

CHROM. 13,868

MEASUREMENT OF RETENTION DATA ON OPEN TUBULAR COLUMNS COUPLED IN SERIES

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(Received February 27th, 1981)

SUMMARY

An equation is derived which relates the apparent capacity factor of a series of columns to the capacity factors of the individual columns, their lengths and the inlet pressure. This equation, which gives results in excellent agreement with experimental results, permits the correct prediction of the retentions of compounds on combined columns, and hence the calculation of the lengths of the individual columns to be used to obtain optimal separations of complex mixtures. This equation also explains the moderate variation of the column capacity factor with inlet pressure and that resulting from reversal of the carrier gas flow on columns that are not very homogeneous. It is shown that, at least when the difference in the retention indices of compounds on two stationary phases is not very large, the retention index on a series of two columns varies linearly with the length of one of the columns.

INTRODUCTION

The on-line combination of two or more columns is a common approach in gas chromatography (GC) for solving difficult separation problems, either because it is easier to couple in series two columns packed with the same stationary phase than to prepare a very long single column, or because two different stationary phases are needed in order to achieve the separation of a given mixture. In the latter instance two possibilities arise: the use of a series of different columns coupled on-line, each packed with one of the pure stationary phases selected, or the use of one column packed with a mixed stationary phase. Both methods have advantages and drawbacks.

The first method is very practical as it permits the use of columns already available; also these columns can be separated and employed for different analyses later. On the other hand, the individual retention times and the selectivity of the combined column depend on the order of the different units. The problems arising from the combination of packed columns have been thoroughly discussed by various workers¹⁻⁵.

The second method requires that a column be prepared specifically for each new separation, which restricts its use to certain types of routine analysis. In this instance, however, the selectivity of the column is independent of its length and the retention time and resolving power increase with increasing length, as for classical columns⁵. In a series of papers, Purnell and co-workers described the retention behaviour of solutes analysed on packed columns prepared using mixed stationary phases⁶⁻¹⁰. It was shown that the partition coefficient of a solute chromatographed on a mixed stationary phase can be predicted from its partition coefficients on the pure stationary phases and the composition of the mixed phase, assuming a linear variation of the partition coefficient on a binary solvent with the volume fraction of one of these solvents in the mixture. This assumption is controversial^{6,11-13} and probably holds only in fairly simple cases. Snyder and Poppe¹² showed that it is probably valid for mixtures of stationary phases on which the partition coefficients are close, such as those used by Laub and Purnell¹⁰, mixtures of polymers that are poorly miscible or mixtures of stationary phases for which the solute-solvent interactions are restricted to 1:1 pairs. Martire¹³ showed that the effect observed by Purnell is "... merely an artifact of the insensitive method of data testing used..." Finally, there are many examples of binary solvent GC stationary phases that show poor agreement with this assumption^{14,15}. It is therefore doubtful whether in most instances computer calculations can predict accurately enough the optimal composition of the mixed stationary phase, as suggested by Purnell and co-workers^{16,17}. Hence the main advantage of this method remains controversial.

As far as open-tubular columns are concerned, it is less difficult to couple them in series than to prepare a single column containing a mixture of stationary phases. Although the static method could be used with a solution of the different stationary phases at the required concentration¹⁸, the stability of the liquid film depends on the wettability of the glass surface, a function of the mode of surface treatment, of the nature of the stationary phase, its surface energy, etc. The best surface treatment is not the same when coating a film of silicone grease or of Carbowax 20M. On the other hand, open-tubular columns have been coupled in series easily, using various types of small-volume connections, the simplest one being shrinkable PTFE tubing¹⁹. There is no need in the present application for sophisticated column switching systems, which could be applied, however, to the design of variable-polarity columns³.

The aim of this paper is to point out some of the problems that occur in the use of on-line series of glass capillary columns, with special emphasis on the prediction of retention data.

