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WALL-COATED ADSORBENT OPEN-TUBULAR FUSED-SILICA COLUMNS FOR THE SEPARATION OF COMPLEX PYROLYSIS PRODUCTS

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SUMMARY

Fused-silica capillary columns coated with a layer of non-porous, homogeneous graphitized carbon black, modified with a variety of stationary phases, were prepared. A series of parameters were determined. The selectivity and efficiency of the columns were much improved. These columns were used in the analysis of complex pyrolysis products and the separation of isomers.

INTRODUCTION

Gas–solid chromatography (GSC) has advantages over gas–liquid chromatography (GLC) owing to the high separation factors obtained. However, a drawback is that the elution temperature is usually much higher than that in GLC. For this reason, the use of GSC has been limited to the analysis of permanent gases or low-boiling hydrocarbons. The introduction of graphitized carbon black (GCB), with a suitable amount of liquid stationary phase added, has made liquid-modified GSC competitive with GLC, even with regard to elution temperature[1].

Glass capillary columns coated with carbon black were introduced several years ago by Vidal Madjar *et al.*[2] and Goretti *et al.*[3]. Recently, Bruner *et al.*[4] showed that improved results are obtained by static coating of the inner surface of capillary columns with GCB impregnated with the liquid phase SP-1000. In this study, wall-coated adsorbent open-tubular (WCAOT) columns were prepared with coatings of Carbopack F (B) and Carbonsieve TDX, modified with the stationary phases DC-550, OV-17 and PEG 20M. The selectivity due to the mechanism of gas–liquid–solid chromatography (GLSC) was much improved and the efficiency in terms of HETP was enhanced. By coupling of the high separation factors due to GLSC with the high efficiency of GLC capillary columns, these columns can be used for separating complex pyrolysis products and separating isomers.

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EXPERIMENTAL

Measurements were performed with a Sigma 1B gas chromatograph, coupled with a Sigma 10 microprocessing system (Perkin-Elmer, Norwalk, CT, U.S.A.) and a GC-5A gas chromatograph (Shimadzu, Kyoto, Japan), using hydrogen as the carrier gas. A JMS-D300 gas chromatograph–mass spectrometer (JEOL, Tokyo, Japan) was used for qualitative analysis. Carbopack F and B were obtained from Supelco (Bellefonte, PA, U.S.A.). STH-01 graphitized carbon black (Jilin Carbon Black Factory, Jilin, China) and carbonsieve TDX (Tianjing No. 2 Reagents Plant, China) were used. Fused-silica tubing was obtained from the Hebei Light-Fibre Factory (Hebei, China). The stationary phases DC-550, OV-17, PEG 20M and picric acid were obtained from the Beijing Chemical Agent Shop (Beijing, China).

The method used for the preparation of the column, a modification of that described by Xu and Vermeulen[5], consists in coating by the static method, keeping the column at a temperature higher than the boiling point of the solvent.

The two kinds of carbon black were first ground in a medium of 95% ethanol and then fractionated by flotation with ethanol to obtain fines of <1 μm. A mixture of volatile pentane and methyl chloride (1:2) was chosen as the solvent. A slurry of 300 mg of Carbopack F or B and 80 ml of mixed solvent, with suitable amounts of stationary phase added, was treated by ultrasound for 40 min in a US-150 Ultrasonic device. In this way, the size of carbon black particles was further reduced to about 0.2 μm (see Fig. 1).

A 25 m × 0.25 mm I.D. fused-silica capillary column was filled with a slurry of GCB by nitrogen pressure using a Micro-column Treating Stand (Shimadzu, Kyoto, Japan). After the capillary column had been completely filled, one end was carefully sealed with stearin and the other end was connected via shrinkable PTFE tubing to a 25 m × 0.25 mm I.D. glass capillary column, which served as a damping column. By immersing the columns in a water-bath (75°C), the coating process was started with the evolution of fine bubbles. After 5–6 h, when the solvent had completely evaporated, nitrogen was passed through the column for 1 h, then the column was ready for conditioning overnight at the maximum operating temperature of the stationary phase.

The samples to be analysed were the products of gas-oil pyrolysis, *viz.*, light hydrocarbons (C_1–C_6), pyrolysis gasoline and fuel oil, and were tested separately.

