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WINDOW ANALYSIS OPTIMIZATION OF GAS CHROMATOGRAPHIC SEPARATION USING DIFFERENT POLARITY PACKED COLUMNS

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تطوير عملية فصل المركبات في تقنية الكروماتوجرافي الغازي بتطبيق نظرية (Window Diagram) واستخدام أعمدة معبأة بمذيبات مختلفة القطبية

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في هذا البحث تم تطبيق نظرية (Window Diagram) بمعادلاتها الرياضية لتحقيق فصل تام لخليط من المركبات الكيميائية وبأقصر وقت ممكن ، وذلك باستعمال عمودين متصلين لكل منهما قطبية مختلفة عن الآخر ؛ العمود الأول يحتوي على مادة السكوالين كمذيب غير قطبي والعمود الثاني يحتوي على مادة داي ايزوبيوتايل فثاليت كمذيب قطبي .

وبعد اجراء التجربة تم تحقيق مايلي :

١) فصل كامل - دون أي تداخل - لجميع مكونات الخليط وذلك عند تحديد نسبة أطوال الاعمدة لبعضها وتحديد الطول الكلي اللازم للعمودين عن طريق النظرية السالفة الذكر .

٢) تطابق تام في مواقع المكونات المفصولة في كلتا حالتي ترتيب العمودين المتصلين سواء عمود السكوالين في الامام أو عمود داي ايزوبيوتيل فثاليت في الامام .

Key Words: Window Diagram Theory, Serial Columns, Partition Coefficient

ABSTRACT:

Window diagram theory has been described by Purnell and his research team in various publications. In this paper we apply this theory to optimize a separation of complex mixture containing propylene oxide, 1-hexene, cyclohexene, tert. amylmethyl wther, 4-octene, 1-octyne, 1-nonene, p-xylene and n-decane by using two different polarity serial columns; squalane (SQ) as a non-polar solvent and Diisobutyl phthalate (DBP) as a polar solvent. A baseline separation of all mixture components is achieved following window analysis that defined the necessary relative and total column lengths. Identical chromatograms for both options: (1) SQ = front, (2) DBP=front are successfully obtained.

INTRODUCTION

The partition coefficient of any sample component, K_R, in multi-component substrates is defined by Purnell and his co-workers in the theory called microscopic partitions (MP)[1-4] theory which is based upon the linear equation:

$$K_R = \phi_A K^0_{R(A)} + \phi_S K^0_{R(S)} \text{ (for a binary (A+S) liquid phase)} \quad (1)$$

where K_R is the solute liquid vapor partition coefficent with a binary stationary phase composed of A, of volume fraction, and ϕ_A and $K^O_{R(A)}$ and $K^O_{R(S)}$ pertain to each of the pure liquid phases.

For any pair of sample components (1 and 2) equation 1 can be written:

$$\alpha_{2/1} = \frac{K_{R2}}{K_{R1}} = \frac{\phi_A K^0{}_{R(A)2} + \phi_S K^0{}_{R(S)2}}{\phi_A K^0{}_{R(A)1} + \phi_S K^0{}_{R(S)1}} \quad (2)$$

from which α values of all solute with respect to all other solutes may be calculated as function of ϕ_A.

The windows diagram procedure has been defined in 1975 by Laub and Purnell [5]. We present here experimental results that apply the theory for different polarity columns in Gas - liquid chromotography.

Theory:

In order to facilitate understanding of the analysis of the experimental information cited later, the practically important elements of window diagram theory [6] are presented here.

The total retention of a given solute eluted through a serial pair of columns of any type is the sum of the retentions (t_R) in the individual sections, so for two columns labelled front (F) abd back (B),

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

where t_d represents dead time (k' = 0) and k' represents a capacity factor. It then follows, as a perfectly general results, that

$$\mathbf{k}' = (t_{dF}k'_F + t_{dB}k'_B) / (t_{dF} + t_{dB}) \quad (4)$$

or setting, $t_{dF} / t_{dB} = P$,

$$k' = \frac{Pk'_F + k_B}{P + 1} \quad (5)$$

This is true for binary serial systems of any kind of column and, being independent of assumption is the most useful form of the basic equation for serial retention.