THEORETICAL

We assume we have in series two open-tubular columns of length L_A and L_B (*cf.*, Fig. 1) and identical inner diameters, and hence the same permeability, k . According to Poiseuille's law⁵, the carrier gas velocity at the outlet of this column series is

$$u_0 = \frac{k}{2\eta(L_A + L_B)P_0} \cdot (P_i^2 - P_o^2) \quad (1)$$

The intermediate pressure, P_a can be considered either as the inlet pressure of

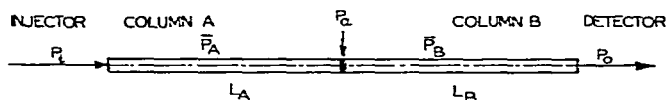


Fig. 1. Schematic diagram of two columns coupled in series. P_i = inlet pressure; P_a = pressure between columns A and B; P_o = outlet pressure; \bar{P}_A = average pressure in the first column; \bar{P}_B = average pressure in the second column; L_A , L_B = column lengths.

the second column or as the outlet pressure of the first column. Mass conservation of the carrier gas demands that the corresponding gas velocity, u_a , be the same, whether it is calculated as the outlet velocity of column 1 or the inlet velocity of column 2:

$$u_a = \frac{k}{2\eta L_A P_a} \cdot (P_i^2 - P_a^2) = \frac{k}{2\eta L_B P_a} \cdot (P_a^2 - P_o^2) \quad (2)$$

Hence

$$\frac{P_i^2 - P_a^2}{L_A} = \frac{P_a^2 - P_o^2}{L_B} = \frac{P_i^2 - P_o^2}{L_A + L_B} \quad (3)$$

The first of these two equations can be solved for P_a^2 :

$$P_a^2 = \frac{P_i^2 L_B + P_o^2 L_A}{L_A + L_B} \quad (4)$$

The retention time over a column of length L is given by

$$t_R = \frac{L}{\bar{u}} (1 + k') \quad (5)$$

with²⁰

$$\bar{u} = ju_o = \frac{3}{2} \cdot \frac{P_o (P_i^2 - P_o^2)}{P_i^3 - P_o^3} \cdot u_o \quad (6)$$

The retention time over the series of two columns is similarly given by

$$t_R = \frac{L_A + L_B}{\bar{u}} (1 + k'_{AB}) = \frac{L_A}{\bar{u}_A} (1 + k'_A) + \frac{L_B}{\bar{u}_B} (1 + k'_B) \quad (7)$$

This equation defines a capacity factor for the series of columns, k'_{AB} , which has no thermodynamic meaning as it will depend on the characteristics of the two columns in addition to the two different retention mechanisms used, but at least it is independent of the flow-rate. Combining eqns. 3, 6 and 7, we obtain⁴

$$k'_{AB} = \frac{k'_A L_A \bar{P}_A + k'_B L_B \bar{P}_B}{(L_A + L_B) \bar{P}} \quad (8)$$

where \bar{P} is the average column pressure⁴:

$$\bar{P} = \frac{P_o u_o}{\bar{u}} = \frac{2}{3} \cdot \frac{P_i^3 - P_o^3}{P_i^2 - P_o^2} \quad (9)$$

Using eqns. 4, 8 and 9, k'_{AB} can be calculated. Eqn. 8 can be further simplified by combination with eqns. 3 and 9:

$$k'_{AB} = \frac{k'_A |P_i^3 - P_a^3| + k'_B |P_a^3 - P_o^3|}{P_i^3 - P_o^3} \quad (10)$$

Eqns. 4 and 10 allow the calculation of k'_{AB} , knowing the capacity ratios of the two columns and their lengths. We note that if the same stationary phase is used but the average film thickness is different for the two columns, the apparent column capacity factor becomes a function of the inlet pressure. This is obviously what should happen on a column that is not homogeneous, having a film thickness function of the position along the column.

The apparent column capacity factor for the column series also depends on the column order for a given flow-rate, as does the intermediate pressure, P_a , as was observed by Hildebrand and Reilley⁴ for packed columns. As the inner diameter of an open-tubular column sometimes varies along the column²¹, as does the film thickness, we may expect that in practice the apparent column capacity factor will deviate from the prediction of eqn. 10 and may even depend on the direction of the gas flow inside each column, their order remaining the same.

In liquid chromatography, the carrier liquid velocity is constant all along the column as the compressibility of liquids can be neglected in calculating this velocity. Then,

$$\bar{u}_A = \bar{u}_B = \bar{u} \quad (11)$$

and eqn. 7 becomes

$$k'_{AB} = \frac{k'_A L_A + k'_B L_B}{L_A + L_B} \quad (12)$$

which is also the limit of eqn. 10 when P_i becomes very close to P_o (and \bar{u} to zero).