RESULTS AND DISCUSSION

In Fig. 2, a typical Van Deemter plot is shown for two columns of the same size (20 m × 0.25 mm I.D.) and the same stationary phase, but one was coated with Carbopack F (GLSC) modified with DC-550 and the other was a DC-550 (GLC) column. Comparative data are presented in Table I. A third column was prepared by coating Carbopack B with PEG 20M. This showed intermediate efficiency between the GLC and Carbopack F columns.

In Table I, the value of the separation number (TZ) is higher for the GLSC column (31.1 or 32.0) than for the GLC column (22.1). This shows that liquid-modified adsorption chromatography offers higher separation factors. The isosteric heat of adsorption (Q_{st}) was measured, and was 14.5 or 15.4 kcal/mol for the GLSC

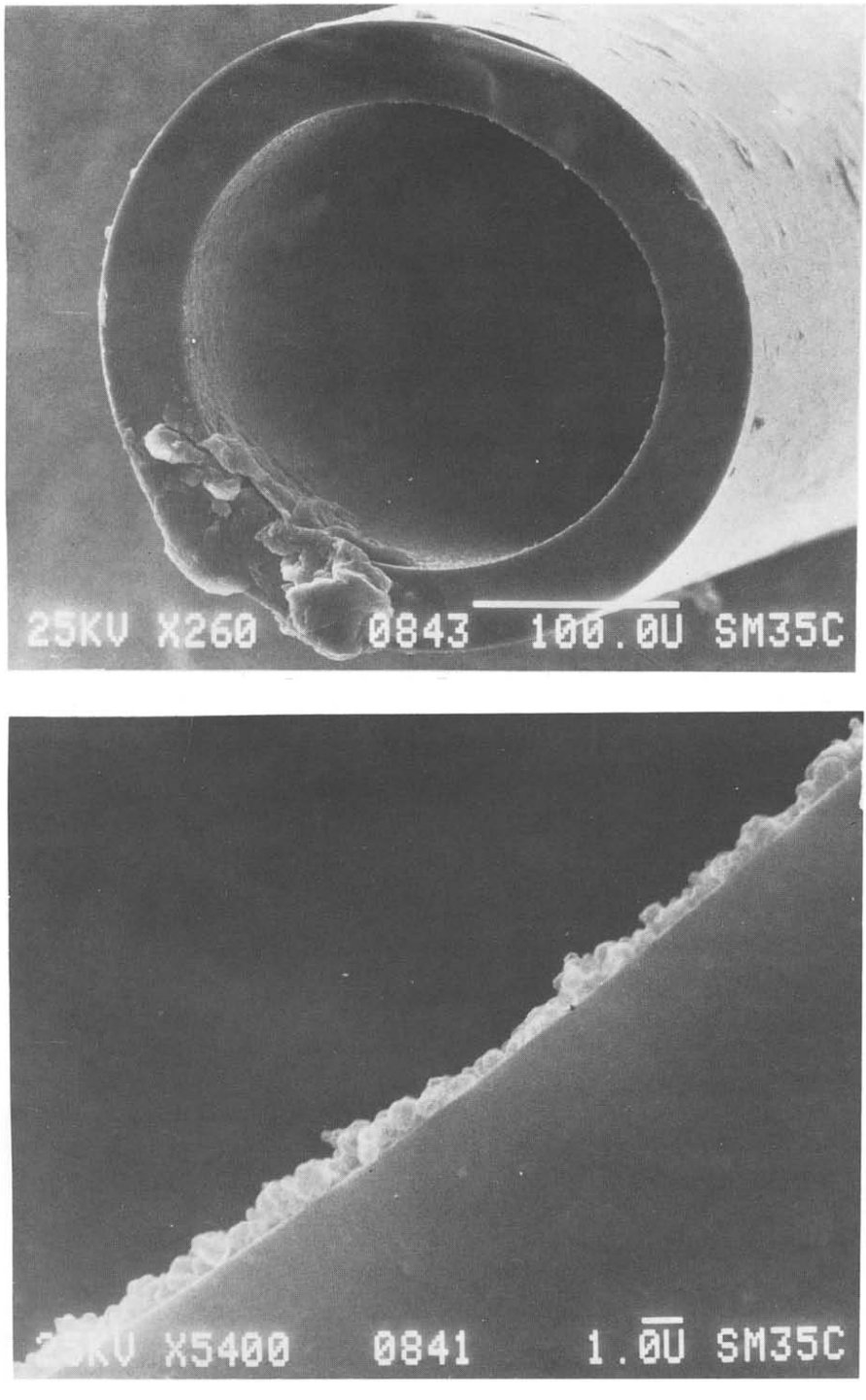

Fig. 1. Micrographs of the internal wall of the fused-silica capillary coated with Carbopack F and DC-550

