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WINDOW ANALYSIS OPTIMIZATION OF GAS CHROMATOGRAPHIC SEPARATIONS USING MIXED PORAPAKS

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SUMMARY

A method is developed for the optimization with respect to analysis time of chromatographic separations using columns of mixed Porapak types. The Rohrschneider approach to classification of sorbent polarity when used in conjunction with window diagram optimization provides an initial selection of potentially good binary combinations. The final selection is influenced by the high temperature stability of the Porapak types studied together with their individual efficiences at high carrier velocities. For the seven-component synthetic mixture examined, it is shown that the speed of analysis may be increased almost ten-fold by using an optimized mixed Porapak column, compared with the best performance of the individual materials.

INTRODUCTION

We have recently presented an approach to analysis time optimization of gas–liquid chromatographic (GLC) separations, encompassing not only optimal choice of packing composition and liquid loading but also the selection of stationary phases[1]. The method was applied, as an example, to the separation of a seven-component C_1–C_3 chlorinated hydrocarbon mixture on conventional packed GLC columns. An optimized baseline separation was achieved in only 73 sec with nitrogen as carrier gas, and this analysis time was further reduced to 56 sec and to 40 sec when helium and hydrogen carriers, respectively, were employed. It was suggested that further improvement in analysis time could be obtained only by improvement of column efficiences and/or the exploitation of some beneficial form of selectivity not exhibited by the range of stationary phases studied.

Some techniques employed in gas chromatography (GC) demand the use of columns with extremely low bleed characteristics, for example, electron-capture detection of traces of pesticides and their metabolites, and the interfacing of GC with mass spectrometry (GC–MS). Low-bleed liquid phases have been developed for such purposes, *e.g.* the OV and Dexil phases. In addition, liquids may be immobilised by bonding with the support surface or by *in situ* cross-linking. An alternative, as least for low-boiling and permanent gas mixtures, exists in the form of gas–solid chromatography (GSC) where column bleed is effectively eliminated. In particular, porous

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polymer beads of the styrene or ethylvinyl benzene, cross-linked with divinyl benzene type have been found to hold several advantages over other adsorbents[2–5]. They are readily produced in spherical bead form, rugged enough to withstand size separation and packing into columns, are chemically homogeneous, have large surface areas (up to 800 $m^2\ g^{-1}$) and large pore volume (up to 1.5 $cm^3\ g^{-1}$) and are relatively stable at high temperatures. Furthermore, having no active sites, highly polar substances such as underivatised fatty acids and even water may be successfully chromatographed. They are commercially available in a variety of polarities under such tradenames as Porapak (Waters Assoc.) and Chromasorb Century Series (Johns-Manville).

It has been demonstrated (*e.g.* refs. 6, 7 and 8) that the combination of different Porapaks in coupled, multi-layer or homogeneous columns can improve certain analyses with respect to both resolution and time. For homogeneously mixed packings, retention was found to be a linear function of composition[8], presumably by weight. This is as we might expect since it can be shown that for mixed adsorbents of equal porosity and mesh size

$$k' = \varphi'_A\, k'_{(A)} + \varphi'_B\, k'_{(B)} \tag{1}$$

where φ'_A, φ'_B are the bulk volume fractions of packings A and B, and $k'_{(A)}$, $k'_{(B)}$ are the capacity factors for some component with columns of pure A and B, respectively. Since the Porapaks do not vary greatly in porosity or bulk density, it follows that k' is very likely in practice, to be linearly dependent on composition expressed as a weight fraction. It was decided to examine the applicability of a methodical optimization of chromatographic parameters, by the window analysis approach, to the Porapaks and their mixtures in order to ascertain whether or not their utility in analysis may be further extended.

THEORY

In chromatography the overall time of elution of some mixture is given by

$$\begin{aligned} t_R &= t_d(1 + k'_1) = \frac{L}{\bar{u}}(1 + k'_1) \\ &= (H/\bar{u})N(1 + k'_1) \end{aligned} \tag{2}$$

where t_d is the time for elution of some non-sorbed substance, k'_1 is the capacity factor of the last component (of retention time t_R), L is the column length, $\bar{u}$ is the mean carrier velocity, N is the number of theoretical plates in the column and H is the plate height. For a separation which is just baseline for the least well resolved pair in the chromatogram,

$$t_R = (H/\bar{u})N_{req}(1 + k'_1) \tag{3}$$

Substituting the well-known equation for N_{req}[9],

$$N_{req} = 36\left(\frac{\alpha}{\alpha - 1}\right)^2\left(\frac{1 + k'}{k'}\right)^2 \tag{4}$$

where α is the relative adjusted retention of the most difficult to separate pair and k' is the capacity factor of the second of this pair gives

$$t_R = 36(H/\bar{u})\left(\frac{\alpha}{\alpha - 1}\right)^2\left(\frac{1 + k'}{k'}\right)^2(1 + k'_1) \tag{5}$$

Following the approach developed by Purnell and Quinn[10] the fastest analysis is obtained by minimizing the terms of the above equation. Now N_{req}, and hence t_R, are extremely sensitive to small changes in α when α is itself small (<1.10). The window diagram approach to optimisation of stationary phase composition[11–17] makes use of this fact. When the smallest α approaches 1.0 the separation becomes impossibly difficult no matter how well other parameters are optimised ($\delta t_R/\delta\alpha \rightarrow -\infty$ as $\alpha \rightarrow 1.0$). The success of window diagram optimization follows from the dominance of this factor α. The capacity factor for the second of the most difficult pair must be set to around 2.0, either by adjusting the liquid loading in GLC, or the temperature in gas–solid chromatography (GSC). Adjustment of temperature may have some effect on relative retentions, and if this is large then once again α may become the dominant factor[18] (for $k' > 2.0$, $\delta t_R/\delta k' \rightarrow 1.0$ as $k' \rightarrow \infty$, and $\delta t_R/\delta k' \rightarrow 0$ as $k' \rightarrow 2.0$). Finally, a column of sufficient length is required such that N_{req} is achieved at a carrier velocity well above optimum flow thereby effectively minimising $(H/\bar{u})$.