Fig. 2 shows plots of k'_{AB}/k'_B as a function of L_A/L_B for different inlet pressures (the outlet pressure is assumed to be atmospheric), for $k'_A/k'_B = 10$ and 0.1. This ratio is expected to be close to 1 at low L_A/L_B and close to either 10 or 0.1 at large L_A/L_B . When $k'_A/k'_B = 1$, k'_{AB}/k'_B is always also equal to 1. The effect of the inlet pressure is important only between 1 and 4 atm. Above about 6 atm, the apparent capacity factor becomes independent of the inlet pressure, and hence of the carrier gas velocity, as shown by the insert in Fig. 2. Assuming that P_o can be neglected in comparison with P_i , we can rewrite eqn. 4:

$$P_a^2 = P_i^2 \cdot \frac{L_B}{L_A + L_B} \quad (13)$$

and eqn. 10 becomes

$$k'_{AB} = k'_A + (k'_B - k'_A) \left(\frac{L_B}{L_A + L_B} \right)^{3/2} \quad (14)$$

Note that P_o is also negligible compared with P_a only if L_A/L_B is not very large, but then k'_{AB} would be nearly equal to k'_A anyway (*cf.*, eqn. 10).

Fig. 3 shows the variation of k'_{AB}/k'_B as a function of L_A/L_B for different values of k'_A/k'_B . It can be seen that the contribution of the first column (column A) is always more important than that of the second (column B).

For example, if we have $L_A/L_B = 3.16$ with $P_i = 2$ atm ($\Delta P = 1$ atm) and $k'_A = 0.2$, $k'_B = 1$, then $k'_A/k'_B = 0.2$ and $k'_{AB}/k'_B = 0.344$. If we reverse the column order by exchanging columns A and B, L_A/L_B becomes equal to 0.316, k'_A is now equal to 1 and $k'_B = 0.2$. The ratio $k'_A/k'_B = 5$ and with $P_i = 2$ atm again we find $k'_{AB}/k'_B = 2.18$, hence $k'_{AB} = 0.436$, *i.e.*, 27% larger. This is a major change in chromatography and two compounds that have accidentally the same k'_{AB} with different k'_A and k'_B will probably have different k'_{BA} .

Unfortunately, there is no simple relationship between the relative retention of two compounds on the two columns and on their combination, except by writing eqn. 10 for the two compounds and dividing the two corresponding equations. A similar conclusion applies to the retention index.

EXPERIMENTAL

Column preparation and measurements

Glass capillary columns were made from soda-lime glass etched with hydrogen chloride as described previously¹⁸. Purified Apiezon L²², hydrocarbon C₈₇²³, polyethylene glycol 20,000 (Carbowax 20M) and polydimethylsiloxane (OV-101) were

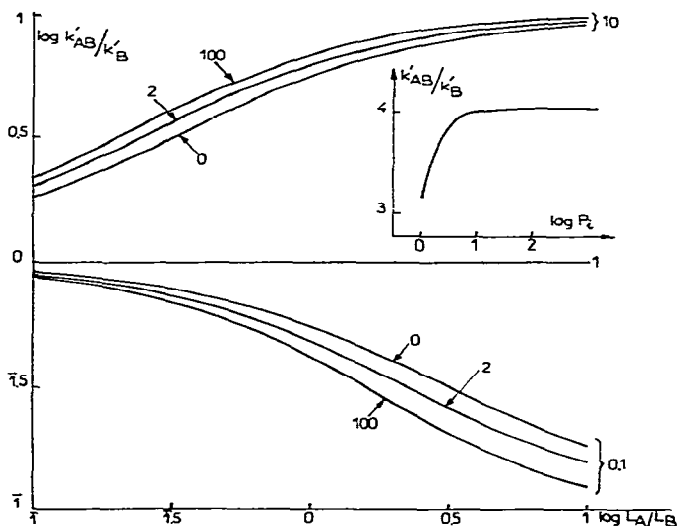


Fig. 2. Logarithmic plots of k'_{AB}/k'_B (ratio of the apparent capacity factor of a combination of two columns A and B to the capacity factor of the second column) against the ratio of the lengths of the two columns. The figure on each curve gives the inlet pressure (atm). The outlet pressure was atmospheric. Upper curves, $k'_A/k'_B = 10$; lower curves, $k'_A/k'_B = 0.10$. If $k'_A/k'_B = 1$, k'_{AB} is always equal to k'_A and k'_B . The insert shows a plot of k'_{AB}/k'_B versus $\log P_i$ for $k'_A/k'_B = 10$ and $L_A/L_B = 0.316$.

