

EMPLOYMENT OF RELATIVE RETENTION TIMES AND CAPACITY FACTORS FOR THE PREDICTION OF OPTIMIZED GAS-LIQUID CHROMATOGRAPHIC SEPARATIONS

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SUMMARY

The chromatographic optimization strategy described by us previously for multi-component sorbents is modified so as to permit the use of the directly measurable parameters, solute α values, capacity factors and weight-fractional compositions of binary stationary phases. The procedure is illustrated with the separation of aromatic amine and hydrocarbon solutes with SE-30 silicone gum and 2,4,7-trinitrofluorenone stationary phases.

INTRODUCTION

Recent¹⁻⁴ investigations of a wide variety of systems, several of which involve supposed charge transfer complexation, have led us to propose a model of solutions, called microscopic partition (MP) theory, which is based upon the linear equation

$$K_R = \varnothing_A K_{R(A)}^0 + \varnothing_S K_{R(S)}^0 \quad (1)$$

where K_R is the solute liquid-vapour partition coefficient with a binary stationary phase composed of A , of volume fraction, \varnothing_A , and S , of volume fraction, \varnothing_S , and $K_{R(A)}^0$ and $K_{R(S)}^0$ pertain to each of the pure liquid phases.

Eqn. 1 has proved to be of considerable utility in isothermal analytical gas chromatography: since the relative volatility, α , of two solutes, 1 and 2, is given by

$$\alpha_{2/1} = \frac{K_{R_2}}{K_{R_1}} = \frac{\varnothing_A \Delta K_{R_2}^0 + K_{R(S)_2}^0}{\varnothing_A \Delta K_{R_1}^0 + K_{R(S)_1}^0} \quad (2)$$

where $\Delta K_R^0 = K_{R(A)}^0 - K_{R(S)}^0$, relative retention data can be predicted as a function of \varnothing_A over the entire range of (binary) stationary-phase composition, $\varnothing_A = 0$ to 1, from data for the two pure liquids^{5,6}. In practice, a rearranged form of eqn. 2:

$$\varnothing_A = \frac{K_{R(S)_2}^0 - \alpha_{2/1} K_{R(S)_1}^0}{\alpha_{2/1} \Delta K_{R_1}^0 - \Delta K_{R_2}^0} \quad (3)$$

was found to be simpler to apply: ϕ_A was calculated at specified values of α within the limits: $1.1 \geq \alpha_{1/2} \geq 1.0 \leq \alpha_{2/1} \leq 1.1$. Plots of α vs. ϕ_A , called window diagrams, were then used to predict the optimum column composition for a given separation which, in addition, also specified the most difficult pair to resolve. This, in turn, allowed calculation of the minimum number of theoretical plates, N , required to effect baseline resolution of the mixture from the relation⁷:

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

where k' is the solute capacity factor [= $(t_R - t_{\text{air}})/t_{\text{air}}$]. The window diagram procedure has been applied with complete success to the gas-liquid chromatographic (GLC) separation of multi-component mixtures^{5,8} (including underivatized sterols⁹), to separations with multi-component sorbents⁹⁻¹², and to what has to date proved its most powerful application, the analysis of complex mixtures of unknown composition¹³. It has, further, been computerized^{6,8,14}.

While there may be some doubt as to the linearity of eqn. 1 when intimately mixed stationary phases, that is, (support + A + S), are employed^{15,16}, there is no doubt that mechanically mixed phases, *i.e.*, (support + A) plus (support + S), must conform exactly to it¹⁷. This, in itself, facilitates the use of our procedure since the analyst may well need to employ two or more stationary phases which exhibit only partial macroscopic miscibility and/or large excess volumes of mixing (although we have yet to encounter the latter situation). The use of mechanical mixtures obviates both of these difficulties while at the same time simplifying the preparation of mixed packings.

