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Theoretical calculation of the retention of chlorobenzenes on non-polar and polar capillary columns connected in series

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ABSTRACT

The retention values of chlorobenzenes on serially linked wide-bore open tubular columns were theoretically calculated and compared with experimental data. The capacity factors measured with the two columns (non-polar SPB 1 and polar Supelcowax 10) connected in direct and reversed order were found to agree with those predicted by theory.

INTRODUCTION

The retention values on serially linked gas chromatographic (GC) columns or on mixed stationary phases, prepared in order to separate complex samples with a unique analysis, can be predicted by approximate theories [1–3] or tentative methods [4,5]. The serial arrangement of polar and non-polar packed columns for the analysis of halocarbons in drinking water by the headspace extraction technique [6–9] was optimized with the window diagram procedure devised by Laub and Purnell [10–12].

Further research was carried out on the optimization procedures of mixed-phase packed columns [13] and of wide-bore capillary columns [14]. In the latter instance, two wide-bore (60 m × 0.75 mm I.D.) columns of different polarity (polydimethylsiloxane and polyglycol bonded phases, respectively) whose individual behaviour for the separation of 30 halomethanes, -ethanes and -ethenes has been previously investigated [15], were connected in series in direct and reversed order, and the results were linearly interpolated as a function of the relative lengths of the two columns. This "practical" procedure permitted the best resolution of the proposed mixture.

A theoretical evaluation of the performance of serially connected wide-bore open-tubular columns for the separation of 25 aromatics, halogenated alkanes and alkenes, acetates, ketones and alcohols, was carried out [16] using the procedure developed in a series of papers by Purnell and co-workers [17–23].

This paper describes the development of the procedure via the analysis of chlorobenzenes at different column temperatures, in order to verify whether the theory is valid for the prediction of the behaviour of the retention when both the column polarity and the analysis temperature are changed.

The main advantages of using large diameter open-tubular columns are their greater capacity, the

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possibility of direct injection of the whole sample, and the avoidance of discrimination between compounds with different boiling points in the splitting system [14,15,24,26]. Routine analysis of environmental samples is therefore more simple and reliable.

EXPERIMENTAL

The analyses were carried out by using a Varian (Palo Alto, CA, USA) Model 3400 gas chromatograph equipped with a standard flame ionization detector and a split–splitless capillary injector. Two wide-bore bonded-phase glass capillary column (60 m × 0.75 mm I.D.) with a film thickness of 1 μm were used: a non-polar dimethylpolysiloxane (SPB 1) and a polar polyethylene glycol, Supelcowax 10 (WAX 10) obtained from Supelco (Bellefonte, PA, USA). The columns were connected to the injector and to the detector with short pieces of flexible fused-silica deactivated capillary tubing (0.32 mm I.D.) and zero-volume connections obtained by inserting the fused-silica tubing into the end of the glass capillary. Serial arrangement was made with 10 cm of the same fused-silica tubing.

Table I shows the boiling temperatures and molecular masses of the analysed compounds; standard solutions in CS$_2$ in concentrations ranging between 0.1 and 1 g l^{-1} were used. Sample volumes up to 1 μl were injected (splitless) in order to verify whether the theoretical procedure is applicable when the use of large samples is necessary for trace analysis. Dead times were determined by methane elution. 1-Bromo-2-chlorobenzene was used as the internal standard.

Flow-rates were measured by a bubble meter and corrected to the column temperature. The column inlet pressure was measured, directly at the injector septum, by means of a mercury micromanometer with a precision of ±2 Torr (226 Pa). The outlet pressure was measured with a Fortin-type precision barometer, supplied by Filotecnica Salmoiraghi (Milan, Italy).

