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### Characterization of adsorbents by high-performance liquid chromatography using aromatic hydrocarbons Porous graphite and its comparison with silica gel, alumina, octadecylsilica and phenylsilica

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#### Abstract

The retention characteristics of 52 aromatic hydrocarbons, mostly alkylbenzenes, were measured on porous graphite using methanol as the mobile phase. There is a linear dependence of log k' on the number of carbon atoms, (i) for polymethylbenzenes whose methyl groups are all in *ortho* positions and (ii) for *n*-alkylbenzenes above butylbenzene. As with alumina and silica gel, the *ortho* effect for graphite was also observed, but graphite shows much higher  $\alpha$  values (the increase in log k' for addition of a carbon atom) than any of the other packing materials studied. The superior selectivity of graphite is in line with its crystalline structure, consisting of a flat, crystalline array of hexagonally arranged carbon atoms. In terms of optimum eluent and retention graphite behaves like a reversed-phase material, but in terms of selectivity towards isomeric compounds it behaves like the oxide adsorbents silica gel and alumina.

### 1. Introduction

Previous papers in this series have reported on the structure-retention relationships for a group of aromatic hydrocarbons on a range of stationary phases, viz., silica gel [1], alumina [2], octadecylsilica [3,4] and phenylsilica [5]. In this paper we report data on the retention of the same group of hydrocarbons on porous graphite (previously known as porous graphitic carbon or PGC).

While Kiselev and co-workers pioneered the

use of graphites as adsorbents in GC [6] and in LC [7], it was only relatively recently that robust graphites have been available for liquid chromatography. Early work on the use of carbons in liquid chromatography was reviewed by Knox *et al.* [8] and more recent work by Knox and Kaur [9]. In particular Knox *et al.* compared the  $\alpha$  values for the addition of a methyl substituent to benzene (0.40–0.45) and of a methylene group to an alkyl chain (0.23–0.26), where the  $\alpha$  value is defined as

$$\alpha = \log[k'(n+1)/k'(n)]$$

k'(n+1) and k'(n) being the k' values for

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hydrocarbons possessing n+1 and n carbon atoms, respectively.

The aim of this study was to obtain HPLC data for aromatic hydrocarbons, mostly alkylbenzenes, in order to study the relationship between their molecular structure and their retention behaviour on porous graphite, and to compare this with their behaviour on silica gel, alumina, octadecylsilica and phenylsilica.

### 2. Experimental

### 2.1. Apparatus

The HPLC equipment consisted of a Model 8500 liquid chromatograph (Varian, Palo Alto, CA, USA) with a syringe pump and a fixedwavelength UV detector (254 nm). Peaks were recorded with a Model TZ 4221 double-channel strip-chart recorder (Laboratory Instruments, Prague, Czech Republic). Retention times of peaks were measured with a Model 3390A integrator (Hewlett-Packard, Avondale, PA, USA).

The porous graphite sample was PGC 70B-CL prepared in the Wolfson Liquid Chromatography Unit (WLCU) according to the procedure of Knox et al. [10]. An equivalent material is now marketed under the trade name Hypercarb by Shandon Scientific (Runcorn, UK). The porous graphite was packed into a  $100 \times 4.7$  mm I.D. stainless-steel column using a standard slurry procedure. The packing materials used in the previous work [1-5] were Silasorb silica gel (Lachema, Brno, Czech Republic), Alusorb 160 neutral alumina (Lachema), ODS Hypersil (Shandon Scientific) and phenylsilica (Laboratory Instruments). The silica, phenylsilica and alumina had mean particle sizes of 7.5  $\mu$ m, the octadecylsilicas had particle sizes of 5 µm and the porous graphite had a nominal particle size of 7  $\mu$ m.

Retention data were analysed and processed on an HP-85 personal computer (Hewlett-Packard) equipped with a Model 82905B impact printer, a Model 82901M disc drive and a Model 7475A plotter. Lotus 1-2-3 was used to prepare, compute and print tables.

