

CHROMSYMP. 301

TOTAL OPTIMIZATION OF THE SEPARATION OF C₁-C₃ CHLOROHYDROCARBONS BY GAS-LIQUID CHROMATOGRAPHY

M. Y. B. OTHMAN, J. H. PURNELL*, P. WAINWRIGHT and P. S. WILLIAMS
University College of Swansea, Singleton Park, Swansea SA2 8PP (U.K.)

SUMMARY

Window analysis optimization is applied to allow the fastest possible analysis by the gas-liquid chromatography of a seven-component mixture of C₁-C₃ chlorinated hydrocarbons of environmental concern. It is established that the fastest analysis is not necessarily achieved with the column substrate that provides the largest relative retentions as the overall analysis time is determined by the retention volume of the last component to emerge and the column length by the most difficult pair to separate. Hence the retention ratio of these components is determining, as also is the value of H/\bar{U} at high velocities.

INTRODUCTION

The number of theoretical plates required for a baseline separation (N_{req}) may be taken to define the difficulty of that separation. Where there is a choice of chromatographic system, N_{req} is likely to be the determining factor in making the decision between the systems. Now, the relative adjusted retention (α) is likely to be small (< 1.10) for separations of chromatographic interest, and N_{req} is highly sensitive to small changes in α in this range. The window diagram approach to optimization of stationary phase composition¹⁻⁵ was developed on the strength of this, and the linear relationship.

$$K_R = \varphi_A K_{R(A)} + \varphi_B K_{R(B)} \quad (1)$$

where the K_R define the liquid-gas partition coefficients for a solute with liquids A or B and their mixtures, and φ represents the volume fractions of A and B. Eqn. 1 must apply when A and B are immiscible and thus, from an analytical point of view, the general applicability of eqn. 1 to intimately mixed liquids is irrelevant because, in gas-liquid chromatography (GLC), A and B may be physically separated through the use of mechanically mixed packings. Knowing $K_{R(A)}$ and $K_{R(B)}$ for all components of a mixture to be separated one can calculate α for all pairs of components as a function of solvent composition. It is arranged that $\alpha \geq 1$ at all times so that the lower envelope of the diagram defines the minimum α (α_{min}) arising at any solvent combination. If the orders of elution for some complex mixture are different for the

two solvents, then the resultant window diagram shows the discontinuous function α_{\min} as it varies with solvent composition. If the capacity factors are large (> 10), the largest window (corresponding to the maximum in α_{\min}) indicates the optimum composition at which N_{req} is a minimum and given by

$$N_{\text{req}} = 36 \left(\frac{\alpha}{\alpha - 1} \right)^2 \quad (2)$$

As is well known, N_{req} becomes increasingly dependent on the magnitude of the capacity factors of the components of difficult pairs when their values fall below 10. N_{req} is then more accurately given by⁶

$$N_{\text{req}} = 36 \left(\frac{\alpha}{\alpha - 1} \right)^2 \left(\frac{k' + 1}{k'} \right)^2 \quad (3)$$

where k' is the capacity factor of the second eluted of the pair of α_{\min} . This equation is still essentially an approximation, but for Gaussian peaks the accuracy improves with decrease in both α and k' . In fact, in the region of interest ($\alpha < 1.10$ and, as we shall see later, k' in the region of 2.0) the accuracy is excellent. Incidentally, if the minimization of N_{req} is the only criterion for optimization, then capacity factors may be increased if necessary by adjustment of the solvent loading so that eqn. 1 once again becomes a good approximation, α being ideally independent of solvent loading.

We have shown in a number of publications⁷⁻¹⁰ how this optimization approach provides a rapid and simple method of optimizing mixed solvent composition and how it may be employed in terms of "practical" quantities such as α , k' or V_{R}^* rather than K_{R} . The method is, in addition, well adapted to computation and we have described^{11,12} computer programs that can accommodate solvent mixtures of up to five components.

We take this opportunity to point out a small modification to the window diagram approach so far described. This modification concerns the optimization of binary packing composition for the separation of a complex mixture in which some or all of the components have very low capacity factors (< 10), and is of direct relevance to this work. It may be shown that for mechanical mixtures of packings of equal bulk density, porosity and mesh size (likely to be a good approximation for identical support and similar solvent loading)

$$k' = W_{\text{A}} k'_{\text{A}} + W_{\text{B}} k'_{\text{B}} \quad (4)$$

where W_{A} and W_{B} are weight fractions of packings A and B (not solvent weight fractions) and k'_{A} and k'_{B} are the capacity factors measured for A and B. It may also be shown that eqn. 3 is exactly equivalent to

$$N_{\text{req}} = 36 \left(\frac{\alpha'}{\alpha' - 1} \right)^2 \quad (5)$$

where α' is the ratio of retentions for any eluted pair uncorrected for dead time, *i.e.*, the raw retention ratio, so that

$$\alpha' = \frac{t_{R2}}{t_{R1}} = \frac{k'_2 + 1}{k'_1 + 1} \quad (6)$$

From eqn. 4, it follows that

$$(k' + 1) = W_A(k'_A + 1) + W_B(k'_B + 1) \quad (7)$$

i.e., $(k' + 1)$ varies linearly with the packing weight composition. Data in the form of $(k' + 1)$ would yield a window diagram showing the discontinuous function of α'_{\min} with packing composition. Maximization of α'_{\min} takes proper account of the various magnitudes of the component capacity factors and results in the true optimum composition for the mixed packing where alteration of liquid loading is undesired. Jones and Wellington¹³ have recently presented an alternative modification to the simple window diagram approach for such conditions (principally for liquid chromatography where capacity factors are often small). Briefly, it entails the maximization of an *S*-factor defined by

$$S = \frac{t_{R2} - t_{R1}}{t_{R2} + t_{R1}} \quad (8)$$

i.e.,

$$S = \frac{\alpha' - 1}{\alpha' + 1} \quad (9)$$

Clearly, the maximization of the *S*-factor and of α' are concomitant, so that the resultant optimum composition will be identical. Maximization of *S* is therefore an unnecessary complication, as the computer programs already constructed^{11,12} for maximizing α may be used unchanged for the maximization of α' ; only the nature of the data need be altered.