Highly purified nitrogen was used as the carrier gas. Helium or hydrogen are superior to nitrogen because they offer faster analysis times and provide more resolving power at flow-rates higher than optimum [26], but nitrogen is used as the carrier and make-up gas in routine analyses carried out with the electron capture detector, and therefore we were able to ascertain the true resolution that one can reasonably obtain without special flow systems and

TABLE I

BOILING TEMPERATURE AND MOLECULAR MASSES OF THE ANALYSED COMPOUNDS, AND THEIR ADJUSTED RETENTION TIMES AT 150°C, ON SPB 1 AND WAX 10 COLUMNS

Compound	Boiling temperature (°C)	Molecular mass	t'_R, SPB 1 (min)	t'_R, WAX 10 (min)
(1) Chlorobenzene (**1**)	132	112.5	0.58	1.45
(2) 1,3-Dichlorobenzene (**2**)	172	147.0	1.37	3.43
(3) 1,4-Dichlorobenzene (**3**)	173	147.0	1.37	3.83
(4) 1,2-Dichlorobenzene (**4**)	179	147.0	1.58	4.72
(5) 1,3,5-Trichlorobenzene (**5**)	208	181.4	2.59	5.18
(6) 1,2,4-Trichlorobenzene (**6**)	214	181.4	3.15	8.60
(7) 1,2,3-Trichlorobenzene (**7**)	218	181.4	3.73	12.18
(8) 1,2,3,5-Tetrachlorobenzene (**8**)	246	215.9	6.41	14.90
(9) 1,2,4,5-Tetrachlorobenzene (**9**)	243–246	215.9	6.44	15.51
(10) 1,2,3,4-Tetrachlorobenzene (**10**)	254[a]	215.9	7.88	25.28
(11) Pentachlorobenzene (**11**)	276	250.3	15.02	36.99
(12) Hexachlorobenzene (**12**)	332	284.8	33.53	79.44
(13) 1-Bromo-2-chlorobenzene (**13**)	204[b]	191.45	2.31	8.54

[a] At 761 mmHg.

[b] At 765 mmHg.

different carrier and make-up gas. The make-up gas flow-rate to the detector was set at a constant 30 ml/min, independent of the flow-rate through the column. The injector and detector temperatures were 200 and 250°C, respectively. Column temperatures ranging from 120 to 195°C were used.

The chromatograms were integrated with a Varian Model 4290 integrating printer–plotter, and the calculations carried out on IBM personal computers by using LOTUS 123 programs (Lotus Development, Cambridge, MA, USA).

The calculation method followed the theory described fully in refs. 16 and 23. The main definitions and equations are reported here.

The overall retention time, t_R, of a solute on two columns linked together is:

$$t_R = t_{RF} + t_{RB} \qquad (1)$$

where F and B indicate the front and back column, respectively. The partition factor, k', is related to the fundamental partition coefficient, k_R, and to the retention time, by

$$k' = k_R V_1/V_m = (t_R/t_d) - 1 \qquad (2)$$

where V_1 is the volume of liquid phase, V_m is the volume of gas phase and t_d is the retention time of unretained solute or dead time. The overall retention time on the linked system is therefore

$$t_R = (t_{dF} + t_{dB})(1 + k') = t_{dF}(1 + k'_F) + t_{dB}(1 + k'_B) \qquad (3)$$

By introducing the function $P = t_{dF}/t_{dB}$ and rearranging eqn. 3:

$$k' = (Pk'_F + k'_B)/(P + 1) \qquad (4)$$

it is possible to predict k' for each solute by measuring its k'_F and k'_B values on the single column and determining P for the combination.

P can be obtained [23] from the equation

$$P = (L_B R_{FB}/L_F R_{FF})(V_{MF}/V_{MB})^2(p_i^3 - p^3)/(p^3 - p_o^3) \qquad (5)$$

where L_B and L_F are the column lengths, V_{MB} and V_{MF} the column free volumes, p_i and p_o the inlet and outlet pressure, R_{FF} and R_{FB} the resistance to gas flow, and p the junction pressure.

The following equation

$$t_d = (2LR_F/3)(p_i^3 - p_o^3)/(p_i^2 - p_o^2)^2 \qquad (6)$$

shows that, for an ideal gas, the plot of t_d against the pressure function $(p_i^3 - p_o^3)/(p_i^2 - p_o^2)^2$ is linear, and has a slope $(2LR_F/3)$. R_F and V_M can be calculated by measuring t_d at various pressures:

$$V_M = JF_c t_d \qquad (7)$$

where J is the James–Martin compressibility factor and F_c the volumetric flow-rate corrected at the column temperature.