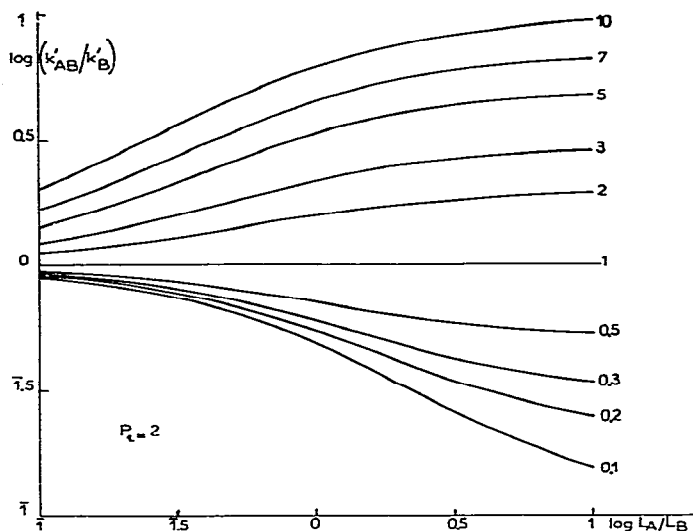


Fig. 3 Plot of $\log(k'_{AB}/k'_B)$ versus $\log(L_A/L_B)$ for various values of k'_A/k'_B , as given on the different curves. $P_i = 2$ atm; $P_o = 1$ atm.

used as stationary phases. Columns were coated by the dynamic method using a mercury plug¹⁹. The solution of stationary phase (0.15–0.30 ml of 5–26% solutions) was sucked into the capillary tube followed by a plug of mercury (*ca.* 30 cm). The vacuum was then disconnected and the mercury plug was pushed through the column by compressed nitrogen at 0.5–5 cm/sec.

The columns were conditioned with nitrogen at a flow-rate of 0.5 ml/min, with temperature programming at the rate of 4°C/min from 50 to 190°C, the latter temperature being maintained for 60 min.

The gas chromatograph was a Fractovap Model 2150 (Carlo Erba, Milan, Italy) equipped with a flame-ionization detector (FID) and an inlet stream splitter. The column tip was carefully inserted into the jet of the FID. Samples were injected using a 10- μ l Hamilton microsyringe. Hydrogen or nitrogen was used as the carrier gas.

The capillary columns were characterized by the capacity factors (k') and the efficiency was expressed as the number of theoretical (n) and effective (N) plates and the separation numbers (TZ) for hydrocarbons and polychlorinated biphenyls (PCBs). Most characteristics were derived from distances measured on paper charts; a magnifying glass was used for peak-width measurements. Retention times of the PCBs and of n -alkanes used for the calculation of retention indices were measured with a stop-watch.

Column characteristics

Column A (122 m \times 0.25 mm I.D.). The column was coated with 0.3 ml of a 15% solution of Apiezon L in n -hexane, using a pressure of 30 cmHg and a velocity of 3 cm/sec (other data are given in Table I).

Column B (93 m \times 0.25 mm I.D.). The column walls were deactivated with hexamethyldisilazane (HMDS) (2 h at 180°C) and the excess of HMDS was removed

by rinsing the column with 3 ml of dichloromethane. The column was further treated with 0.3 ml of a 5% solution of Carbowax 20M in dichloromethane using a pressure of 30 cmHg and a velocity of 0.3 cm/sec. The excess of Carbowax 20M was removed by rinsing the column with 3 ml of dichloromethane²⁴. The column was coated with 0.3 ml of a 5% solution of hydrocarbon C₈₇²³ in *n*-hexane using a pressure of 30 cmHg with a velocity of 3 cm/sec (other data are given in Table I).

Column C (116.4 m × 0.24 mm I.D.). The column was coated with 0.3 ml of a 15% solution of Apiezon L in *n*-hexane using a pressure of 30 cmHg and a velocity of 3 cm/sec. The original column was cut into six parts and the regularity of the film thickness was checked by analysing *n*-octadecane at 180°C. The capacity ratios of the four centre pieces agreed to within ±2% relative²⁵. These four pieces when coupled together with PTFE shrinkable tubing gave a 77.6-m column (column C in Table I).