In this paper we extend the window technique to the choice of optimum binary solvent composition from a range of available solvents, with the eventual objective now being the attainment of the shortest possible analysis time rather than simply of the minimum N_{req} . As we shall see, the conditions corresponding to these optima may be totally different.

We have shown elsewhere¹⁴ that the approach developed by Rohrschneider^{15,16} to the selection of an optimum solvent for some complex mixture separations is amenable to window diagram solution. In this approach the logarithms of solute retentions relative to some standard are plotted vertically at some point on a horizontal linear 0-100 scale, the extremes being originally defined by the retention characteristics of squalane (SQ) and β,β' -oxydipropionitrile (ODPN). The objective is then to place intermediate solute solvent data at points such that linear plots for each solute may be constructed over the full range 0-100. We retain Rohrschneider's identification of this scale as one of solvent polarity, although some alternative term might be preferable. Provided that the plots of logarithms of relative retentions are approximately linear over the chosen range of solvents then a window diagram of

In α_{\min} against polarity allows an initial selection of solvent or solvent pairs based on the magnitude of α_{\min} alone. It will be shown later that, in spite of the importance of α'_{\min} for correctly optimizing the packing composition of some fixed solvent loading, it is α_{\min} that finally determines N_{req} when the solvent loading has been optimized. It will become apparent, however, that N_{req} is just one of the factors, albeit an important one, that influence the ultimate optimized analysis time.

The theory of minimum analysis time (fastest analysis) received considerable attention about 20 years ago. Of the several approaches developed, that offered by Purnell and Quinn¹⁷, although subject to approximation, is the least complex and the most facile in practical application.

Briefly, they showed that fastest analysis does not correspond to working at H_{\min} , *i.e.*, \bar{U}_{opt} , of the characteristic theoretical plate height *versus* flow velocity curve, but at the average velocity \bar{U} corresponding to the point at which a line from the origin effectively becomes the asymptote to the high velocity end of the Van Deemter curve. Thus, in the simplest possible terms, if

$$H = A + B/\bar{U} + C\bar{U} \quad (10)$$

then

$$(H/\bar{U}) \rightarrow C \text{ as } \bar{U} \rightarrow \infty \quad (11)$$

Thus for the elution of the second component of the most difficult pair to separate in any mixture

$$t = \frac{L}{\bar{U}}(1 + k') = \left(\frac{H}{\bar{U}}\right) N_{\text{req}}(1 + k') \quad (12)$$

i.e.

$$t = 36 \left(\frac{H}{\bar{U}}\right) \left(\frac{\alpha}{\alpha - 1}\right)^2 \frac{(1 + k')^3}{(k')^2} \quad (13)$$

Provided that H/\bar{U} is independent of k' , t has a minimum at $k' = 2$. For our present purposes we shall assume this is so, although in practice it is rarely the case. Hence for minimized analysis time for this difficult pair

$$t = 243 \left(\frac{H}{\bar{U}}\right)_{\min} \left(\frac{\alpha}{\alpha - 1}\right)^2 \quad (14)$$

The overall analysis time, t_{R} , for the complex mixture is given by

$$t_{\text{R}} = t \cdot \frac{(1 + nk')}{(1 + k')} \quad (15)$$

where n is the ratio of the adjusted elution time of the last component to that of the second of the most difficult pair to separate. For conditions optimised as above, this reduces to

$$t_R = 81 \left(\frac{H}{\bar{U}} \right)_{\min} \left(\frac{\alpha}{\alpha - 1} \right)^2 (1 + 2n) \quad (16)$$

It is now evident that in addition to α , both n and $(H/\bar{U})_{\min}$ are factors in the expression for optimized analysis time. Now, α and n are, ideally, independent of solvent loading, leaving only $(H/\bar{U})_{\min}$ requiring measurement for a column made up at the optimized composition and loading.

EXPERIMENTAL

The solute mixture chosen was a seven-component C₁-C₃ chlorinated hydrocarbon mixture, first because such mixtures are of environmental interest and second because the literature contains a sufficiency of data to allow a ready choice of a small selection of solvents providing a wide range of both retention and relative retention.

The chromatographic experiments were conducted on a Varian Vista 6000 chromatograph coupled to a Varian Vista 401 data system. Nitrogen was used as the carrier gas for the initial experiments with helium and hydrogen used later; supplementary flows of hydrogen and clean air were used for the flame-ionization detector.

Packed columns were constructed of 3.2 mm O.D. stainless steel, the solid support being Chromosorb G (AW DMCS) of 120-140 mesh. The column packing procedure has been described¹⁸. For the initial gathering of data, all packings were made up at 2.9% (w/w) solvent/support in 183 cm (6 ft.) columns. Sample components were run both singly and together and averaged values for k' emerged from at least six determinations. All data refer to elution at 50°C.

The five solvents, squalane (SQ), di-*n*-butyl tetrachlorophthalate (DBTC), dinonyl phthalate (DNP), tricresyl phosphate (TCP) and polyethylene glycol 1500 (PEG), were used as received. In the Rohrschneider scheme, β, β' -oxydipropionitrile (ODPN) is normally taken as the solvent of highest polarity ($P = 100$) but, owing to the marked liquid surface (Gibbs) adsorption characteristic of this liquid, relative retentions are extremely sensitive to the solvent/support ratio. This is certainly undesirable for our purposes and the use of ODPN was therefore ruled out.

