of polycyclic aromatic hydrocarbons (SRM869) were obtained from Perkin-Elmer (Norwalk, CT, USA) and the National Institute of Standards and Technology (Gaithersburg, MD, USA), respectively. Other test solutes were obtained from several sources and made up in the mobile phase. Unless otherwise specified, the void volume, t_o, was determined by injecting potassium nitrate as a maker.

The retention factor, k, was calculated using the expression $k=(t_R-t_o)/t_o$, where t_R is the retention time of the solute. The selectivity factor, α, was determined from the equation $\alpha=k_{n+1}/k_n$, where n is the peak number and $k_{n+1}>k_n$. The peak asymmetry, A_s, was calculated from the expression $A_s=w/w-\Delta w$, where w is the peak width at 10% peak height and Δw is the absolute difference defined as $\Delta w=l-t$; l and t are the leading and tailing half width at 10% peak height.

3. Results and discussion

3.1. Surface coverage

The carbon content of the product obtained at the end of each reaction step are presented in Table 1 together with those of the reference columns as supplied by the manufacturers. The surface coverage of the bonded phase was calculated using the expression [28]:

$$\text{surface coverage } (\mu\text{mol m}^{-2}) = \frac{\%\text{C} \times 10^6}{1200 N_c \times S_{BET}} \quad (1)$$

where N_c is the number of carbon atoms in the bonded cyclic siloxane or alkyl silane and S_{BET} is the specific surface area ($m^2 g^{-1}$) of the bare silica. It can be seen that the carbon content and hence the surface coverage of the new phases followed the reactivity of the cyclic siloxanes in the presence of acidic protons in which $D_3^{Me} > D_4^{Ph}$ [25]. While the surface coverage of the intemediate products as well as those of the reference packings are readily obtained from Eq. (1), the amount of the bonded octadecyl groups in D_3^{Me}–C_{18} and D_4^{Ph}–C_{18} can, to a good approximation, be determined from the difference in the percentage carbon content of the intermediate and the final products with this equation. An examination of the data presented in Table 1, therefore, showed that incorporation of the octadecyl groups on the deactivated support produced additional 1.96 and 2.01% C in D_3^{Me}–C_{18} and D_4^{Ph}–C_{18}, respectively. These values correspond to 0.77 and 0.62 μmol m^{-2} of the bonded ligands which are substantially lower than those of the reference columns assuming that the surfaces of the latter consists mainly of the octadecyl groups which might not hold since the TES–C_{18} column is prepared on a triethoxysilane (TES) deactivated silica [9,10] and the Nova-Pak C_{18} column is endcapped.

3.2. Retention characteristics

The chromatographic properties of the bonded phases were evaluated with (i) the 'Perkin-Elmer Mix' consisting of sodium chloride, benzene, toluene, ethylbenzene, isopropylbenzene, *tert.*-butylbenzene and anthracene and (ii) a polar mixture containing aniline, *N*-methylaniline (*N*-MA) and *N,N*-dimethylaniline (*N,N*-DMA). The anilines were chosen because they show strong interactions with residual silanols and hence poor peak symmetry. Fig. 2 shows the separation of the 'Perkin-Elmer Mix' with an eluent of 70% methanol in water on a volume basis. (Notice that this mixture can only be resolved on the TES-C_{18} column with 60% methanol). As illustrated in the figure, all the sample components were baseline resolved with good peak shapes. The columns retention data in terms of retention factor, k, selectivity, a, and theoretical plate number, N, defined as $N = 5.54\ (t_R/w_h)^2$ (where w_h is the peak width at half-height in time units) are listed in Table 2. It can be seen that the solutes' retention factors and selectivities are slightly greater on D_4^{Ph}-C_{18} compared with D_3^{Me}-C_{18}. However, column efficiencies are significantly higher on D_3^{Me}-C_{18} than

Table 1
Surface coverage of the bonded phases

Bonded phase	%C	Surface coverage (μmol m^{-2})
Silica + hexamethylcyclotrisiloxane (D_3^{Me})[a]	1.90	2.49
D_3^{Me}-C_{18}	3.86	–
Silica + octaphenylcyclotetrasiloxane (D_4^{Ph})[a]	4.54	0.74
D_4^{Ph}-C_{18}	6.55	–
TES-C_{18}[b]	5.61	2.21
Nova-Pak C_{18}[c]	7.00	1.72

[a] Intermediate product.
[b] Same silica gel as described in the Section 2.
[c] Particle size, $d_p = 4.0$ μm.
–: Not determined (see Section 3.1 for detail).