The junction pressure p is:

$$p = \left(\frac{p_i^2 - l_F[P_i^2 - (V_{MB}R_{FF}/V_{MF}R_{FB})p_o^2]}{1 - l_F[1 - (V_{MB}R_{FF}/V_{MF}R_{FB})]}\right)^{1/2} \qquad (8)$$

where $l_F = L_F/(L_F + L_B)$ is the length fraction of the front column.

It is then possible (eqn. 5) to obtain P, if some values of p_i, p_o, L_F and L_B are selected and the values of R_F and V_M are known from eqns. 6 and 7 for the individual columns.

By introducing the function f_F, so that

$$k' = f_F k'_F + f_B k'_B \qquad (9)$$

where $f_F + f_B = 1 f_F$ can be obtained by combination of eqns. 4 and 9:

$$f_F = P/(P + 1) \qquad (10)$$

As k' for the serial system is linear, it is possible to plot k' as a function of f_F over the range 0–1.

RESULTS AND DISCUSSION

Table I lists the physical properties and the adjusted retention times of the analysed compounds on the two columns at the same temperature, 150°C, in order to show the performance of the columns in isothermal analysis conditions. Some pairs of compounds are not resolved on the non-polar column, whereas the polar column can separate all the chlorobenzenes but requires a long analysis time, owing to the maximum temperature limit of the column, that cannot be overcome.

Table II shows the values of the capacity factor, k', for the two columns in the range 120–180°C for the non-polar (SPB 1) and 150–195°C for the polar (WAX 10), in order to obtain three values of k' at reasonable temperature interval and with acceptable retention times.

The V_M values, calculated from eqn. 7 starting from the t_d measured in the pressure range between 3 and 13 p.s.i., were 21.13 ± 1.05 on SPB 1 and 22.69 ± 1.02 on WAX 10. The R_F values, previously

TABLE II

CAPACITY FACTORS FOR SPB 1 AND WAX 10 COLUMNS AT DIFFERENT TEMPERATURES

Column lengths, 60 m; carrier gas, nitrogen.

Compound	k'					
	SPB 1			WAX 10		
	120°C	150°C	180°C	150°C	180°C	195°C
Chlorobenzene	0.283	0.133	0.065	0.394	0.209	0.157
1,3-Dichlorobenzene	0.712	0.315	0.153	0.934	0.449	0.329
1,4-Dichlorobenzene	0.729	0.315	0.153	1.044	0.493	0.357
1,2-Dichlorobenzene	0.837	0.364	0.177	1.286	0.603	0.434
1,3,5-Trichlorobenzene	1.463	0.596	0.278	1.410	0.647	0.463
1,2,4-Trichlorobenzene	1.827	0.725	0.336	2.342	1.023	0.715
1,2,3-Trichlorobenzene	2.199	0.859	0.389	3.318	1.407	0.966
1,2,3,5-Tetrachlorobenzene	4.086	1.477	0.630	4.057	1.676	1.139
1,2,4,5-Tetrachlorobenzene	4.112	1.482	0.634	4.223	1.736	1.172
1,2,3,4-Tetrachlorobenzene	5.149	1.815	0.759	6.878	2.700	1.788
Pentachlorobenzene	10.691	3.446	1.341	10.080	3.790	2.463
Hexachlorobenzene	26.634	7.689	2.744	21.646	7.577	4.771
1-Bromo-2-chlorobenzene	1.198	0.530	0.265	2.324	1.026	0.720

calculated for the same columns [16], were $2.78 \cdot 10^5$ Nsm^{-3} (SPB 1) and $2.33 \cdot 10^5$ Nsm^{-3} (WAX 10). By using these values and the above equations, the k' values of the linked 60 + 60 m columns, connected in the two sequences SPB 1 + WAX 10 and WAX 10 + SPB 1 were calculated. These are compared with the experimental results in Tables III and IV. The fractional differences Δ%, calculated from

TABLE III

COMPARISON OF CALCULATED AND EXPERIMENTAL k' VALUES ON SERIALLY LINKED SPB 1 AND WAX 10 COLUMNS

Column lengths, 60 m; P value at 150 and 180°C, 1.185.