The dependence of k' and thus of relative retention α, on column sequence FB or BF and on k'_F and k'_B is totally described by eqn. 5, and given that we know k'_F , k'_B and P, there is no problem in calculating either absolute or relative retentions in serial systems. The determination of k'_F and k'_B is straightforward but that of P is not, since we require to know not only the values of the inlet p_i and outlet p_o pressures, but of the junction pressure P, as shown below.

Hilderbrand and Reilley [7] introduced the concept of a resistance to gas flow function R_F defined in terms of average carrier velocity, u, by

$$R_F = (p_i^2 - p_0^2) / pu \quad (6)$$

and it is a simple matter then to show [6, 7] that t_d is given by

$$t_d = \left[\frac{2LR_F}{3}\right]\left[\frac{p_i^3 - p_0^3}{(p_i^2 - p_0^2)^2}\right] \quad (7)$$

where L is column length. Both eqns. 6 and 7 are, again perfectly general, applying to both packed and open tube columns. Thus, for an open tube clumn (Poiseuille's law).

$$R_F = 32L\eta/3r^2$$

where r is the radius and η the carrier gas viscosity. For a packed column (D'Arcy's law), corresponding [7],

$$R_F = 2\eta\varepsilon L/B_0$$

where ε is the total porosity of the column packing and B_o is its specific permeability.

R_F is, thus, very readily measured experimentally for any column by determining t_d as a function of p_i and evaluating $2lR_f/3$ as the slope of a plot of t_d against $(p_i^3 - p_o^3 / p_i^2 - p_o^2)$ [2].

Turning now to the situation where two columns are serially linked with pressure drop p_i -- p in column F and of p -- p_o in column B, it is a straight forward matter to show[8] that, on account of conservation of mass,

$$\frac{V_{MF}}{L_F R_{fF}}(p_i^2 - p^2) = \frac{V_{MB}}{L_B R_{fB}}(p^2 - p_0^2) \qquad (8)$$

whence,

$$p^2 = \left\{ \frac{p_i^2 - I_F\left[p_i^2 - (\bar{V}_{MB}\bar{R}_{fF}/\bar{V}_{MF}\bar{R}_{fB})p_o^2\right]}{1 - I_F\left[1 - (\bar{V}_{MB}\bar{R}_{fF}/\bar{V}_{MF}\bar{R}_{fB})\right]} \right\} \qquad (9)$$

where V_{MF} and V_{MB} are the mobile phase (void) volumes of columns F and B and I_F is the length fraction, $L_F/(L_F + L_B)$, note also $I_F + I_B = 1$. V_{MF} and V_{MB} are easily measured directly via the usual relationship.

$V_M = jF_c t_d$

Where j is the James-Martin compressibility correction and F_c is the temperature corrected column flow-rate. Hence, p is readily evaluated for any I_F or pressures.

Eqns. 7 and 9 now allows us to calculate P since [8]

$$P = t_{dF} / t_{dB} = \left(\frac{L_B R_{fB}}{L_F R_{fF}}\right)\left(\frac{V_{MF}}{V_{MB}}\right)^2\left[\frac{(p_i^3 - p^3)}{(p^3 - p_0^3)}\right] \qquad (10)$$

All the quantities needed to evaluate P can be determined experimentally. We can subsequently, via eqn. 5, calculate k' for any column combination and any pi and po and, hence, α for solute pairs.

Calculating Column Lenghts for Optimizing Separations. Purnell and Williams [8] optimisation theory starts by defining a function, f_F, corresponding to some true length fraction, l_f such that

$$k' = f_F k'_F + f_B k'_B = (Pk'_F + k'_B)/(P+1) \qquad (11)$$

where $f_F + f_B = 1$

From above, $f_F = P / (P + 1)$ or $P = f_F / (1 - f_F)$.