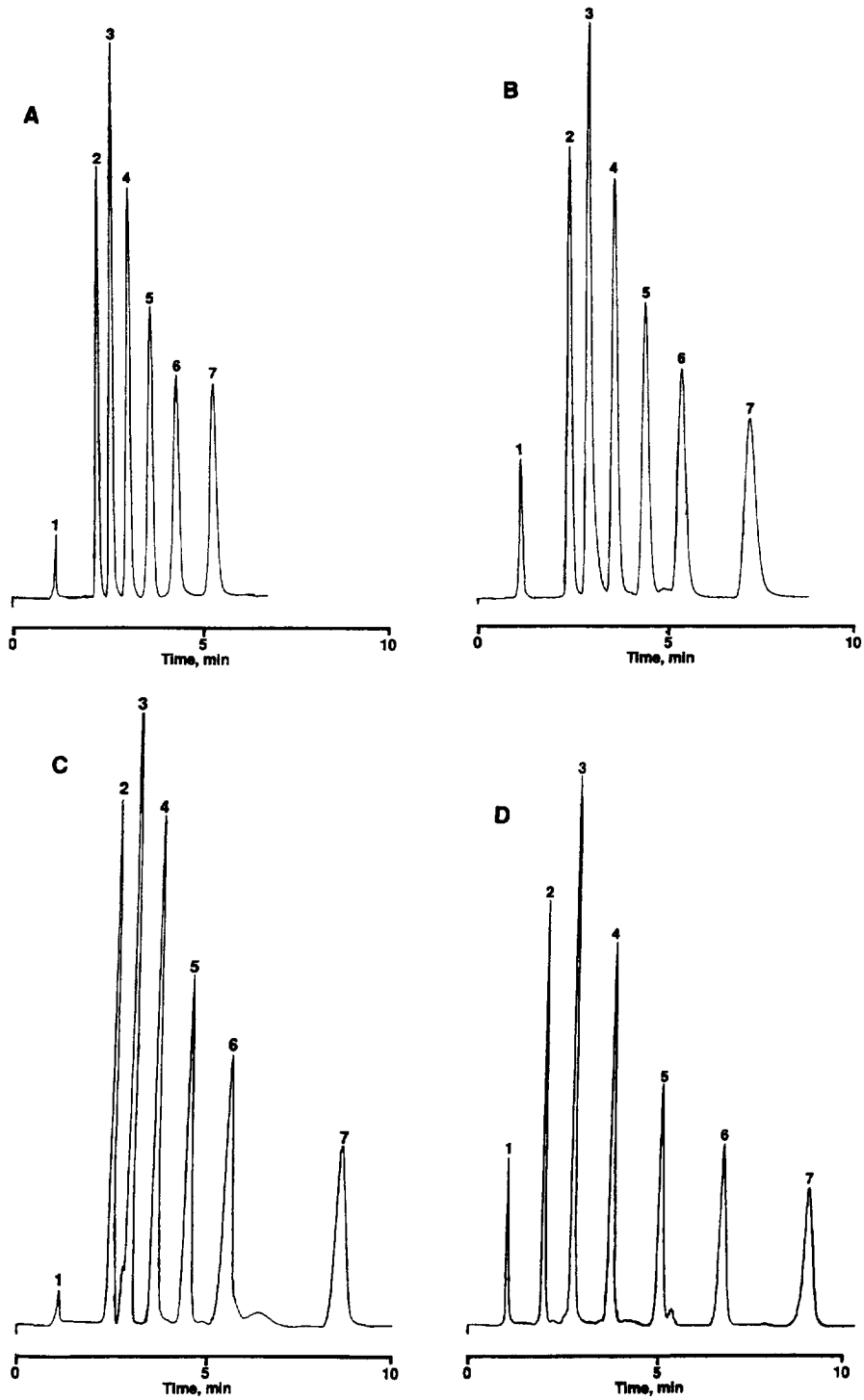


Fig. 2. Chromatograms of 'Perkin-Elmer Mix' on (A) D_3^{Me}-C_{18}, (B) D_4^{Ph}-C_{18}, (C) TES-C_{18}, and (D) Nova-Pak C_{18} columns. Mobile phase: methanol–water (70:30, v/v), (60:40 for C) 25°C. Flow-rate: 1.0 ml min^{-1}. UV detection at 254 nm. Peaks: (1) sodium chloride, (2) benzene, (3) toluene, (4) ethylbenzene, (5) isopropylbenzene, (6) *tert.*-butylbenzene, (7) anthracene.