Once liquid loading or temperature has been fixed t_R may be considered as

$$t_R = 36(H/\bar{u})\left(\frac{\alpha'}{\alpha' - 1}\right)^2(1 + k'_1) \tag{6}$$

where α' is the relative non-adjusted retention of the most difficult pair *i.e.*

$$\alpha' = \frac{t_{R_i}}{t_{R_j}} = \frac{k'_i + 1}{k'_j + 1} \tag{7}$$

As explained in our earlier publication[1], the optimum packing composition is obtained by maximising α' which simply involves supplying solute retention data in the form of $(k' + 1)$ to our computer program[17].

EXPERIMENTAL

A synthetic seven-component solute mixture of ethanol, acetonitrile, acrylonitrile, dichloromethane, trichloromethane, tetrachloromethane and *n*-hexane was chosen, representing a variety of solute types and polarities. Four Porapaks (Q-S, S, N and T, all 100–120 mesh) and their mixtures were considered for the optimization of the mixture separation.

The chromatographic experiments were conducted with a Perkin-Elmer F-33 gas chromatograph. Nitrogen was employed as the carrier gas, with supplementary hydrogen and clean air for the flame-ionization detector. Column oven temperature was continuously monitored with a Hewlett-Packard Model 2802A platinum resistance digital thermometer fitted with a fast response probe.

The Porapaks require conditioning before routine use, and since conditioning is accompanied by a certain amount of shrinkage this was carried out in bulk in a 6.35-mm ($\frac{1}{4}$ in.) O.D. stainless-steel column with a flow of (oxygen-free) nitrogen. The manufacturers recommend maximum operating temperatures of 190°C for Porapak types N and T, and 230°C for types Q-S and S. For this work, types N and T were conditioned at 180°C, and types Q-S and S at 220°C. The analytical columns were constructed of 3.2 mm (1/8 in.) O.D. stainless steel. The packing procedure has been described[19] and involves packing under several hundred p.s.i. of nitrogen.

Initial measurements showed that capacity factors were large (ranging from 3 to 25) even at our self-imposed upper limit of 180°C. Since the object of the exercise was to obtain a fast baseline separation, all subsequent measurements and analyses were performed at 180°C. Even at this temperature Porapak T showed a slow but progressive increase in apparent polarity, accompanied by an overall decrease in solute capacity factors. This decrease in capacity factors was not attributable to further shrinkage of the polymer beads thereby creating a larger mobile-phase volume, since the observation was confirmed on repacking the column. This is entirely consistent with the observations of Castello and D'Amato[20] for Porapak T at 200°C. Interestingly, these same authors found that type N was stable at 200°C over an extended period (30 days).

Sample components were chromatographed both singly and as mixtures, and retentions were averaged over several determinations. Capacity factors were determined by taking methane retention as corresponding to dead time, considered to be a good approximation even for the Porapaks at 180°C.

RESULTS

Table I lists k' data for the seven solutes measured on 6 ft. (183 cm) columns of each of the four well-conditioned Porapaks. Fig. 1 shows typical chromatograms of the full seven-component mixture eluted from the four columns at 180°C with carrier inlet pressures of around 20 p.s.i. The chromatograms obtained with Porapaks Q-S, N and T each contain an effectively complete overlap. Only S partially resolves all seven components and consideration of the capacity factor data of Table I and the approximate formula exactly equivalent to eqn. 4

$$N_{req} = 36\left(\frac{\alpha'}{\alpha' - 1}\right)^2 \tag{8}$$

TABLE I

CAPACITY FACTORS OF NAMED MIXTURE COMPONENTS MEASURED AT 180°C WITH 6-ft. (183 cm) PORAPAK COLUMNS

	Compound	*Q-S*	*S*	*N*	*T*
1	Ethanol	3.36	4.00	6.44	6.40
2	Acetonitrile	4.35	4.89	9.49	10.4
3	Dichloromethane	6.42	6.33	9.27	8.15
4	Acrylonitrile	6.51	6.89	13.0	12.3
5	Trichloromethane	13.8	13.7	20.2	15.7
6	*n*-Hexane	19.9	15.5	19.5	9.23
7	Tetrachloromethane	22.3	19.0	24.7	15.0