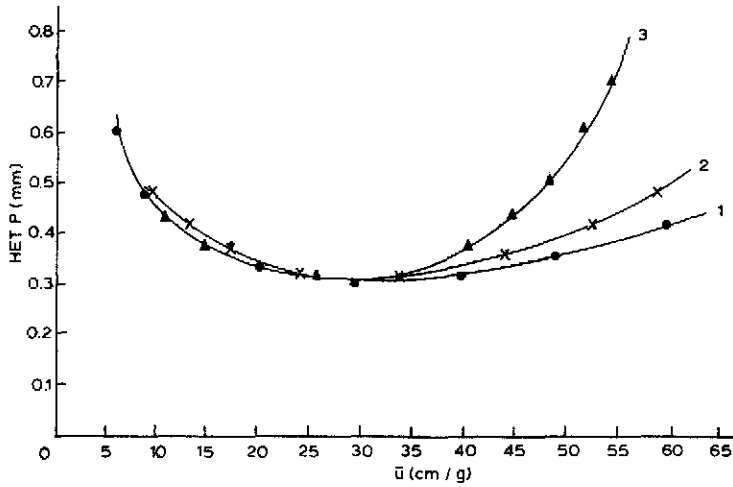

Fig. 2. Typical example of Van Deemter plot for Carbopack F (B), modified with Carbowax PEG 20M and DC-550. Sample: n-C_{12} at 135°C (k' = 6.5). Carrier gas: hydrogen. Lines 1–3 correspond to columns 1–3 in Table I.

column and 9.8 kcal/mol for the GLC column. The column with the higher Q_{st} was operating with a GLSC mechanism. This is further confirmed by the value obtained from bleeding of the stationary phase. For the GLSC column, the bleeding was lower by a factor of 3.4, which means that the GLSC column has good thermal stability. These columns have been used over a period of 6 months and no significant changes in retention time and selectivity have been observed.

Fig. 3 shows the separation of pyrolysis gasoline (b.p. <180°C cut), performed on the WCAOT column with Carbopack F modified with 10% DC-550. Pyrolysis gasoline is a complex mixture containing large amounts of paraffins, olefins, diolefins and aromatic hydrocarbons. Qualitative analysis was performed by gas chromatography–mass spectrometry and the use of Kováts retention indices. More than 93 components were identified. Compared with conventional GLC capillary columns with non-polar squalane, the analysis time with the GLSC column is reduced by one third, while the same resolution is achieved. Alkylbenzenes in pyrolysis gasoline are listed in

TABLE I

COMPARISON OF CHROMATOGRAPHIC PARAMETERS FOR GLSC AND GLC COLUMNS

Columns: 1 = fused-silica capillary (20 m × 0.25 mm I.D.) coated with Carbopack F + 10% DC-550 (GLSC 1); 2 = fused-silica capillary (20 m × 0.25 mm I.D.) coated with Carbopack B + 15% PEG 20M (GLSC 2); 3 = fused-silica capillary (20 m × 0.25 mm I.D.) coated with 10% DC-550, film thickness 0.5 μm (GLC).

Column No.	H_{min} *(mm)*	$\bar{u}$ *(cm/s)*	*TZ* (k' = 6)	*Coating efficiency (%)*	$k'_{(n\text{-}C_{16})}$ *(105°C)*	$Q_{st\,(n\text{-}C_{12})}$ *(kcal/mol)*	*Bleeding at 240°C (% full-scale)*
1	0.29	35	31.1	76	5.2	14.5	6
2	0.32	34	32.0	70	5.0	15.4	5
3	0.29	34	22.1	76	8.5	9.8	18