Column D (92 m × 0.25 mm I.D.). The column walls were etched with methyl trifluorochloroethyl ether as described by Tesarik and Novotny²⁶. The column walls were deactivated with Carbowax 20M²⁴ and coated with 0.3 ml of a 10% solution of Carbowax 20M in dichloromethane using a pressure of 30 cmHg and a velocity of 3 cm/sec. The original column was cut into six parts and the four centre pieces were coupled to produce a 56.6-m column (column D in Table I).

TABLE I

CHARACTERISTICS OF THE GLASS CAPILLARY COLUMNS FOR *n*-OCTADECANE (180°C)

Characteristic	Apiezon L		Hydrocarbon C ₈₇ : column B	Carbowax 20M: column D
	Column A	Column C		
\bar{u} (cm/sec)	22.7	13.7*	18.5	11.0*
k'	3.45	3.86	1.07	4.38
n	346,700	289,700	342,000	123,300
n/L (m ⁻¹)	2840	3730	3670	2670
N	208,400	182,700	91,400	123,000
N/L (m ⁻¹)	1700	2350	980	2170
TZ	86**	41***	76**	38**

* Measured with nitrogen as carrier gas; hydrogen was used with the other columns.

** Found between *n*-C₁₈ and *n*-C₂₀.

*** Found between *n*-C₂₀ and *n*-C₂₁.

RESULTS AND DISCUSSION

To test the applicability of eqns. 4 and 10, the capacity factor (k') for *n*-octadecane was determined on two glass capillary columns coated with Apiezon L (column A) and hydrocarbon C₈₇ (column B). The capacity ratios measured under the given conditions for C₁₀–C₂₀ *n*-alkanes were almost independent of the inlet pressure, which is in contradiction to the results published for packed columns⁴ and suggests that the inner diameter of the column and the film thickness of the stationary phase are fairly uniform along the whole column.

Knowing the capacity factors on the individual columns, measurements were

TABLE II
CHARACTERISTICS OF THE COMBINATIONS OF COLUMNS A AND B (180°C)

	Column order	
	AB	BA
\bar{v} (cm/sec)	19.7	12.5
k'	2.66	2.31
k'_{calc}	2.71	2.49
n	567,000	736,000
n/L (m ⁻¹)	2640	3420
N	299,500	342,000
N/L (m ⁻¹)	1390	1590
TZ^*	109	115

* Found between $n\text{-C}_{18}$ and $n\text{-C}_{20}$.

performed on the two columns coupled in series, in the two possible orders (AB and BA). The results are given in Table II, together with the capacity factors of n -octadecane (k'_{calc}) calculated from eqns. 4 and 10 and the data in Table I. The agreement between the measured and calculated capacity factors is within $\pm 2\%$ relative for the column combination AB and within $\pm 8\%$ relative for the column combination BA, and thus seems to depend on the column order. It is better when the column having the larger capacity ratio (column A) precedes that with the smaller capacity ratio (B), which agrees with results published for packed columns⁴ and corresponds to the fact that the solute spends a much longer time on the first column, on which it is more retained and through which the gas velocity is smaller than on the second column.

Thus, as predicted from eqn. 10, the change in the capacity factor with the

TABLE III
CHARACTERISTICS OF COMBINATIONS OF COLUMN C AND DIFFERENT PARTS OF COLUMN D (180°C)

	Carbowax 20M column (D) lengths (m)			
	15.5	29.8	44.5	56.6
\bar{u}^* (cm/sec)	12.6	12.8	13.3	11.8
k'^{**}	3.91	3.98	4.09	4.26
k'_{calc}^{**}	3.90	3.94	3.97	4.02
n	323,000	380,000	400,000	420,000
n/L (m ⁻¹)	3480	3500	3270	3260
N	205,000	242,000	258,000	275,000
N/L (m ⁻¹)	2200	2200	2100	2050
TZ^{***}	46	48	50	52

* Carrier gas was nitrogen.

** Found for 3,4,4'-trichlorobiphenyl (peak 33 in Fig. 4 and in Table IV), values calculated from eqn. 14.

*** Found between $n\text{-C}_{20}$ and $n\text{-C}_{21}$.

column order is due only to the change in the average column pressures \bar{P}_A and \bar{P}_B resulting from reversal of the column order.

It is generally accepted that the separation number (TZ) characterizes the column separation power; however, TZ depends on the n -alkanes chosen for its calculation. For instance, on column A at 100°C we found $TZ = 75$ between n -C₁₀

TABLE IV

RETENTION INDICES OF SOME POLYCHLOROBIPHENYLS AT 180°C ON COMBINATIONS OF AN APIEZON L COLUMN AND CARBOWAX 20M COLUMNS OF VARIOUS LENGTHS (L_B)

Linear relationship between retention indices and Carbowax 20M column length.