From the stand-point of the analyst, the more serious impediment to the use of the window-diagram procedure is that it requires solute partition coefficients and stationary-phase densities. The latter may be particularly difficult to measure when, for example, silicone gums are employed at high temperatures. The need for density data may be overcome by recognizing that, since

$$\frac{\phi_i q_i^0}{\rho_{i,j}} = W_i \quad (5)$$

and

$$V_{g(i)}^{T,0} = \frac{K_{R(i)}^0}{\rho_i^0} \quad (6)$$

eqn. 1 may be cast in the form (*e.g.* refs. 18-21):

$$V_g^T = W_A \Delta V_g^{T,0} + V_{g(S)}^{T,0} \quad (7)$$

where V_g^T is the solute specific retention volume at the column temperature, ρ_i^0 is the density of pure stationary phase, i , W_A is the weight fraction of component A of the binary (A + S) stationary phase, a superscript, 0, refers to a pure phase, and $\Delta V_{g(A)}^{T,0} = V_{g(A)}^{T,0} - V_{g(S)}^{T,0}$. Thus, plots of V_g^T vs. W_A will be linear and $V_{g(A)}^{T,0}$ and W_A may therefore be employed in place of K_{R}^0 and ϕ_A for the purposes of eqns. 2 and 3.

While offering a useful simplification, eqn. 7 still necessitates measurement of the parameter $V_g^{T,0}$ which, in industrial analytical laboratories especially is unsatisfactory from the stand-point of the required time and equipment. The problem can be circumvented, however, by the use of capacity factors and relative retention times. Parenthetically, we view this strategy as self-evident but, because of its importance from the practical view, we now present in detail its derivation.

Table I gives the retention data for five hypothetical solutes whose V_g^T values (inner ordinate) are plotted vs. W_A in Fig. 1. As Hildebrand and Reilley¹⁹ pointed out, α values alone cannot be used to predict optimum binary stationary-phase compositions for a given separation unless the specific retention volumes of the standard solute with each of the pure phases are identical (i.e., a horizontal line in Fig. 1). However, for two columns, each of which we specify (for simplicity at this point)

TABLE I

SPECIFIC RETENTION VOLUMES, $V_g^{T,0}$, AND RELATIVE RETENTION VALUES, α^0 (No. 1 = 1.000), FOR FIVE HYPOTHETICAL SOLUTES AND STATIONARY PHASES, A AND S

Solute	$V_g^{T,0}$ (ml/g) _(S)	$\alpha_{(S)11}^0$	$V_g^{T,0}$ (ml/g) _(A)	$\alpha_{(A)11}^0$	$\alpha_{(A)11}^0 \times \frac{k'_{(A)1}}{k'_{(S)1}}$ *
1	75	1.000	100	1.000	1.333
2	75	1.000	150	1.500	2.000
3	100	1.333	60	0.600	0.800
4	125	1.667	160	1.600	2.133
5	200	2.667	100	1.000	1.333

* $V_g^{T,0} / V_{g(S)1}^{T,0}$ is equal to $k'_{(A)1} / k'_{(S)1}$ for columns of assumed equivalent weight percent liquid loading and dead space per unit length.

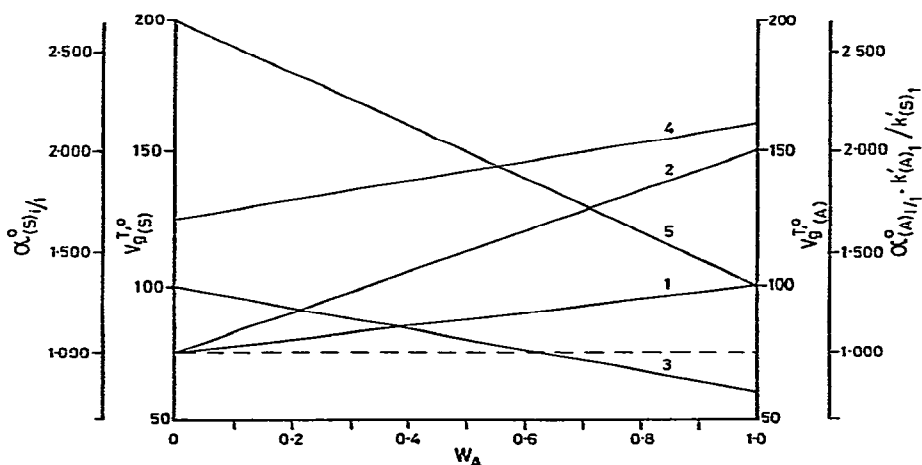


Fig. 1. Plots of V_g^T (inner ordinates) and outer ordinates: (left), $\alpha_{(S)11}^0$, and (right), $\alpha_{(A)11}^0 \times k'_{(A)1} / k'_{(S)1}$ vs. W_A for hypothetical 5-component mixture of Table I.