TABLE I

CAPACITY FACTORS MEASURED ON THE FIVE PURE PHASE 183 cm COLUMNS AT 50°C, ALL PACKINGS BEING LOADED AT 2.9% (w/w)

Solute	Stationary phase				
	SQ	DBTC	DNP	TCP	PEG
1-Chloropropane	2.52	2.43	3.35	2.22	1.53
Tetrachloromethane	8.92	8.48	8.42	5.86	4.33
Dichloromethane	1.75	3.11	4.20	3.39	6.14
Trichloroethylene	12.3	13.2	15.9	11.0	10.0
<i>cis</i> -1,2-Dichloroethylene	3.76	6.54	8.63	6.84	9.83
Trichloromethane	4.57	7.87	10.2	8.48	12.2
1,2-Dichloroethane	5.68	10.6	13.7	11.9	17.4

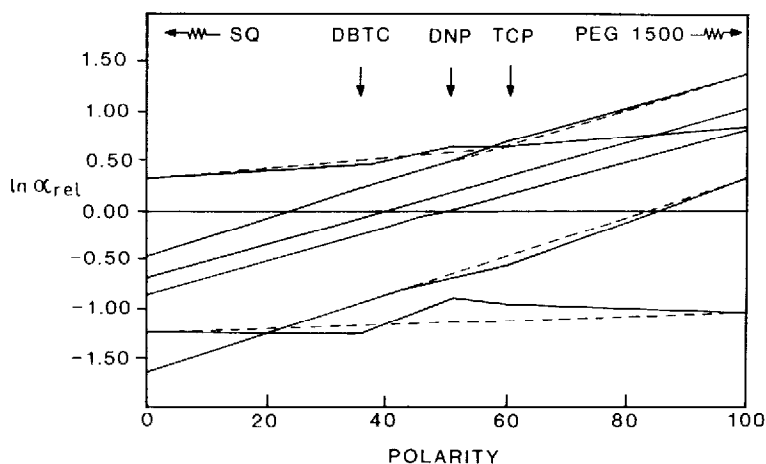


Fig. 1. Rohrschneider plot for elution at 50°C of (1) 1-chloropropane, (2) tetrachloromethane, (3) dichloromethane, (4) trichloroethylene, (5) *cis*-1,2-dichloroethylene, (6) trichloromethane and (7) 1,2-dichloroethane. Solvents: squalane (SQ); di-*n*-butyl tetrachlophthalate (DBTC); dinonyl phthalate (DNP); tricresyl phosphate (TCP); polyethylene glycol 1500 (PEG). All retentions relative (α) to that for tetrachloromethane (2).

RESULTS

Table I lists k' data for the seven solutes with each of the solvents, loaded at 2.9% (w/w) and packed into 183 cm columns. Fig. 1 shows the Rohrschneider plot in terms of $\ln \alpha$ (CCl_4 being reference solute) against the arbitrary polarity scale, the individual solvents being located at the polarities providing closest approach to linearity of all data. All except 1-chloropropane fall very close to the straight lines

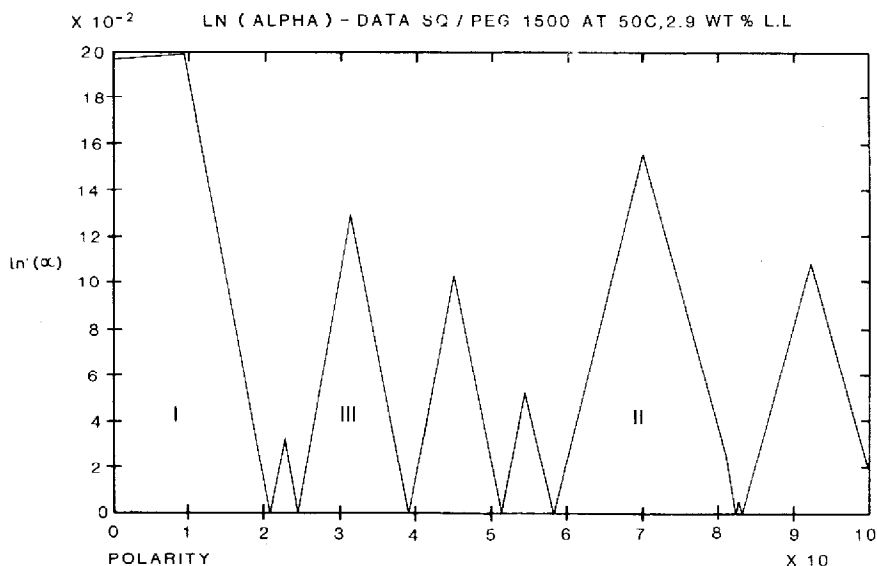


Fig. 2. Window diagram from data in Fig. 1. Linearity of Rohrschneider plots assumed.

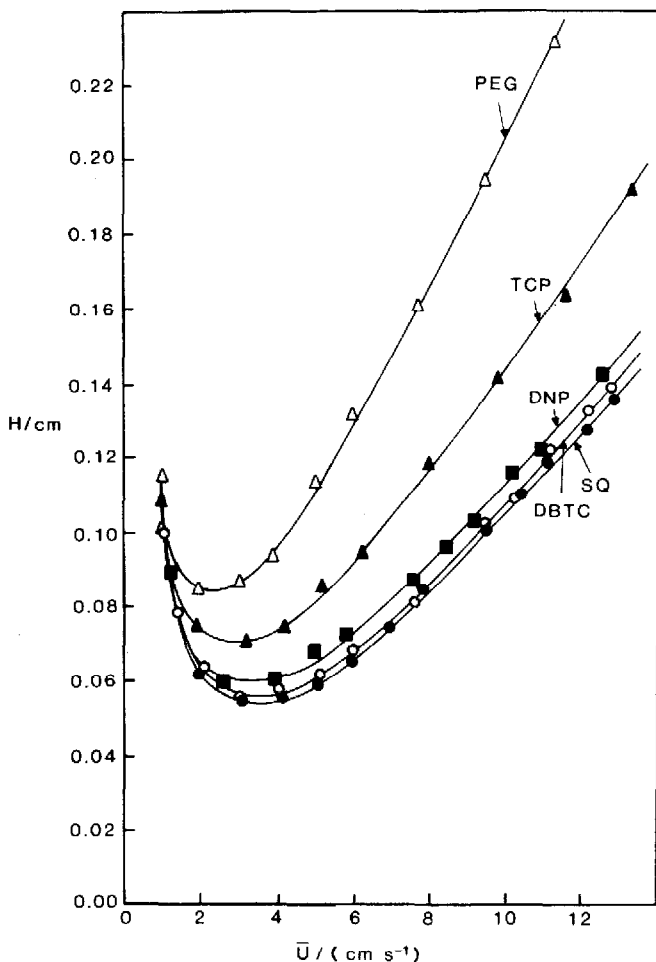


Fig. 3. H/\bar{U} curves for 183 cm, 2.9% (w/w) columns of the five solvents for elution of tetrachloromethane by nitrogen at 50°C.

connecting the data points at the extremes of polarity, *i.e.*, squalane to polyethylene glycol, and its deviation is greatest when it is well separated from the rest of the mixture. Fig. 2 shows the window diagram of $\ln \alpha_{\min}$ against polarity obtained when exact linearity of the Rohrschneider plots is assumed. In terms of maximizing relative retention, the windows labelled I, II and III are the three best in order of decreasing α_{\min} . Window I we may take to correspond to pure squalane, as little improvement is to be expected on adding a portion of some other packing. Window II lies between TCP and PEG and window III between SQ and DBTC. In the interests of simplicity we shall concern ourselves here with the comparison between windows I and II.