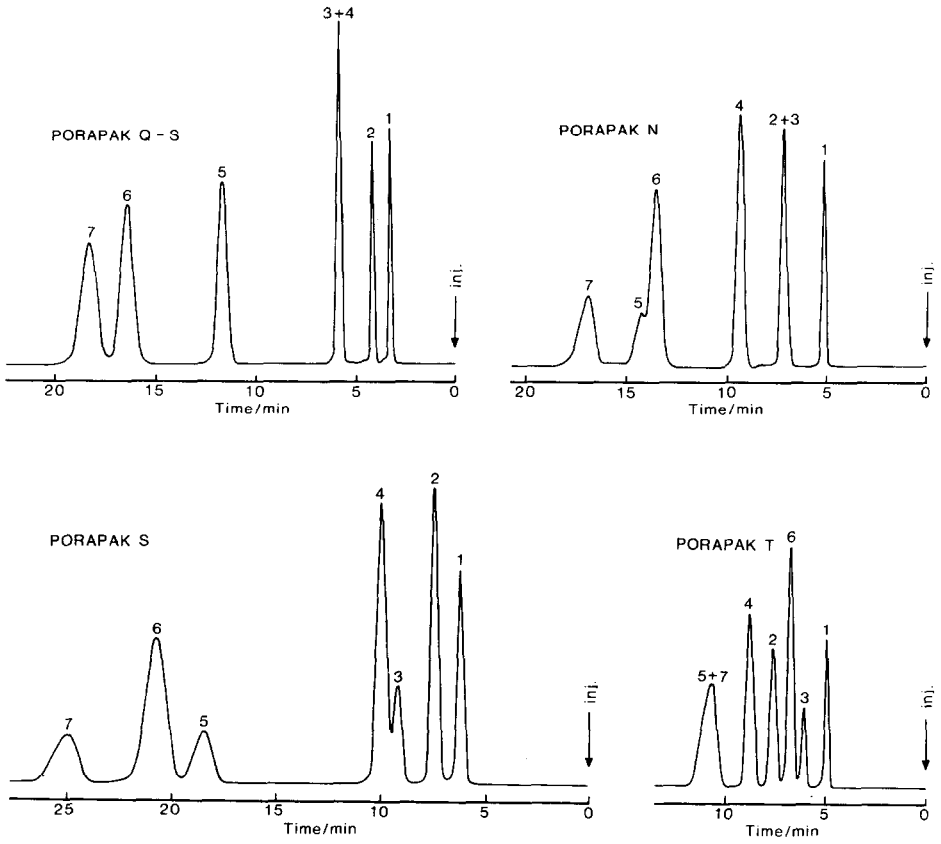

Fig. 1. Chromatograms of the seven-component mixture obtained with 6-ft. (183 cm) columns of the four Porapaks as labelled. (Column temperature 180°C, inlet pressure 20 p.s.i.). Component identity: 1 = ethanol; 2 = acetonitrile; 3 = dichloromethane; 4 = acrylonitrile; 5 = trichloromethane; 6 = *n*-hexane; 7 = tetrachloromethane.

where α' is the relative non-adjusted retention of the most difficult to separate pair, *i.e.*, $\alpha' = (k_i' + 1)/(k_j' + 1)$, indicates that 7150 plates are required for baseline separation. Acrylonitrile (4) appears to reflect a column efficiency of around 1770 plates in this chromatogram which suggests that a baseline separation could be obtained on a Porapak S column if the length was extended by a factor of 4, *i.e.* a 732-cm column. The analysis time expected would be correspondingly four times as long, *i.e.* 100 min; as we shall see, a great waste of time and materials.

Fig. 2 shows the Rohrschneider plot[21,22] in terms of ln α (taking tetrachloromethane as reference solute) against an arbitrary polarity scale. Porapak Q-S was assigned zero polarity and the most polar, type T, a polarity of 100. Polarities of types S and N were assigned those values (22 and 53, respectively) providing closest approach to linearity of all the data.

The four 6-ft. (183 cm) individual Porapak columns were characterised in terms of efficiency as a function of linear carrier velocity. Column efficiencies for *n*-hexane, trichloromethane and tetrachloromethane were determined for inlet pressures of 10,

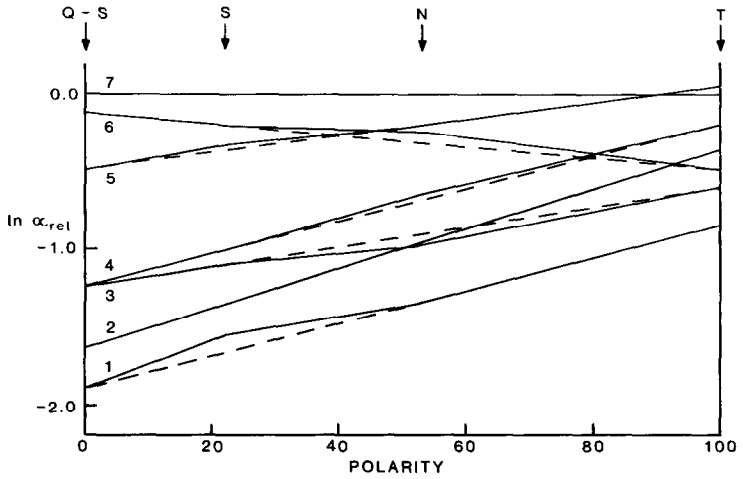

Fig. 2. Rohrschneider plot for elution of seven-component mixture from four Porapaks at 180°C. Component identity as for Fig. 1, and all retentions relative (α) to that for tetrachloromethane (7).