Compound	T = 150°C			T = 180°C		
	k' (calc)	k' (exp)	Δ%	k' (calc)	k' (exp)	Δ%
Chlorobenzene	0.252	0.247	−2.02	0.129	0.129	0
1,3-Dichlorobenzene	0.598	0.591	−1.18	0.288	0.289	0.35
1,4-Dichlorobenzene	0.648	0.644	−0.62	0.308	0.311	0.96
1,2-Dichlorobenzene	0.785	0.780	−0.64	0.372	0.373	0.27
1,3,5-Trichlorobenzene	0.968	0.964	−0.41	0.446	0.448	0.45
1,2,4-Trichlorobenzene	1.464	1.464	0	0.650	0.651	0.15
1,2,3-Trichlorobenzene	1.984	1.988	0.20	0.854	0.860	0.70
1,2,3,5-Tetrachlorobenzene	2.657	2.672	0.56	1.108	1.119	0.98
1,2,4,5-Tetrachlorobenzene	2.736	2.758	0.80	1.138	1.145	0.61
1,2,3,4-Tetrachlorobenzene	4.131	4.169	0.91	1.647	1.662	0.90
Pentachlorobenzene	6.481	6.509	0.43	2.461	2.492	1.24
Hexachlorobenzene	14.075	14.124	0.35	4.957	5.018	1.21
1-Bromo-2-chlorobenzene	1.351	1.366	1.10	0.613	0.619	0.97

TABLE IV

COMPARISON OF CALCULATED AND EXPERIMENTAL k' VALUES ON SERIALLY LINKED SPB 1 AND WAX 10 COLUMNS

Column lengths, 60 m; $P = 1.398$ at 150°C; $P = 1.396$ at 180°C.

Compound	T = 150°C			T = 180°C		
	k' (calc)	k' (exp)	Δ%	k' (calc)	k' (exp)	Δ%
Chlorobenzene	0.285	0.295	3.37	0.149	0.158	5.69
1,3-Dichlorobenzene	0.676	0.682	0.87	0.325	0.335	2.98
1,4-Dichlorobenzene	0.740	0.746	0.80	0.351	0.361	2.77
1,2-Dichlorobenzene	0.901	0.906	0.55	0.425	0.434	2.07
1,3,5-Trichlorobenzene	1.070	1.079	0.83	0.493	0.504	2.18
1,2,4-Trichlorobenzene	1.668	1.671	0.18	0.736	0.743	0.94
1,2,3-Trichlorobenzene	2.292	2.289	−0.13	0.982	0.989	0.71
1,2,3,5-Tetrachlorobenzene	2.981	2.986	0.17	1.239	1.251	0.96
1,2,4,5-Tetrachlorobenzene	3.080	3.087	0.23	1.276	1.283	0.54
1,2,3,4-Tetrachlorobenzene	4.767	4.759	−0.17	1.890	1.893	0.18
Pentachlorobenzene	7.313	7.325	0.16	2.768	2.776	0.29
Hexachlorobenzene	15.826	15.844	0.11	5.562	5.571	0.16
1-Bromo-2-chlorobenzene	1.576	1.588	0.75	0.708	0.718	1.39