The efficiency curves for the five 2.9% (w/w) loaded 183 cm columns are shown in Fig. 3. It can be seen that a line drawn from the origin becomes asymptotic to all the curves in the velocity region 8–10 cm sec⁻¹; the values of $(H/\bar{U})_{\min}$ being 0.0106 sec (SQ), 0.0108 sec (DBTC), 0.0113 sec (DNP), 0.0143 sec (TCP) and 0.0205 sec

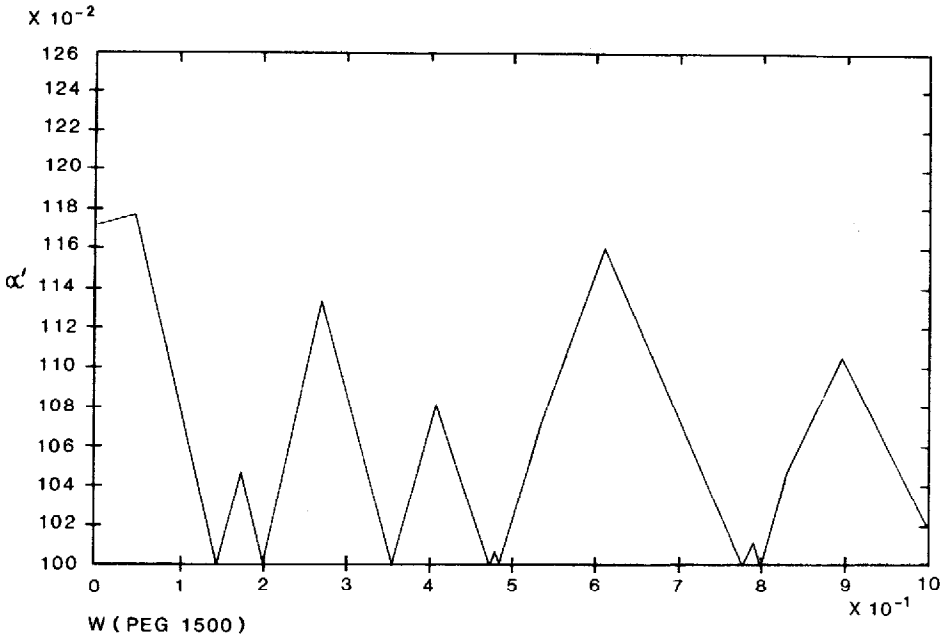


Fig. 4. Window diagram for SQ/PEG mixtures plotted as weight fraction (W) of PEG packing. Data as in Fig. 1. This diagram exemplifies those obtainable for all solvent mixtures capable of giving the optimum polarity of window II of Fig. 2.

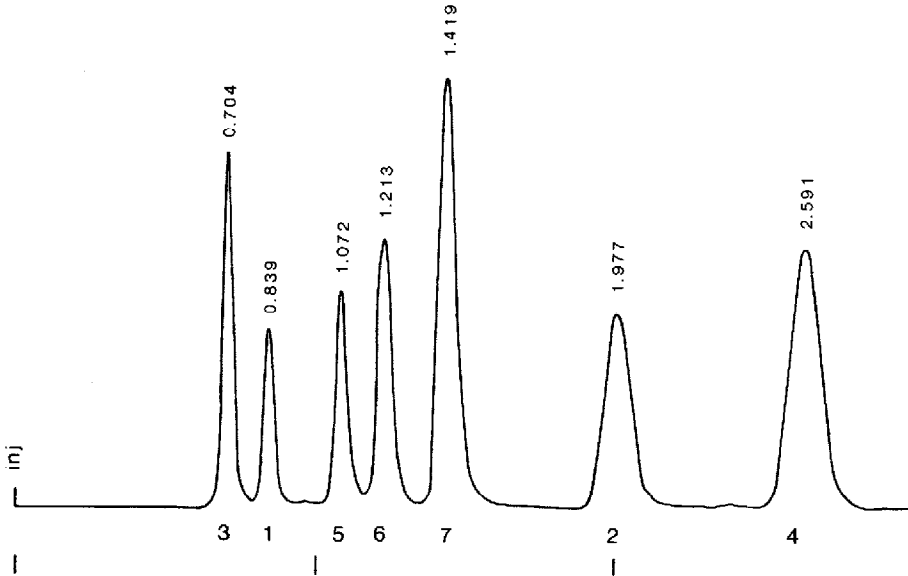


Fig. 5. Chromatogram for sample mixture eluted at 50°C by nitrogen from a 183 cm column of 1.273% (w/w) of SQ alone. Predicted optimum analysis time, 158 sec; actual, 156 sec.

