

Note

Capillary gas chromatography of some polycyclic aromatic compounds on several stationary phases

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The analytical study of polycyclic aromatic compounds (PACs) is of great interest as (1) they are widespread in the environment, in natural water, in foods and in oil- and coal-derived materials¹, (2) many of these compounds are suspected mutagens and/or carcinogens² and (3) their presence and concentration in some coal-derived materials, such as pitches, plays a very important rôle with regard to the future use of these materials³.

The determination of PACs has been carried out by different chromatographic techniques^{4,5}, but the most important tools are high-performance liquid chromatography and gas chromatography (GC)¹; with the latter the best separations of PACs are achieved with temperature programming. However, to the best of our knowledge, only linear-temperature-programmed retention indices of PACs on the slightly polar stationary phase SE-52 are available⁶⁻⁹.

In this paper linear-temperature-programmed retention indices of a group of 25 PACs, obtained on OV-101, SE-54 and OV-1701 as stationary phases, are reported. The influence of the polarity of the stationary phase and the temperature programme on the chromatographic retention of these PACs is discussed. Also relationships between retention indices on the above mentioned stationary phases and some properties of these compounds are discussed.

EXPERIMENTAL

Retention times were determined with a Model 8320 gas chromatograph (Perkin-Elmer, Beaconsfield, U.K.) equipped with flame ionization detection (FID). The separation was carried out on three fused-silica capillary columns coated with OV-101, SE-54 and OV-1701 stationary phases respectively. The characteristics of these columns, the polarity of the stationary phases on the McReynolds scale¹⁰ and working conditions are given in Table I.

The compounds were co-chromatographed with naphthalene, phenanthrene and crysene, which were used as internal standards for calculation of the retention indices. The latter were calculated by using a linear retention index scale for linear-temperature-programmed GC, suggested by Van Den Dool and Kratz¹¹ and used by others⁶⁻⁹. The equation was

TABLE I
CAPILLARY COLUMNS AND WORKING CONDITIONS

Parameter	Column		
	1	2	3
Stationary phase (McReynolds polarity)	OV-1701 ($P_M=789$)	OV-101 ($P_M=229$)	SE-54 $P_M=337$)
Length (m)	25	25	20
Internal diameter (mm)	0.22	0.22	0.22
Carrier gas (hydrogen) flow-rate (ml/min)	1.8	0.7	1.4
Splitting ratio	1:120	1:64	1:64
Detector and injector temperatures ($^{\circ}\text{C}$)	300	300	300
Temperature programme from 50 to 300 $^{\circ}\text{C}$ ($^{\circ}\text{C}/\text{min}$)	4	4	4

$$I = 100 \left[n + \frac{t_{R(\text{compound})} - t_{R(n)}}{t_{R(n+1)} - t_{R(n)}} \right] \quad (1)$$

where I is the retention index, n is the number of rings in the hydrocarbon standard eluted before the substance of interest, $t_{R(\text{compound})}$ is the measured retention time of the substance for which the retention index is to be determined and $t_{R(n)}$ and $t_{R(n+1)}$ are the measured retention times of the hydrocarbon standards eluted just before and after the compound studied. The solutes were obtained from Fluka, Aldrich, Merck and Janssen. The calculated retention indices are given in Table II.

Table III shows the boiling points, T_b , molecular polarizabilities, α , molecular connectivities, ${}^1\chi$, Van der Waals volumes, V_w , and molecular weights, W_M , of these compounds. The boiling points were taken from the literature^{12,13}; α , ${}^1\chi$ and V_w were calculated as indicated in refs. 14, 15 and 16, respectively.

RESULTS AND DISCUSSION

Table II shows the retention indices obtained on OV-101 (McReynolds polarity = 229), SE-54 (McReynolds polarity = 337) and on OV-1701 (McReynolds polarity = 789). Also in Table II the difference, δ , between the retention indices on OV-1701 and on OV-101 are given, indicating that the retention of the PACs is clearly affected by the stationary phase polarity.

The nitrogenated compounds are in general more strongly retained on the more polar stationary phase, especially the indole derivatives (compounds 21 and 23), 2-aminoanthracene and diphenylamine (compounds 13 and 24); among the pyridine derivatives, compounds 1, 2, 6, 8 and 18, are the more influenced in their retention by the stationary phase polarity.

