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RELATIVE RETENTION IN SERIALLY CONNECTED BINARY GAS CHROMATOGRAPHIC CAPILLARY COLUMN SYSTEMS AND THE IMPLICATIONS FOR WINDOW DIAGRAM OPTIMIZATION OF SUCH SYSTEMS

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SUMMARY

The application of the window diagram technique to the optimization of the relative length of serially coupled binary capillary columns has recently been attempted. However, no proper account was taken of the effects of carrier gas compressibility, empirical means being relied upon in the final optimization. We show here that compressibility effects can in fact be quantitatively accounted for. The strategy for optimization and relevant equations are derived for the general use of differing phase ratios and inner diameters of the column sections, as well as for certain special cases of relevance to the aforementioned recently published work.

INTRODUCTION

The method of window analysis optimization of chromatographic separation, initiated by Laub and Purnell¹, has subsequently been extended widely by Laub, Purnell, Williams and their collaborators (*e.g.*, ref. 2). This development initially concentrated on packed columns, for either gas or liquid chromatography, and included accounts of the application of the technique to optimizing the choice of multi-substrate systems, column temperature, eluent pH, etc. Insofar as multi-substrate operation was concerned these workers, recognizing the effect of carrier gas compressibility on relative retention, eschewed the use of serially connected packed columns and strongly advocated mechanical mixing of the various packing materials in a single column such that each experienced exactly the same pressure regime. However, in a relatively recent publication, Purnell *et al.*³ described the application of the window method to the optimization of multi-capillary column systems, which are most conveniently operated serially. To obviate the difficulty alluded to above, these workers employed very short lengths of capillary such that the pressure drop was trivial, no concern for compressibility effects would then be needed and it was unimportant in which order columns were connected. The results were entirely consistent with prediction.

Recently, Ingraham *et al.*⁴ and Takeoka *et al.*⁵ have also attempted to employ window analysis to optimize serially connected capillary column systems. They concluded that window analysis provided a useful, but no more than first-approximation

result, so that subsequent empirical adjustment of column lengths was required. As we have pointed out elsewhere⁶, this conclusion is incorrect, being founded on an erroneous derivation, disregard of the carrier compressibility effect and, finally, the use in some experimental tests of columns of unequal diameter, a factor that complicates the theory and practice still further.

In the light of the above situation, it seems worthwhile to present the correct theory and to show that window analysis then provides precise information regarding serial capillary column optimisation. In presenting this theory we deal first with the situation where compressibility effects are ignored and column diameters are equal. This is the model adopted by Jennings and his colleagues and this analysis, accompanied by extension to the case where diameters are unequal, allows a direct assessment of the extent of error in their treatment. We then discuss briefly the case of columns of equal diameter but subject to compressibility effects in order to show that our approach is entirely consistent with the corresponding early development by Hildebrand and Reilley⁷ recapitulated later by Buys and Smuts⁸. Finally, we treat the general case where diameters, pressure drops and film thicknesses are all variables. This treatment provides a basis for detailed evaluation of the data of Jennings and his collaborators, which can then be shown to be in excellent accord with theoretical prediction.

CASE A. NO CARRIER GAS COMPRESSIBILITY EFFECT

Columns of equal inner diameter

Let us assume that the volume of liquid phase is negligible in comparison with that of the mobile phase, *i.e.*, that phase ratios (β) are very large. Then, for a dual-column system, F (inlet end) followed by B (outlet end), the mobile phase volume (V_{MF}) in column F is given by

$$V_{MF} = \bar{V}_M L_F \quad (1)$$

where \bar{V}_M is the mobile phase volume per unit length, which is the same for both columns. Correspondingly, the liquid phase volume (V_F) is

$$V_F = V_{MF}/\beta_F = \bar{V}_M L_F/\beta_F \quad (2)$$

or

$$L_F = V_F \beta_F / \bar{V}_M \quad (3)$$

and, for column B,

$$L_B = V_B \beta_B / \bar{V}_M \quad (4)$$

The volume fraction (ϕ_F) of liquid F in the composite system is

$$\phi_F = V_F / (V_F + V_B)$$

whence

$$L_B = \frac{V_F \beta_B}{\bar{V}_M} \left(\frac{1}{\varphi_F} - 1 \right) \quad (5)$$

and so, the length fraction, *e.g.*, $l_F = L_F / (L_F + L_B)$, is

$$l_F = \frac{\varphi_F \beta_F}{\varphi_F \beta_F + \varphi_B \beta_B} \quad (6)$$