Table 2
Retention properties of aromatic hydrocarbons

Column	Property	Peaks[a]					
		2	3	4	5	6	7
D_3^{Me}-C_{18}	k	1.01	1.34	1.77	2.28	2.89	3.76
	α	–	1.33	1.32	1.29	1.27	1.30
	N (plates/m)	38100	40400	50300	36700	41100	33400
D_4^{Ph}-C_{18}	k	1.06	1.50	2.08	2.79	3.65	5.18
	α	–	1.41	1.39	1.34	1.31	1.42
	N (plates/m)	15500	15800	21100	20400	19600	17700
TES-C_{18}	k	1.19	1.64	2.25	3.03	3.98	6.61
	α	–	1.38	1.37	1.35	1.31	1.66
	N (plates/m)	25200	23300	35400	33200	22500	33700
Nova-Pak C_{18}	k	0.91	1.67	2.65	3.89	5.45	7.65
	α	–	1.84	1.59	1.47	1.40	1.40
	N (plates/m)	29500	57500	60600	55600	47300	45000

[a] See Fig. 2 for peak identification and chromatographic conditions.

D_4^{Ph}-C_{18}. This result suggests that the bonded octadecyl groups in D_3^{Me}-C_{18} are less sterically protected by the methyl groups on the siloxane chains and hence more readily available for interactions with the analytes. The appreciably high theoretical plate numbers of the solutes on Nova-Pak C_{18} can, to a greater extent, be due to the small particle size of the packing material.

The chromatograms of the polar compounds are shown in Fig. 3. Similar to those observed for the aromatic hydrocarbons, the solutes' retention are slightly higher on D_4^{Ph}-C_{18} column than D_3^{Me}-C_{18}. Nevertheless, the two columns provide excellent peak shape similar to that observed on TES-C_{18}. It is, however, interesting to note that the anilines are eluted with severe peak tailing on Nova-Pak C_{18} column. The peak asymmetry, A_s, of the compounds together with their k and a values are listed in Table 3. With the exception of Nova-Pak C_{18}, the asymmetry factor for each of the solutes is about unity even for the last eluting peak without any additives in the mobile phase. The observed tailing of the anilines on the Nova-Pak column indicate that the silanols on Nova-Pak silica are either more acidic or less shielded by the bonded ligands. The values of A_s obtained on D_3^{Me}-C_{18} and TES-C_{18} show that solute retention on these columns is essentially controlled by hydrophobic interactions.

3.3. Separation of polycyclic aromatic hydrocarbons (PAHs)

The selectivity of the phases towards PAHs was investigated with a standard reference mixture (known as SRM869) containing benzo[*a*]pyrene (BaP), 1,2:3,4:5,6:7,8-tetrabenzonaphthalene (TBN) and phenanthro[3,4*c*]phenanthrene (PhPh). The elution order of these compounds has been shown to be very useful for assessing the monomeric or polymeric nature of stationary phases in LC [29,30]. Thus, under isocratic conditions of 85% acetonitrile–water at 2 ml min^{-1}, monomeric and polymeric phases should elute in the order BaP≤PhPh<TBN and PhPh<TBN≤BaP, respectively. For phases with intermediate surface coverage, the elution order of this mixture is PhPh<BaP<TBN. Based on the selectivity factor $\alpha_{TBN/BaP}$, a quantitative measure of phase selectivity towards PAHs was also developed in which high values for $\alpha_{TBN/BaP}$ (>1.7) indicate monomeric-like phases, low values (<1) suggest polymeric-like phases, and for intermediate phases $1<\alpha_{TBN/BaP}\leq 1.7$.