The behaviour of the oxygenated compounds shows two trends: the ethers (compounds 7, 10 and 11) are more strongly retained on the less polar stationary phases, whereas this effect is opposite for aromatic ketones (compounds 19, 22 and 25).

The sulphur compounds (14 and 20) show a very similar chromatographic relative retention on the three stationary phases. However, they show the highest relative retention on SE-54.

TABLE II
RETENTION INDICES OF SOME PACs ON SEVERAL STATIONARY PHASES

Compound number	Name	$f^{OV-1701}$ $P_M = 789$	f^{SE-54} $P_M = 337$	f^{SE-52} $P_M = 334$	f^{OV-101} $P_M = 229$	δ^a
1	Quinoline	215.90	210.95	210.26 ^b	209.51	+ 6.39
2	Isoquinoline	220.35	214.49	214.14 ^b	213.19	+ 7.16
3	8-Methylquinoline	226.51	225.86	225.18 ^b	225.49	+ 1.02
4	2-Methylquinoline	227.38	224.12	224.13 ^b	223.47	+ 3.91
5	7-Methylquinoline	235.36	231.80	231.37 ^b	230.99	+ 4.37
6	6-Methylquinoline	235.85	232.19	229.82 ^c	230.75	+ 5.10
7	Diphenyl ether	236.94	240.83	—	241.16	- 3.82
8	4-Methylquinoline	241.41	236.82	235.77 ^b	235.54	+ 5.87
9	2,2'-Bipyridyl	248.27	246.71	247.15 ^b	245.68	+ 2.59
10	Dibenzofuran	257.68	259.14	258.77 ^b	259.57	- 1.89
11	Dibenzyl ether	280.99	281.12	—	281.19	- 0.20
12	5H-Indeno[1,2- <i>b</i>]pyridine	282.77	279.70	279.85 ^b	278.75	+ 4.02
13	Diphenylamine	283.77	276.68	—	275.74	+ 8.03
14	Dibenzothiophene	296.00	296.15	295.39 ^b	295.95	+ 0.05
15	Acridine	306.41	303.79	304.04 ^b	303.18	+ 3.23
16	7,8-Benzoquinoline	306.90	303.45	301.94 ^b	302.57	+ 4.33
17	Phenanthridine	311.81	308.01	307.94 ^b	307.45	+ 4.36
18	5,6-Benzoquinoline	313.25	308.01	307.94 ^b	306.96	+ 6.29
19	9-Xanthenone	318.12	314.04	—	313.05	+ 5.07
20	Thianthrene	328.61	329.88	330.13 ^c	328.58	+ 0.03
21	Carbazole	330.07	311.18	311.71 ^b	309.63	+20.44
22	Anthraquinone	336.30	332.19	—	331.38	+ 4.92
23	2-Phenylindole	361.97	343.80	346.18 ^b	343.02	+18.95
24	2-Aminoanthracene	379.92	366.78	367.45 ^b	365.89	+14.03
25	Phenanthrenequinone	380.49	363.39	—	362.04	+18.45

$$^a \delta = f^{OV-1701} - f^{OV-101}$$

^b Retention indices taken from ref. 6.

^c Retention indices taken from ref. 9.

Therefore, the elution order of this group of compounds on the moderately polar stationary phase OV-1701 is not the same as on the less polar stationary phases SE-54 and OV-101. Inversions in the elution order can be observed: 8- and 2-methylquinoline (compounds 3 and 4), 7- and 6-methylquinoline (compounds 5 and 6), diphenyl ether and 4-methylquinoline (compounds 7 and 8), dibenzyl ether and diphenylamine (compounds 11 and 13), acridine and 7,8-benzoquinoline (compounds 15 and 16), phenanthridine and 5,6-benzoquinoline (compounds 17 and 18), 2-aminoanthracene and phenanthrenequinone (compounds 24 and 25), and carbazole (compound 21) which on OV-101 is eluted after 5,6-benzoquinoline. The elution order on the moderately polar stationary phase OV-1701 follows the increasing order of the boiling point more closely than the elution order on the less polar stationary phases. That is, the chromatographic process on OV-1701 is more similar to distillation, than on the less polar stationary phase OV-101 or SE-54 (see data in Tables II and III).