as containing equivalent weight percent liquid loadings and dead space per unit length,

$$\frac{V_{g(S)_i}^{T,0}}{V_{g(A)_i}^{T,0}} = \frac{k'_{(S)_i}}{k'_{(A)_i}} \quad (8)$$

that is, the ratio of capacity factors of the standard solute will be equal to the ratio of the solute specific retention volumes. The product of this ratio and the α values obtained with pure stationary phase A (6th column of Table I) correctly orders the relative retention data with respect to those found with pure S irrespective of the magnitude of the $k'_{(A)}/k'_{(S)}$ ratio of the standard solute. This procedure is equivalent to defining a horizontal line (dashed in Fig. 1) which intercepts the ordinate of the plot of $V_{g(S)_i}^{T,0}$ vs. W_A at the value of $V_{g(S)_i}^{T,0}$ of the internal standard. Thus, the order and magnitude of the data in columns 3 ($\alpha_{(S)_{i/1}}^0$) and 6 ($\alpha_{(A)_{i/1}}^0 \cdot k'_{(A)_i}/k'_{(S)_i}$) are made to conform precisely to those of columns 2 ($V_{g(S)_i}^{T,0}$) and 4 ($V_{g(A)_i}^{T,0}$). The data of column 3 may now be treated as $V_{g(S)_i}^{T,0}$ values and the data of column 6 as $V_{g(A)_i}^{T,0}$ values (outer ordinate) from which a window diagram may be constructed according to eqns. 2, 3, 6 and 7. For example, taking solute 1 as the internal standard, the value of W_A at which solutes 2 and 3 overlap is given by:

$$W_A^{2=3} = \frac{\alpha_{(S)_{3/1}}^0 - \alpha_{(S)_{2/1}}^0}{\Delta_{2/1} - \Delta_{3/1}} = \frac{1.333 - 1.000}{1.000 + 0.533} = 0.217$$

where:

$$\Delta_{i/1} = \frac{\alpha_{(A)_{i/1}}^0 k'_{(A)_1}}{k'_{(S)_1}} - \alpha_{(S)_{i/1}}^0 \quad (9)$$

Fig. 2 presents the complete window diagram for the five solutes of Table I, which shows that an $A + S$ stationary phase such that $W_A = 0.810$ will baseline-separate the mixture provided the column yields a number of plates sufficient to resolve an α value of 1.128 ($N_{\text{req}} = 2800$ for $k' > 10$).

While seeming to be a useful practice, the employment of equal liquid loadings in the reference columns may, in some instances, pose a serious difficulty in that retention times with one or the other of the phases may be unduly long, each (or both) may exhibit interfacial adsorption effects (thus necessitating the use of high loadings so that retention corresponds mainly to that of bulk solution), and so forth. This can be overcome, however, by recognising that, in such cases where different liquid loadings are used, eqn. 8 must be modified to:

$$\frac{V_{g(S)_i}^{T,0}}{V_{g(A)_i}^{T,0}} = \frac{k'_{(S)_i}}{k'_{(A)_i}} \cdot \frac{W_A}{W_S} \quad (10)$$

where W_A and W_S are the weight percent liquid loadings of packings A and S , respectively.