### 2.2. Chemicals

The eluent throughout was analytical-reagent grade methanol (Lachema) distilled in glass before use. Most of the hydrocarbons were kindly provided by the Institute of Chemical Technology (Prague, Czech Republic); the reminder were purchased from UK chemical suppliers.

### 2.3. Procedure

On the basis of preliminary chromatographic runs, mixtures containing two to four completely resolved hydrocarbons were prepared in methanol. Injections of between 2 and 10  $\mu$ l of each mixture were made in triplicate. Column capacity factors, k', were calculated from the retention times measured by the integrator according to

$$k' = (t_{\rm R} - t_0)/t_0$$

where  $t_{\rm R}$  is the retention time of a solute peak and  $t_0$  is that of the unretained solvent peak;  $t_0$ was taken as the time from injection to the moment when the trace for the solvent disturbance crossed the baseline. The solvent disturbance peak was generated by the 2,2,4-trimethylpentane in which the samples were dissolved. Retention data were reproducible to better than 2% from run to run provided that an entire set of data were obtained over a period of 20 h. The column activity was checked several times during each experiment by injecting a standard mixture of benzene, toluene, *n*-propylbenzene and *n*-butylbenzene.

Table 1 lists the packing materials and the eluents used in this and previous studies in the series.

### 3. Results and discussion

Table 2 gives the values of the capacity factors for the 52 hydrocarbons eluted by methanol from graphite at 20°C. Each value represents the average of at least three measurements. Most of the compounds examined were alkylbenzenes

Material	Eluent	Ref.	
Graphite (PGC 70B-CL)	Methanol	This work	
Alumina	Pentane	2	
Silica gel	Pentane	1	
ODS-silica	Methanol-water <sup>a</sup>	3	
Phenylsilica	Methanol-water <sup>b</sup>	5	

Table 1 Packing materials and eluents

<sup>a</sup> Proportions 70:30, 80:20 and 90:10 (w/w) were used.

<sup>b</sup> Proportions 50:50, 60:40, 70:30 and 80:20 (w/w) were used.

and had the empirical formula  $C_nH_{2n-6}$ , but compounds with the following empirical formulae were also characterized:  $C_nH_{2n-8}$  (indane, tetralin, cyclohexylbenzene),  $C_nH_{2n-10}$  (indene),  $C_nH_{2n-12}$  (naphthalene),  $C_nH_{2n-14}$  (biphenyl and acenaphthene) and so on up to  $C_nH_{2n-22}$ (o-terphenyl).

We examined the following aspects of the structure-retention relationship for the 52 solutes: (i) the general relationship between  $\log k'$  and the number of carbon atoms in each molecule; (ii) effects of the various structural features on  $\log k'$ , *viz.*, (a) the length of the alkyl chain and the number of alkyl groups, (b) the arrangement of the alkyl groups (the *ortho* effect) and (c) the shape of the alkyl groups; and (iii) differences between various stationary phases, *viz.*, (a) graphite, (b) alumina, (c) silica gel, (d) octadecylsilica bonded phase and (e) phenylsilica bonded phase.

### 3.1. Relationship between $\log k'$ and carbon number

Fig. 1 shows the dependence of log k' on carbon number for the 52-hydrocarbon set using graphite as the packing material and methanol as the eluent. Similar plots have been reported previously [1-3,5] for the other stationary phases listed in Table 1. In general, there is no universal relationship between log k' and carbon number, although there is the expected trend (except for silica gel with pentane as eluent) towards higher retention with the larger carbon numbers. When-

ever a further carbon atom is added to a molecule, its k' value is increased (except for silica gel). There are, however, a number of linear or near-linear relationships for specific series of compounds. Examples are shown by the broken line drawn through points for the all-ortho-polymethylbenzenes and the full lines drawn through points for *n*-alkylbenzenes (upper) and cyclohexylbenzenes (lower), the dependence for *n*alkylbenzenes becoming linear only above amylbenzene. To elucidate the effects of the various structural features mentioned above it is necessary to consider more limited sets of data.