The separations of these compounds on the cyclic siloxane-based C_{18} columns are shown in Fig. 4. Under the operating conditions, the three compounds are baseline resolved on both columns at analysis times that are significantly less than those reported in

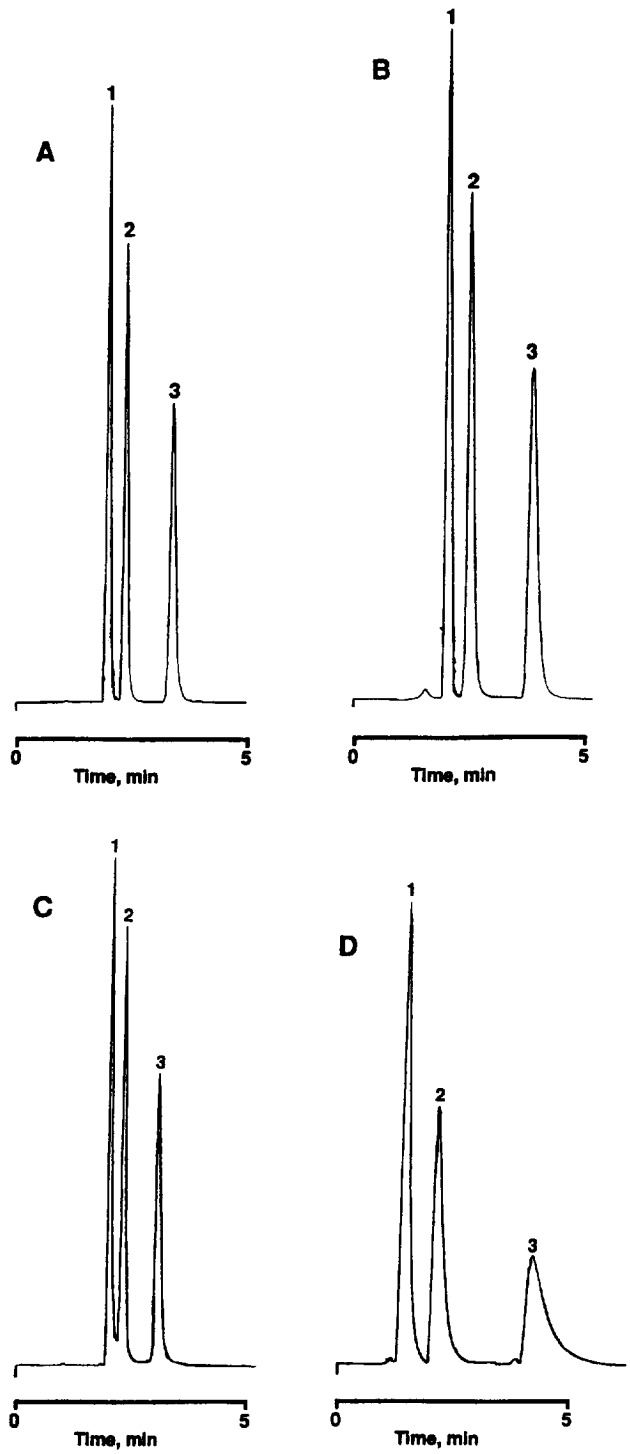


Fig. 3. Separation of polar compounds on (A) D_3^{Me}-C_{18}, (B) D_4^{Ph}-C_{18}, (C) TES-C_{18}, and (D) Nova-Pak C_{18}. Mobile phase: methanol–water (60:40, v/v), 25°C. Flow-rate: 1.0 ml min^{-1}. UV detection 254 nm. Peaks: (1) aniline, (2) *N*-methylaniline, (3) *N,N*-dimethylaniline.

Table 3
Retention properties of polar solutes

Column	Retention factor[a]			Selectivity factor		Peak asymmetry, A_s		
	k_1	k_2	k_3	α_1^2	α_2^3	1	2	3
D_3^{Me}-C_{18}	0.23	0.47	1.08	2.04	2.30	1.00	1.03	1.09
D_4^{Ph}-C_{18}	0.23	0.52	1.36	2.26	2.62	1.00	1.08	1.13
TES-C_{18}	0.27	0.46	0.92	1.70	2.00	1.00	1.02	1.06
Nova-Pak C_{18}	0.53	1.37	3.72	2.58	2.72	1.50	2.67	3.40

[a] Solutes: 1 = aniline, 2 = *N*-methylaniline, and 3 = *N*,*N*-dimethylaniline.