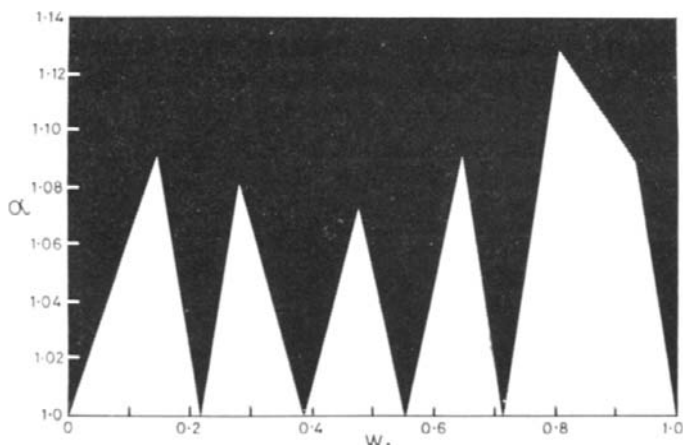


Fig. 2. Window diagram calculated from data of Table I (columns 3 and 6) with solute 1 as the internal standard.

We illustrate below the application of the described procedure with the data reported by Cooper and co-workers²² for aromatic amine and hydrocarbon solutes with GE SE-30 silicone gum and 2,4,7-trinitrofluorenone (TNF) stationary phases, since these are representative of several of the difficulties encountered in the use of eqns. 1-3 yet which are overcome by the method outlined above.

EXPERIMENTAL

The solutes were obtained from BDH (Poole, Great Britain), Aldrich (Milwaukee, Wisc., U.S.A.), or Eastman-Kodak (Rochester, N.Y., U.S.A.). The GE SE-30 silicone gum was purchased from Applied Science Labs. (State College, Pa., U.S.A.) and TNF from Aldrich. The gas chromatograph was a Pye Model 104 fitted with a single flame ionization detector. The carrier gas was nitrogen. Packings were coated by rotary evaporation in the usual manner with 120-140-mesh Chromosorb G (AW DMCS treated) as the solid support. Because the original work by Cooper and co-workers²² did not specify the type of silicone oil employed, we measured the solute specific retention volumes used in this study with SE-30. Our V_g values were at variance by some 10% with those reported, but retention data relative to any one of the solutes agreed with the data of Cooper and co-workers to, on average, $\pm 2\%$. Relative retention data for TNF were calculated from the reported²² specific retention volumes and, although not verified, were assumed to be accurate to $\pm 2\%$.

RESULTS AND DISCUSSION

The retention data of the solutes used in this study are reported in Table II relative to N,N-dimethylaniline (D), the $k'_{(TNF)D}/k'_{(SE-30)D}$ ratio of which was calculated on the basis of columns of equal liquid loadings. Fig. 3 shows the straight-line plot of the relative retention data vs. W_{TNF} , which was constructed using only the two end points ($\alpha^0_{(SE-30)I/D}$ at $W_{TNF} = 0$ and $\alpha^0_{(TNF)I/D} \cdot k'_{(TNF)D}/k'_{(SE-30)D}$ at $W_{TNF} = 1$), thus

TABLE II
RETENTION DATA FOR LISTED SOLUTES RELATIVE* TO N,N-DIMETHYLANILINE (D) WITH SE-30 AND TNF STATIONARY PHASES AT 180°

Solute	SE-30	TNF ²²	$\alpha_{i/D} \times \frac{k'_{(A)D}}{k'_{(S)D}}$
	$\alpha_{i/D}$	$\alpha_{i/D}$	
A Aniline	0.609	1.192	5.622
B N-Methylaniline	0.840	1.418	6.687
C <i>o</i> -Toluidine	0.903	1.936	9.130
D N,N-Dimethylaniline	1.000	1.000	4.716
E <i>cis</i> -Decalin	1.221	0.075	0.354
F <i>trans</i> -Decalin	1.007	0.075	0.354
G Indane	0.856	0.302	1.424
H Indene	0.876	0.723	3.410
I 2,3-Benzofuran	0.722	0.706	3.330

* $k'_{(A)D}/k'_{(S)D} = 4.716$ for reference columns packed, respectively, with identical liquid loadings of pure A and of pure S.