$$\varphi_F = \frac{l_F \beta_B}{l_F \beta_B + l_B \beta_F} \quad (7)$$

The overall phase ratio (β) is defined as the total mobile phase volume/total liquid phase volume, *i.e.*,

$$\beta = \frac{\bar{V}_M L_F + \bar{V}_M L_B}{\frac{\bar{V}_M L_F}{\beta_F} + \frac{\bar{V}_M L_B}{\beta_B}}$$

and so

$$\frac{1}{\beta} = \frac{l_F}{\beta_F} + \frac{l_B}{\beta_B} \quad (8)$$

By appropriate substitution from eqn. 6 into eqn. 8, it then follows that

$$\beta = \varphi_F \beta_F + \varphi_B \beta_B \quad (9)$$

As carrier gas compressibility effects are ignored, we can now identify the overall partition coefficient (K_R) unambiguously in terms of the liquid volume fractions, and the relevant values of K_R for pure F and B, via

$$K_R = \varphi_F K_{R(F)}^0 + \varphi_B K_{R(B)}^0 \quad (10)$$

and as the capacity factor $k' = K_R / \beta$, substituting for φ_F and φ_B and replacing K_R by the appropriate k' yields

$$k' = l_F k'_F + l_B k'_B \quad (11)$$

Ingraham *et al.*⁴ employed this model only and, in conclusion, commented adversely on our use of eqn. 11 when we presented the first example of optimization of length fraction of coupled capillaries³. First we should note that, unhappily, these workers

perpetrated an algebraic error in going from eqn. 7 to 8 and represented eqn. 8 as

$$\beta = l_F \beta_F + l_B \beta_B$$

which is true only when $\beta_F = \beta_B$, which, as the diameters are equal, so too must be the film thicknesses. Thus, their general equation for l_F is wrong, a matter of some consequence as in their experiments film thicknesses differed by a factor of four.

In our initial example³ the column diameters were, in fact, identical and the composite column was so permeable to flow that the pressure drop was trivial. Thus, eqn. 11 does apply and in this particular situation it is valid to carry out window analysis via length fractions, *i.e.*, eqn. 11, as we did.

Columns of unequal diameter but equal film thickness

Jennings and his later co-workers⁴ actually carried out their attempted window analysis with such columns. Therefore, it is valid to assess the errors that will arise, even without taking account of the compressibility correction.

Again we assume that the liquid phase volume is small relative to that of the mobile phase and so, generally, mobile phase volume = $L\pi r^2$ and liquid phase volume = $2\pi r L d$, where r is the internal column radius and d is the liquid film thickness. Thus, the overall phase ratio is

$$\beta = r/2d$$

and

$$V_M = \pi r^2 L = 4\pi d^2 \beta^2 L \quad (12)$$

For column F, therefore,

$$V_{MF} = 4\pi d^2 \beta_F^2 L_F$$

and

$$V_F = 4\pi d^2 \beta_F L_F \quad (13)$$

with corresponding equations for column B.

Now, as we have equal film thickness, for F and B, eqn. 13 leads to

$$l_F = L_F / (L_F + L_B) = (V_F / \beta_F) / [(V_F / \beta_F) + (V_B / \beta_B)]$$

In other words,

$$l_F = \frac{\varphi_F \beta_B}{\varphi_F \beta_B + \varphi_B \beta_F} \quad (14)$$

or

$$\varphi_F = \frac{l_F \beta_F}{l_F \beta_F + l_B \beta_B} \quad (15)$$

Eqns. 13 and 15 then lead to

$$\beta = \varphi_F \beta_F + \varphi_B \beta_B \quad (16)$$

exactly as derived for the first model.

Appropriate substitutions as those in going from eqn. 10 to eqn. 11 then gives

$$k' = \frac{l_F r_F^2 k'_F + l_B r_B^2 k'_B}{l_F r_F^2 + l_B r_B^2} \quad (17)$$

in considerable contrast with eqn. 11 and emphasizing the error introduced by assuming in theory that $r_F = r_B$, when it is not the case in practice. Indeed, even before attempting to include a compressibility correction we see that there is no simple relationship between l_F and the various k' . Even allowing that compressibility corrections were negligible it is, therefore, clear that failure to use eqn. 17 would lead to gross error in the evaluation of k' and thus of l_F via the window analysis procedure.