the literature on some C_{18} columns [27,30–32]. Since the phases are synthesized by a monomeric surface modification process, their selectivity towards the solutes is typical of a monomeric-like phase, that is BaP<PhPh<TBN. The solutes' retention and selectivity factors are listed in Table 4

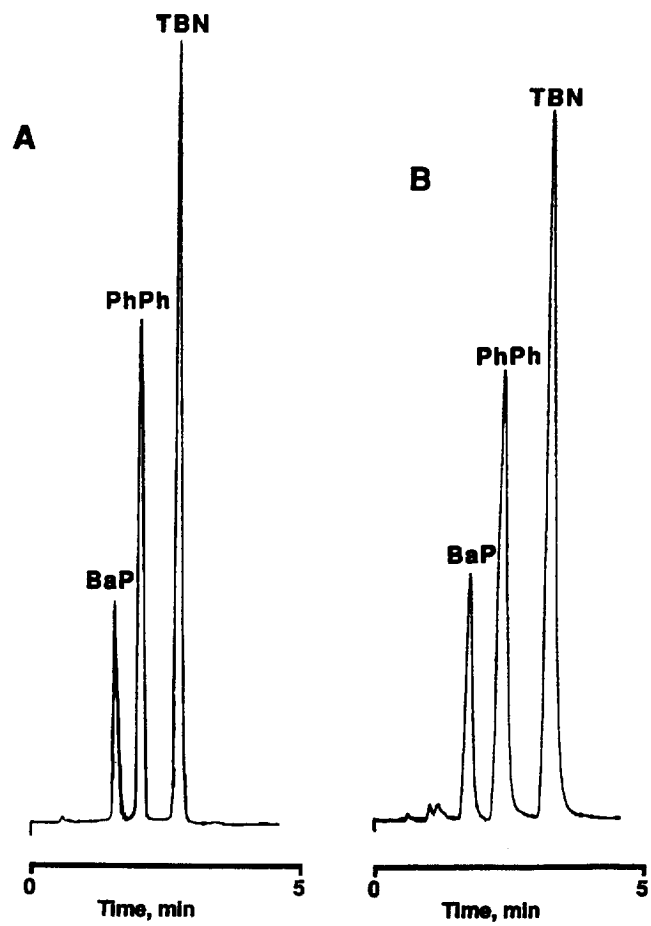


Fig. 4. Separation of phase-type test mixture (SRM869) on (A) D_3^{Me}-C_{18}, and (B) D_4^{Ph}-C_{18} phases. Mobile phase: acetonitrile–water (85:15, v/v), 25°C. Flow-rate: 2.0 ml min^{-1}. UV detection at 254 nm.

Table 4
Retention properties of PAHs (SRM869)

Column	Retention factor			Selectivity factor		
	k_{BaP}	k_{PhPh}	k_{TBN}	α_{BaP}^{PhPh}	α_{PhPh}^{TBN}	α_{BaP}^{TBN}
D_3^{Me}-C_{18}	1.78	3.22	4.61	1.18	1.43	2.59
D_4^{Ph}-C_{18}	1.77	3.44	5.12	1.94	1.49	2.89
TES-C_{18}^{a}	0.99	0.81	1.74	0.82	2.15	1.76

[a] Data from Ref. [33].

together with those of TES-C_{18} column reported by Pesek et al. [33]. As can be seen, the monomeric nature of the new phases is substantiated by their $\alpha_{TBN/BaP}$-values which are substantially greater than 1.7. Hence, partial deactivation of the silica support with cyclic siloxanes does not change the surface structure of the bonded phases but enhances their separation efficiencies as earlier reported [26]. As indicated by their high retention and selectivity factors, the PAHs are better resolved on D_3^{Me}-C_{18} and D_4^{Ph}-C_{18} columns compared with TES-C_{18} column.