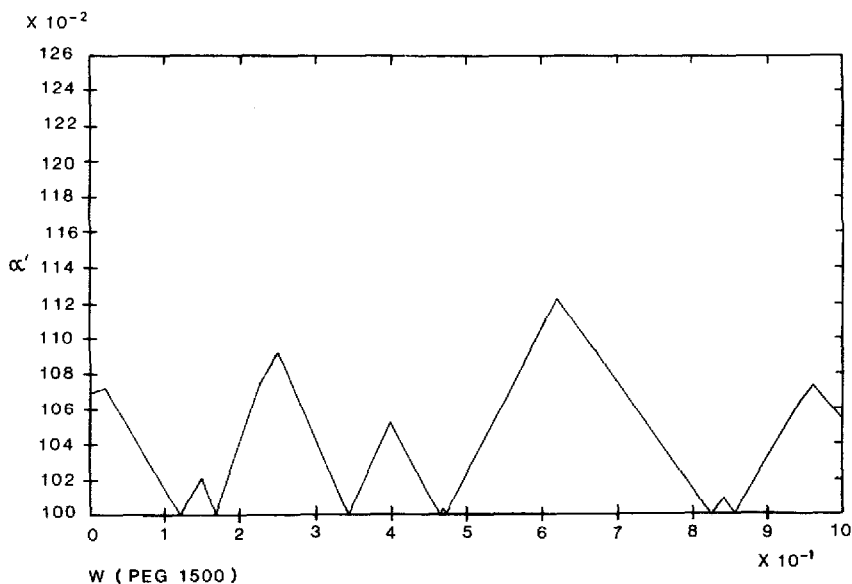


Fig. 6. Window diagram for SQ/PEG constructed using data acquired with columns more lightly loaded than for Figs. 1-3.

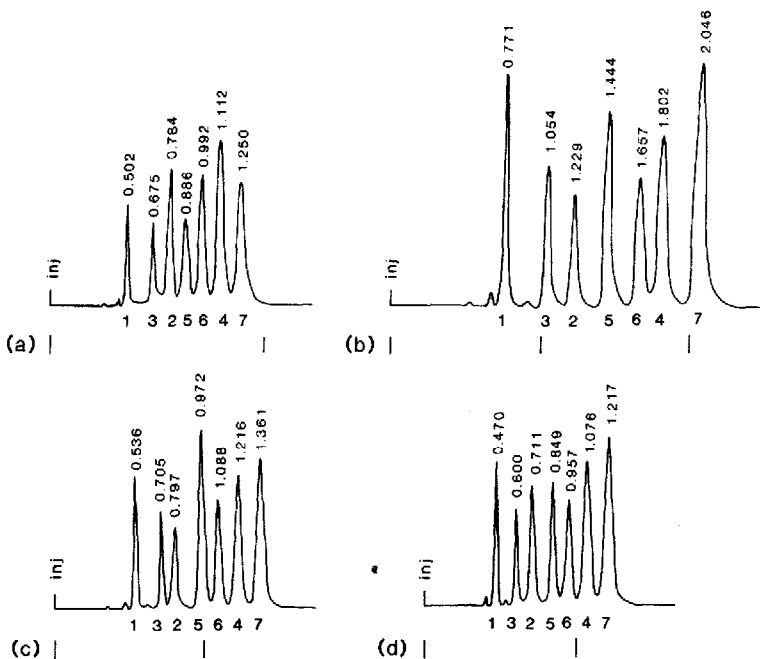


Fig. 7. Chromatograms obtained with mixed substrate columns corresponding to window II of Fig. 2. Solvent loadings as theoretically calculated for fastest analysis using nitrogen as carrier gas. Experimental analysis times agree with those predicted. (a) SQ/PEG ($W_{\text{PEG}} = 0.610$); (b) DBTC/PEG ($W_{\text{PEG}} = 0.469$); (c) DNP/PEG ($W_{\text{PEG}} = 0.534$); (d) TCP/PEG ($W_{\text{PEG}} = 0.207$), giving a fastest analysis of 73 sec.

TABLE II
OPTIMUM CONDITIONS FOR SEPARATION PREDICTED FROM DATA MEASURED ON THE 2.9% (w/w) PACKINGS

Packing	Loading (%, w/w)	2nd of difficult pair	α_{\min}	N_{req}	n	$N_{\text{req}}(1 + k')$	$(H/\bar{U})_{\min}^*$ (sec)	t_R^{**} (sec)
SQ	1.27	4th eluted	1.135	2530	2.69	16,100	0.0106	171
SQ/PEG, $W_{\text{PEG}} = 0.610$	0.534	6th eluted	1.112	3530	1.18	11,900	0.0166	198
DBTC/PEG, $W_{\text{PEG}} = 0.469$	0.498	6th eluted	1.113	3510	1.18	11,800	0.0154	181
DNP/PEG, $W_{\text{PEG}} = 0.466$	0.443	6th eluted	1.111	3580	1.17	12,000	0.0156	187
TCP/PEG, $W_{\text{PEG}} = 0.169$	0.538	6th eluted	1.118	3220	1.19	10,900	0.0153	167

* $(H/\bar{U})_{\min}$ given for a 2.9% (w/w) column calculated where necessary by assuming a linear dependence of the value on the weight fraction of packing components.

** t_R represents the analysis time to be expected for $(H/\bar{U})_{\min}$ values corresponding to those quoted for 2.9% (w/w) packing.

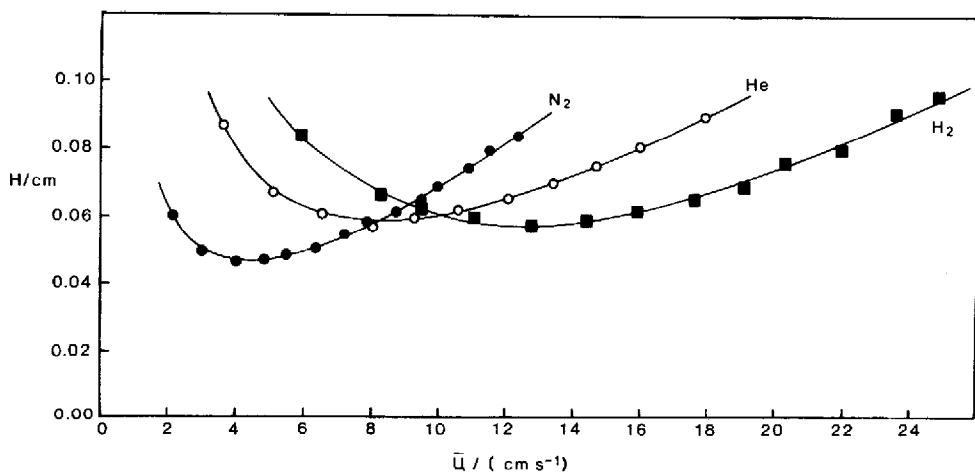


Fig. 8. H/\bar{U} curves for elution by nitrogen, helium or hydrogen of tetrachloromethane from column of SQ/PEG packings ($W_{\text{PEG}} = 0.610$) loaded at 0.534% (w/w).