Rearranging eq (10) then gives us

$$p^3 = \frac{p_i^3 + p\gamma p_o^3}{1 + P\gamma} \qquad (12)$$

where

$$\gamma = \frac{L_F R_{fF}}{L_B R_{fB}}\left[\frac{V_{MB}}{V_{MF}}\right]^2 = \frac{\bar{R}_{fF}}{\bar{R}_{fB}}\left[\frac{\bar{V}_{MB}}{\bar{V}_{MF}}\right]^2 \qquad (13)$$

where $\bar{R}_f$ and $\bar{V}_M$ are the respective quantities per unit lenght for each column and are, ideally, constants. It follows, therefore, that γ is also a constant, being independent of the individual column lengths comprising any whole column.

Substituting for $P(f_F / 1 - f_F)$ in the equation for p^3 leads to

$$p^3 = \frac{p_i^3 - f_F(p_i^3 - \gamma p_0^3)}{1 - f_F(1 - \gamma)} \qquad (14)$$

Finally, rearranging the equation for p^2, we get the length fraction corresponding to Fat fixed p_i and p_o via rearrangement of equation (8) as

$$I_F = \left\{ \frac{\bar{R}_{fF}\bar{V}_{MB}}{\bar{R}_{fB}\bar{V}_{MF}}\left(\frac{p^2 - p_0^2}{p_i^2 - p^2}\right) + 1 \right\}^{-1} \qquad (15)$$

and p can now be calculated for any F so as to yield the corresponding value of I_F.

Knowing the α_{min} (at the maximum window), we identify the correseponding optimum solvent composition, and knowing α_{min} for baseline resolution of all components of the mixture, the number of plates can be calculated from [9]

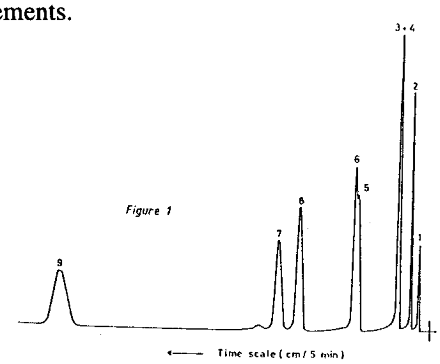
$$N_{req} = 36\left(\frac{\alpha}{\alpha - 1}\right)^2\left(\frac{k' + 1}{k'}\right)^2 \qquad (16)$$

where k' is the capacity factor of the second component of the most difficult to separate pair.

Experimental Section:

Squalane (SQ), Diisobutyl phthalate (DBP) and 60-80 mesh Chromosorb-G (AW-DMCS) were procured from phase separations (Queensferry, U.K.) and used as received. Sample components were of Laboratory grade. Columns of both SQ and DBP were made up in 270 cm and 300 cm lenghths, respectively, of 3.2 mm O.D. Stainless-steel tube, the liquid substrates being deposited on the Chromosorb by standard means. Swagelock fittings, to which packing was added if possible, minimized extraneous or coupling dead volumes. When used either alone or serially, columns, irrespective of mode, were always used with flow in the same direction to avoid void creation, which can occur on reversal of packed columns.

The two column packings each contained 5% (W/W) solvent and elution was by nitrogen. A Perkin-Elmer (Beaconsfield, U. K.) F.33 system equiped with flame ionisation detection (FID) and modified precision pressure gauges were used, and all experiments cited were conducted at 90°C. Since FID was used, dead-volumes were measured by methane injection, data quoted are the means of numerous measurements.



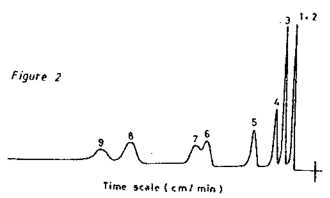


Figure 1. Chromatogram of the nine component mixture with SQ at 90°C.

Figure 2. Chromatogram of the nine component mixture with DBP at 90°C.

RESULTS

Fig. 1,2 illustrate typical chromatograms obtained for the nine-component mixture with each column in turn. We see that in no case is complete resolution of the sample achieved. Thus, the pair of these two columns provides a possible combination for isothermal series column separation.

Table 1 summarizes the chromatograms shown, for SQ there is a pair of identical k' (3/4) and 5 and 6 are seriously overlapped. DBP overs difficulty in separating a different pair (6/7) with identical k' for a pair of (1/2).

Table 1:

Data of predicted k' values for the original columns at 90o C.