## 3.2. Effects of specific structural changes on retention

# Chain length in alkylbenzenes and number of methyl groups in all-ortho-polymethylbenzenes

Figs. 2 and 3 show the dependence of  $\log k'$ for all-ortho-polymethylbenzenes and n-alkylbenzenes on carbon number for the five stationary phases listed in Table 1. Broken lines are drawn through points for the ortho-polymethylbenzenes and full lines through points for n-alkylbenzenes. With graphite (Fig. 2), the retention times of ortho-polymethylbenzenes and n-alkylbenzenes both increase with increasing number of carbon atoms in the substituent groups. For the ortho-polymethyl benzenes the dependence is linear but for the *n*-alkylbenzenes the dependence becomes linear only with amylbenzene and higher homologues. With alumina (Fig. 3) there is a linear increase in log k' for the ortho-polymethylbenzenes, but in-

Table 2			
Retention	data	on	carbon

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No.	Compound	С	Н	t <sub>R</sub> (min)	k'	
1	Benzene	6	6	1.77	0.18	
2	Toluene	7	8	2.17	0.45	
3	Ethylbenzene	8	10	2.20	0.47	
4	n-Propylbenzene	9	12	2.50	0.67	
5	n-Butylbenzene	10	14	3.04	1.03	
6	n-Amylbenzene	11	16	4.34	1.89	
7	n-Hexylbenzene	12	18	6.21	3.14	
8	n-Heptylbenzene	13	20	10.16	5.77	
9	n-Octylbenzene	14	22	17.02	10.35	
10	n-Nonylbenzene	15	24	29.94	18.96	
11	n-Decylbenzene	16	26	52.44	33.96	
12	n-Tridecylbenzene	19	32	а	a	
13	o-Xylene	8	10	3.39	1.26	
14	<i>m</i> -Xylene	8	10	3.06	1.04	
15	<i>p</i> -Xylene	8	10	3.33	1.22	
16	Isopropylbenzene	9	12	2.03	0.35	
17	o-Ethyltoluene	9	12	3.64	1.43	
18	p-Ethyltoluene	9	12	3.12	1.08	
19	1,2,3-Trimethylbenzene	9	12	7.22	3.81	
20	1,2,4-Trimethylbenzene	9	12	6.41	3.27	
21	1,3,5-Trimethylbenzene	9	12	4.96	2.31	
22	Isobutylbenzene	10	14	2.45	0.63	
23	secButylbenzene	10	14	2.21	0.47	
24	tertButylbenzene	10	14	2.08	0.39	
25	<i>m</i> -Cymene	10	14	2.55	0.70	
26	<i>p</i> -Cymene	10	14	2.51	0.67	
27	o-Diethylbenzene	10	14	3.62	1.41	
28	m-Diethylbenzene	10	14	2.98	0.99	
29	p-Diethylbenzene	10	14	2.96	0.97	
30	1,2,3,4-Tetramethylbenzene	10	14	21.36	13.24	
31	1,2,3,5-Tetramethylbenzene	10	14	15.08	9.05	
32	1,2,4,5-Tetramethylbenzene	10	14	16.17	9.78	
33	Pentamethylbenzene	11	16	57.26	37.17	
34	4-tertButyltoluene	11	16	2.34	0.56	
35	Isopentylbenzene	11	16	3.39	1.26	
36	tertAmylbenzene	11	16	2.22	0.48	
37	Neopentylbenzene	11	16	2.59	0.73	
38	m-Diisopropylbenzene	12	18	2.12	0.41	
39	p-Diisopropylbenzene	12	18	2.42	0.61	
40	Hexamethylbenzene	12	18	а	а	
41	1,2,4-Triethylbenzene	12	18	5.72	2.81	
42	1,3,5-Triethylbenzene	12	18	4.01	1.67	
43	Cyclohexylbenzene	12	16	4.04	1.69	
44	p-Di-tertbutylbenzene	14	22	2.53	0.69	
45	Pentaethylbenzene	16	26	3.57	1.38	
46	p-Dicyclohexylbenzene	18	26	30.93	19.62	
47	Hexaethylbenzene	18	30	2.46	0.64	
48	1,3,5-Tri-tertbutylbenzene	18	30	1.94	0.29	
49	Indane	9	10	3.45	1.30	
50	Indene	9	8	4.85	2.23	
51	I etrahydronaphthalene	10	12	4.43	1.95	
52	Naphthalene	10	8	11.70	6.80	