20, 40 and 70 p.s.i. Injection of methane (assumed to be non-retained) provided a measure of carrier velocity. The theoretical plate height (H) against mean linear carrier velocity ($\bar{u}$) curves for tetrachloromethane are shown in Fig. 3 and Table II lists $(H/\bar{u})_{min}$ for each of the solutes with each column. The Porapak S column proved

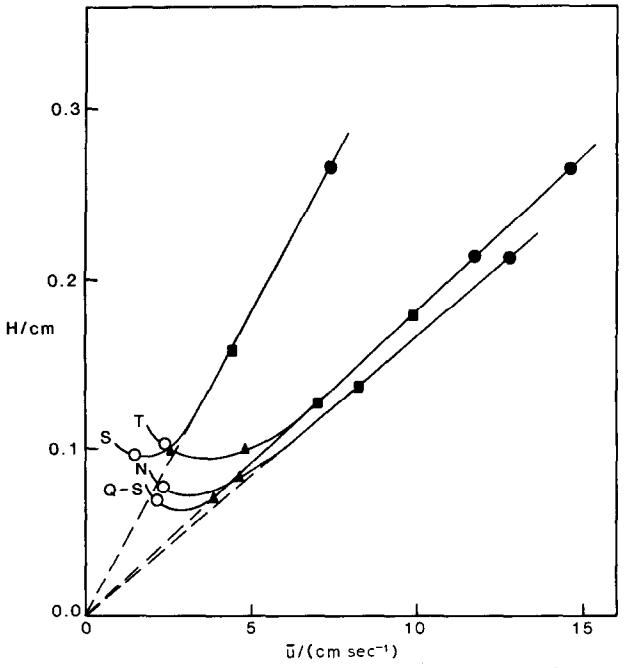

Fig. 3. $H/\bar{u}$ curves for elution of tetrachloromethane from 6-ft. (183 cm) columns of the four Porapaks at 180°C. ○, 10 p.s.i.; ▲, 20 p.s.i.; ■, 40 p.s.i.; ●, 70 p.s.i.

TABLE II

VALUES OF MINIMUM ($H/\bar{u}$) (sec) FOR NAMED MIXTURE COMPONENTS WITH 6-ft. (183 cm) PORAPAK COLUMNS AT 180°C

Component	*Q-S*	*S*	*N*	*T*
n-Hexane	0.0148	0.0330	0.0125	0.0135
Trichloromethane	0.0158	0.0337	0.0125	0.0140
Tetrachloromethane	0.0183	0.0358	0.0166	0.0182

to be less permeable than the others and also markedly less efficient for all solutes. This observation was confirmed by repacking of the column.

Proceeding with the optimization, the window diagram of ln α *versus* polarity is shown in Fig. 4. The largest window has its maximum at a polarity of 27 on our arbitrary scale, *i.e.* between Porapak S and N. The maximum of the second largest window falls at a polarity of 74, *i.e.* between Porapaks N and T. In order to approximate some intermediate polarity it is necessary to mix different Porapaks in correctly determined proportions. The most obvious binary mixture would be composed of those Porapaks closest to, and bounding the desired polarity, although we are not restricted to this choice, since, obviously, mixture of the Porapaks of 0 and 100 polarity can provide any value in principle. The optimum composition for some binary mixture is obtainable from a window diagram of α' *versus* bulk volume composition of the packing. Solute retention data submitted in the form of ($k' + 1$) to our computer program results in such diagrams, those for S with N and for N with T being shown in Fig. 5 and 6. The apparent discrepancies between these and the relevant sections of the polarity window diagram of Fig. 4 (principally the reduction of the window at polarity 49 and increase of that at 74) are attributable to the compromises which are always necessary in the construction of a Rohrschneider diagram

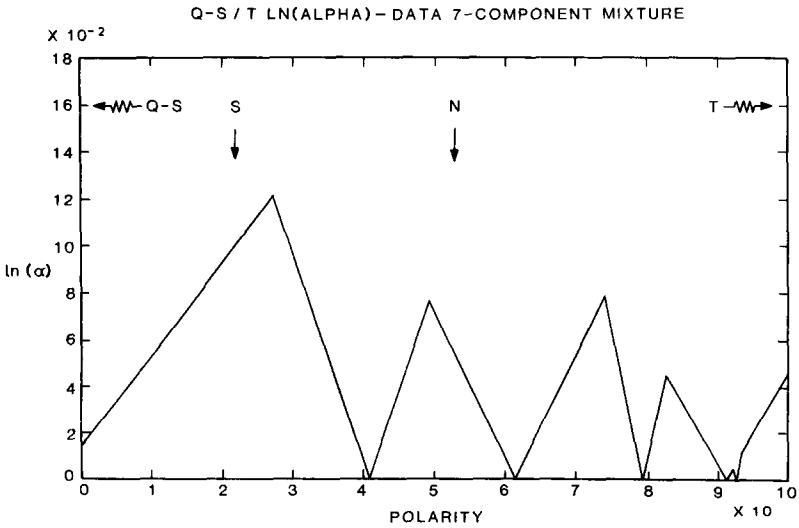

Fig. 4. Window diagram for Rohrschneider plot of Fig. 2. Perfect linearity of plots assumed (broken lines).

