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OPTIMIZATION OF STATIONARY PHASE SELECTIVITY FOR THE GAS-LIQUID CHROMATOGRAPHIC SEPARATION OF C₈ CYCLIC AND AROMATIC HYDROCARBONS USING SQUALANE AND LIQUID CRYSTAL GLASS CAPILLARY COLUMNS IN SERIES

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SUMMARY

A procedure is described for the computer optimization of the selectivity of capillary columns in series for the gas chromatographic separation of cyclic and aromatic hydrocarbons. The selectivity of two columns in series is given by the column length fraction: $x_B = L_B / (L_A + L_B)$, where L is the column length and A and B denote a non-polar stationary phase (squalane) and a polar stationary phase (liquid crystal), respectively. Columns of various lengths were coupled in series using shrinkable PTFE tubing. The optimization criterion used was derived from the Kováts retention indices of the solutes. At the optimum column selectivity few peak pairs were not resolved.

INTRODUCTION

The aim of the chromatography of a complex mixture is the complete separation of the sample constituents in the shortest time. Therefore, the role of optimization procedures is to establish experimental conditions that allow this aim to be achieved. The basic experimental conditions that influence capillary gas chromatographic (GC) separations are following: (1) the separation temperature; (2) the column selectivity; (3) the column separation efficiency; and (4) the column phase ratio. In addition to these main factors, capillary GC separation can be influenced by several side factors, *e.g.*, the nature of the carrier gas and its inlet pressure and the quality of the capillary column walls.

We previously published¹ an optimization algorithm for the calculation of the optimum selectivity of a chromatographic system for the separation of polychlorinated biphenyls by capillary GC. The selectivity was changed by connecting different lengths of Carbowax 20M glass capillary column to a constant length of glass capillary column coated with Apiezon L.

The aim of this paper is to show how the selectivity of the columns can be changed by connecting various lengths of both squalane and liquid crystal glass capillary columns for the separation of cyclic and aromatic hydrocarbons. The optimum selectivity of the separation system was calculated using a computer.

THEORETICAL

In a previous paper¹ we derived a relationship between the column resolution (R_{ji}) and the Kováts retention index difference (ΔI_{ji}) of two adjacent peaks (i, j):

$$\Delta I_{ji} = \frac{400}{\sqrt{N_j}} \cdot \frac{R_{ji}}{\ln \alpha} \quad (1)$$

where N_j is the number of effective plates of the column and α is the relative retention of two consecutive n -alkanes ($\alpha = t'_{R,z+1}/t'_{R,z}$), chosen such that for retention the relationship $t'_{R,z+1} > t'_{R,j} > t'_{R,i} > t'_{R,z}$ is valid.

The smallest difference in Kováts retention indices ($\Delta I_{ji,\min} = \delta$) which corresponds to a resolution $R_{ji,\min}$ was taken as a basis for the calculation of the optimization criterion (C_p). Peak pairs for which $\Delta I_{ji} > \delta$ were considered as resolved and those for which $\Delta I_{ji} < \delta$ not resolved. The optimization criterion was calculated using the equation

$$C_p = P + \left(\frac{\Delta I_k}{\delta} - 1 \right) \quad (2)$$

where P is the number of not resolved peak pairs and ΔI_k is the smallest difference in Kováts retention indices for which $\Delta I_k > \delta$.

The first term on the right-hand side of eqn. 2 (P) is the main part and the second term $[(\Delta I_k/\delta) - 1]$ a secondary part of the optimization criterion. The selectivity of two capillary columns in series can be expressed by the column length fraction^{2,3}:

$$x_B = \frac{L_B}{L_A + L_B} \quad (3)$$

where L is the column length and A and B denote a non-polar and a polar stationary phase, respectively. Kováts retention indices (I) of compounds separated on columns A and B in series can be calculated using the equation

$$I_{AB} = x_A I_A + x_B I_B \quad (4)$$

where $x_A = 1 - x_B$. The interactions of a solute with stationary phases of different polarity in two columns in series are better studied using a rearranged form of eqn. 4:

$$I_{AB} = I_A + (I_B - I_A)x_B \quad (5)$$

EXPERIMENTAL

A Fractovap 2350 gas chromatograph (Carlo Erba, Milan, Italy), equipped with a flame ionization detector and all-glass inlet splitter, was used. The velocity of the nitrogen used as the carrier gas was 7–10 cm/s in all the experiments; this is slightly above the optimum velocity or close to it. Glass capillary columns were made of soft glass, the inner wall being etched prior to phase coating, using gaseous hydrogen chloride, according to a procedure described elsewhere⁴. Single columns were coupled in series using shrinkable PTFE tubing. Retention times were measured using a stop-watch. The samples contained C₅–C₈ *n*-alkanes and C₈ cyclic and aromatic hydrocarbons (see Table I). The temperature of all the GC runs was 60°C. Five column series were used (Table II).

Columns A

A 98 m × 0.25 mm I.D. glass capillary column was coated dynamically with 0.3 ml of 15% squalane solution in *n*-pentane. In the coating procedure a mercury plug was pushed through the column at a velocity 2 cm/s using nitrogen⁵. The coated

TABLE I
SYSTEMATIC NAMES AND ABBREVIATIONS OF SAMPLE COMPONENTS

<i>Peak No.*</i>	<i>Systematic name</i>	<i>Abbreviation</i>
8	1,1,3-Trimethylcyclopentane	1,1,3-TriMeCyPe
13	1- <i>trans</i> -2- <i>cis</i> -4-Trimethylcyclopentane	1- <i>tr</i> -2- <i>cis</i> -4-TriMeCyPe
15	1- <i>trans</i> -2- <i>cis</i> -3-Trimethylcyclopentane	1- <i>tr</i> -2- <i>cis</i> -3-TriMeCyPe
17	1,1,2-Trimethylcyclopentane	1,1,2-TriMeCyPe
20	1- <i>cis</i> -2- <i>trans</i> -4-Trimethylcyclopentane	1- <i>cis</i> -2- <i>tr</i> -4-TriMeCyPe
21	1- <i>cis</i> -2- <i>cis</i> -4-Trimethylcyclopentane	1- <i>cis</i> -2- <i>cis</i> -4-TriMeCyPe
22	1- <i>cis</i> -2- <i>trans</i> -3-Trimethylcyclopentane	1- <i>cis</i> -2- <i>tr</i> -3-MeCyPe
27	1-Methyl- <i>cis</i> -3-ethylcyclopentane	1-Me- <i>cis</i> -3-EtCyPe
26	1-Methyl- <i>trans</i> -3-ethylcyclopentane	1-Me- <i>tr</i> -3-EtCyPe
28	1-Methyl- <i>trans</i> -2-ethylcyclopentane	1-Me- <i>tr</i> -2-EtCyPe
29	1-Methyl-1-ethylcyclopentane	1-Me-1-EtCyPe
34	Isopropylcyclopentane	IsoProCtPe
35	1-Methyl- <i>cis</i> -2-ethylcyclopentane	1-Me- <i>cis</i> -2-EtCyPe
37	<i>n</i> -Propylcyclopentane	<i>n</i> -ProCyPe
31a	1- <i>cis</i> -2- <i>cis</i> -3-Trimethylcyclopentane	1- <i>cis</i> -2- <i>cis</i> -3-TriMeCyPe
24	1- <i>trans</i> -4-Dimethylcyclohexane	1- <i>tr</i> -4-DiMeCyHex
25	1,1-Dimethylcyclohexane	1,1-DiMeCyHex
23	1- <i>cis</i> -3-Dimethylcyclohexane	1- <i>cis</i> -3-DiMeCyHex
31	1- <i>trans</i> -2-Dimethylcyclohexane	1- <i>tr</i> -2-DiMeCyHex
32	1- <i>trans</i> -3-Dimethylcyclohexane	1- <i>tr</i> -3-DiMeCyHex
33	1- <i>cis</i> -4-Dimethylcyclohexane	1- <i>cis</i> -4-DiMeCyHex
36	1- <i>cis</i> -2-Dimethylcyclohexane	1- <i>cis</i> -2-DiMeCyHex
39	Ethylcyclohexane	Et-CyHex
38	Ethylbenzene	EtBe
41	1,4-Dimethylbenzene	<i>p</i> -Xyl
42	1,3-Dimethylbenzene	<i>m</i> -Xyl
43	1,2-Dimethylbenzene	<i>o</i> -Xyl

* See Figs. 2 and 3.