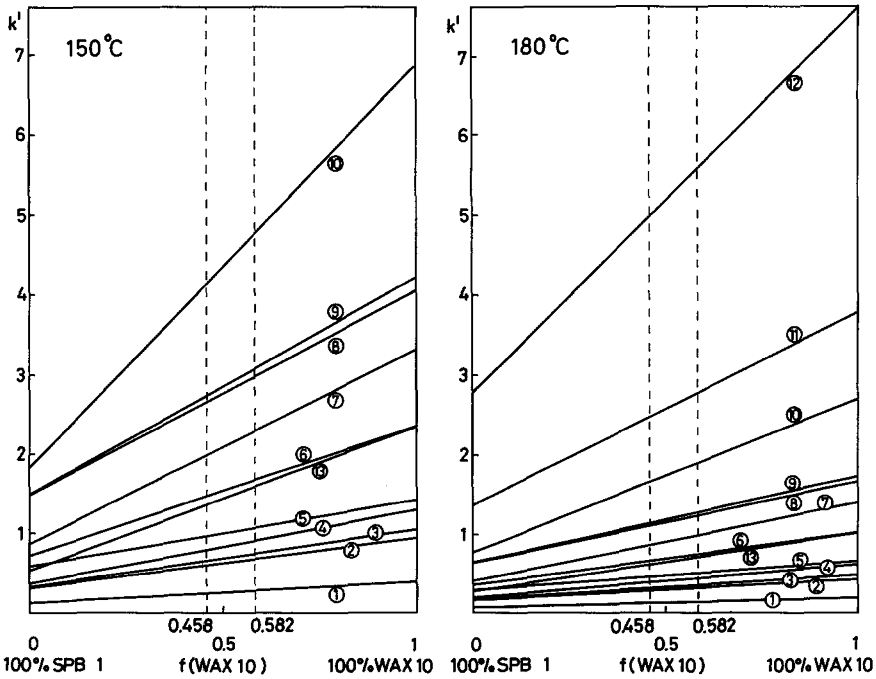

Fig. 1. Values of k' on non-polar (SPB 1) and polar (WAX 10) columns at two temperatures of analysis. The compound numbers are as in Table I.

the ratio of the difference between the two values to the experimental value are also shown.

Fig. 1 shows the change of k' values at 150 and 180°C as a function of the composition of the column, expressed as the fraction f of the WAX 10, ranging from zero to one. The values of f equal to 0.458 and to 0.582 marked on the abscissa correspond to the SPB 1 + WAX 10 and to the reversed sequence of the two 60 m columns, respectively.

These results confirm that the theory is suitable for the prediction of the k' values in a range of boiling temperatures of the compounds in the sample (132–332°C), which is much wider than that investigated by Jones and Purnell [23] for phenols (191–227°C) and by us in a previous work [16] for various compounds (40–155°C). The capacity factors shown in Table II and the discussed theory permit the calculation of k' values for every compound in the f_F range between 0 and 1, either by using eqn. 9 or by graphical interpolation from Fig. 1. From k' values for two solutes 1 and 2 at a given temperature as a function of f_F, the solvent efficiency $\alpha = k'_2/k'_1$ can be obtained. By plotting α values for the $m!/2(m-2)!$ pairs of solutes as a function of f_F, the so-called window diagram is obtained [28], which permits the f_F value giving the best separation of the less resolved pair to be calculated.

By the following this procedure, an optimum f_F value of 0.75 for the polar column was obtained, corresponding to $\alpha = 1.037$ for the less resolved pair, the compounds **8** and **9** of Table I. A capacity factor $k' = 3.54$ for compound **9** can also be calculated.

By using the equation

$$N_{\text{req}} = 16R^2 \left(\frac{\alpha}{\alpha - 1}\right)^2 \left(\frac{1 + k'_2}{k'_2}\right)^2 \tag{11}$$

that is useful in determining the number of plates required for the baseline separation of two peaks, with an absolute resolution $R = 1.5$ (percentage resolution 99.7%), one obtains a number of theoretical plates $N = 46\,481$. An experimental value of