Table II also shows retention indices of 19 PACs obtained on SE-52 (McReynolds polarity = 334) at 2°C/min^{6,9}. These data are in very good agreement

TABLE III
 PROPERTIES OF PACs UTILIZED IN THIS STUDY

Compound number	Name	$T_b(^{\circ}C)$	$\alpha(\text{\AA}^3)$	W_M	$^1\chi$	$V_w(\text{ml/mol})$
1	Quinoline	238.0	17.11	129	3.0145	71.39
2	Isoquinoline	243.0	17.11	129	3.0044	71.39
3	8-Methylquinoline	—	18.96	143	3.6811	82.54
4	2-Methylquinoline	247.6	18.96	143	3.6852	82.54
5	7-Methylquinoline	257.6	18.96	143	3.6752	82.54
6	6-Methylquinoline	258.6	18.96	143	3.6752	82.54
7	Diphenyl ether	259.0	20.31	170	4.2296	94.88
8	4-Methylquinoline	264.2	18.96	143	3.6811	82.54
9	2,2'-Bipyridyl	272.5	18.20	156	3.7909	86.54
10	Dibenzofuran	285.0	22.47	168	4.3129	86.64
11	Dibenzyl ether	298.0	24.36	198	5.1058	115.84
12	5H-Indeno[1,2-b]pyridine	306.0	20.22	167	4.4716	94.30
13	Diphenylamine	302.0	21.14	169	4.3213	99.76
14	Dibenzothiophene	332.3	24.24	184	4.9339	94.24
15	Acridine	346.0	24.79	179	4.6792	96.99
16	7,8-Benzoquinoline	—	24.79	179	4.6752	96.99
17	Phenanthridine	349.0	24.79	179	4.6752	96.99
18	5,6-Benzoquinoline	—	24.79	179	4.6752	96.99
19	9-Xanthenone	—	24.27	196	4.7671	98.34
20	Thianthrene	364.6	26.23	216	5.2132	105.04
21	Carbazole	355.0	23.36	167	4.4047	91.52
22	Anthraquinone	379.8	25.86	208	5.0629	106.84
23	2-Phenylindole	—	25.32	193	5.0653	109.24
24	2-Aminoanthracene	—	26.82	193	5.0087	107.58
25	Phenanthrenequinone	—	25.86	208	5.0629	106.84

with those obtained on SE-54 (McReynolds polarity = 337) at 4°C/min. The relationship between the two sets of data shows a correlation coefficient of 0.9998, indicating that the variation from 2 to 4°C/min in the temperature programme does not affect, in any appreciable way, the relative retention of these compounds.

Relationships between retention indices of PACs and some of their properties have been reported. Retention indices of a group of PACs have been related to molecular connectivity, but the equations obtained have no value because of their high standard deviations¹⁷. More rigorous contributions have been made by other authors¹⁸⁻²⁰.

The properties selected in this paper in order to study their relationships with the chromatographic retention have a clear meaning and are as follows. The boiling point, T_b , is the temperature at which the vapour pressure of a compound reaches 1 atm. This property gives information about the magnitude of the intermolecular attractions in each compound, and can be measured experimentally. The molecular polarizability, α , provides information about the intermolecular dispersive and inductive forces in the interactions with other compounds²¹. It is usually obtained from experimental data on the density and refractive index, but unfortunately these data are not available for

most of the compounds studied here and were calculated additively¹⁴. The molecular weight, W_M , is the sum of the atomic weights of all atoms in a molecule. The first order molecular connectivity, ${}^1\chi$, is a quantification of the branching, atom connections, shape and size of the molecule, and is determined by additive calculation¹⁵. Finally the Van der Waals volume, V_W , is the volume occupied by a molecule impenetrable to other molecules with thermal energies at ordinary temperatures. Its determination is by additive calculation¹⁶. The Van der Waals volume and the first order connectivity have been related previously with dispersive solute-stationary phase interactions²²⁻²⁵.

Table IV gives the correlation coefficients between these properties for 25 and 18 compounds, respectively. The more and the less correlated parameters with T_b are α and V_W respectively, but each one has a different physico-chemical meaning, and therefore provides different kinds of information; among the other parameters the least close relationship is between α and V_W , and the closest is between W_M and ${}^1\chi$.