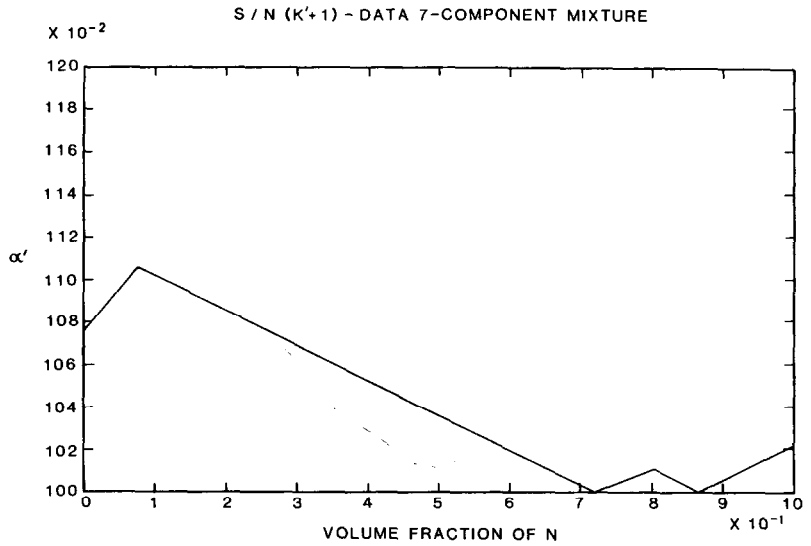

Fig. 5. Window diagram for optimizing mixtures of Porapaks S and N.

and assignment of polarities, principally to be seen in the fact that Fig. 4 assumes exact linearity of the Rohrschneider plots. The optimum N–T mixture is now predicted to be slightly superior with respect to minimum α' compared to the optimum S–N mixture (minimum α' of 1.114 and 1.106, respectively).

Optimization by using mixtures of Porapaks N and T

Fig. 6 indicates an optimum composition of 0.443 of T by volume, with minimum α' of 1.114, *i.e.* baseline separation predicted to require 3440 plates. Free-fall

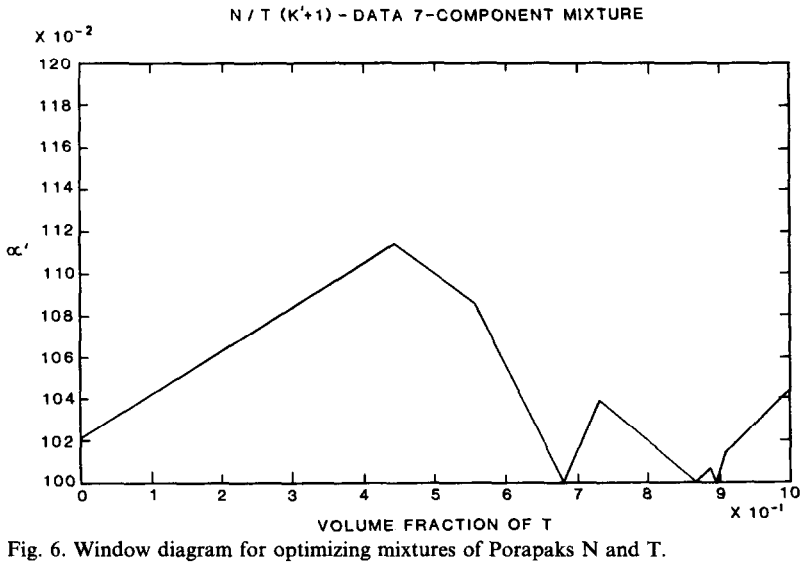

Fig. 6. Window diagram for optimizing mixtures of Porapaks N and T.

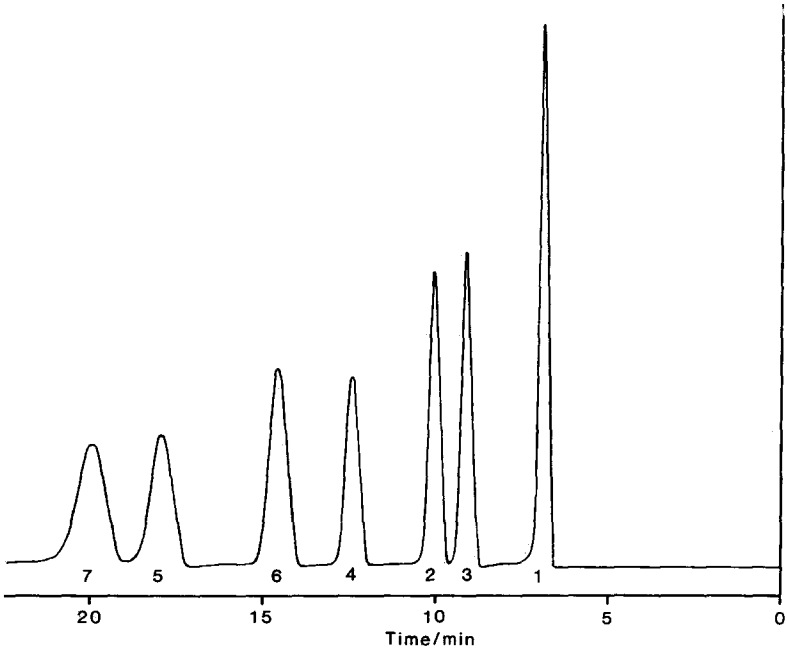

Fig. 7. Chromatogram of seven-component mixture (identities as for Fig. 1) obtained with 12-ft. (366 cm) column of empirically optimized mixture of Porapaks N and T. Column temperature 180°C, inlet pressure 60 p.s.i.

