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EXPERIMENTAL VERIFICATION OF THE THEORY OF SERIALLY COUPLED GAS CHROMATOGRAPHIC COLUMNS

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SUMMARY

The general theory of serially coupled gas chromatographic columns previously offered by the authors is experimentally tested. It is shown to be entirely valid and free of all assumption other than that of carrier gas ideality. The application of the theory in practice is illustrated and shown to be simple and straightforward in providing accurate values of capacity factors and relative retentions for coupled columns from readily measured parameters for the individual columns. The main obstacle to rapid development of practically useful serial column systems is thus removed.

INTRODUCTION

One of the most interesting, and potentially important, developments of the immediate past has been the revival of interest in the serial operation of gas chromatographic columns, in particular, of open tubes. Put in the simplest terms, this has arisen as a result of a growing appreciation that little further improvement in column efficiency (theoretical plate height) can now be envisaged and that, in consequence, a search for higher selectivity offers a more effective route to improved analysis than the use of ever longer columns.

Historically, work in this area can be traced to the outstanding innovative studies of Hildebrand and Reilly¹, essentially overlooked at the time. The only subsequent contribution of note, until very recently, was that of Buys and Smuts², although, as we point out later, this work did not lead to advance. The recent revival of practical interest starts with the work of Jennings and co-workers^{3,4} who, while establishing the practical value of serial open tube column systems, were unable to reconcile their results quantitatively with existing theory. We have, since, presented assumption free general^{5–8} and approximate⁹ (practical) theories of serial column operation in gas chromatography. Most recently, Mayfield and Chesler¹⁰ have reported a comprehensive attempt to test the value of theory in predicting retention in coupled open tube columns. Their results allowed them to conclude no more than

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that they could be "cautiously optimistic that one or other of the three approaches adopted could serve as a basis for coupled column optimisation". Their caution is reasonably based since each of the approaches they tested involve simplifying and thus limiting, assumptions which preclude their general applicability.

We present here experimental results that confirm the correctness of our own approach, one that was not tested by Mayfield and Chesler¹⁰. Further, we show the practical simplicity of its use in predicting, from readily measured experimental data, absolute capacity factors (k') and, hence, relative retention (α), as a function of both inlet pressure and column mode. This opens the route to quantitative and straightforward optimisation of column lengths in serially coupled systems.

THEORY

Only the practically important elements of our general theory⁵⁻⁷ are presented here in order to facilitate understanding of the analysis of the experimental information cited later.

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) and back (B),

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

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

$$k' = (t_{dF}k'_F + t_{dB}k'_B)/(t_{dF} + t_{dB}) \quad (2)$$

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

$$k' = \left(\frac{Pk'_F + k'_B}{P + 1} \right) \quad (3)$$

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. 3, 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.

Hildebrand and Reilley¹ introduced the concept of a resistance to gas flow function (R_F) defined in terms of average carrier velocity, \bar{u} , by

$$R_F = (p_i^2 - p_o^2)/\bar{p}\bar{u} \quad (4)$$

and it is a simple matter then to show^{6,7} that t_d is given by

$$t_d = \left[\frac{2LR_F}{3} \right] \left[\frac{p_i^3 - p_o^3}{(p_i^2 - p_o^2)^2} \right] \quad (5)$$

where L is column length. Both eqns. 4 and 5 are, again, perfectly general, applying to both packed and open tube columns. Thus, for an open tube column (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), correspondingly⁷,

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

where ε is the total porosity of the column packing and B_0 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 $p_i \rightarrow p$ in column F and of $p \rightarrow p_o$ in column B, it is a straightforward matter to show⁷ that, on account of conservation of mass,

$$\frac{V_{MF}}{L_F R_{FF}} (p_i^2 - p^2) = \frac{V_{MB}}{L_B R_{FB}} (p^2 - p_o^2) \quad (6)$$

whence,

$$p^2 = \left\{ \frac{p_i^2 - l_F [p_i^2 - (V_{MB} R_{FF} / V_{MF} R_{FB}) p_o^2]}{1 - l_F [1 - (V_{MB} R_{FF} / V_{MF} R_{FB})]} \right\} \quad (7)$$

where V_{MF} and V_{MB} are the mobile phase (void) volumes of columns F and B and l_F is the length fraction, $L_F/(L_F + L_B)$, note also $l_F + l_B = 1$. 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 l_F or pressures.

Eqns. 5 and 7 now allow us to calculate P since⁷

$$P = t_{dF}/t_{dB} = \left(\frac{L_B R_{FB}}{L_F R_{FF}} \right) \left(\frac{V_{MF}}{V_{MB}} \right)^2 \left[\frac{(p_i^3 - p^3)}{(p^3 - p_o^3)} \right] \quad (8)$$

All the quantities needed to evaluate P can be determined experimentally. We can subsequently, via eqn. 3, calculate k' for any column combination and any p_i and p_o and, hence, α for solute pairs.

We have pointed out earlier⁷ that eqn. 8, again, is perfectly general, depending for its validity only upon adherence of the carrier to the ideal gas laws, and that the equations of Hildebrand and Reilley¹ and of Buys and Smuts² represent special cases covered by eqn. 8. The equation derived by the former authors is valid only when V_M/L is the same for both columns F and B, that is, the serial columns must have equal $r^2\varepsilon$. The equation presented by the latter authors is of even more limited validity since it demands that, in addition, the columns involved must have equal ε/B_0 , that is, identical flow resistance per unit length (R_F/L). It is not, therefore, surprising that recent attempts¹⁰ to correlate these earlier theoretical approaches with experiment have failed; given ignorance of the constraints imposed by assumption in these early theoretical derivations, failure of the equations in practice was almost inevitable.