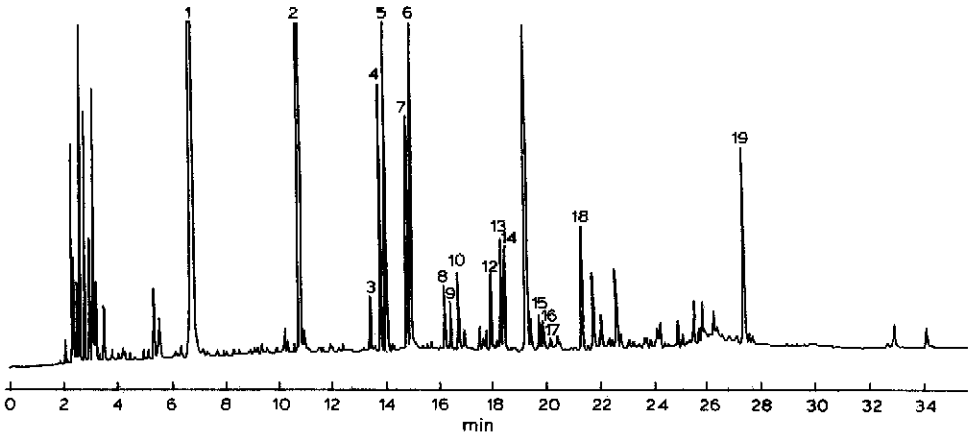

Fig. 3. Separation of the pyrolysis gasoline (b.p. < 180°C cut). Fused-silica capillary column, 20 m × 0.25 mm I.D., Carbopack F + DC-550. Temperature programme, 40°C for 5 min, raised at 4°C/min to 180°C. For peak identifications, see Table II.

Table II. By increasing the polarity of the stationary phase and using Carbowax PEG 20M, paraffins, naphthenes and olefins were eluted before benzene, methylbenzene and dimethylbenzene and dimethylbenzene isomers were easily separated. The column is suitable for the determination of hydrocarbon types.

Fig. 4 shows a chromatogram of pyrolysis fuel oil (b.p. 180–300°C). In order to determine the amounts of individual alkylnaphthalenes present, a conventional method of analysis was established. C_{10}–C_{12} alkylnaphthalenes were isolated from the fuel oil by liquid chromatography and separated on a WCAOT column with Carbopack B modified with OV-17. Naphthalene, two methylnaphthalenes, two ethylnaphthalenes and eight dimethylnaphthalenes were identified. The separation of alkylnaphthalene mixtures has been reported by numerous investigators[6,7]; it seems to be difficult to separate all the compounds (see Table III) because they have similar structures. In this work, owing to the GSC mechanism, the column used is superior in plate number

TABLE II

DETERMINATION OF ALKYLBENZENES IN PYROLYSIS GASOLINE

Peak No.	*Compound*	*Wt. – %*	*Peak No.*	*Compound*	*Wt. – %*
1	Benzene	19.2	11	1,3,5-Trimethylbenzene	0.4
2	Toluene	18.5	12	1-Methyl-2-ethylbenzene	0.5
3	Ethylbenzene	2.5	13	1,2,4-Trimethylbenzene	0.2
4	*p*-Xylene	1.4	14	α-Methylstyrene	0.3
5	*m*-Xylene	3.7	15	1,3-Methylisopropylbenzene	0.5
6	Styrene	7.8	16	*n*-Butylbenzene	0.3
7	*o*-Xylene	1.7	17	Indane	0.5
8	Isopropylbenzene	0.5	18	Indene	3.1
9	*n*-Propylbenzene	0.2	19	Naphthalene	2.5
10	1-Methyl-3-ethylbenzene	1.3			