bulk density measurements of the Porapaks gave results of 0.367 and 0.416 g ml^{-1} for N and T, respectively. Since the mesh size of each was the same, the weight fraction of T, w_T is given by

$$\frac{1}{w_T} = 1 + \frac{\rho_N}{\rho_T}\left(\frac{1}{\varphi'_T} - 1\right) \tag{9}$$

where ρ_N, ρ_T are the free-fall bulk densities, and φ'_T is the bulk volume fraction of T. It is assumed that the ratio of free-fall densities will not differ greatly from the ratio of packed densities. A 12-ft. (366 cm) column of the optimum mixture of N and T (w_T = 0.474) proved to be unstable in use at 180°C, the changes in retention characteristics being consistent with further increase in polarity of the Porapak T component. An empirical adjustment of the column composition resulted in a best chromatogram shown in Fig. 7; the final composition of the column corresponded to a w_T of around 0.36. With an inlet pressure of 60 p.s.i. a baseline separation was achieved in 20 min. The uncertainty in final w_T is due to the possible selective loss of one or other of the components on unpacking, adjusting composition and repacking the column. The most difficult pair to separate for this column comprises dichloromethane (3) and acetonitrile (2) (k' of 9.05 and 10.1, respectively) having α' of 1.105.

Optimization by using mixtures of Porapaks S and N

Fig. 5 indicates an optimum bulk volume fraction of N of 0.076 with minimum α' of 1.106, N_{req} of 3920. This corresponds to a w_N of 0.077 (free-fall bulk density of

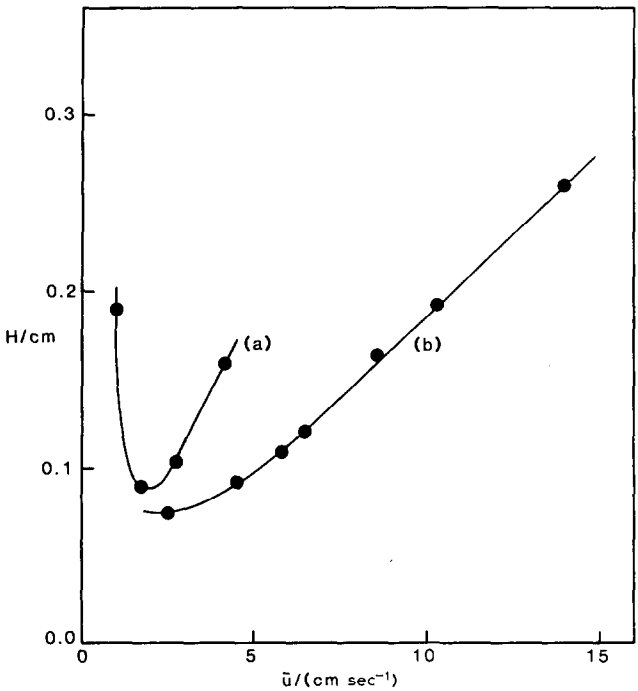

Fig. 8. $H/\bar{u}$ curves for elution of tetrachloromethane at 180°C from (a) 12-ft. (366 cm) column of Porapaks S and N, $\varphi'_N = 0.076$, (b) 6-ft. (183 cm) column of Porapaks Q-S and N, $\varphi'_N = 0.375$.

TABLE III

COMPARISON OF OBSERVED CAPACITY FACTORS AND RELATIVE NON-ADJUSTED RETENTIONS FOR 12-ft. (366 cm) COLUMN OF MIXED PORAPAKS S AND N ($\varphi'_N = 0.076$), WITH PREDICTIONS FROM DATA OF TABLE I

	Compound	*Predicted*		*Observed*		$k'\Delta\%$*
		k'	α'	k'	α'	
1	Ethanol	4.19		4.14		−1
			1.202		1.235	
2	Acetonitrile	5.24		5.35		2
			1.210		1.211	
3	Dichloromethane	6.55		6.69		2
			1.106		1.107	
4	Acrylonitrile	7.35		7.51		2
			1.820		1.810	
5	Trichloromethane	14.2		14.4		1
			1.105		1.104	
6	*n*-Hexane	15.8		16.0		1
			1.214		1.141	
7	Tetrachloromethane	19.4		18.4		−5

* $k'\Delta\% = 100\,(k'_{obs} - k'_{pred})/k'_{pred}$.