3.4. Separation of barbiturates

To further demonstrate the application of the phases for the separation of different types of compounds, the chromatograms of a standard mixture of alkaloids containing five barbital derivatives are shown in Fig. 5. As can be seen, the sample components are completely separated on both columns. While the analysis compared well with those of Montes et al. [27], the D_3^{Me}-C_{18} column clearly

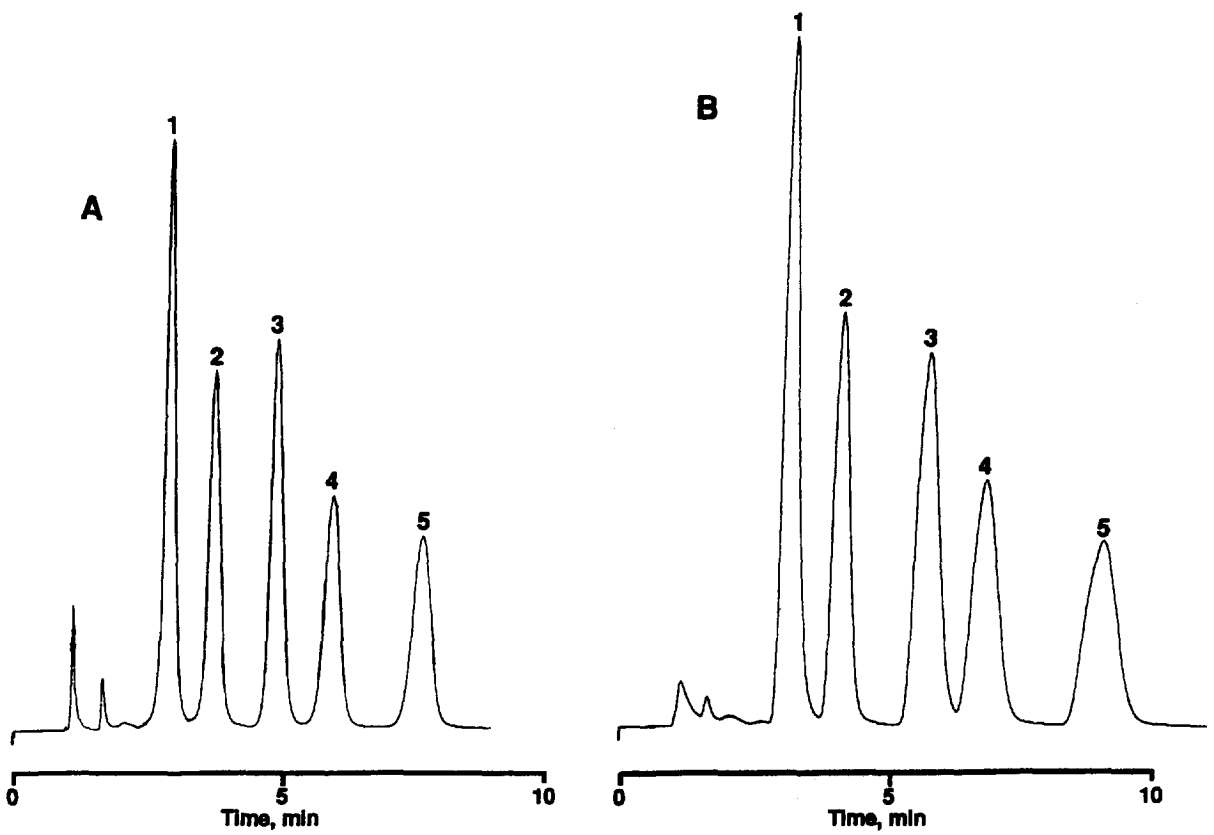


Fig. 5. Separation of a standard barbiturate mixture on (A) D_3^{Me}-C_{18}, and (B) D_4^{Ph}-C_{18} phases. Mobile phase: methanol–water (40:60, v/v), 25°C. Flow-rate: 1.0 ml min^{-1}. UV detection at 220 nm. Peaks: (1) butabarbital, (2) amobarbital, (3) secobarbital, (4) phenobarbital, (5) hexobarbital.

exhibits better resolution and good peak symmetry for the sample.

3.5. Analysis of tricyclic antidepressants

Fig. 6 shows the separation of a standard mixture of four tricyclic antidepressants. As can be seen, the D_3^{Me}-C_{18} column appears to provide a better separation of the sample components with good peak shapes. Also, the analysis time on D_4^{Ph}-C_{18} is about 52% longer than that on D_3^{Me}-C_{18}. Hence, the latter phase could be advantageous for fast analysis of these compounds. Since imipramine and clomipramine are even more sensitive to the presence of residual silanols than anilines, the observed peak tailing on D_4^{Ph}-C_{18}, therefore, may be the result of a relatively few accessible silanols on the column packings.