(PEG). Now, provided the efficiency behaviour is independent of column length, it is possible to determine for some N_{req} the minimum length of column needed so that operation at $(H/\bar{U})_{\text{min}}$ is ensured. Incidentally, this minimum length corresponds to the maximum that is worthwhile using in that, at any greater length, H/\bar{U} being constant, no gain in speed of analysis can be achieved. Finally, we note that, to an acceptable degree of approximation, H is proportional to composition for a mechanically mixed packing.

As has already been stated, window II falls between TCP and PEG. A combination of TCP and PEG packings is therefore the most obvious solution. However,

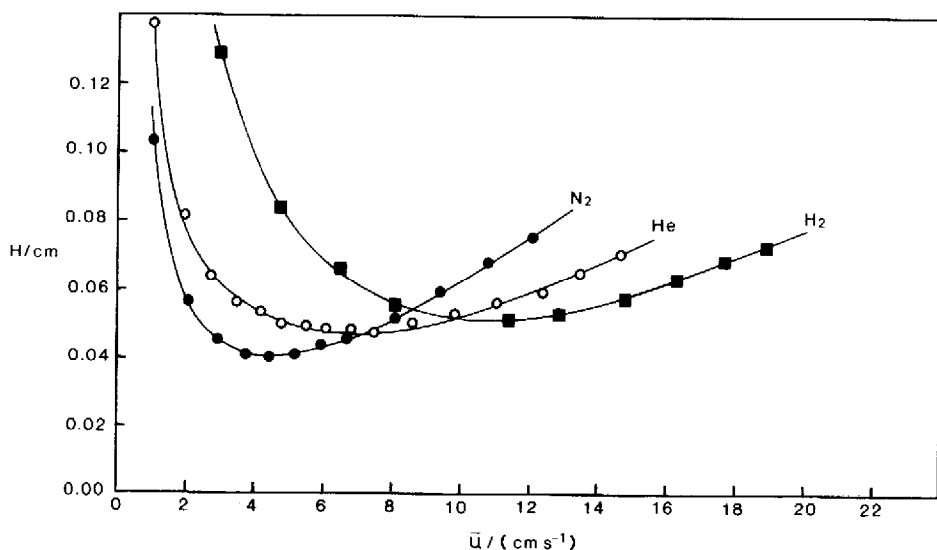


Fig. 9. H/\bar{U} curves for elution by nitrogen, helium or hydrogen of tetrachloromethane from column of DNP/PEG packings ($W_{\text{PEG}} = 0.466$) loaded at 0.443% (w/w).

TABLE III
EXPERIMENTAL RESULTS WITH NITROGEN AS CARRIER GAS

Packing	k' for 2nd of difficult pair	α'_{min}	N_{req}	n	$N_{req} (1 + k'_i)^*$	$(H/\bar{U})_{min}$ (sec)	$t_{R\ pred}$ (sec)	$t_{R\ obs}$ (sec)
SQ	2.14	1.132	2660	2.67	17,900	0.0088	158	155
SQ/PEG, $W_{PEG} = 0.610$	2.18	1.121	3090	1.18	11,000	0.0068	75	75
DBTC/PEG, $W_{PEG} = 0.470$	2.41	1.105	4010	1.16	15,200	0.0078	119	123
DNP/PEG, $W_{PEG} = 0.466$	2.45	1.118	3250	1.17	12,600	0.0062	78	82
TCP/PEG, $W_{PEG} = 0.207$	2.42	1.124	2940	1.19	11,400	0.0066	75	73

* k'_i refers to the capacity factor of the last eluted component in this and all following tables.

three other binary packings are possible, *viz.*, SQ/PEG, DBTC/PEG and DNP/PEG. In order to determine the approximate optimum weight compositions and solvent loadings for each of these binary combinations it is necessary to construct α' window diagrams for all four. An example, for SQ/PEG, is given in Fig. 4; note that here the horizontal scale represents the real packing weight fraction, unlike that of Fig. 2. It is then simple to calculate the expected capacity factors of the components for the indicated optimum compositions at 2.9% (w/w) loading. The optimum required liquid loadings may be calculated as $2.9(2/k'_2)$, where k'_2 is the expected capacity factor for the second of the first eluted difficult pair if $k'_2 > 2$, or the second of the second eluted difficult pair if $k'_2 < 2$ (at the apex of a window two pairs must have the same α'_{min}). For a final composition optimization, the adjusted $(k' + 1)$ data for the optimum loaded pure packings need to be subjected to a further window analysis

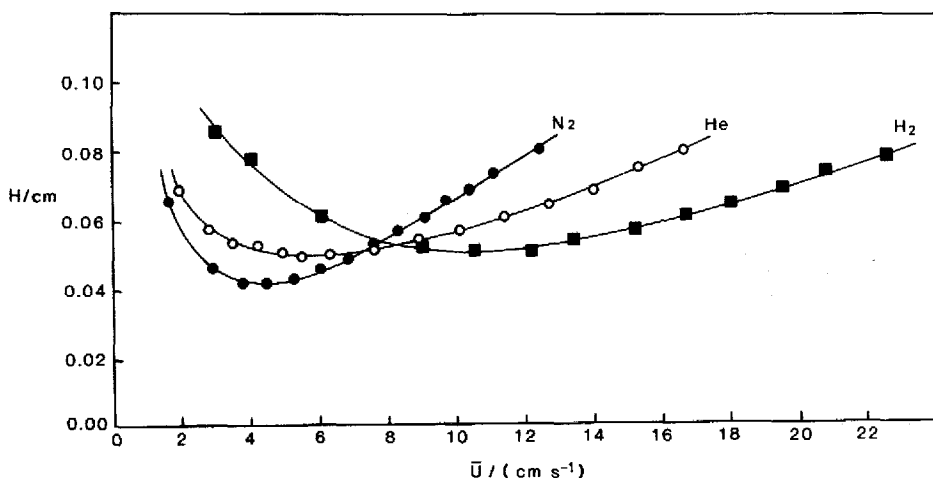


Fig. 10. H/\bar{U} curves for elution by nitrogen, helium or hydrogen of tetrachloromethane from column of TCP/PEG packings ($W_{PEG} = 0.169$) loaded at 0.538% (w/w).