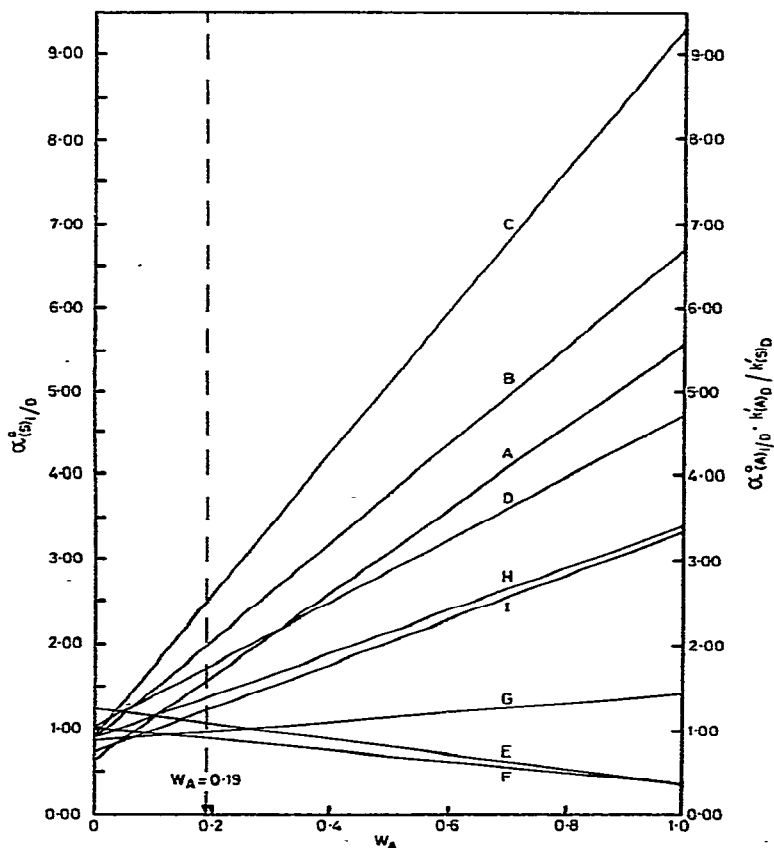


Fig. 3. Plot of relative retention data of solutes of Table II vs. W_{TNF} at 180°. Dashed line at $W_{TNF} = 0.19$.

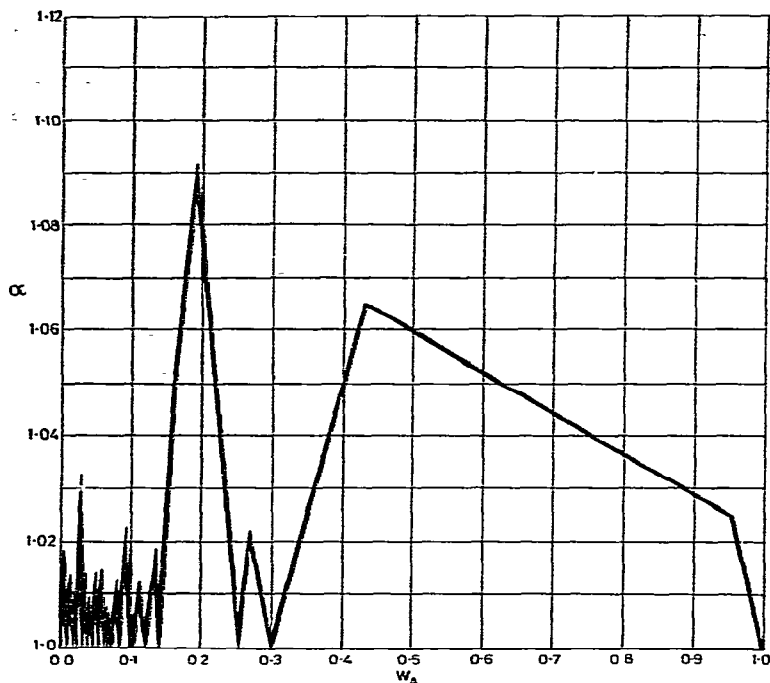


Fig. 4. Window diagram calculated from relative retention data of Table II, columns 2 and 4, with N,N-dimethylaniline as the internal standard. Optimum predicted weight fraction of TNF is 0.19, at which the most difficult pair to resolve has an α value of 1.092.