In what follows, we present evidence to show that the several equations presented above describe real behaviour correctly. We have chosen to use packed columns, each containing Chromosorb G supported squalane but differing in support particle size and/or solvent-support ratio. Manipulation of eqn. 3 readily establishes that relative retentions should remain constant in serial operation of the columns containing similar packing but capacity factors, of course, will change. It is, intuitively obvious that relative retention cannot be changed by serial column operation unless the relevant α values are different in the component parts. Thus, the experimental test here involves accuracy of prediction of k' values, a sufficient objective since, given that this is achieved, it will evidently be equally true where α values differ.

EXPERIMENTAL

Squalane and Chromosorb G (AW-DCMG) of both 60–80 and 100–120 ASTM mesh, were procured from Phase Separations. They were used as received. Columns were fabricated in 3 m lengths of 1/8th in O.D. stainless steel, squalane being coated on the support by standard methods. Column connexions were made via Swagelock fittings, packing being added where necessary to minimise dead volume. Columns were always used with gas flow in the same direction in order to eliminate any possible void creation during use.

The columns used were: (1) 0.5% (w/w) squalane on 100–120 mesh; (2) 3.5% (w/w) squalane on 100–120 mesh; (3) 0.5% (w/w) squalane on 60–80 mesh; (4) 5.0% (w/w) squalane on 60–80 mesh. This nomenclature is used throughout what follows.

The gas chromatograph comprised a Perkin-Elmer F.33 system, equipped with flame ionization detection and modified to allow inclusion of precision pressure gauges and a platinum resistance thermometer probe. The carrier gas was nitrogen and all experiments were conducted at 90°C.

Dead volumes were measured by methane injection via a 100- μ l syringe whilst the four liquid test solutes, benzene, toluene, ethylbenzene and propylbenzene, were injected singly in amounts in the range 0.01–0.10 μ l. No sample size effect on retention was detectable.

RESULTS

Basic retention data for elution from individual columns at 90°C were as listed in Table I; values of k' cited are the mean of numerous elutions.

The individual values of α are sufficiently close to the arithmetic means to confirm that α is independent of solvent-support ratio and of support mesh size.

Plots of t_d against $(p_i^3 - p_o^3)/(p_i^2 - p_o^2)^2$ are shown in Figs. 1 and 2. The linearity is clearly excellent and the derived values of R_F in $N\ s\ m^{-3}$ ($= 1.01 \cdot 10^7\ atm\ s\ cm^{-1}$) are: columns, (1) $9.05 \cdot 10^6$; (2) $8.56 \cdot 10^6$; (3) $3.60 \cdot 10^6$; (4) $3.79 \cdot 10^6$; the agreement of the data for columns 1 and 2 (100–120 mesh) and of those for columns 3 and 4 (60–80 mesh) is as close as reasonable expectation could demand. The corresponding mobile phase volumes, V_M in ml were: 7.79; 7.71; 7.74; 7.91; values that show, from a different point of view, the excellent reproducibility of the packing procedures.

TABLE I
 k' AND α VALUES FOR TEST SOLUTES WITH INDIVIDUAL COLUMNS

| Solute | Column | | | | | | | | |
|---------------|--------|----------|------|----------|-------|----------|------|----------|-----------------|
| | 1 | | 2 | | 3 | | 4 | | α_{over} |
| | k' | α | k' | α | k' | α | k' | α | |
| Benzene | 0.400 | 0.209 | 2.79 | 0.208 | 0.432 | 0.196 | 3.86 | 0.209 | 0.206 |
| Toluene | 0.916 | 0.480 | 6.51 | 0.486 | 1.08 | 0.491 | 9.03 | 0.488 | 0.486 |
| Ethylbenzene | 1.91 | 1.00 | 13.4 | 1.00 | 2.20 | 1.00 | 18.5 | 1.00 | 1.00 |
| Propylbenzene | 3.77 | 1.97 | 26.8 | 2.00 | 4.23 | 1.92 | 36.7 | 1.98 | 1.97 |

In Tables II–V, we present values of k'_{exp} and k'_{calc} , for the four solutes eluted from each of eight column combinations. Included also are the relevant values of p_i , p_o and P since, in combination with the data presented earlier, all necessary calculations may be reproduced.

DISCUSSION

The data of Tables II–V illustrate a number of general features of serial column operation. Consider the values of k' listed. First, we see that for a given binary column mode, the effect of increasing the inlet pressure is proportionately the same for all solutes. Table VI lists the ratios of the values of k' for each column mode over the approximate range 25–105 p.s.i.

Over this substantial inlet pressure range we see that absolute k' values vary from around 2 to 14%, depending on the intrinsic k' of the individual columns. Since the test columns involve pairs in which intrinsic k' varies by an order of magnitude, it is unlikely that, in practice, greater variation will be commonly met with.