No.	The Components	Columns of DBP k'	Column of SQ k'
1	Propylene oxide	1.35	0.850
2	1-Hexene	1.35	2.41
3	Cyclo-hexane	2.22	4.78
4	Tert-amyl methyl ether	3.09	4.78
5	4-Octene	5.55	12.0
6	1-Octyne	10.2	12.6
7	1-Nonene	11.3	26.3
8	p-Xylene	18.1	22.5
9	n-Decane	21.2	65.1

Having established capacity factor data for the columns we now go on to determine the flow parameters of the test columns. Flow rates were determined at 10 psi intervals form 10 psig for both columns with one extra measurement a 5 psig for the SQ column as shown in Table 2.

Table 2.

Values of H and u for SQ and DBP columns at 90°C.

SQ			DBP		
p(psi)	H (cm)	u(cms-1)	p(psi)	H(cm)	u(cms-1)
5	0.255	2.00	..	..	..
10	0.210	4.02	10	0.320	3.88
20	1.05	8.3	20	0.220	7.19
30	1.32	10.0	30	0.144	11.4
40	2.78	15.0	40	0.228	14.3

In Table 3 we list the measured values of t_d, v_m and f(p) where this is defined as:

$$f(p) = \frac{{}_{pi}3 - p_o 3}{({}_{pl}2 - p_o 2)2}$$

Table 3

Values of td, Vm, u and f(p) for test columns at 90°C.

	SQUALANE			DIISOBUTYL PHTHALATE		
p (psi)	t_d (sec)	v_m (ml)	10^6f(p) (m^2 IV^{-1})	t_d (sec)	v_m (ml)	10^6 f(p) (m^2 IV^{-1})
10	70.7	7.50	11.2	78.0	7.33	11.1
15	48.2	7.46	7.5	53.2	7.76	7.5
20	35.8	7.14	5.8	42.0	7.63	5.8
25	29.8	7.17	4.6	35.2	7.94	4.6
30	26.1	7.59	3.9	29.6	7.94	3.9
35	22.6	7.59	3.5	26.2	7.91	3.5
40	20.1	7.41	3.0	22.5	7.91	3.0

In figure 3 we show plots of H against u for the two columns to determine lowest H value by the curves.

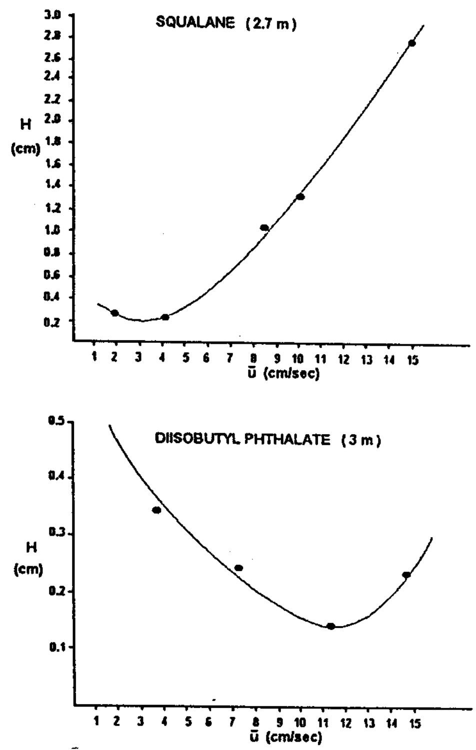


Figure 3: Van Deemter plots for test columns.

In plots of t_d against (pi3 - po3) / (pi2 - po2)2 for the two columns which are evidently, of excellent linearity and provide the values of R_f for SQ and DBP listed in Table 4, values of V_M for the two columns, predicted from plots of $1/t_d$ against j. F_c, are cited in table 4.

Table 4

Values of R_f and V_M for the row columns at 90° C.

Carrier gas, N_2.