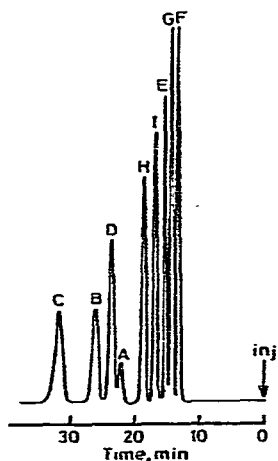


Fig. 5. First-time chromatogram of solutes of Table II with a 30-ft. glass column containing a mechanical mixture of packings of SE-30 and TNF such that $W_{TNF} = 0.2$. Temperature, 180°; inlet pressure, 20 p.s.i.g.

assuming, for mechanically mixed binary stationary phases, linear behaviour over the entire range, $W_A = 0$ to 1. Fig. 4 gives the window diagram calculated from columns 2 and 4 of Table II, which predicts that baseline separation of all solutes will be obtained, given a number of plates sufficient to separate a solute pair of $\alpha = 1.092$ ($N_{req.} = 5100$ for $k' > 10$), with a column containing a mixture of SE-30 and TNF such that $W_{TNF} = 0.19$. Since we found approximately 175 plates per foot for these solutes with these phases, eqn. 4 indicates that a 30-ft. column will resolve all components. Fig. 5 shows the first-time chromatogram obtained with the prescribed column and packing where, clearly, baseline resolution has been achieved and where, further, the order of elution is precisely that predicted from Fig. 3 (dashed line). The minimal amount of work required to produce a window diagram (approximately one day turn-around at our computer installation) is thus fully justified in that our method makes possible the first-time separation of mixtures with binary stationary phases, the computer-optimized composition of which can be predicted solely from relative retention and capacity factor data.

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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 R. J. Laub and J. H. Purnell, *Tenth Int. Symp. Advan. Chromatogr., Munich, 1975*.
- 7 J. H. Purnell and C. P. Quinn, in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 184.
- 8 R. J. Laub, J. H. Purnell and P. S. Williams, *J. Chromatogr.*, 134 (1977) 249.
- 9 W. K. Al-Thamir, R. J. Laub and J. H. Purnell, *J. Chromatogr.*, 142 (1977) 3.
- 10 W. K. Al-Thamir, R. J. Laub and J. H. Purnell, *Twelfth Int. Symp. Advan. Chromatogr., Amsterdam, 1977*.
- 11 W. K. Al-Thamir, R. J. Laub and J. H. Purnell, *J. Chromatogr.*, in preparation.
- 12 R. J. Laub and J. H. Purnell, *Anal. Chem.*, 48 (1976) 799.
- 13 R. J. Laub and J. H. Purnell, *Anal. Chem.*, 48 (1976) 1720.
- 14 R. J. Laub, J. H. Purnell and P. S. Williams, *Anal. Chim. Acta*, 95 (1977) 135.
- 15 R. J. Laub, D. E. Martire and J. H. Purnell, *J. Chem. Soc. Farad., Trans. I*, 73 (1977) 1686; 74 (1978) 213.
- 16 M. W. P. Harbison, D. E. Martire, R. J. Laub, J. H. Purnell and P. S. Williams, *J. Chem. Soc. Farad., Trans. I*, in preparation.
- 17 R. J. Laub, J. H. Purnell and D. M. Summers, *J. Chem. Soc. Farad., Trans. I*, submitted.
- 18 G. R. Primavesi, *Nature (London)*, 184 (1959) 2010.
- 19 G. P. Hildebrand and C. N. Reilley, *Anal. Chem.*, 36 (1964) 47.
- 20 A. S. Melnikov and B. V. Aivazov, *Zh. Anal. Khim.*, 28 (1973) 791.
- 21 J. Klein and H. Widdecke, *J. Chromatogr.*, 147 (1978) 384.
- 22 A. R. Cooper, C. W. P. Crowne and P. G. Farrell, *Trans. Farad. Soc.*, 62 (1966) 2725; 63 (1967) 447.