No.	Compound	С	Н	$t_{\rm R}$ (min)	k'	
53	Phenanthrene	14	10	a	a	
54	Biphenyl	12	10	17.12	10.41	
55	Fluorene	13	10	а	a	
56	Acenaphthene	12	10	a	a	
57	o-Terphenyl	18	14	28.48	17.99	

Table 2 (continued)

Mobile phase, methanol; temperature, 20°C. C = No. of carbon atoms in molecule; H = No. of hydrogen atoms;  $t_{R}$  = retention time;  $k' = \text{capacity factor} = (t_R - t_0)/t_0$ ;  $t_0$  (retention time of an unretained compound) = 1.50. <sup>4</sup> Data obtained under different conditions.



Fig. 1. Dependence of  $\log k'$  for 52 aromatic hydrocarbons on carbon number. Packing material, graphite; elucnt, methanol; temperature, 20°C. Broken line drawn through points for the all-ortho-polymethylbenzenes; full lines drawn through points for (top) n-alkylbenzenes and (bottom) cyclohexylbenzenes. The names of compounds represented by numbers are listed in Table 2 (46 = p-dicyclohexylbenzene; 47 = hexaethylbenzene; 48 = tri-tert.-butylbenzene; 57 = o-terphenyl).

creasing the chain length in the *n*-alkylbenzenes gives no change in  $\log k'$ . With silica gel there is only a slight increase in  $\log k'$  for the orthopolymethylbenzenes, but a decrease in  $\log k'$ with increase in chain length for the n-alkylbenzenes. Fig. 3 further shows that ODS-silica provides no selectivity between ortho-polymethylbenzenes and *n*-alkylbenznes of the same carbon number: for both series there is the same dependence of  $\log k'$  on carbon number. The increase in log k' with increasing carbon number is similar to that for the alkyl-substitution line with graphite. With phenylsilica there is again



Fig. 2. Dependence of log k' for ortho-polymethylbenzenes and n-alkylbenzenes on carbon number. Packing material, graphite; eluent, methanol; temperature, 20°C. Broken line drawn through points for the ortho-polymethylbenzenes; full line drawn through points for *n*-alkylbenzenes.

selectivity between ortho-polylittle the methylbenzenes and the n-alkylbenzenes, and the dependence of  $\log k'$  on carbon number is much weaker than with ODS-silica, being similar to that of the ortho-polymethylbenzenes on underivatized silica gel.

In general, the position of benzene is anomalous. For graphite the log k' value for benzene lies on the line for the ortho-polymethylbenzenes. For alumina and silica gel log k' for benzene lies between the lines for the orthopolymethylbenzenes and n-alkylbenzenes. For ODS and phenylsilica gels the point for benzene lie on the lines for both series.

The data in Figs. 2 and 3 may be summarized by listing the  $\alpha$  values for methyl substitution at



Fig. 3. As Fig. 2, except packing material: silica gel, eluent pentane; alumina, eluent pentane; octadecylsilica, eluent methanol-water (80:20, w/w); and phenylsilica, eluent methanol-water (80:20, w/w).

an *ortho* position and for addition of a methylene group to the alkyl chain in benzene. These values are given in Table 3.