CASE B. INCLUSION OF THE GAS COMPRESSIBILITY EFFECT

Columns of the same diameter

This particular problem was first addressed in 1964 by Hildebrand and Reilly⁷ and later by Buys and Smuts⁸. We have shown elsewhere⁶ a simplified and assumption free-treatment which leads to the same basic result as obtained by these earlier workers, that is, for a given solute,

$$k' = \frac{Pk'_F + k'_B}{P + 1} \quad (18)$$

where

$$P = \frac{t_{dF}}{t_{dB}} = \frac{p_1^3 - p^3}{p^3 - p_0^3} = \frac{p j_B l_F}{p_0 j_F l_B} \quad (19)$$

and p_1 , p and p_0 are the prevailing pressures at the inlet, the junction and outlet, respectively, j_F and j_B are the James-Martin compressibility factors over columns F and B and t_{dF} and t_{dB} are the dead times for the columns.

As a consequence of eqn. 18, the relative retention of a solute pair (X, Y) is

$$\alpha_{YX} = \frac{k'_Y}{k'_X} = \frac{Pk'_{Y(F)} + k'_{Y(B)}}{Pk'_{X(F)} + k'_{X(B)}} \quad (20)$$

from which it can be seen that relative retention depends in practice on whether column F or column B is at the inlet end. A numerical illustration of the extent of variation in α was given elsewhere⁶.

Thus, in attempting optimization of values of l_F it is insufficient to know only

k'_F and k'_B but also imperative to define the sequence of the columns as they are to be used in experiment.

We now extend earlier work to show how the actual value of l_F is related to pressure drops in the system.

It is self-evident from eqn. 18 that, when the pressure drop is significant, we can no longer express k' in terms of l_F and l_B as in eqn. 11 but, rather, as

$$k' = l'_F k'_F + l'_B k'_B \quad (21)$$

and, correspondingly,

$$K_R = \varphi'_F K_{R(F)}^0 + \varphi'_B K_{R(B)}^0 \quad (22)$$

where the newly primed quantities represent "effective" length fractions and volume fractions where

$$l'_F = P/(P + 1) \quad (23)$$

or

$$P = l'_F/(1 - l'_F) \quad (24)$$

and where φ'_F and l'_F are related thus (*cf.*, eqns. 6 and 7):

$$\varphi'_F = \frac{l'_F \beta_B}{l'_F \beta_B + l'_B \beta_F}$$

$$l'_F = \frac{\varphi'_F \beta_F}{\varphi'_F \beta_F + \varphi'_B \beta_B}$$

The linear relationships described by eqns. 21 and 22, and later eqn. 33, permit the direct application of window diagram optimization, and are introduced with this sole purpose in mind.

From eqn. 24 and the earlier definition of P , we then have

$$(p_i^3 - p^3)/(p^3 - p_o^3) = l'_F/(1 - l'_F)$$

whence

$$p^3 = p_i^3 - l'_F(p_i^3 - p_o^3) \quad (25)$$

However, for a column of constant diameter, we know also⁹ that the pressure, p , at any point of fractional distance l_F from the inlet, is given by

$$p^2 = p_i^2 - l_F(p_i^2 - p_o^2)$$

Hence,

$$l_F = [p_i^2 - [p_i^3 - l_F^3(p_i^3 - p_o^3)]^{2/3}]/(p_i^2 - p_o^2) \quad (26)$$

l_F can thereby be calculated for some optimum l_F and any experimental pressure data.

Thus, for columns of equal diameter with a significant pressure drop, the means of exploiting window analysis quantitatively are at hand. The contrast between this result and that where compressibility was ignored is sufficiently clear to establish that Jennings and co-workers could not possibly have achieved a reasonable window optimization.

CASE C

The general case

The three models dealt with up to this point will each be met with in practice but, of course, represent particular aspects of the general case. We now present the general model from which solutions for particular models can be derived.