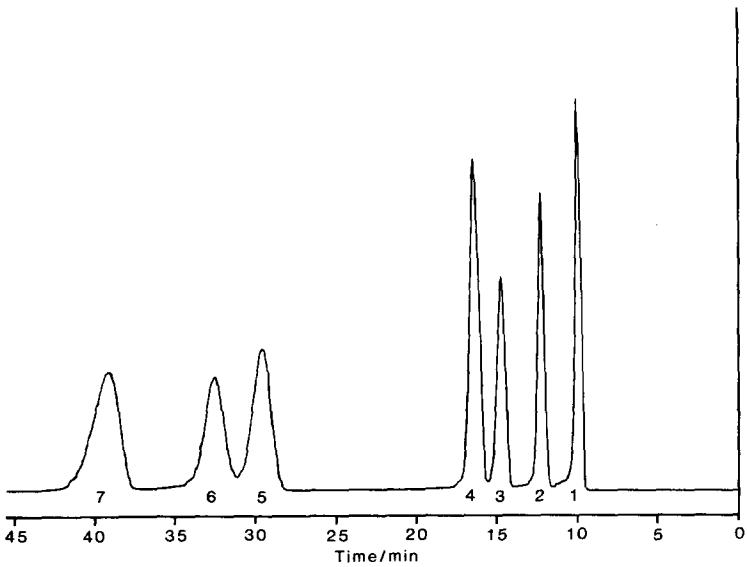

Fig. 9. Chromatogram of seven-component mixture (identities as for Fig. 1) obtained with 12-ft. (366 cm) column of mixed Porapaks S and N, $\varphi'_N = 0.076$. (Column temperature 180°C, inlet pressure 60 p.s.i.).

S measured as 0.362 g ml^{-1}). Mixing of these materials was not recommended by Castello and D'Amato[8] and indeed there was some aggregation of the particles. However, packing of columns under high-pressure nitrogen offered no difficulty and the 12-ft. (366 cm) column (two 6-ft. sections connected in series) exhibited a minimum ($H/\bar{u}$) for tetrachloromethane of 0.0375 sec (as shown in Fig. 8), not significantly worse than characterised the 6-ft. pure Porapak S column (Table II). Predicted and observed capacity factors and relative non-adjusted retentions are compared in

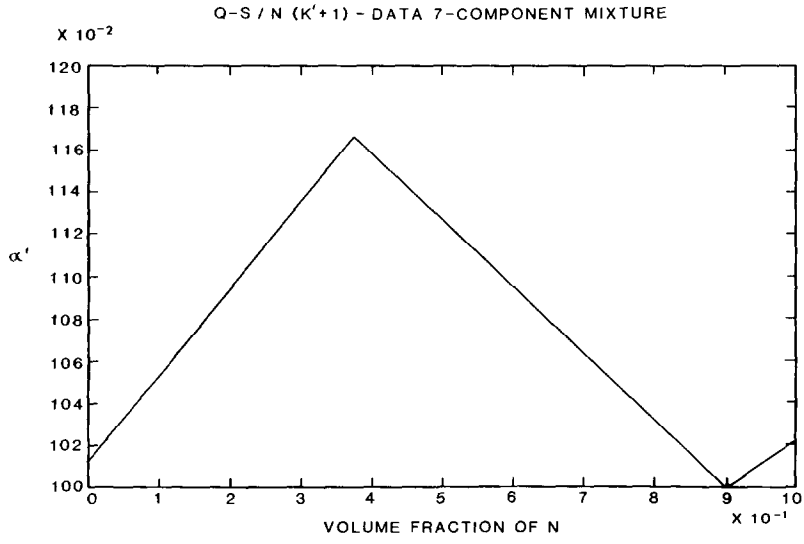

Fig. 10. Window diagram for optimizing mixtures of Porapaks Q-S and N.

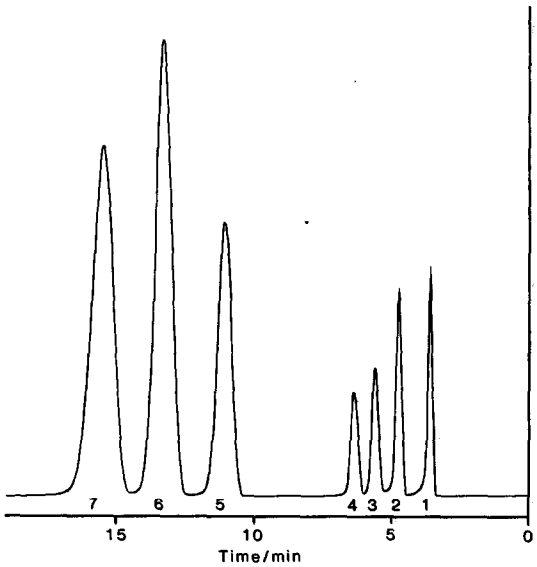

Fig. 11. Chromatogram of seven-component mixture (identities as for Fig. 1) obtained with 6-ft. (183 cm) column of mixed Porapaks Q-S and N, $\varphi'_N = 0.375$. (Column temperature 180°C, inlet pressure 20 p.s.i.).

Table III. The agreement is excellent. Fig. 9 shows a chromatogram of the mixture run at 60 p.s.i., a pressure where $(H/\bar{u})$ is effectively minimised. At this carrier velocity (3 cm sec^{-1}) the column would be expected to exhibit only 3250 plates for tetrachloromethane but this component is not itself involved in either of the two difficult separations. *n*-Hexane (6) and trichloromethane (5) would both be expected to show better efficiencies (Table II) and hence the separation of this pair is close to baseline.