Table 3 shows clearly that graphite is unique in that it provides a very strong dependence of log k' on carbon number, especially for the *ortho*-polymethylenzenes, and at the same time by far the greatest selectivity between methyl substitu-

tion at an ortho position and methylene addition. The  $\alpha$  values agree with those reported by Knox et al. [8], namely 0.40-0.45 for methyl substitution and 0.23-0.26 for methylene addition. Alumina shows the next strongest retention and selectivity and silica the least of the three adsorbents. When silica is derivatized with ODS the  $\alpha$  values are increased but the selectivity

Table 3

 $\alpha$  Values for methylene substitution at an ortho position and for addition of a methylene group to the alkyl chain of benzene

Packing	Eluent	Methyl substitution	Methylene addition	Difference
Graphite	Methanol	0.46	0.22 <sup>a</sup>	0.24
Alumina	Pentane	0.195	0.00	0.195
Silica gel	Pentane	0.046	-0.014 to $-0.03$	0.05 to 0.06
ODS-silica	Methanol-water (80:20, w/w)	0.17	0.17	0.00
Phenylsilica	Methanol-water (70:30, w/w)	0.10	0.10	0.00

<sup>*a*</sup> From  $C_5$  to  $C_{10}$  chain. The values for  $C_8$  to  $C_{10}$  are 0.25.

shown by the naked adsorbents is lost. Phenylsilica shows slight selectivity but weak retention.

### Arrangement of alkyl groups, the ortho effect

The *ortho* effect is an effect observed with alumina and silica gel whereby the retention of substances with substituents in the *ortho* position is greater than that of isomers with substituents in other positions [1,2]. With the ODS- and

phenylsilica a reversed ortho effect has been observed [3,5].

The effect for graphite is illustrated in Fig. 4, which shows a substitution scheme for generation of all the polymethylbenzenes along with the k' values for each compound and the  $\alpha$  values for each substitution. In Fig. 4, each substitution step has been termed *ortho*, *meta* or *para* according to whether the nearest group to the newly added group is *ortho*, *meta* or *para*. When the



PARA 0.45 0 0.43 0 0.43

Fig. 4. Substitution scheme for polymethylbenzenes retained by graphite. Numbers on formulae are k' values; numbers above arrows are  $\alpha$  values. Elution conditions as in Fig. 2.

new methyl group is inserted between two methyl groups which are *meta* to one another, the new methyl group will be *ortho* to both of the original groups. We have termed this a "double *ortho*" substitution. Fig. 4 shows that on average the  $\alpha$  values for different types of substitution are as follows: double *ortho* substitution,  $\alpha = 0.59$ ; *ortho* substitution,  $\alpha = 0.47$ ; *meta* substitution,  $\alpha = 0.37$ ; and *para* substitution,  $\alpha = 0.43$ .

Although graphite behaves with regard to retention more like a reversed-phase material, it nevertheless shows the same *ortho* effect as the other adsorbents, silica and alumina. In this respect graphite behaves like the classical adsorbents, giving the highest retention for isomeric polymethylbenzenes having the largest number of methyl groups in *ortho* positions.

The data for the five stationary phases are summarized in Table 4. Table 4 shows that all three adsorbents (graphite, alumina and silica gel) show similar trends in that double ortho substitution provides the largest  $\alpha$  value, ortho substitution the next largest followed by para substitution and finally meta substitution with the lowest  $\alpha$  value. Graphite is chiefly distinct from the other adsorbents in having much larger  $\alpha$ values for all substitutions and, on the whole, slightly grater selectivity with respect to isomeric polymethylbenzenes (*i.e.*, a wider variation in the bracketed values). With graphite the polymethylbenzenes are eluted as groups of isomers according to carbon number, whereas with the

Table 4  $\alpha$  Values for methyl substitution in benzene

other packing materials there is considerable overlap of groups and with silica complete overlap occur.