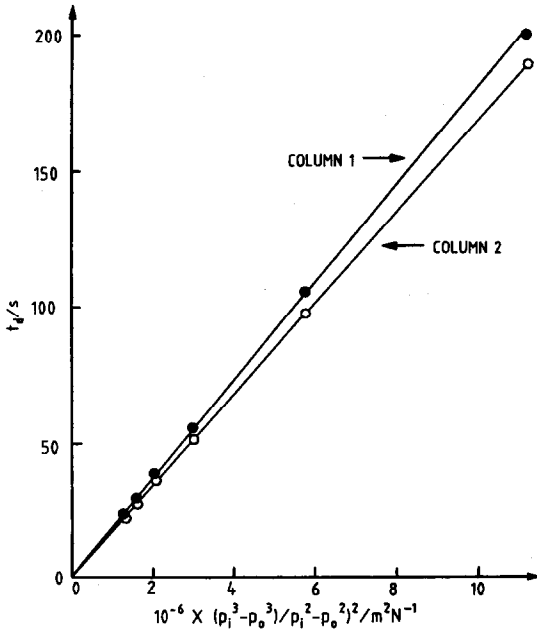


Fig. 1. Plot of dead time (t_d) against $(p_i^3 - p_o^3)/(p_i^2 - p_o^2)^2$ for columns 1 and 2 (100–120 mesh). Carrier gas, nitrogen; temperature, 90°C. $R_F = 1.5 \times \text{slope}/L$ (cf. eqn. 5).

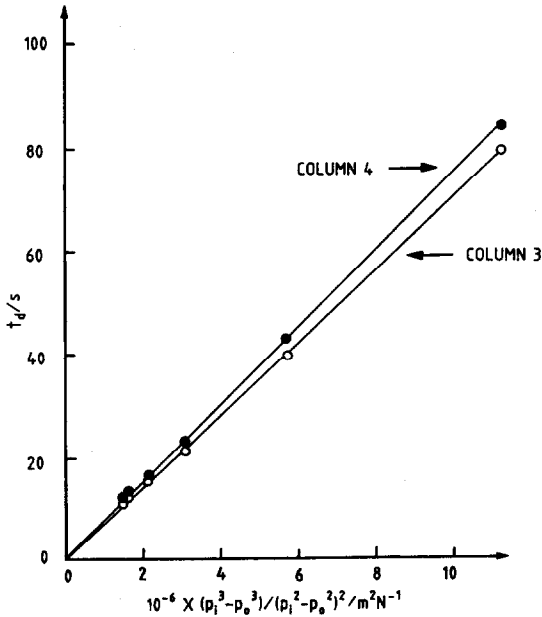


Fig. 2. Plot of dead time (t_d) against $(p_i^3 - p_o^3)/(p_i^2 - p_o^2)^2$ for columns 3 and 4 (60–80 mesh). Carrier gas, nitrogen; temperature, 90°C. $R_F = 1.5 \times \text{slope}/L$ (cf. eqn. 5).

TABLE II

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF k' FOR COMBINATIONS OF COLUMNS 2 AND 3 OVER A RANGE OF p_i AT 90°C

Pressures in p.s.i.; carrier gas, nitrogen.

| Mode: F/B = 2:3 | | | | | | Mode: F/B = 3:2 | | | | | |
|----------------------|-------|------|------|------------|-------------|-----------------|-------|------|------|------------|-------------|
| p_i | p_o | p | P | k'_{exp} | k'_{calc} | p_i | p_o | p | P | k'_{exp} | k'_{calc} |
| <i>Propylbenzene</i> | | | | | | | | | | | |
| 24.7 | 14.7 | 18.2 | 1.30 | 16.9 | 17.0 | 24.5 | 14.5 | 22.0 | 1.20 | 14.8 | 14.5 |
| 34.7 | 14.6 | 22.5 | 1.53 | 17.9 | 17.9 | 34.6 | 14.6 | 30.2 | 1.33 | 14.0 | 13.9 |
| 54.6 | 14.6 | 32.1 | 1.81 | 18.6 | 18.8 | 54.7 | 14.7 | 46.6 | 1.45 | 13.6 | 13.4 |
| 74.6 | 14.6 | 42.3 | 1.94 | 18.7 | 19.1 | 74.8 | 14.8 | 63.3 | 1.50 | 13.0 | 13.3 |
| 94.6 | 14.6 | 52.8 | 2.02 | 18.8 | 19.3 | 94.8 | 14.8 | 80.0 | 1.52 | 13.0 | 13.2 |
| 104.6 | 14.6 | 58.1 | 2.05 | 18.9 | 19.4 | 104.9 | 14.9 | 88.4 | 1.53 | 12.7 | 13.1 |
| <i>Ethylbenzene</i> | | | | | | | | | | | |