TABLE II
CHARACTERIZATION OF THE COLUMN SERIES USED

Series No.	Abbreviation*	Stationary phase	Length (m)	x_B
1	A ₁ + A ₂	Squalane	97.9	0.00
2	B ₁ + A ₁ + A ₂	Liquid crystal + squalane	124.3	0.21
3	B ₂ + B ₁ + A ₁ + A ₂	Liquid crystal + squalane	150.3	0.35
4	B ₂ + B ₁ + A ₁	Liquid crystal + squalane	98.7	0.53
5	B ₂ + B ₁	Liquid crystal	52.4	1.00

* The abbreviations correspond to the order of columns in the oven, starting from the injection part and ending at the detector.

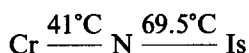
column was split into two parts: column A₁ with a length of 46.3 m and column A₂ with a length of 51.6 m.

Columns B

A 52.4 m × 0.25 mm I.D. glass capillary column was split into two parts: column B₁ with a length of 26.0 m was coated statically⁶ with a 0.25% solution of liquid crystal in methylene chloride and column B₂ with a length of 26.4 m was coated statically⁶ similarly to column B₁.

Characterization of liquid crystal

4-*n*-Pentylacetophenone (O-4-*n*-heptylbenzyl oxime) was first investigated by GC elsewhere⁷. The transition temperatures of this compound are as follows:



(Cr = solid crystalline, N = nematic, Is = isotropic).

Calculation of threshold (δ)

The threshold δ was calculated for the squalane column (A₁ + A₂ in Table II). For compounds with capacity ratio $k > 2$ it was found from eqn. 1 that $\delta = 1.00$ for $R_{ji} = 0.75$.

RESULTS AND DISCUSSION

Kováts retention indices of all compounds present in the sample mixture were determined at 60°C on the first four column series (Table II). As the column with the liquid crystal was only 52.4 m long (B₁ + B₂ in Table II) and exhibited too low a separation power, retention indices only for aromatic hydrocarbons were measured and further evaluated on this column. From the experimental Kováts retention indices the computer calculated the coefficients of eqn. 5 using the method of least squares subroutine in the OPTCOX program (Table III). From the $\Delta I = I_B - I_A$

TABLE III

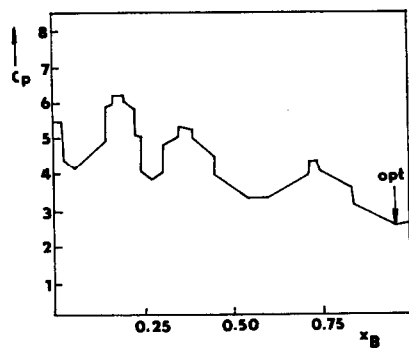
COEFFICIENTS OF EQN. 5 FOUND BY THE METHOD OF LEAST SQUARES AT 60°C AND THE CORRESPONDING CORRELATION COEFFICIENTS