#### Shape of alkyl groups

Branching of the alkyl group generally decreases the retention both in adsorption chromatography and in chromatography on reversed phases. This is clearly illustrated for graphite by the chromatogram of  $C_9$  hydrocarbons shown in Fig. 5, which includes peaks for indane and indene, and by Fig. 6 for  $C_{10}$  hydrocarbons, which includes tetrahydronaphthalene.

Fig. 7 shows that, for two-ring hydrocarbons,



Fig. 5. Chromatogram of selected  $C_9$  hydrocarbons showing selectivity effects. Packing material, graphite; eluent, methanol; temperature, 20°C.

Material	Type of substitution					
	Double ortho	ortho	meta	para		
Graphite	0.59 (+0.12)	0.47	0.37 (-0.10)	0.43 (-0.04)	· · · · · · · · · · · · · · · · · · ·	
Alumina	0.28(+0.085)	0.195	0.08(-0.115)	0.09 (-0.105)		
Silica gel	0.08(+0.034)	0.046	0.00(-0.08)	0.01(-0.07)		
ODS-silica"	0.15(-0.02)	0.17	0.19(+0.02)	0.40(+0.23)		
Phenylsilica <sup>b</sup>	0.10 (0.00)	0.10	0.09 (-0.01)	0.08 (-0.02)		

Values in parentheses are the deviations in  $\alpha$  from the values for ortho substitution (in italics).

<sup>a</sup> Mobile phase: methanol-water (80:20, w/w).

<sup>b</sup> Mobile phase: methanol-water (70:30, w/w).



Fig. 6. Chromatogram of selected  $C_{10}$  hydrocarbons showing selectivity effects. Conditions as in Fig. 5.

retention on graphite is increased by (a) increased unsaturation, peaks 2 and 5, peaks 3 and 7 and peaks 4 and 6; and (b) an increase in the number of carbon atoms in a ring, peaks 2 and 3.

However, the transition from a isolated-ring system to a condensed-ring system does not produce a consistent effect, as seen by comparing peaks 3 and 4 (cyclohexylbenzene and tetrahydronaphthalene) with peaks 6 and 7 (naphthalene and biphenyl).



RETENTION TIME [min]

Fig. 7. Chromatogram of selected mixture showing the effect of addition of hydrogen atoms for pairs of compounds with the same carbon numbers: indane-indene; cyclohexylbenzene-biphenyl; tetrahydronaphthalene-naphthalene. Conditions as in Fig. 5.

# 3.3. Correlation with other stationary phases: the nature of graphite

The original objective in preparing graphites for liquid chromatography was to provide a nearly perfect reversed-phase material that would not suffer from the defects of alkylsilicas such as solubility in eluents, hydrolysis of bonded groups and effects of underivatized silanol groups. In the event, graphite proved to be unique and to show properties both of reversed-phase silica gels and of classical adsorbents.

We may note first that, in order to obtain reasonable elution times for the 52 hydrocarbons used in this and previous studies, it was necessary to use pentane as the eluent for the oxide adsorbents but methanol or methanol-water for graphite and the derivatized silica gels. In this respect graphite must fall into the class of a predominantly reversed-phase material. On the other hand, graphite is clearly an adsorbent, and one with properties that distinguish it from the other adsorbents. It is an extremely strong adsorbent, showing higher  $\alpha$  values for addition of a further carbon atom to any molecule than any of the other materials, and it shows much greater selectivity towards isomers. This is thought to be due to its possessing a flat, crystalline surface (a hexagonal array of carbon atoms like a giant aromatic molecule), which can clearly distinguish between molecules that show good and poor fits to the surface. Both alumina and amorphous silica have geometrically heterogeneous surfaces, which will be far from flat at the atomic level and can distinguish molecules only on the basis of specific effects such as dipole and hydrogenbonding interactions. Likewise, the bonded phases, and particularly ODS-silica, behave more like viscous liquids than adsorbents (especially when in contact with a swelling solvent such as hexane) and therefore show little scope for stereospecific interactions.