| 24.6 | 14.6 | 18.1 | 1.30 | 8.84 | 8.53 | 24.6 | 14.6 | 22.2 | 1.20 | 7.17 | 7.39 |
| 34.6 | 14.6 | 22.4 | 1.53 | 8.93 | 9.00 | 34.6 | 14.6 | 30.1 | 1.33 | 6.94 | 7.01 |
| 54.6 | 14.5 | 32.1 | 1.81 | 9.36 | 9.41 | 54.5 | 14.5 | 46.4 | 1.45 | 6.60 | 6.77 |
| 74.5 | 14.5 | 42.3 | 1.94 | 9.55 | 9.59 | 74.5 | 14.5 | 63.0 | 1.50 | 6.63 | 6.68 |
| 94.6 | 14.5 | 52.8 | 2.02 | 9.50 | 9.69 | 94.5 | 14.5 | 79.7 | 1.52 | 6.45 | 6.64 |
| 104.6 | 14.5 | 58.1 | 2.05 | 9.43 | 9.73 | 104.5 | 14.5 | 88.1 | 1.53 | 6.55 | 6.63 |
| <i>Toluene</i> | | | | | | | | | | | |
| 24.6 | 14.6 | 18.1 | 1.30 | 4.26 | 4.15 | 24.4 | 14.4 | 21.9 | 1.20 | 3.59 | 3.55 |
| 34.6 | 14.6 | 22.4 | 1.53 | 4.43 | 4.36 | 34.4 | 14.4 | 29.9 | 1.33 | 3.42 | 3.41 |
| 54.6 | 14.6 | 32.1 | 1.81 | 4.63 | 4.58 | 54.4 | 14.4 | 46.3 | 1.45 | 3.37 | 3.30 |
| 74.6 | 14.6 | 42.3 | 1.94 | 4.70 | 4.67 | 74.5 | 14.5 | 63.1 | 1.50 | 3.23 | 3.25 |
| 94.6 | 14.6 | 52.8 | 2.02 | 4.68 | 4.71 | 94.5 | 14.5 | 79.7 | 1.52 | 3.16 | 3.23 |
| 104.7 | 14.7 | 58.2 | 2.05 | 4.63 | 4.72 | 104.5 | 14.5 | 88.1 | 1.53 | 3.20 | 3.23 |
| <i>Benzene</i> | | | | | | | | | | | |
| 24.7 | 14.7 | 18.2 | 1.30 | 1.75 | 1.77 | 24.6 | 14.6 | 22.1 | 1.20 | 1.49 | 1.50 |
| 34.7 | 14.7 | 22.5 | 1.53 | 1.84 | 1.86 | 34.6 | 14.6 | 30.1 | 1.33 | 1.40 | 1.44 |
| 54.7 | 14.7 | 32.2 | 1.81 | 1.96 | 1.95 | 54.6 | 14.6 | 46.5 | 1.45 | 1.37 | 1.39 |
| 74.7 | 14.7 | 42.4 | 1.94 | 1.99 | 1.99 | 74.6 | 14.6 | 63.2 | 1.50 | 1.36 | 1.38 |
| 94.7 | 14.7 | 52.9 | 2.02 | 1.99 | 2.00 | 94.6 | 14.6 | 79.8 | 1.52 | 1.32 | 1.37 |
| 104.7 | 14.7 | 58.2 | 2.05 | 1.98 | 2.01 | 104.6 | 14.6 | 88.2 | 1.53 | 1.37 | 1.36 |