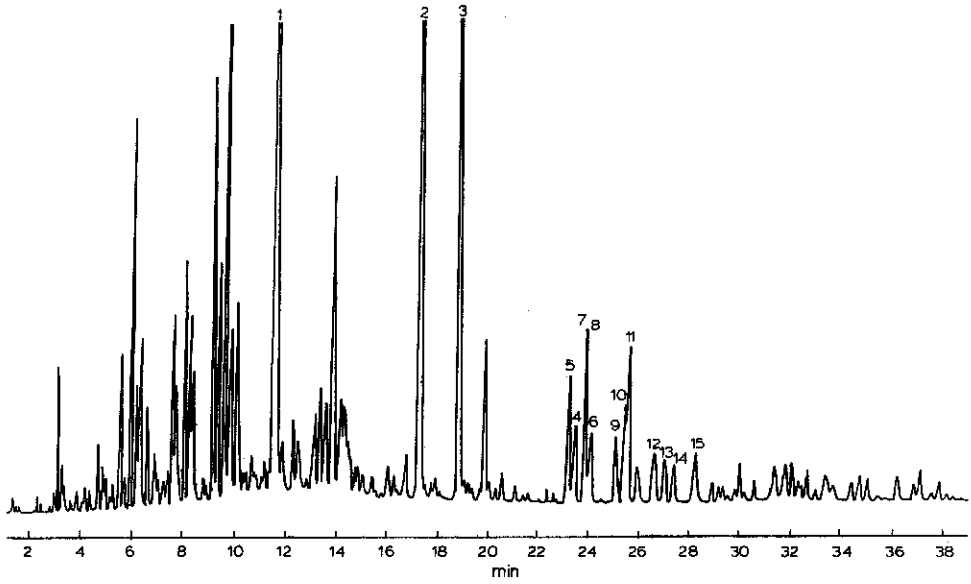

Fig. 4. Separation of pyrolysis fuel oil (b.p. 180–300°C cut). Fused-silica capillary column, 20 m × 0.25 mm I.D., Carbopack B + OV-17. Temperature programme, 95°C for 10 min, raised at 4°C/min to 200°C. For peak identifications, see Table III.

and separation factors to those used previously[6,7]; 2,6- and 2,7-dimethylnaphthalene (DMN) are hardly separated, 1,6- and 1,3-DMN are partially separated and 2,3-, 1,4-, 1,5- and 1,2-DMN are completely separated (Fig. 5).

Fig. 6 shows the separation of pyrolysis gas on a fused-silica capillary column coated with carbon sieve (TDX). The elution order follows the carbon number. C_1–C_5 hydrocarbons are well separated, except the butene isomers. It is difficult to separate butene isomers by using only carbon black as the stationary phase.

TABLE III

ALKYLNAPHTHALENES ISOLATED FROM PYROLYSIS FUEL OIL (b.p. 180–300°C)

Peak No.	*Compound*[a]	*RRT*[b]	*b.p. (°C)*	*Peak No.*	*Compound*[a]	*RRT*[b]	*b.p. (°C)*
1	Naphthalene	1.00	217.96	9	1,7-DMN	2.87	262.90
2	2-MN	1.65	241.14	10	1,3-DMN	2.95	265.50
3	1-MN	1.87	244.18	11	1,6-DMN	2.99	265.5
4	Diphenyl	2.54	255.00	12	2,3-DMN	3.20	268.0
5	2-EN	2.50	257.90	13	1,4-DMN	3.30	268.5
6	1-EN	2.65	258.67	14	1,5-DMN	3.37	270.1
7	2,6-DMN	2.61	262.00	15	1,2-DMN	3.57	271.1
8	2,7-DMN	2.62	262.00	16	Acenaphthane	4.20	277.2

[a] MN = methylnaphthalene; EN = ethylnaphthalene; DMN = dimethylnaphthalene.

[b] RRT = relative retention time (naphthalene = 1.00).The retention time of naphthalene was 11.7 min.

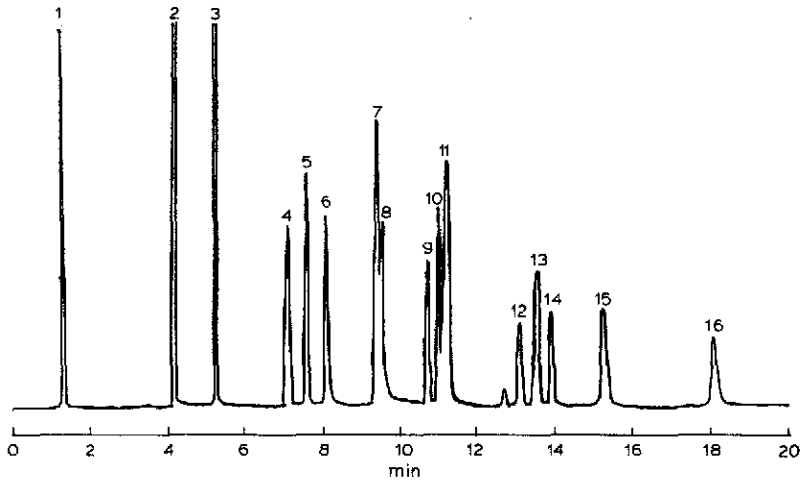

Fig. 5. Separation of C_{10}–C_{12} alkylnaphthalenes. Fused-silica capillary column, 20 m × 0.25 mm I.D., Carbopack B + DC-550. Temperature, 200°C. For peak identifications, see Table III.