Peak No.	Identification*	Equation	Correlation coefficient
1	2,2'-	$I = 2.122 L_B + 1630.2$	0.9996
2	2,3'-	$I = 1.804 L_B + 1719.9$	0.9999
3	2,4'-	$I = 1.789 L_B + 1739.9$	0.9997
4	2,2',6'-	$I = 2.305 L_B + 1731.6$	0.9995
5	2,2',5'-	$I = 1.906 L_B + 1792.9$	0.9997
6	2,2',4'-	$I = 1.789 L_B + 1805.8$	0.9997
7	2,3',6'-	$I = 1.910 L_B + 1809.8$	0.9997
8	2,2',3'-	$I = 2.189 L_B + 1816.6$	0.9995
9	2,4',6'-	$I = 1.917 L_B + 1834.8$	0.9997
10	4,4'-	$I = 1.806 L_B + 1845.7$	0.9997
11	2,2',5,6'-	$I = 2.042 L_B + 1881.0$	0.9996
12	2,3',5'-	$I = 1.617 L_B + 1890.5$	0.9997
13	2,2',4,6'-	$I = 1.534 L_B + 1897.4$	0.9996
14	2,5,4'-	$I = 1.925 L_B + 1903.4$	0.9996
15	2,4,3'-	$I = 2.028 L_B + 1904.8$	0.9986
16	2,5,4'-	$I = 1.632 L_B + 1908.8$	0.9997
17	2,3,3'-	$I = 2.234 L_B + 1911.1$	0.9998
18	2,4,4'-	$I = 1.532 L_B + 1917.4$	0.9994
19	3,4,2'-	$I = 1.741 L_B + 1918.5$	0.9997
20		$I = 1.883 L_B + 1931.2$	0.9997
21		$I = 1.584 L_B + 1955.0$	0.9996
22	2,2',5,5'-	$I = 1.732 L_B + 1954.9$	0.9998
23	2,2',4,5'-	$I = 1.619 L_B + 1968.1$	0.9996
24		$I = 1.542 L_B + 1969.8$	0.9996
25	2,2',3,5'-	$I = 1.984 L_B + 1977.9$	0.9997
26	2,2',4,4'-	$I = 1.517 L_B + 1983.0$	0.9996
27	2,3',5',6'-	$I = 1.829 L_B + 1985.6$	0.9994
28	2,2',3,4'-	$I = 1.867 L_B + 1992.4$	0.9997
29	3,4',5'-	$I = 1.953 L_B + 1998.5$	0.9996
30	3,5,4'-	$I = 1.881 L_B + 2001.6$	0.9992
31		$I = 2.229 L_B + 2003.4$	0.9998
32	2,6,3',4'-	$I = 1.833 L_B + 2012.8$	0.9997
33	3,4,4'-	$I = 1.789 L_B + 2035.9$	0.9997
34	2,5,3',5'-	$I = 1.914 L_B + 2046.4$	0.9996
35	2,4,3',4'-	$I = 1.591 L_B + 2090.0$	0.9997
36		$I = 1.352 L_B + 2091.5$	0.9995
37	3,4,5,2'-	$I = 1.500 L_B + 2098.8$	0.9996
38	2,3',4,4'-	$I = 1.821 L_B + 2112.2$	0.9997
39	2,3,3',4'-	$I = 1.716 L_B + 2119.4$	0.9996
40		$I = 1.512 L_B + 2131.4$	0.9987

* Positions of chlorine atoms in PCB molecule.