Turning to the effect of mode alone, again we see that the effect on k' is proportionately the same for all solutes, but the effect of p_i is now much more pronounced, as Table VII shows.

The effect of inverting the column sequence is to induce changes in k' ranging from 4 to 17% at the lower inlet pressure but of 10 to 65% at the higher pressure. This effect, obviously, is greatest when the intrinsic k' of the individual columns comprising the pair are most different; self-evidently, if these were equal, k' would not change at all. For the reason cited above, this again indicates the probable range of variation likely to be met with in practice.

The foregoing observations provide, for the first time, theoretical and practical insight into the extent of change of k' to be anticipated as a function of both p_i and

TABLE III

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF k' FOR COMBINATIONS OF COLUMNS 1 AND 4 OVER A RANGE OF p_i AT 90°C

Pressures in p.s.i.; carrier gas, nitrogen.

| Mode: F/B = 1:4 | | | | | | Mode: F/B = 4:1 | | | | | |
|----------------------|-------|------|------|------------|-------------|-----------------|-------|------|------|------------|-------------|
| p_i | p_o | P | P | k'_{exp} | k'_{calc} | p_i | p_o | P | P | k'_{exp} | k'_{calc} |
| <i>Propylbenzene</i> | | | | | | | | | | | |
| 24.8 | 14.8 | 18.3 | 1.29 | 18.5 | 18.2 | 25.0 | 15.0 | 22.5 | 1.27 | 22.9 | 22.2 |
| 34.9 | 14.9 | 22.7 | 1.51 | 17.5 | 16.9 | 35.0 | 15.0 | 30.6 | 1.42 | 23.0 | 23.0 |
| 55.0 | 15.0 | 32.3 | 1.78 | 15.8 | 15.6 | 55.0 | 15.0 | 47.0 | 1.54 | 24.0 | 23.7 |
| 74.9 | 14.9 | 42.4 | 1.92 | 15.0 | 15.1 | 75.1 | 15.1 | 67.7 | 1.59 | 23.1 | 24.0 |
| 94.9 | 14.9 | 52.8 | 2.00 | 14.7 | 14.8 | 95.1 | 15.1 | 80.4 | 1.62 | 23.4 | 24.1 |
| 104.9 | 14.9 | 58.0 | 2.02 | 14.8 | 14.7 | 105.1 | 15.1 | 88.8 | 1.63 | 23.0 | 24.2 |
| <i>Ethylbenzene</i> | | | | | | | | | | | |
| 24.6 | 14.6 | 18.1 | 1.29 | 9.20 | 9.15 | 25.0 | 15.0 | 22.5 | 1.27 | 10.8 | 11.2 |
| 34.6 | 14.6 | 22.4 | 1.51 | 8.56 | 8.49 | 34.6 | 14.6 | 30.2 | 1.42 | 11.6 | 11.6 |
| 54.6 | 14.6 | 32.0 | 1.78 | 7.95 | 7.86 | 54.6 | 14.6 | 46.6 | 1.54 | 12.0 | 12.0 |
| 74.4 | 14.4 | 42.0 | 1.92 | 7.42 | 7.57 | 74.6 | 14.6 | 63.3 | 1.59 | 11.8 | 12.1 |
| 94.4 | 14.4 | 52.4 | 2.00 | 7.21 | 7.42 | 94.6 | 14.6 | 80.0 | 1.62 | 11.6 | 12.2 |
| 104.4 | 14.4 | 57.7 | 2.02 | 7.03 | 7.39 | 104.6 | 14.6 | 88.3 | 1.63 | 11.6 | 12.2 |
| <i>Toluene</i> | | | | | | | | | | | |
| 24.4 | 14.4 | 17.9 | 1.29 | 4.50 | 4.46 | 24.7 | 14.7 | 22.2 | 1.27 | 5.48 | 5.46 |
| 34.4 | 14.4 | 22.2 | 1.51 | 4.22 | 4.14 | 34.6 | 14.6 | 30.1 | 1.42 | 5.78 | 5.68 |
| 54.4 | 14.4 | 31.8 | 1.78 | 3.93 | 3.82 | 54.6 | 14.6 | 46.6 | 1.54 | 5.82 | 5.84 |
| 74.4 | 14.4 | 42.0 | 1.92 | 3.78 | 3.69 | 74.6 | 14.6 | 63.2 | 1.59 | 5.88 | 5.90 |
| 94.8 | 14.8 | 52.7 | 2.00 | 3.59 | 3.62 | 94.5 | 14.5 | 79.9 | 1.62 | 5.82 | 5.93 |
| 104.6 | 14.6 | 57.8 | 2.02 | 3.60 | 3.59 | 104.5 | 14.5 | 88.3 | 1.63 | 5.86 | 5.94 |
| <i>Benzene</i> | | | | | | | | | | | |
| 24.8 | 14.8 | 18.3 | 1.29 | 1.90 | 1.91 | 24.6 | 14.6 | 22.2 | 1.27 | 2.21 | 2.34 |
| 34.9 | 14.9 | 22.6 | 1.51 | 1.72 | 1.78 | 34.6 | 14.6 | 30.2 | 1.42 | 2.38 | 2.43 |
| 54.9 | 14.9 | 32.2 | 1.78 | 1.61 | 1.64 | 54.6 | 14.6 | 46.6 | 1.54 | 2.47 | 2.50 |
| 74.9 | 14.9 | 42.4 | 1.92 | 1.55 | 1.58 | 74.6 | 14.6 | 63.2 | 1.59 | 2.36 | 2.52 |
| 94.9 | 14.9 | 52.8 | 2.00 | 1.52 | 1.55 | 94.6 | 14.6 | 80.0 | 1.62 | 2.44 | 2.54 |
| 104.9 | 14.9 | 58.1 | 2.02 | 1.51 | 1.54 | 104.6 | 14.6 | 88.3 | 1.63 | 2.49 | 2.54 |

column sequence. But they provide also a background against which the extent of agreement between the experimental observations and theoretical prediction may be judged.

If we define the discrepancy function Δ as

$$\Delta(\%) = 100(k'_{exp} - k'_{calc})/k'_{calc}$$

we note, first, that the number of individual data having positive Δ is closely equal to that of negative Δ and that there are no obvious trends. Secondly, that the extreme deviations are $\pm 6\%$, and such large deviations are few. Finally, listing the arithmetic

TABLE IV

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF k' FOR COMBINATIONS OF COLUMNS 1 AND 2 OVER A RANGE OF p_i AT 90°C

Pressures in p.s.i.; carrier gas, nitrogen.