TABLE IV

EXPERIMENTAL RESULTS WITH HELIUM AS CARRIER GAS

Packing	k' for 2nd of difficult pair	α'_{min}	N_{req}	n	$N_{req} (1 + k'_i)$	$(H/\bar{U})_{min}$ (sec)	$t_{R\ pred}$ (sec)	$t_{R\ obs}$ (sec)
SQ/PEG, $W_{PEG} = 0.610$	2.18	1.119*	3200*	1.17	11,400	0.0050	57	59
DNP/PEG, $W_{PEG} = 0.466$	2.43	1.121*	3110*	1.17	12,000	0.0047	56	61
TCP/PEG, $W_{PEG} = 0.207$	2.52	1.129*	2750*	1.18	10,900	0.0048	52	56

* These values refer to the last eluted pair.

to equalize α'_{min} once again for the two difficult pairs. In practice, it is better to re-measure capacity factors on columns packed with the fresh optimum loaded pure packings. In this way, any errors in absolute loading together with discrepancies due to surface adsorption effects are allowed for.

Table II shows the results of calculations possible from the initial set of data obtained with the 2.9% (w/w) pure phase columns. For squalane, the most difficult

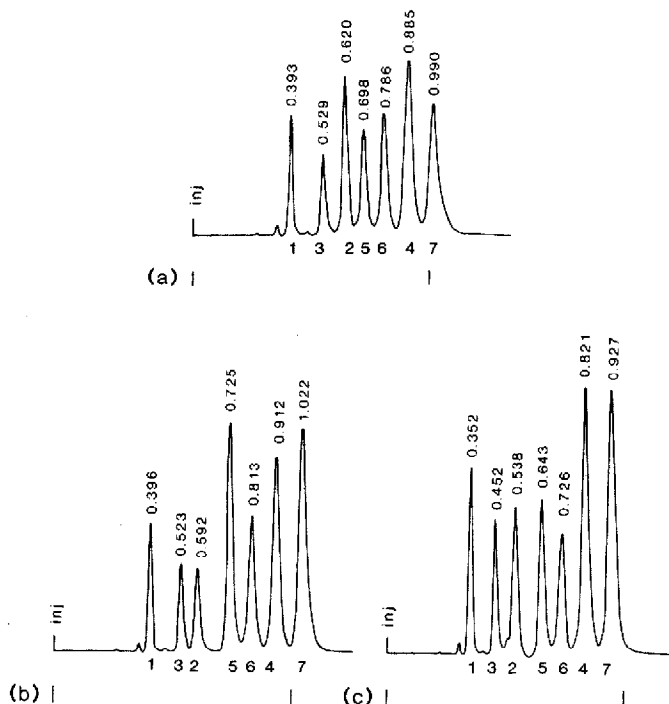


Fig. 11. Chromatograms for elution of sample from columns: (a) SQ/PEG [$W_{PEG} = 0.610$, 0.534% (w/w), 205 cm]; (b) DNP/PEG [$W_{PEG} = 0.466$, 0.443% (w/w), 204 cm]; (c) TCP/PEG [$W_{PEG} = 0.169$, 0.538% (w/w), 210 cm]. Fastest analysis, 56 sec with (c).

to separate pair corresponds to the third and fourth eluted, *i.e.*, *cis*-1,2-dichloroethylene and trichloromethane. For the four binary packings corresponding to window II, the fifth and sixth, and the sixth and seventh eluted are equally difficult at 2.9% (w/w), and therefore for reduced solvent loading the fifth and sixth are the most difficult pair, *i.e.*, tetrachloromethane followed by 1,2-dichloroethane. As far as N_{req} at the adjusted liquid loadings is concerned, SQ offers less difficulty than window II, which is consistent with the larger $\ln \alpha_{min}$ in Fig. 2 and with eqn. 16. However, once n has been taken into account, the speed of separation is favoured by window II {window II is favoured by the ratio of $[1 + 2(1.18)]/[1 + 2(2.69)]$, *i.e.*, 3.36/6.38}. The final factor of $(H/\bar{U})_{min}$ remains. At 2.9% (w/w), SQ is the most efficient of the packings and PEG the least (see Fig. 3). All the binary packings must contain some proportions of PEG packing which at first might lead one to suppose that the packings corresponding to window II would have relatively large values for $(H/\bar{U})_{min}$. The optimized loadings are all lower than 2.9% (w/w), however, the window II packings markedly so. It is impossible to predict the efficiencies of the lower loaded columns as it is possible for the efficiency to improve owing to faster equilibration within the thinner liquid film but to become very much worse once a point is reached where droplet formation is favoured. If $(H/\bar{U})_{min}$ is assumed not to change, then SQ may be seen to have a marginal advantage over window II (except possibly for the TCP/PEG combination), requiring a shorter column as well as separating the mixture more quickly.

Table III shows the actual results obtained with the lower loaded columns. The combinations differ slightly from those reported in Table II as they derive from window optimization of retention data measured on the freshly made lightly loaded columns. The values of α'_{min} are improved for SQ/PEG, DNP/PEG and TCP/PEG combinations, as expected, the last two pairs eluted now being the most difficult. DBTC/PEG provided some problems in that the columns appeared to be unstable. Over a period of time, the retention behaviour slowly approached that for an intimately mixed liquid phase, which suggests some mobility of the solvent in the column.