Nevertheless, the elution orders of hydrocarbons on graphite are very similar to those on alumina and silica, namely, more aromatic hydrocarbons are more retained, *e.g.*, naphthalene is more retained then tetrahydronaphthalene, indene more than indane and biphenyl more than cyclohexylbenzene.

In contrast, the elution order of the same groups of compounds on ODS-silica [4] is the reverse, with the alkanes showing the greatest retention. However, as far as the effect of isomerization is concerned, retention decreases with isomerization, cyclization, dehydrogenation, dehydrocyclization and aromatization.

Graphite thus resembles the other adsorbents more than it does ODS-silica with regard to its selectivity for different hydrocarbon types.

The comparison of graphite with other packing materials can also be clarified by plots of  $\log k'$  on graphite against  $\log k'$  on the other adsorbents. Fig. 8 shows plots for the *n*-alkylbenzenes and the *ortho*-polymethylbenzenes. There is a marked distinction between graphite and the two oxide adsorbents compared with the relative

similarity of the plots for the two bonded silica gels.

### 4. Conclusions

In terms of retention and the type of eluent required, graphite behaves most like a reversedphase material. In terms of selectivity towards isomeric compounds, graphite behaves more like oxide adsorbents, such as silica gel and alumina.

Graphite combines good selectivity for species with different carbon numbers with good isomer selectivity within groups. For the polymethylbenzenes this enables essentially all isomers to be separated in groups according to their carbon numbers. This is not possible with either the bare adsorbents or the derivatized silica gels.

The  $\alpha$  values for graphite are 0.22-0.25 for



Fig. 8. Correlation of log k' on graphite with log k' on silica gel, alumina, octadecylsilica and phenylsilica. Conditions: for graphite, as in Fig. 1; for silica gel, alumina, octadecylsilica and phenylsilica, as in Fig. 3.

addition of a methylene group to the carbon chain and 0.46 for addition of a methyl group into an *ortho* position to the benzene ring. These are much higher than the corresponding values for the other adsorbents and for the bonded silica gels.

General behavioural patterns found with all the packing materials studied (graphite, silica gel, alumina, octadecylsilica and phenylsilica) are as follows: (a) higher aromatics are more retained than the lower aromatics (number of aromatic rings); (b) compounds with a larger number of methyl groups (*e.g.*, polymethylbenzenes) are more retained; and (c) branching of a substituent alkyl group decreases the retention.

### 5. References

 J. Kříž, L. Vodička, J. Punčochářová and M. Kuraš, J. Chromatogr., 219 (1981) 53.

- [2] J. Kříž, J. Punčochářová, L. Vodička and J. Vařeka, J. Chromatogr., 437 (1988) 178.
- [3] J.H. Knox, J. Kříž and E. Adamcová, J. Chromatogr., 447 (1988) 13.
- [4] J. Kříž, M. Kuraš, L. Vodička and J. Burda, Ropa Uhlie, 31 (1989) 645.
- [5] J. Kříž, E. Adamcová and L. Obal, in preparation.
- [6] A.V. Kiselev and Ya.I. Yashin, Adsorbtsionnaya Gazovaya i Zhidkostnaya Khromatografya, Khimiya, Moscow, 1979.
- [7] A.V. Kiselev, Yu.S. Nikitin, I.I. Frolov and Ya.I. Yashin J. Chromatogr., 91 (1974) 187.
- [8] J.H. Knox, K.K. Unger and H. Mueller, J. Liq. Chromatogr., 6 (S-1) (1983) 1.
- [9] J.H. Knox and B. Kaur, in R.A. Hartwick and P.R. Brown (Editors), *High Performance Liquid Chromatog-raphy*, Wiley, New York, 1989, pp. 189–222.
- [10] J.H. Knox, B. Kaur and G.R. Millward, J. Chromatogr., 352 (1986) 3.