| Mode: $F/B = 1:2$ | | | | | | Mode: $F/B = 2:1$ | | | | | |
|----------------------|-------|------|------|------------|-------------|-------------------|-------|------|------|------------|-------------|
| p_i | p_o | p | P | k'_{exp} | k'_{calc} | p_i | p_o | p | P | k'_{exp} | k'_{calc} |
| <i>Propylbenzene</i> | | | | | | | | | | | |
| 24.8 | 14.8 | 20.4 | 1.29 | 14.3 | 13.8 | 24.8 | 14.8 | 20.6 | 1.27 | 15.6 | 16.6 |
| 34.9 | 14.9 | 26.6 | 1.47 | 13.7 | 13.1 | 34.8 | 14.8 | 26.9 | 1.43 | 16.2 | 17.3 |
| 54.9 | 14.9 | 39.8 | 1.65 | 12.7 | 12.5 | 54.7 | 14.7 | 40.5 | 1.60 | 16.9 | 17.9 |
| 74.9 | 14.9 | 53.4 | 1.73 | 12.5 | 12.2 | 74.8 | 14.8 | 54.4 | 1.68 | 17.4 | 18.2 |
| 94.9 | 14.9 | 67.2 | 1.78 | 12.3 | 12.1 | 94.7 | 14.7 | 68.5 | 1.72 | 17.3 | 18.3 |
| 114.9 | 14.9 | 81.0 | 1.80 | 12.2 | 12.0 | 104.8 | 14.8 | 75.6 | 1.73 | 17.2 | 18.4 |
| <i>Ethylbenzene</i> | | | | | | | | | | | |
| 24.7 | 14.7 | 20.2 | 1.29 | 7.43 | 6.93 | 24.7 | 14.7 | 20.4 | 1.27 | 8.81 | 8.34 |
| 34.8 | 14.8 | 26.5 | 1.47 | 6.81 | 6.56 | 34.7 | 14.7 | 26.9 | 1.43 | 9.26 | 8.67 |
| 54.9 | 14.9 | 39.9 | 1.65 | 6.63 | 6.25 | 54.7 | 14.7 | 40.5 | 1.60 | 9.41 | 8.98 |
| 74.7 | 14.7 | 53.3 | 1.73 | 6.36 | 6.12 | 74.6 | 14.6 | 54.3 | 1.68 | 9.37 | 9.11 |
| 94.7 | 14.7 | 67.0 | 1.78 | 6.10 | 6.04 | 94.6 | 14.6 | 68.4 | 1.72 | 9.03 | 9.18 |
| 114.7 | 14.7 | 80.0 | 1.80 | 6.08 | 6.01 | 104.6 | 14.6 | 75.5 | 1.73 | 8.99 | 9.18 |
| <i>Toluene</i> | | | | | | | | | | | |
| 24.7 | 14.7 | 20.2 | 1.29 | 3.51 | 3.35 | 24.7 | 14.7 | 20.4 | 1.27 | 4.08 | 4.05 |
| 34.7 | 14.7 | 26.4 | 1.47 | 3.45 | 3.18 | 34.7 | 14.7 | 26.8 | 1.43 | 4.43 | 4.21 |
| 54.7 | 14.7 | 39.6 | 1.65 | 3.13 | 3.03 | 54.7 | 14.7 | 40.4 | 1.60 | 4.42 | 4.36 |
| 74.7 | 14.7 | 53.3 | 1.73 | 3.03 | 2.97 | 74.7 | 14.7 | 54.4 | 1.68 | 4.48 | 4.42 |
| 94.7 | 14.7 | 67.0 | 1.78 | 3.00 | 2.93 | 94.8 | 14.8 | 68.5 | 1.72 | 4.45 | 4.45 |
| 104.8 | 14.8 | 74.1 | 1.80 | 2.96 | 2.92 | 104.8 | 14.8 | 75.6 | 1.73 | 4.49 | 4.46 |
| <i>Benzene</i> | | | | | | | | | | | |
| 24.7 | 14.7 | 20.2 | 1.29 | 1.43 | 1.44 | 24.5 | 14.8 | 20.5 | 1.27 | 1.68 | 1.73 |
| 34.6 | 14.6 | 26.3 | 1.47 | 1.41 | 1.37 | 34.9 | 14.9 | 27.0 | 1.43 | 1.83 | 1.81 |
| 54.5 | 14.5 | 39.5 | 1.65 | 1.32 | 1.30 | 54.9 | 14.9 | 40.6 | 1.60 | 1.85 | 1.87 |
| 74.5 | 14.5 | 53.1 | 1.73 | 1.29 | 1.27 | 74.9 | 14.9 | 54.5 | 1.68 | 1.90 | 1.90 |
| 94.5 | 14.5 | 66.9 | 1.78 | 1.26 | 1.26 | 94.9 | 14.9 | 68.6 | 1.72 | 1.91 | 1.91 |
| 114.5 | 14.5 | 80.7 | 1.80 | 1.27 | 1.25 | 104.9 | 14.9 | 75.7 | 1.73 | 1.90 | 1.91 |

mean of all calculated values of Δ , as in Table VIII, we see that agreement of experimental and calculated k' is good to ca. 2%, a figure very substantially less than the variations of k' with p_i and mode illustrated in Tables VI and VII. Bearing in mind that at 90°C, (a) temperature variation of $\pm 1^\circ\text{C}$ can induce a change of $\pm 3\%$ in the observed value of k' , (b) that at long retention temporal flow variation can be around $\pm 1\%$, and (c) that the use of methane as a dead time marker must induce some small error, agreement to better than about that observed is hardly to be expected.

The data thus confirm the theory remarkably well and provide a secure base for binary column optimisation via prediction of α as a function of mode and pressures.

TABLE V

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF k' FOR COMBINATIONS OF COLUMNS 2 AND 4 OVER A RANGE OF p_i at 90°C

Pressures in p.s.i.; carrier gas, nitrogen.