For SQ the predicted optimum analysis time is reduced to 158 sec owing to the better performance of the lower loaded column [$(H/\bar{U})_{min}$ reduced to 0.0088 sec], the chromatogram being shown in Fig. 5. Fig. 6 shows the α' window diagram for the newly acquired SQ and PEG retention data and the optimum separations for the

TABLE V
EXPERIMENTAL RESULTS WITH HYDROGEN AS CARRIER GAS

Packing	k' for 2nd of difficult pair	α'_{min}	N_{req}	n	$N_{req} (1 + k'_1)$	$(H/\bar{U})_{min}$ (sec)	$t_{R\ pred}$ (sec)	$t_{R\ obs}$ (sec)
SQ/PEG, $W_{PEG} = 0.610$	2.15	1.117*	3300*	1.17	11,600	0.0036	42	45
DNP/PEG, $W_{PEG} = 0.466$	2.39	1.116*	3340*	1.16	12,600	0.0038	48	49
TCP/PEG, $W_{PEG} = 0.207$	2.43	1.123	3000	1.18	11,600	0.0035	41	40

* These values refer to the last eluted pair.

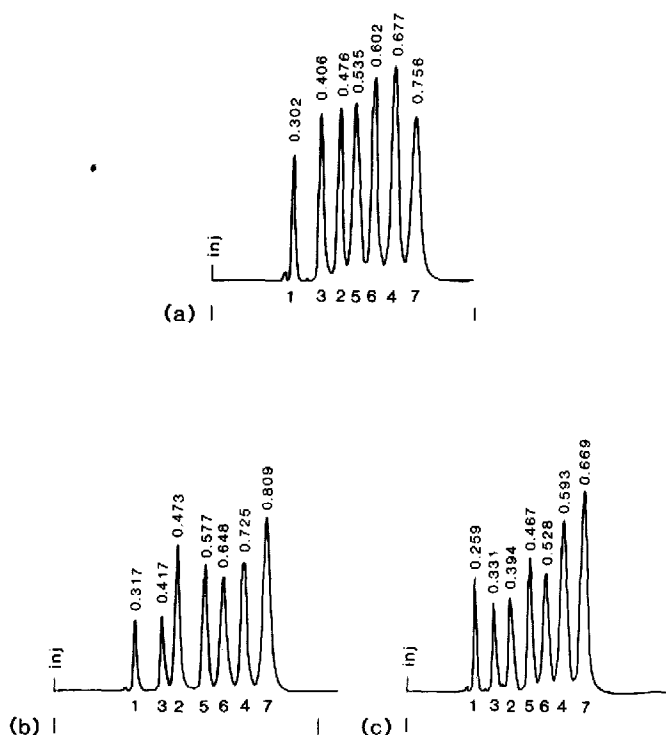


Fig. 12. Chromatograms for elution of sample from columns as described for Fig. 11. Fastest analysis, 40 sec with (c).

four binary packings are shown in Fig. 7. Note that column lengths had to be extended to ensure operation at a high enough carrier velocity (SQ/PEG 205 cm, DBTC/PEG 183 cm, DNP/PEG 204 cm, TCP/PEG 210 cm). The efficiencies of all four were excellent, better in fact than the optimum loaded SQ column, with the result that, except for DBTC/PEG, analysis was completed in about half the time required with SQ.

Finally, we note that a change of carrier gas to helium or hydrogen can improve the analysis time still further. Their greater diffusivity results in smaller contributions to plate height from resistance to mass transfer in the gas phase. Hence $(H/\bar{U})_{\min}$ may be expected to be lower, as indeed is the case as seen from the Figs. 8, 9 and 10, which show the nitrogen, helium and hydrogen efficiency curves for the binary packings SQ/PEG, DNP/PEG and TCP/PEG, respectively. Table IV gives the predicted optimum analysis times for helium as carrier gas and Fig. 11 illustrates the chromatograms. Table V gives the predicted optimum analysis times for hydrogen as carrier gas and Fig. 12 showing the corresponding chromatograms. Baseline separation is essentially achieved in around 40 sec with hydrogen as carrier gas.

Incidentally, no problems were encountered with the flame-ionization detector when hydrogen was used as the carrier gas. A splitter system was found to be unnecessary, and in fact supplementary hydrogen was required for the flame for much of the range of carrier gas flow-rates studied.

REFERENCES

- 1 J. H. Purnell and J. M. Vargas de Andrade, *J. Amer. Chem. Soc.*, 97 (1975) 3585.
- 2 J. H. Purnell and J. M. Vargas de Andrade, *J. Amer. Chem. Soc.*, 97 (1975) 3590.
- 3 R. J. Laub and J. H. Purnell, *J. Amer. Chem. Soc.*, 98 (1976) 30.
- 4 R. J. Laub and J. H. Purnell, *J. Amer. Chem. Soc.*, 98 (1976) 35.
- 5 R. J. Laub and J. H. Purnell, *J. Chromatogr.*, 112 (1975) 71.
- 6 J. H. Purnell, *J. Chem. Soc.*, (1960) 1268.
- 7 R. J. Laub and J. H. Purnell, *Anal. Chem.*, 48 (1976) 799.
- 8 R. J. Laub and J. H. Purnell, *Anal. Chem.*, 48 (1976) 1720.
- 9 W. K. Al-Thamir, R. J. Laub and J. H. Purnell, *J. Chromatogr.*, 142 (1977) 3.
- 10 R. J. Laub, J. H. Purnell, D. M. Summers and P. S. Williams, *J. Chromatogr.*, 155 (1978) 1.
- 11 R. J. Laub, J. H. Purnell and P. S. Williams, *J. Chromatogr.*, 134 (1977) 249.
- 12 R. J. Laub, J. H. Purnell and P. S. Williams, *Anal. Chim. Acta*, 95 (1977) 135.
- 13 P. Jones and C. A. Wellington, *J. Chromatogr.*, 213 (1981) 357.
- 14 J. H. Purnell, P. S. Williams and G. A. Zabierek, in R. E. Kaiser (Editor), *Proceedings of the 4th International Symposium on Capillary Chromatography*, Huthig, Heidelberg, 1981, p. 573.
- 15 L. Rohrschneider, *Z. Anal. Chem.*, 170 (1959) 256.
- 16 L. Rohrschneider, *J. Chromatogr.*, 39 (1969) 383.
- 17 J. H. Purnell and C. P. Quinn, in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Butterworths, London, 1961, p. 184.
- 18 R. J. Laub and J. H. Purnell, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 195.