4. Conclusion

This paper has shown that cyclic siloxane bonded phases incorporated with *n*-alkyl groups are valuable packing materials in reversed-phase liquid chromatography as in GC. As a result of better accessibility of the analytes to the bonded ligands, the hexamethylcyclotrisiloxane–octadecyl phase (D_3^{Me}-C_{18})

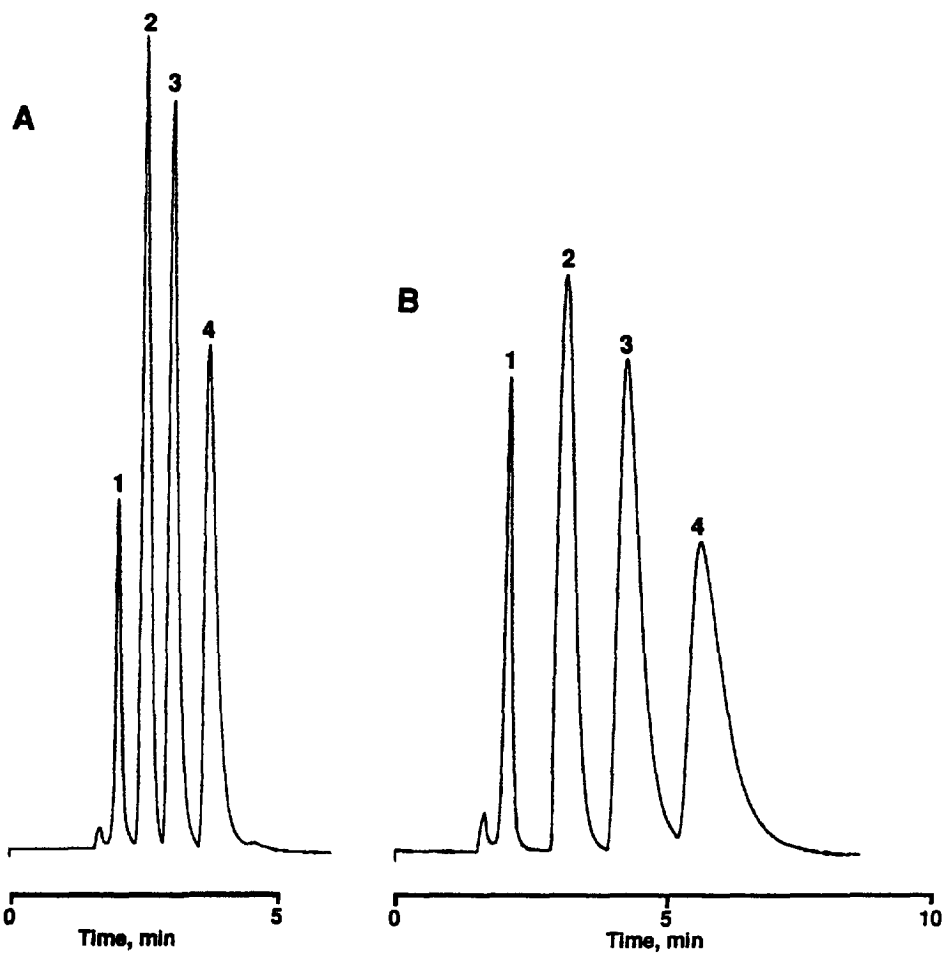


Fig. 6. Separation of basic drugs (tricyclic antidepressants) on (A) D_3^{Me}-C_{18}, and (B) D_4^{Ph}-C_{18} phases. Mobile phase: methanol–0.025 *M* K_2HPO_4 (70:30, v/v), 25°C. Flow-rate: 1.0 ml min^{-1}. UV detection at 230 nm. Peaks: (1) desipramine, (2) nortriptyline, (3) imipramine, (4) clomipramine.

exhibits good retention characteristics compared to octaphenylcyclotetrasiloxane–octadecyl phase (D_4^{Ph}-C_{18}). While solute retention, especially for the polar compounds, appears to be less affected by residual silanols on D_3^{Me}-C_{18}, its chromatographic characteristics compared favourably with those of the reference columns. The rapid and efficient analysis of barbiturates and tricyclic antidepressants on hexamethylcyclotrisiloxane–octadecyl phase demonstrates its usefulness in phamaceutical analysis.