| Mode: F/B = 2:4 | | | | | | Mode: F/B = 4:2 | | | | | |
|----------------------|-------|------|------|------------|-------------|-----------------|-------|------|------|------------|-------------|
| p_i | p_o | p | P | k'_{exp} | k'_{calc} | p_i | p_o | p | P | k'_{exp} | k'_{calc} |
| <i>Propylbenzene</i> | | | | | | | | | | | |
| 24.5 | 14.5 | 18.1 | 1.27 | 32.1 | 31.2 | 24.7 | 14.7 | 22.2 | 1.29 | 34.4 | 32.4 |
| 34.3 | 14.3 | 22.3 | 1.50 | 32.0 | 30.8 | 34.8 | 14.8 | 30.2 | 1.43 | 34.1 | 32.6 |
| 54.3 | 14.3 | 32.1 | 1.76 | 31.2 | 30.4 | 54.7 | 14.7 | 46.4 | 1.56 | 33.5 | 32.8 |
| 74.6 | 14.6 | 42.7 | 1.89 | 31.0 | 30.2 | 74.7 | 14.7 | 63.0 | 1.62 | 32.4 | 32.9 |
| 94.6 | 14.6 | 53.4 | 1.96 | 29.8 | 30.1 | 94.8 | 14.8 | 79.7 | 1.64 | 32.6 | 33.0 |
| 104.7 | 14.7 | 58.8 | 1.99 | 29.9 | 30.1 | 104.8 | 14.8 | 88.0 | 1.65 | 32.4 | 33.0 |
| <i>Ethylbenzene</i> | | | | | | | | | | | |
| 24.2 | 14.2 | 17.8 | 1.27 | 16.3 | 15.6 | 24.7 | 14.7 | 22.2 | 1.29 | 16.9 | 16.3 |
| 34.9 | 14.9 | 22.9 | 1.50 | 16.1 | 15.5 | 34.7 | 14.7 | 30.1 | 1.43 | 17.0 | 16.4 |
| 54.7 | 14.7 | 32.5 | 1.76 | 16.5 | 15.3 | 54.5 | 14.5 | 46.3 | 1.56 | 16.7 | 16.5 |
| 74.7 | 14.7 | 42.9 | 1.89 | 15.2 | 15.2 | 74.3 | 14.3 | 62.6 | 1.62 | 16.5 | 16.5 |
| 94.7 | 14.7 | 53.5 | 1.96 | 15.1 | 15.1 | 94.6 | 14.6 | 79.5 | 1.64 | 16.6 | 16.6 |
| 104.7 | 14.7 | 58.8 | 1.99 | 15.1 | 15.1 | 104.8 | 14.8 | 87.9 | 1.65 | 16.5 | 16.6 |
| <i>Toluene</i> | | | | | | | | | | | |
| 24.7 | 14.7 | 18.3 | 1.27 | 7.78 | 7.62 | 24.7 | 14.7 | 22.2 | 1.29 | 8.48 | 7.93 |
| 34.6 | 14.6 | 22.6 | 1.50 | 7.73 | 7.52 | 34.7 | 14.7 | 30.1 | 1.43 | 8.29 | 7.99 |
| 54.6 | 14.6 | 32.4 | 1.76 | 7.63 | 7.42 | 54.7 | 14.7 | 46.4 | 1.56 | 8.14 | 8.05 |
| 74.6 | 14.6 | 42.8 | 1.89 | 7.49 | 7.38 | 74.7 | 14.7 | 62.9 | 1.62 | 8.13 | 8.07 |
| 94.6 | 14.6 | 53.4 | 1.96 | 7.43 | 7.36 | 94.8 | 14.8 | 79.6 | 1.64 | 8.10 | 8.08 |
| 104.7 | 14.7 | 58.8 | 1.99 | 7.30 | 7.35 | 104.9 | 14.8 | 88.0 | 1.65 | 8.08 | 8.08 |
| <i>Benzene</i> | | | | | | | | | | | |
| 24.7 | 14.7 | 18.3 | 1.27 | 3.23 | 3.26 | 24.8 | 14.8 | 22.3 | 1.29 | 3.46 | 3.39 |
| 34.7 | 14.7 | 22.7 | 1.50 | 3.34 | 3.22 | 34.8 | 14.8 | 30.2 | 1.43 | 3.57 | 3.42 |
| 54.7 | 14.7 | 32.4 | 1.76 | 3.26 | 3.18 | 54.8 | 14.8 | 46.5 | 1.56 | 3.48 | 3.44 |
| 74.7 | 14.7 | 42.8 | 1.89 | 3.19 | 3.16 | 74.8 | 14.8 | 63.0 | 1.62 | 3.45 | 3.45 |
| 94.6 | 14.6 | 53.4 | 1.96 | 3.20 | 3.15 | 94.9 | 14.9 | 79.0 | 1.64 | 3.42 | 3.45 |
| 104.6 | 14.6 | 58.7 | 1.99 | 3.15 | 3.15 | 104.9 | 14.9 | 88.1 | 1.65 | 3.38 | 3.46 |

Finally it will be observed in Tables II-V that, as p_i increases, the change in k' diminishes progressively to the point where k' becomes effectively pressure independent. We illustrate this in Fig. 3 where the data for all four solutes eluted at various p_i in column modes 2:3 and 3:2 are illustrated. These are typical, and we see plateaux reached at around 50 p.s.i. This behaviour is theoretically predictable.

When $p_i \gg p_o$, eqn. 7 reduces to

$$p \rightarrow \left\{ \frac{p_i^2 - l_F p_i^2}{1 - l_F [1 - (V_{MB} R_{FF} / V_{MF} R_{FB})]} \right\}^{1/2}$$

TABLE VI

VARIATION (RATIO) OF k' FOR ANY SOLUTE WITH p_i (25–105 p.s.i.) FOR A GIVEN BINARY COLUMN AND MODE

| Column mode (F/B) | k' ratio (p_i105/p_i25) |
|----------------------|----------------------------------|
| 3:2 | 0.907 |
| 2:3 | 1.14 |
| 1:4 | 0.808 |
| 4:1 | 1.09 |
| 1:2 | 0.870 |
| 2:1 | 1.10 |
| 2:4 | 0.966 |
| 4:2 | 1.02 |

TABLE VII

CHANGE OF k' FOR ANY SOLUTE WITH CHANGE OF COLUMN MODE

| Inlet pressure (p_i) (p.s.i.) | k' ratio | | | |
|--------------------------------------|------------|-----------|-----------|-----------|
| | 2:3 → 3:2 | 4:1 → 1:4 | 2:1 → 1:2 | 4:2 → 2:4 |
| 25 | 1.17 | 1.22 | 1.20 | 1.04 |
| 105 | 1.48 | 1.65 | 1.53 | 1.10 |