First, the relationships between retention indices and each of the above-mentioned properties were studied. Table V shows the statistics of the $I = f(\theta)$ equations, where $\theta = T_b, \alpha, W_M, {}^1\chi$ or V_W . The parameter most closely connected with the chromatographic retention is the boiling point, T_b . The relationships between retention indices and the other parameters $\alpha, W_M, {}^1\chi$ or V_W are very poor, and the equations obtained have no predictive value, in accordance with similar previous results¹⁷.

However the different rôles of these parameters on the several stationary phases is noteworthy. The additively calculated parameters $\alpha, W_M, {}^1\chi$ or V_W show a closer relationship with retention indices obtained on the slightly polar stationary phases, than with the retention indices obtained on the moderately polar stationary phase. On the other hand, the T_b values are more closely related with retention indices obtained on the moderately polar stationary phase, than with retention indices obtained on the less polar stationary phase. This behaviour is not an exception, and has been observed previously for other groups of compounds^{26,27}. The equations $I = f(T_b)$ were obtained with only 18 compounds, owing to the fact that the boiling point data of the other compounds were not available in the literature^{12,13}.

Although retention indices on OV-1701 are very closely connected with boiling point values, T_b , the former are not a linear function of the latter (see compounds 12

TABLE IV
CORRELATION COEFFICIENTS BETWEEN SEVERAL PROPERTIES FOR 18 AND 25 COMPOUNDS RESPECTIVELY

	$N = 18$					$N = 25$				
	T_b	α	W_M	${}^1\chi$	V_W	α	W_M	${}^1\chi$	V_W	
T_b	1.0000	0.9178	0.8449	0.8538	0.7243	α	1.0000	0.9277	0.9489	0.8669
α		1.0000	0.9289	0.9426	0.8333	W_M	1.0000	0.9674	0.9295	
W_M			1.0000	0.9674	0.9258	${}^1\chi$		1.0000	0.9452	
${}^1\chi$				1.0000	0.9330	V_W			1.0000	
V_W					1.0000					

TABLE V

STATISTICAL DATA FOR THE $I = f(\theta)$ EQUATIONS, WHERE $\theta = T_b, \alpha, W_M, {}^1\chi$ OR V_W

R = Correlation coefficient, s = standard deviation, N = number of experimental points and F = F-test.

Stationary phase	P_M	T_b	α	W_M	${}^1\chi$	V_W
OV-101	229	$R = 0.9897$	$R = 0.9438$	$R = 0.8997$	$R = 0.9067$	$R = 0.8494$
		$s = 5.51$	$s = 15.27$	$s = 20.16$	$s = 19.47$	$s = 24.37$
		$N = 18$	$N = 25$	$N = 25$	$N = 25$	$N = 25$
		$F_{1,16}^a = 766.6$	$F_{1,23}^b = 187.4$	$F_{1,23} = 97.7$	$F_{1,23} = 106.4$	$F_{1,23} = 59.6$
SE-54	337	$R = 0.9909$	$R = 0.9414$	$R = 0.8970$	$R = 0.9033$	$R = 0.8461$
		$s = 5.19$	$s = 15.59$	$s = 20.43$	$s = 19.83$	$s = 24.64$
		$N = 18$	$N = 25$	$N = 25$	$N = 25$	$N = 25$
		$F_{1,16} = 866.3$	$F_{1,23} = 179.3$	$F_{1,23} = 94.8$	$F_{1,23} = 101.9$	$F_{1,23} = 57.9$
OV-1701	789	$R = 0.9921$	$R = 0.9142$	$R = 0.8581$	$R = 0.8664$	$R = 0.8185$
		$s = 4.92$	$s = 20.04$	$s = 25.39$	$s = 24.70$	$s = 28.41$
		$N = 18$	$N = 25$	$N = 25$	$N = 25$	$N = 25$
		$F_{1,16} = 1001.0$	$F_{1,23} = 117.0$	$F_{1,23} = 64.2$	$F_{1,23} = 69.2$	$F_{1,23} = 46.7$

^a $F_{1,16}(\alpha=0.01) = 8.53$.

^b $F_{1,23}(\alpha=0.01) = 7.88$.