Acknowledgments

This work was funded in part by NASA-Ames Research Center through the Exobiology Program (Contract NCC 2-650), the National Science Foundation (CHE 9119933), and the Camille and Henry Dreyfus Foundation through a Scholar (JJP) award. We gratefully acknowledge the donation of the Vydac silica by the Separations Group.

References

[1] I. Halász, I. Sebastian, Angew. Chem. Int. Ed. Engl. 8 (1969) 453.
[2] J.J. Kirkland, J.J. DeStefano, J. Chromatogr. Sci. 8 (1970) 309.
[3] H. Engelhardt, H. Löw, W. Götzinger, J. Chromatogr. 544 (1991) 371.
[4] T.M. Khong, C.F. Simpson, Chromatographia 24 (1987) 385.
[5] S.O. Akapo, A. Furst, T.M. Khong, C.F. Simpson, J. Chromatogr. 471 (1989) 283.
[6] D.B. Marshall, K.A. Stutler, C.H. Lochmüller, J. Chromatogr. Sci. 22 (1984) 217.
[7] S.O. Akapo, C.F. Simpson, J. Chromatogr. Sci. 28 (1990) 186.
[8] J.E. Sandoval, J.J. Pesek, Anal. Chem. 61 (1989) 2067.
[9] J.E. Sandoval, J.J. Pesek, Anal. Chem. 63 (1991) 2634.
[10] C. Chu, E. Jonsson, M. Auvinen, J.J. Pesek, J.E. Sandoval, Anal. Chem. 65 (1993) 808.
[11] H.O. Fatunmbi, M.J. Wirth, Anal. Chem. 64 (1992) 822.
[12] H.O. Fatunmbi, M.J. Wirth, Anal. Chem. 65 (1992) 2783.
[13] J.J. Kirkland, J.L. Glajch, R.D. Farlee, Anal. Chem. 61 (1989) 2.
[14] J.J. Kirkland, C.H. Dilks Jr., J.E. Henderson, LC·GC 11 (1993) 290.
[15] K.K. Unger (Editor), Packings and Stationary Phases in Chromatographic Techniques (Chromatographic Science Series, Vol. 47), Marcel Dekker, New York, 1990.
[16] R.P.W. Scott, Silica Gel and Bonded Phases: Their Production, Properties and Use in LC, Wiley, New York, 1993.
[17] G.E. Berendsen, L. DeGalan, J. Chromatogr. 196 (1980) 21.
[18] N. Tanaka, K. Sakagami, M. Araki, J. Chromatogr. 199 (1980) 327.
[19] L.C. Sander, S.A. Wise, J. Chromatogr. 316 (1984) 163.
[20] J. Köhler, P.D. Chase, R.D. Farlee, J. Vega, J.J. Kirkland, J. Chromatogr. 352 (1986) 275.
[21] K.D. Lork, K.K. Unger, J.N. Kinkel, J. Chromatogr. 352 (1986) 199.
[22] P. Roumeliotis, K.K. Unger, J. Chromatogr. 149 (1978) 211.
[23] S.A. Wise, W.E. May, Anal. Chem. 55 (1983) 1479.
[24] R. Spack, M. Kubin, S. Vozka, B. Porsch, J. Liq. Chromatogr. 3 (1980) 1465.
[25] S.O. Akapo, J.-M.D. Dimandja, M.T. Matyska, J.J. Pesek, J. Microcol. Sep. 42 (1996) 189.
[26] S.O. Akapo, J.-M.D. Dimandja, M.T. Matyska, J.J. Pesek, Anal. Chem. 68 (1996) 1954.
[27] M.C. Montes, C. van Amen, J.J. Pesek, J.E. Sandoval, J. Chromatogr. A 688 (1994) 31.
[28] S.O. Akapo, C.F. Simpson, J. Chromatogr. Sci. 32 (1994) 86.
[29] L.C. Sander, S.A. Wise, Anal. Chem. 56 (1984) 504.
[30] L.C. Sander, S.A. Wise, Anal. Chem. 59 (1987) 2309.
[31] L.C. Sander, J. Chromatogr. Sci. 26 (1988) 380.
[32] L.C. Sander, S.A. Wise, J. High Resolut. Chromatogr. Chromatogr. Commun. 11 (1988) 383.
[33] J.J. Pesek, M.T. Matyska, H. Hemphälä, Chromatographia 43 (1996) 10.