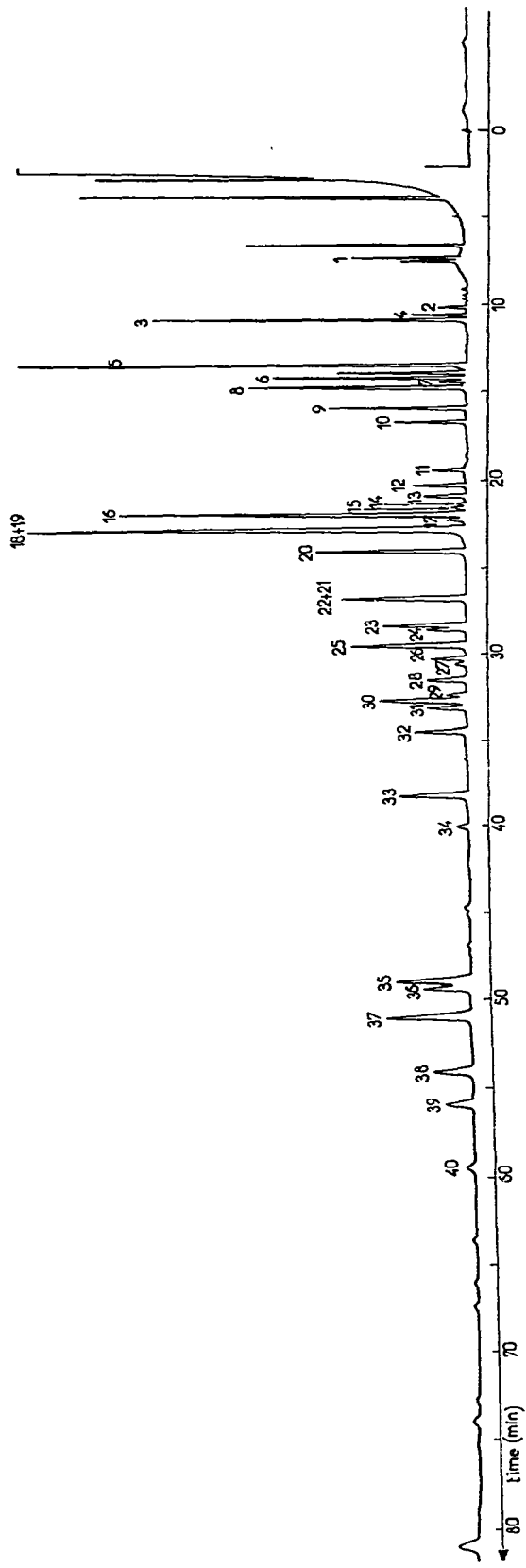


Fig. 4. Separation of a mixture of PCBs and *n*-alkanes on Apiezon L (column C) at 180°C. Peak numbers correspond to those in Table IV.

and $n\text{-C}_{11}$ whereas at 180°C we obtained $TZ = 86$ between $n\text{-C}_{18}$ and C_{20} (cf., Table I). Therefore, the separation numbers given in Tables I–III do not characterize the maximal separation power of the columns, but permit an estimation of the column performances under the test conditions. As the evaluation of column separation power depends on several factors, our results concerning this problem will be discussed separately²⁷.

Some characteristics of the combinations of column C and an increasing number of pieces of column D are given in Table III. In this column series the first column (column C) contains Apiezon L but, owing to the smaller film thickness, it has a smaller capacity factor for n -octadecane than the various segments of column D, which are coated with Carbowax 20M. In spite of this the measured and calculated capacity factors are in very good agreement, as shown in Table III (difference 0.2–5% relative). It can also be seen that the capacity factor does not vary linearly with the length of the Carbowax 20M column added to the Apiezon L column, but markedly faster.

Although there is no theoretical reason for this, it was interesting to examine whether the retention indices which are relatively independent of the average column pressure vary linearly with the length of Carbowax column added to the Apiezon L