Peak No.*	Abbreviation of solute**	$I_{A,i}$	ΔI_B	ΔI	r
8	1,1,3-TriMeCyPe	724.7	721.3	-3.34	-0.9930
13	1-tr-2-cis-4-TriMeCyPe	741.9	741.4	-0.52	-0.9327
15	1-tr-2-cis-3-TriMeCyPe	748.5	748.4	-0.15	-0.5204
17	1,1,2-TriMeCyPe	765.2	759.2	-5.41	-0.9913
21	1-cis-2-tr-4-TriMeCyPe	775.8	777.6	1.76	0.9811
22	1-cis-2-tr-3-TriMeCyPe	779.8	781.8	2.02	0.9922
23	1-cis-3-DiMeCyHex	786.0	791.3	5.29	0.9962
24	1-tr-4-DiMeCyHex	786.1	795.8	9.67	0.9989
25	1,1-DiMeCyHex	788.4	789.6	1.23	0.5655
26	1-Me-tr-3-EtCyPe	788.5	793.7	5.21	0.9983
27	1-Me-cis-3-EtCyPe	791.1	795.8	4.69	0.9987
28	1-Me-tr-2-EtCyPe	791.7	795.1	3.43	0.9816
29	1-Me-1-EtCyPe	794.9	798.2	3.29	0.9844
31	1-tr-2-DiMeCyHex	802.9	808.5	5.59	0.9942
32	1-cis-4-DiMeCyHex	806.5	810.2	3.65	0.9918
33	1-tr-3-DiMeCyHex	806.5	810.2	3.65	0.9918
34	IsoProCyPe	813.1	819.7	6.64	0.9892
35	1-Me-cis-2-EtCyPe	821.6	827.5	5.88	0.9838
36	1-cis-2-DiMeCyHex	830.7	835.4	4.71	0.9506
37	<i>n</i> -ProCyPe	830.7	839.8	9.08	0.9820
38	EtBe	834.5	916.0	81.54	0.9990
39	EtCyHex	835.2	842.8	7.63	0.9794
41	<i>p</i> -Xyl	848.8	940.7	91.90	0.9986
42	<i>m</i> -Xyl	851.1	935.7	84.62	0.9988
43	<i>o</i> -Xyl	869.3	960.6	91.31	0.9959

* See Figs. 2 and 3.

** See Table I.

values in Table III, the differences between the selectivities of the liquid crystal and squalane for cyclic and aromatic hydrocarbons can be seen. It is surprising that the ΔI values are not too high for cyclic hydrocarbons [less than 10 retention index units (i.u.)] and there are pairs of cyclic compounds that are not resolved on squalane as

Fig. 1. Dependence of optimization criterion (C_p) on the column length fraction (x_B) as found by computer.

well as on the liquid crystal. The highest ΔI values are found for aromatic hydrocarbons, from which one could conclude that the contribution of solute-solvent polar interactions to the retention is much higher than that of solute-solvent steric hindrance when separating aromatics on liquid crystals. However, one would then expect a much higher ΔI value for ethylbenzene than for *o*-xylene, which is not the case, the values being 81.54 and 91.31, respectively.

Knowing the coefficients of eqn. 5, the computer calculated Kováts retention indices of all solutes from all x_B values in the range 0–1 in steps of 0.005. For each x_B , the computer (i) arranged the compounds in order of increasing retention index, (ii) calculated all ΔI increments and (iii) calculated the optimization criterion from eqn. 2.

Optimal column selectivity determined by the computer as a minimum of the dependence of the optimization criterion (C_p) on the column length fraction (x_B) is shown in Fig. 1.

The reconstructed chromatograms in Figs. 2 and 3 show the dependence of the model mixture separations on the composition of the column series. For formal reasons the reconstructed chromatograms were transformed to the axes detector response (R), column B length fraction (x_B) and Kováts retention index (I). Such chromatograms illustrate only the influence of column composition selectivity on the separation and there is no direct relationship between the peak widths and Kováts retention indices in Figs. 2 and 3. The peak widths in all chromatograms are equal to those found on the squalane column ($A_1 + A_2$ in Table II).

From Fig. 1 it can be seen that the optimum selectivity corresponds to $x_B = 0.95$ if a capillary column coated with liquid crystal stationary phase had a separation