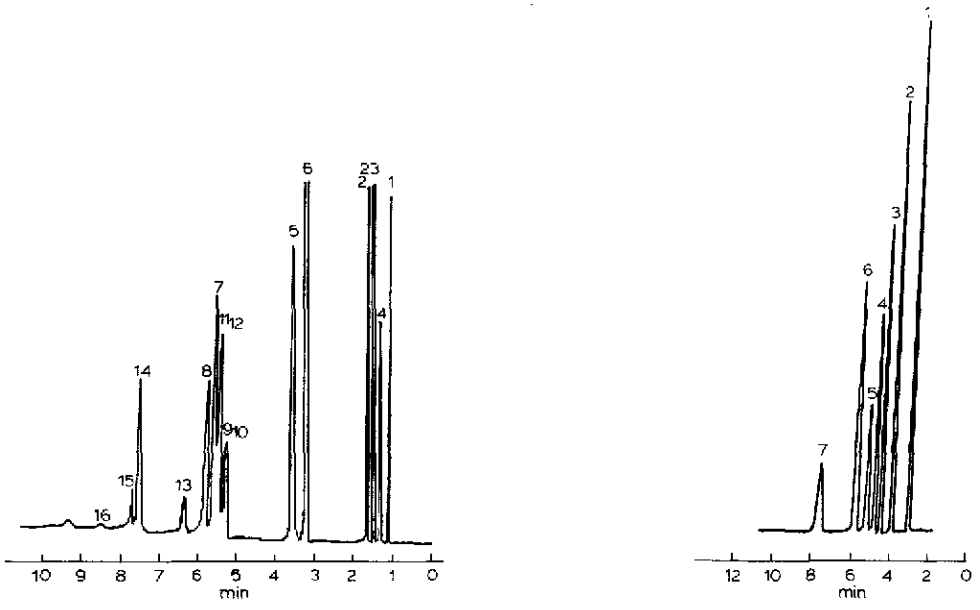

Fig. 6. Separation of C_1–C_5 hydrocarbons. Fused-silica capillary column, 10 m × 0.25 mm I.D., carbon molecular sieve (TDX). Temperature programme, 40°C for 2 min, raised at 25°C/min to 350°C. Peaks: 1 = methane; 2 = ethane; 3 = ethylene; 4 = acetylene; 5 = propane; 6 = propylene; 7 = isobutane; 8 = *n*-butane; 9 = isobutene; 10 = 1-butene; 11 = *trans*-2-butene; 12 = *cis*-2-butene; 13 = 1,3-butadiene; 14 = isopentane; 15 = *n*-pentane; 16 = 1-pentene.

Fig. 7. Separation of C_4 hydrocarbons. Fused-silica capillary column, 8 m × 0.25 mm I.D., STH-01 + 0.2% picric acid. Temperature, 30°C. Peaks: 1 = isobutene; 2 = *n*-butene; 3 = *n*-butane; 4 = isobutene; 5 = *cis*-2-butene; 6 = *trans*-2-butene; 7 = 1,3-butadiene.

Using STH-01 modified with 0.2% picric acid, seven isomers were completely separated at room temperature (Fig. 7).

These examples have shown that, by using a coating of a non-porous, non-specific adsorbent, such as GCB, with a polar stationary phase, the analytical potential of GSC is preserved to a great extent when non-polar hydrocarbons are eluted. This is due to the fact that if the molecules to be eluted are poorly soluble in the liquid stationary phase, the effect of the liquid modifier is to deactivate the surface and to reduce the retention time. Further, the interactions of the analyte molecules with the adsorbent–modifier system are such that a higher selectivity can be achieved than with the pure adsorbent.

REFERENCES

1 A. Di Corcia and A. Liberti, *Adv. Chromatogr.*, 14 (1976) 305.
2 C. Vidal Madjar, S. Bekassa, M. F. Gonnord, P. Arpino and G. Guiochon, *Anal. Chem.*, 49 (1977) 768.
3 G. Goretti, A. Liberti and G. Pili, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1978) 143.
4 F. Bruner, G. Crescentini, F. Mangani, P. Palma and M. Xiang, *J. Chromatogr.*, 399 (1987) 87.
5 B. Xu and N. P. E. Vermeulen, *Chromatographia*, 18 (1984) 520.
6 K. Kasamatsu, *Bull. Jpn. Pet. Inst.*, 17 (1975) 28.
7 M. C. Pankova, R. S. Milina, R. P. Belcheva and A. S. Ivanov, *J. Chromatogr.*, 137 (1977) 198.