Again we take columns F and B, operating over the pressure ranges p_i to p and p to p_o . Let them have internal radii r_F and r_B , and the viscosity of the carrier be η . Then, from the Poiseuille equation, the outlet velocity is given by

$$u_o = \frac{r^2}{16\eta L} \left(\frac{p_i^2 - p_o^2}{p_o} \right)$$

Let the relevant velocities at the various points be u_{Fi} , u_{Fo} , u_{Bi} and u_{Bo} . Then, as mass flow-rate is constant throughout the system,

$$p_i u_{Fi} r_F^2 = p u_{Fo} r_F^2 = p u_{Bi} r_B^2 = p_o u_{Bo} r_B^2$$

Since, in addition, as shown above, we can set

$$u_{Fo} = \frac{r_F^2(p_i^2 - p^2)}{16\eta L_F p}$$

and

$$u_{Bo} = \frac{r_B^2(p^2 - p_o^2)}{16\eta L_B p_o}$$

constancy of mass flow demands that

$$\frac{r_F^4}{L_F} (p_i^2 - p^2) = \frac{r_B^4}{L_B} (p^2 - p_o^2) \quad (27)$$

i.e.,

$$p^2 = \left\{ \frac{p_i^2 - l_F [p_i^2 - (r_B/r_F)^4 p_o^2]}{1 - l_F [1 - (r_B/r_F)^4]} \right\} \quad (28)$$

The dead times in the two column sections are

$$t_{dF} = L_F/\bar{u}_F = L_F/j_F u_{F0} = \frac{32\eta L_F^2}{3r_F^2} \left[\frac{p_i^3 - p^3}{(p_i^2 - p^2)^2} \right]$$

and

$$t_{dB} = L_B/\bar{u}_B = L_B/j_B u_{B0} = \frac{32\eta L_B^2}{3r_B^2} \left[\frac{(p^3 - p_o^3)}{(p^2 - p_o^2)^2} \right]$$

and then, introducing eqn. 27, we obtain

$$t_{dF} = \frac{32\eta L_B^2}{3r_B^2} \left(\frac{r_F}{r_B} \right)^6 \left[\frac{(p_i^3 - p^3)}{(p^2 - p_o^2)^2} \right] \quad (29)$$

Thus,

$$k' = \frac{t_{dF}k'_F + t_{dB}k'_B}{t_{dF} + t_{dB}} = \frac{P'k'_F + k'_B}{P' + 1} \quad (30)$$

where

$$P' = \frac{t_{dF}}{t_{dB}} = \left(\frac{r_F}{r_B} \right)^6 \left(\frac{p_i^3 - p^3}{p^3 - p_o^3} \right) \quad (31)$$

Eqns. 30 and 31 are the analogues of eqns. 18 and 19 and, indeed, when $r_F = r_B$, reduce to these.

Correspondingly, in analogy with eqn. 20,

$$\alpha_{YX} = \frac{k'_Y}{k'_X} = \frac{P'k'_{Y(F)} + k'_{Y(B)}}{P'k'_{X(F)} + k'_{X(B)}} \quad (32)$$

It is again evident that the experimental value of α for any pair is very much dependent on the sequence in which the columns are used. Thus, α for any solute pair eluted in the mode FB may differ very significantly from the corresponding α observed in elution in the mode BF.

Finally, let us set

$$k' = f_F k'_F + f_B k'_B \quad (33)$$

where $f_F + f_B = 1$. From eqn. 30, we then derive the results

$$f_F = P'/(P' + 1) \text{ and } P' = f_F/(1 - f_F)$$

and eqn. 31, in turn, leads to the result

$$p^3 = \frac{p_i^3 + P' \left(\frac{r_B}{r_F} \right)^6 p_o^3}{1 + P' \left(\frac{r_B}{r_F} \right)^6}$$

or

$$p^3 = \frac{p_i^3 - f_F \left[p_i^3 - \left(\frac{r_B}{r_F} \right)^6 p_o^3 \right]}{1 - f_F \left[1 - \left(\frac{r_B}{r_F} \right)^6 \right]} \quad (34)$$

Finally, setting mass flows at the column outlets equal (*cf.*, eqn. 27) leads eventually to

$$l_F = \frac{p_i^2 - p^2}{p_i^2 - p^2 + \left(\frac{r_B}{r_F} \right)^4 (p^2 - p_o^2)} \quad (35)$$

When $r_B = r_F$, eqns. 34 and 35 reduce to the corresponding equations derived in the last section.

A true optimization of column length fractions now becomes apparent. A window analysis dependent on the linear relationship expressed by eqn. 33 will indicate the optimum f_F . Hence p can then be calculated for some overall pressure drop via equation 34. The optimum true length fraction l_F is then obtainable through use of eqn. 35. The theory presented is quantitative so long as the phase ratios are large and the carrier gas behaviour approaches ideal.

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