TABLE VI

EQUATIONS $I = f(T_b)$ AND $I = f(T_b, \theta)$, WHERE $\theta = \alpha, W_M, {}^1\chi$ OR V_W

Stationary	P_M	No.	Equation	R	s	N	F
OV-101	229	1	$I = 13.38 + 0.85T_b$	0.9897	5.51	18	$F_{1,16}^a = 767.6$
		2	$I = 4.45 + 0.68T_b + 2.78\alpha$	0.9934	4.42	18	$F_{2,15}^b = 564.8$
		3	$I = 3.39 + 0.68T_b + 0.35W_M$	0.9971	2.91	18	$F_{2,15} = 1311.4$
		4	$I = 6.19 + 0.67T_b + 14.73{}^1\chi$	0.9983	2.22	18	$F_{2,15} = 2250.2$
		5	$I = -9.51 + 0.73T_b + 0.63V_W$	0.9980	2.46	18	$F_{2,15} = 1839.9$
SE-54	337	6	$I = 14.23 + 0.85T_b$	0.9909	5.19	18	$F_{1,16} = 866.3$
		7	$I = 6.51 + 0.70T_b + 2.40\alpha$	0.9937	4.33	18	$F_{2,15} = 586.4$
		8	$I = 5.03 + 0.70T_b + 0.33W_M$	0.9972	2.87	18	$F_{2,15} = 1340.4$
		9	$I = 7.67 + 0.68T_b + 13.44{}^1\chi$	0.9980	2.38	18	$F_{2,15} = 1949.9$
		10	$I = 7.16 + 0.74T_b + 0.59V_W$	0.9981	2.37	18	$F_{2,15} = 1975.4$
OV-1701	789	11	$I = 12.52 + 0.87T_b$	0.9921	4.92	18	$F_{1,16} = 1001.0$
		12	$I = 12.52 + 0.87T_b - 0.001\alpha$	0.9921	4.92	18	$F_{2,15} = 469.2$
		13	$I = 10.92 + 0.84T_b + 0.06W_M$	0.9923	4.86	18	$F_{2,15} = 480.6$
		14	$I = 10.53 + 0.82T_b + 4.08{}^1\chi$	0.9927	4.72	18	$F_{2,15} = 511.0$
		15	$I = 1.58 + 0.81T_b + 0.30V_W$	0.9939	4.32	18	$F_{2,15} = 611.6$
OV-1701	789	16	$I = 17.25 + 0.85T_b$	0.9953	3.74	16	$F_{1,14}^c = 1473.1$
		17	$I = 15.38 + 0.74T_b + 8.09{}^1\chi$	0.9977	2.58	16	$F_{2,13}^d = 1440.7$
		18	$I = 4.64 + 0.77T_b + 0.40V_W$	0.9984	2.14	16	$F_{2,13} = 2087.9$

^a $F_{1,16}(\alpha=0.01) = 8.53$.

^b $F_{2,15}(\alpha=0.01) = 6.36$.

^c $F_{1,14}(\alpha=0.01) = 8.86$.

^d $F_{2,13}(\alpha=0.01) = 6.70$.

and 13 and 20 and 21 in Tables II and III). In order to find better predictive equations, biparametric regressions were tested (Table VI).

For slightly polar stationary phases satisfactory predictive biparametric equations $I = f(T_b, \theta)$, where $\theta = {}^1\chi$ or V_M (eqns. 4, 5 and 9, 10), have been found for all kinds of compounds. The statistics of these equations are better than those of the monoparametric ones and their standard deviations are very close to the experimental values.

For the moderately polar stationary phase none of the biparametric equations improves the statistics of the monoparametric ones; examination of the retention indices predicted with eqns. 12–15 indicates that the compounds that show the highest deviations from experimental data are those whose heteroatoms support hydrogen atoms, *i.e.*, diphenylamine and carbazole. Biparametric equations obtained without the introduction of these compounds show satisfactory statistical data (eqns. 17 and 18). The PACs, whose heteroatoms support hydrogen atoms, give rise to hydrogen-bonding interactions. The dipole–dipole and hydrogen-bonding interactions of these compounds with the stationary phase must be taken into account in order to find valuable predictive equations for calculating approximate retention indices of all kinds of PACs on a polar or moderately polar stationary phase.

These results agree with previous quantitative structure–retention relationship studies on solutes which have the capacity to give rise to hydrogen-bonding interactions²⁷.

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