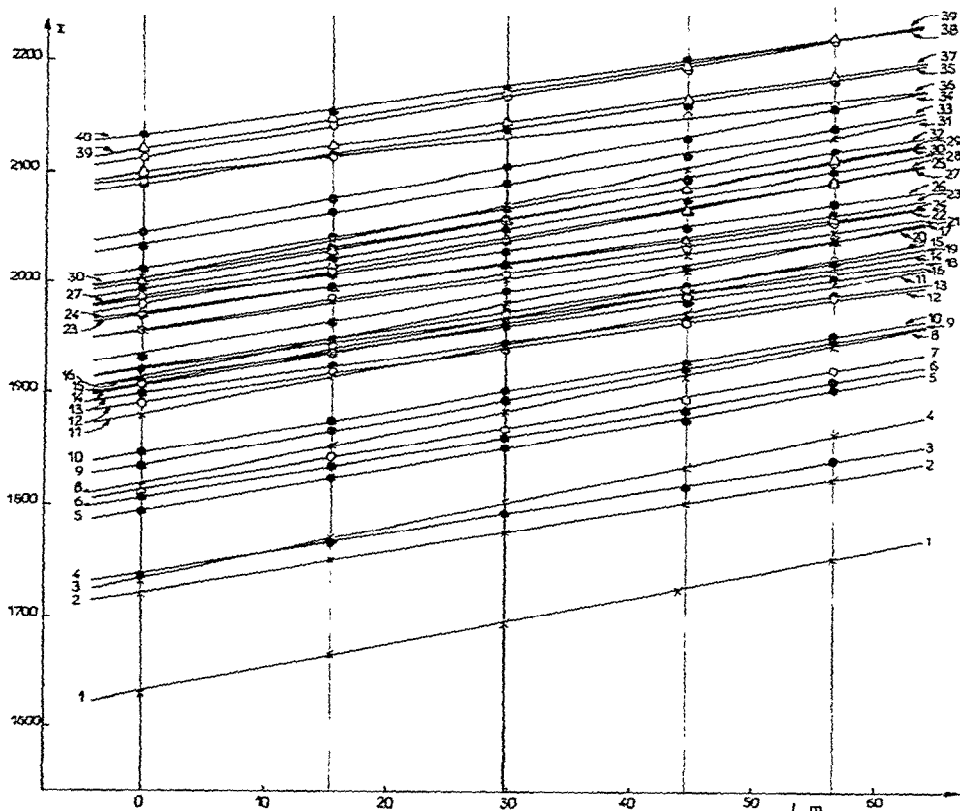


Fig. 5. Variation of retention indices of PCBs on a combination of column C (Apiezon L) and various sections of column D (Carbowax 20M) with the length of the columns (180°C).

column. Fig. 4 shows a chromatogram for the separation of a mixture of PCBs and *n*-alkanes on the Apiezon L column (column C), and the variation in the retention indices with increasing length of the Carbowax 20M column added to the Apiezon L column is given in Table IV. It can be seen that the retention indices increase linearly under the conditions used. The equations derived for these linear relationships are given in Table IV. The values of the correlation coefficients are excellent and there is an extremely small scatter of the experimental results, which originates mainly from experimental errors in the measurements and fluctuations in the experimental parameters during the analysis, as it is of the same order of the reproducibility of retention indices.

The slopes of the linear equations depend on the number of chlorine atoms and their positions on the diphenyl ring system. Use of the data in Table IV or Fig. 5 allows the determination of the optimal length of the Carbowax 20M column that permits complete resolution of the mixture. This optimization also involves the selection of the column temperature and the length of the Apiezon L column.

It must be emphasized that the linear dependence of the retention indices on the length of one of the two columns in the series is an experimental result valid for the particular analysis studied here, and it may be extrapolated to other situations only with caution. This is explained by the fact that the variation of the retention index is relatively slow, the largest change when a 56-m Carbowax 20M column is added to the Apiezon L column being an increase of 131 units, and the smallest change an increase of 85 units. More polar compounds could exhibit larger changes and the plot of *I* versus L_B some curvature.

ACKNOWLEDGEMENTS

We are grateful to E. Kováts (Lausanne) for the gift of a sample of hydrocarbon C₈₇. One of us (J.K.) acknowledges the S.E.A. Foundation for a research grant.

LIST OF SYMBOLS

j	Correction factor for gas compressibility (eqn. 6)
k	Column permeability ($= d_c^2/32$ for open-tubular columns) (eqn. 1)
k'	Column capacity factor (eqn. 5)
k'_A, k'_B	Capacity factors for columns A and B, respectively (eqn. 7)
k'_{AB}	Apparent capacity factor for the combination of column A followed by column B (eqn. 7)
L	Column length (eqn. 5)
L_A, L_B	Lengths of columns A and B, respectively (eqn. 1)
\bar{P}	Average column pressure (eqn. 8)
\bar{P}_A, \bar{P}_B	Average pressures of columns A and B, respectively (eqn. 8)
P_i, P_o	Inlet and outlet pressures of the column or column combination, respectively (eqn. 1)
P_a	Pressure between columns A and B (eqn. 2)
t_R	Retention time of a compound (eqn. 5)
\bar{u}	Average velocity of the carrier gas (eqn. 5)

\bar{u}_A, \bar{u}_B	Average carrier gas velocity through columns A and B, respectively (eqn. 7)
u_o	Carrier gas velocity at the outlet of the column or column combination (eqn. 1)
u_a	Carrier gas velocity between columns A and B (eqn. 2)
η	Carrier gas viscosity (eqn. 1)

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