Column	10^{-6}Rf (Nsm^{-3})	V_M (ml $^{m-1}$)
DBP	1.18 ± 0.25	2.591 ± 0.08
SQ	1.296 ± 0.19	2.74 ± 0.07

Having established the necessary data we can now proceed to construct a plot of k' against f for the solvent pair for all solutes. All this involves is plotting the k' values for a solute on each side of the diagram and connecting the pairs for each solute with a straight line. The relevant plot is shown in Figure 4 where represents the front columns (f_F). Figure 5 illustrates the window diagram for this combination in the same mode (DBP = Front), the relevant values of α having been calculated in steps of f_F ver the range 0-1. This reveals a best α of 1.325 at f_F = 0.818.

Using equations (12, 13, 15) we can calculate ι_F corresponding to the optimum f_F derived from the best window. These calculations produce the following results to provide baseline separation at the α_{min} corresponding to the top of the window ($L = N_{req} H_{min}$).

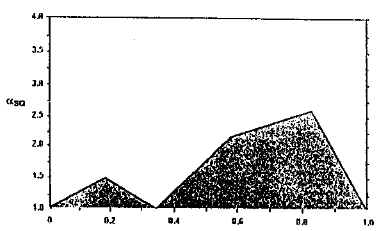
Mode A : SQ(F) / DBP (B) : ι_F = 0.11, L = 3.45 m

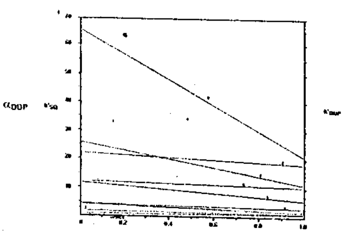
so L_{SQ} = 0.37 m and L_{DBP} = 3.08 m

Mode B : DBP (F) / SQ (B) : ι_F = 0.735 , L = 3.45 m

so L_{DBP} = 2.53 m and L_{SQ} = 0.92 m

Figure 6 shows the chromatograms obtained from the column systems (A/B) as predicted above. These are very sucessful because baseline resolution is to all intents and a purposes achieved. As theory demands, the chromatograms are identical and a reasonable agreement between the experimental and calculated values of k', as shown in table 5. It is notable that despite the column length, total analysis time is only 16 minutes.





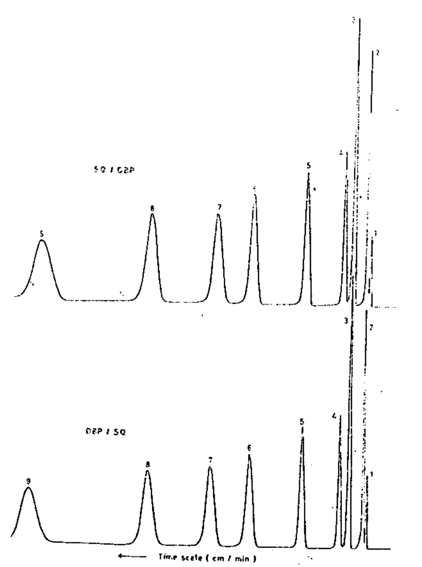


Figure 4 : Plots of k' against f_F for the nine solutes with DBP (F) AND SQ (B).

Figure 5 : Window diagram from figure 5.

Figure 6: Chromatograms of the nine component mixture in each mode SQ/DEP or DBP/SQ.

Operating conditions : 90 °C, 30 p. s. i. g. N_2; columns as in text.

Table 5

Comparison of experimental and calculated values of k' for Column Combination of SQ and DBP at optimum lengths.

Cols. Comb.	SQ / DBP			DBP / SQ		
Comps. No.	K'cal.	k'Exp.	k'Exp. / k'Cal.	K'cal.	K'Exp.	k'Exp. / k'Cal
1	1.27	1.21	0.953	1.26	1.20	0.952
2	1.51	1.53	1.01	1.54	1.575	1.02
3	2.62	2.64	1.01	2.68	2.71	1.01
4	3.36	3.43	1.02	3.40	3.46	1.02
5	6.56	6.59	1.01	6.73	6.54	0.972
6	10.6	11.0	1.04	10.6	10.8	1.02
7	13.6	14.1	1.03	14.0	14.0	1.00
8	18.8	19.7	1.05	18.9	19.3	1.02
9	28	28.9	1.03	29.2	28.7	0.984

Mean 1.02 ± 0.028 Mean 1.00 ± 0.025

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