TABLE VIII

ARITHMETIC MEANS OF Δ (%) FOR ALL COLUMN MODES, ALL SOLUTES AND ALL INLET PRESSURES

| Mode | Mean Δ (%) |
|------|-------------------|
| 2:3 | ±1.3 |
| 3:2 | ±1.7 |
| 1:4 | ±1.7 |
| 4:1 | ±2.4 |
| 1:2 | ±2.8 |
| 2:1 | ±3.0 |
| 2:4 | ±1.8 |
| 4:2 | ±2.0 |

that is,

$$p \rightarrow p_i \left[\frac{1 - l_F}{1 - l_F(1 - C)} \right]^{1/2} \quad (9)$$

where $C = (V_{MB}R_{FF}/V_{MF}R_{FB})$. Substituting this value for p in eqn. 8 for P then yields

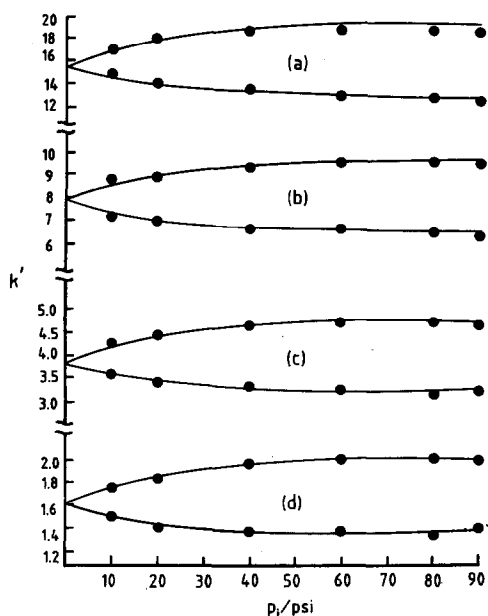


Fig. 3. Plots of k' against p_i for serial combinations of columns 2 and 3. Circles, k'_{exp} ; full lines, k'_{calc} . Upper curves, column mode $F/B = 2:3$; lower curves, column mode $F/B = 3:2$. Elution of (a) propylbenzene, (b) ethylbenzene, (c) toluene and (d) benzene, by nitrogen at 90°C .

TABLE IX

COMPARISON OF CALCULATED AND EXPERIMENTAL HIGH PRESSURE LIMITING VALUES OF k'

| Column mode (F/B) | Solute | k'_{calc} (lim) | k'_{exp} (> 100 p.s.i.) |
|-----------------------|--------------|-------------------|------------------------------|
| 3:2 | Ethylbenzene | 6.42 | 6.63 |
| 2:2 | Ethylbenzene | 9.88 | 9.73 |
| 2:1 | Benzene | 1.94 | 1.91 |
| 1:2 | Benzene | 1.24 | 1.25 |
| 4:2 | Ethylbenzene | 16.6 | 16.6 |
| 2:4 | Ethylbenzene | 15.0 | 15.1 |
| 4:1 | Toluene | 5.99 | 5.94 |
| 1:4 | Toluene | 3.48 | 3.59 |

$$P_{lim} = \left(\frac{L_B R_{FB}}{L_F R_{FF}} \right) \left(\frac{V_{MF}}{V_{MB}} \right)^2 \left\{ \left[\frac{1 - I_F (1 - C)}{1 - I_F} \right] - 1 \right\} \quad (10)$$

in other words, $P \rightarrow \text{constant}$.

The above provides a route to a final test of the theory since P_{lim} can be calculated for any column combination from the data provided earlier and, in turn, provide values of k'_{lim} via eqn. 3, for any chosen solute, for comparison with the values observed at the highest pressures employed. Table IX shows, for a few examples that are typical, the excellence of the agreement achieved.

These last observations are also of practical importance. The plateaux start, to all intents and purposes, at about the inlet pressure level above which fastest analysis is achieved⁸. Thus, whatever optimisation theory is employed is simplified since we are relieved of the need to allow for inlet pressure dependence of k' in serial systems operated in fastest analysis conditions.

The experimental evidence presented leaves no doubt of the validity of our theory and rapid practical progress should now be anticipated since the main obstacle to successful serial column operation in gas chromatography has been removed.

REFERENCES

- 1 G. P. Hildebrand and C. N. Reilly, *Anal. Chem.*, 36 (1964) 47.
- 2 T. S. Buys and T. W. Smuts, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 461.
- 3 D. F. Ingraham, C. F. Shoemaker and W. Jennings, *J. Chromatogr.*, 239 (1982) 39.
- 4 G. Takeoka, H. M. R. Richard, F. M. Mehran and W. Jennings, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 145.
- 5 J. H. Purnell and P. S. Williams, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 569.
- 6 J. H. Purnell and P. S. Williams, *J. Chromatogr.*, 292 (1984) 197.
- 7 J. H. Purnell and P. S. Williams, *J. Chromatogr.*, 321 (1985) 249.
- 8 J. H. Purnell and P. S. Williams, *J. Chromatogr.*, 325 (1985) 1.
- 9 J. H. Purnell, M. Rodriguez and P. S. Williams, *J. Chromatogr.*, 323 (1985) 402.
- 10 H. T. Mayfield and S. N. Chesler, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 595.