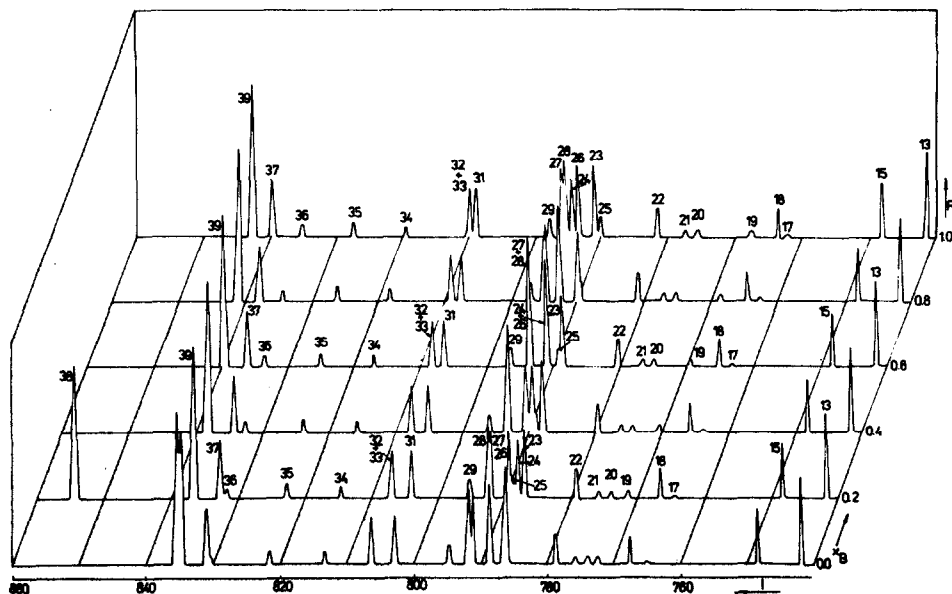


Fig. 2. Reconstructed chromatograms showing the separation of sample constituents at various column length fractions. I = Kováts retention index; x_B = column length fraction (see eqn. 3); R = detector response. For peak identification, see Table I.

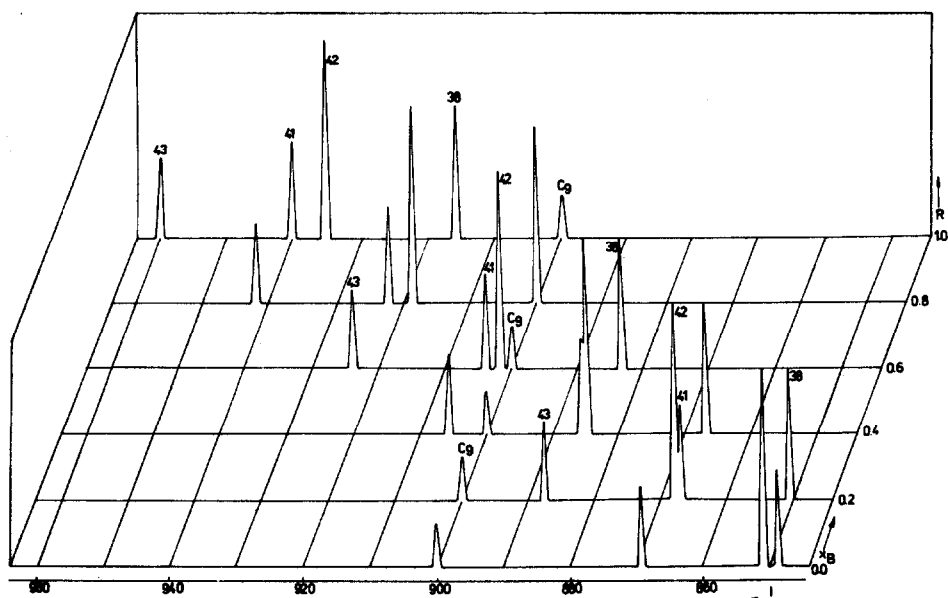


Fig. 3. Reconstructed chromatograms showing the separation of further sample constituents at various column length fractions. Axes as in Fig. 2. For peak identification, see Table I.

power comparable to that of squalane. The value $x_B = 0.95$ corresponds in Fig. 1 is $C_p \approx 2$, which shows that two pairs of peaks are not resolved at the optimal composition of the column series (peak pairs 27, 28 and 32, 33). However, peaks 32 and 33 were resolved by the analysis of the model mixtures in a very long glass capillary column (270 m) coated with squalane at 48°C^8 .

CONCLUSIONS

A computer procedure has been devised for the optimization of the selectivity of columns in series for the separation of complex mixtures. The results obtained on liquid crystal and squalane capillary columns indicate that for the characterization of liquid crystal selectivity xylenes are not the best solutes as the polar solute-solvent interactions are much greater than solute-solvent steric hindrance.

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