TABLE IV

COMPARISON OF OBSERVED CAPACITY FACTORS AND RELATIVE NON-ADJUSTED RETENTIONS WITH PREDICTED VALUES FOR 6-ft. (183 cm) MIXED Q-S–N COLUMN OF $\varphi'_N = 0.375$

	Compound	*Predicted*		*Observed*		$k'\Delta\%$
		k'	α'	k'	α'	
1	Ethanol	4.52		4.41		−2
			1.319		1.333	
2	Acetonitrile	6.28		6.21		−1
			1.166		1.165	
3	Dichloromethane	7.49		7.40		−1
			1.171		1.150	
4	Acrylonitrile	8.94		8.66		−3
			1.730		1.729	
5	Trichloromethane	16.2		15.7		−3
			1.209		1.186	
6	*n*-Hexane	19.8		18.8		−5
			1.163		1.162	
7	Tetrachlomethane	23.2		22.0		−5

Perfect separation could therefore be achieved with a slightly longer column, provided $\bar{u}$ is again set to 3 cm sec^{-1}. An optimised analysis time of around 40 min is to be expected.

Optimization by using a mixture of Porapaks Q-S and N

The minimum relative non-adjusted retentions (α') for the optimized N–T and S–N mixtures are very similar. The poorer performance of the latter system is attributable to lower column efficiency due to the inclusion of a large proportion of Porapak S. The N–T system however had proved to be unstable. These difficulties may be circumvented by consideration of an optimised mixture of Porapak Q-S and N since it had been observed that these materials are relatively stable in use even at 180°C while, in addition, their individual column efficiencies are relatively good.

Fig. 10 shows the window diagram for the Q-S–N combination. The optimum composition corresponds to a φ'_N of 0.375 where the worst α' predicted is 1.166, *i.e.* N_{req} of only 1780 plates. This is fortuitously larger than the optimum window of Fig. 5 for the combination of N with S. Both are approximations to the optimum polarity of 27 shown by Fig. 4 of course. Bulk density of Q-S was found to be 0.371 g ml^{-1} and, hence, the optimum composition corresponds to w_N of 0.372. The efficiency curve for tetrachloromethane eluted from a 6-ft. (183 cm) column packed with such a mixture is shown in Fig. 8, and the $(H/\bar{u})_{min}$ of 0.0185 sec compares very well with the efficiencies of columns of the pure Porapak components (Table II). Assuming the requirement of 1780 plates for tetrachloromethane an inlet pressure of between 20 and 25 p.s.i., resulting in a mean carrier velocity of 5.5 cm sec^{-1} should have separated the mixture in approximately 14 min, and since $(H/\bar{u})$ for this velocity is close to $(H/\bar{u})_{min}$ no improvement in analysis speed may be expected by increase of column length. The chromatogram obtained at 20 p.s.i. is shown in Fig. 11 and is complete in 15.4 min; the predicted and observed k' and α' are compared in Table IV. Although absolute errors in k' reach -5%, relative discrepancies are very much smaller sug-

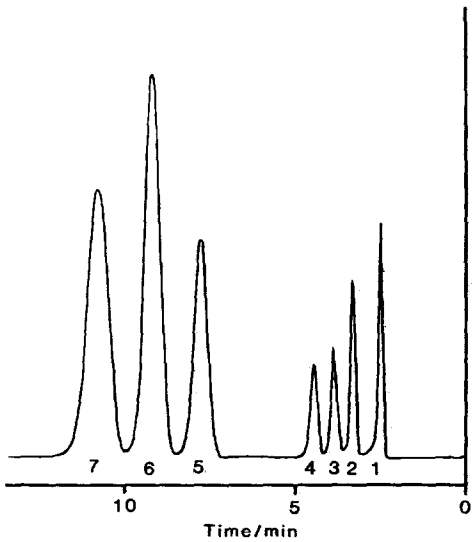

Fig. 12. As for Fig. 11, but with inlet pressure raised to 30 p.s.i.

TABLE V

COMPARISON OF COLUMN EFFICIENCY REQUIRED FOR SEPARATION OF CONSECUTIVE PAIRS OF ELUTED COMPONENTS WITH THE OBSERVED EFFICIENCY FOR EACH COMPONENT WITH THE 6-ft. (183 cm) Q-S-N COLUMN OF φ'_N = 0.375 OPERATED AT 30 p.s.i. INLET PRESSURE

	Compound	α'_{obs}	N_{req}	N_{obs}
1	Ethanol			2660
		1.333	580	
2	Acetonitrile			2770
		1.165	1790	
3	Dichloromethane			2510
		1.150	2120	
4	Acrylonitrile			2680
		1.729	200	
5	Trichloromethane			2190
		1.186	1460	
6	*n*-Hexane			2360
		1.162	1850	
7	Tetrachloromethane			1770

gesting either inaccuracy in measurement of dead time or some small fluctuations in carrier flow. Now tetrachloromethane of all the sample components, is eluted with least efficiency for all the Porapaks studied and it follows that optimum speeds of analysis based on $(H/\bar{u})_{min}$ for tetrachloromethane will err on the conservative side. By increasing the inlet pressure to 30 p.s.i., the analysis is complete in only 10.8 min and is effectively still baseline as may be seen in Fig. 12. Table V shows the comparison of column efficiency required for separation of consecutive pairs with the observed efficiency for each solute at this flow.

CONCLUSION

The advantages of following a methodical optimization are clearly demonstrated. The fastest possible baseline separation of our synthetic mixture on unmixed Porapaks is predicted to be close to 100 min whereas a 10.8-min separation is shown to be possible with an optimized mixed column. A further increase in speed would be possible by increasing the temperature thereby reducing capacity factors towards the optimum level of 2.0. This could however lead to the onset of instability as observed for Porapak T at 180°C which could be accompanied by column bleed.

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