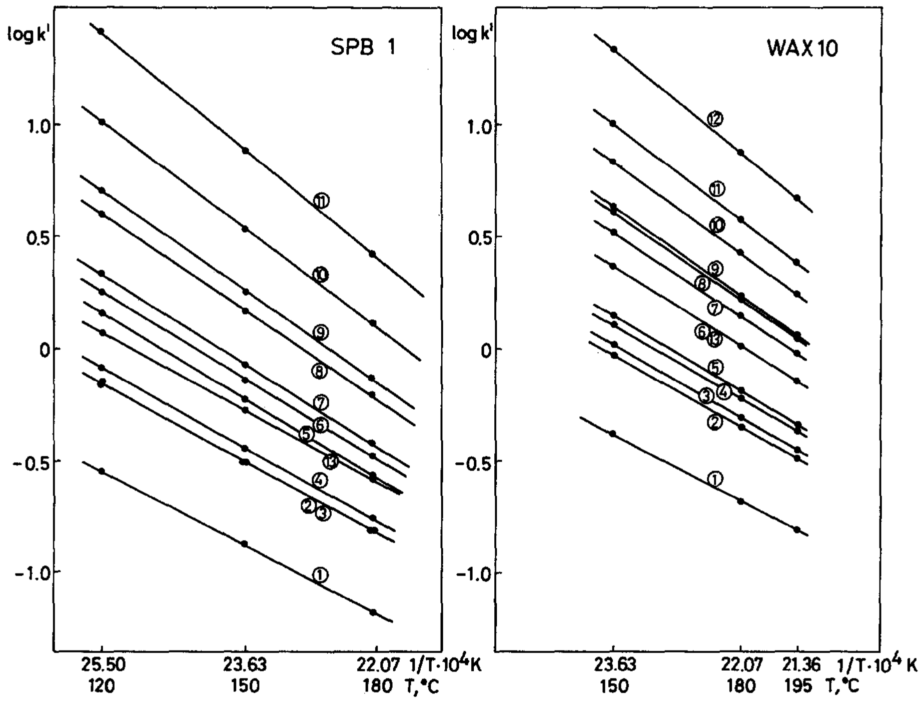

Fig. 2. Arrhenius plots (log k' as a function of the reciprocal of absolute temperature) on non-polar (SPB 1) and polar (WAX 10) columns. The compound numbers are as in Table I.

0.09 cm for the height equivalent to theoretical plate (HETP) was obtained: therefore the baseline resolution of peaks **8** and **9** requires a mixed column with the overall length of 41.83 m.

The l_F value, *i.e.*, the length fraction of the two columns, can be obtained by fixing p_i at the value corresponding to the minimum of the Van Deemter equation, with known p_o, γ and f_F values (in either mode 0.75 or 0.25), and by calculating P'; the value of $l_F = 0.61$ is thus obtained for the series arrangement WAX 10 + SPB 1, and therefore the mixed column having a total length of 41.83 m should be formed by 25.51 m of WAX 10 followed by 16.31 m of SPB 1, being $p = 20.75$ and $P = 1.44$. The non-polar–polar arrangement should be formed by 3.6 m of SPB 1 followed by 38.23 m of WAX 10, being $p = 25.36$ and $P = 1.20$.

From the practical point of view, however, the separation can be obtained by maintaining the columns at full length, because the combination WAX 10 + SPB 1 with $l_F = 0.50$ permits a baseline resolution of the critical pair **8** and **9**; with a $f_F = 0.50$, a value of $\alpha = 1.032$ is obtained with $N_{req} = 61\,580$, corresponding to a total length of 55.4 m, which is much shorter than the 120 m of the two complete columns. The reversed combination, SPB 1 + WAX 10, with $l_F = 0.50$ is also suitable, because calculations give a resolution that is sufficient, although not at the baseline ($R = 0.95$).

This procedure was repeated for all the component pairs of the sample to predict the complete pattern of the chromatogram, by excluding only those pairs with α values greater than 1.1 for all the compositions of the column system, because they do not have interference problems. This procedure may be troublesome when the presence in the sample of compounds of different polarities results in a complicated network of intersecting lines in the diagram (Fig. 1) of k' as a function of f [15,16]. The ideal f value can be theoretically calculated for isothermal conditions and permits the analysis to be optimized for the resolution. The effect of the carrier gas pressure on the resolution was reported previously [16]. Also the column temperature may be used to optimize the separation [29]; in order to check how the analysis temperature can be increased without unacceptable loss of resolution, the effect of temperature on k' values must be known.

The dependence of log k' on the reciprocal of the absolute temperature is linear (Fig. 2). It is therefore possible to calculate the k' value at any column temperature and, owing to the observed linearity as a function of the column composition, to predict the k' value, and then the retention time, for every combination of columns at any temperature.

In order to minimize the analysis time, the column temperature can also be programmed, mainly when the boiling temperatures of the compounds in the sample differ widely. Further research is therefore necessary to find a system that permits the use of retention data collected at various isotherm for calculating the programming rate that gives the best separation in the shortest time on mixed or serially connected columns.

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