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THEORY OF THE EFFICIENCY OF SERIALLY CONNECTED GAS CHROMATOGRAPHIC COLUMNS AND THE EFFECT ON OPTIMIZED SPEED OF ANALYSIS

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SUMMARY

Equations are derived to calculate both minimum (H/\bar{u}) and optimum analysis time of a complex mixture for serially configured binary gas chromatographic columns. The theory presented is essential to optimization of speed of analysis with binary coupled columns, and complements our already published approach to correction for the effects of pressure gradient in the application of window diagram optimization. Through the examination of the derived equations, and with the aid of several graphical examples, we are able to identify those conditions which are not favoured by serial operation. Finally, a comparison is made with columns of mechanically mixed packings and conditions identified where each is likely to be better than the other in terms of attainable speed of analysis.

INTRODUCTION

The difficulty of chromatographic separation of a mixture may be quantified in terms of the number of theoretical plates required for the satisfactory resolution of all desired components. The most demanding separation of consecutively eluting mixture components fixes the overall difficulty. The window diagram technique, introduced for optimizing mixed substrate composition for separation of complex mixtures¹⁻⁵, functions by minimizing overall plate requirement. A window diagram shows, for instance, the variation with substrate composition of some parameter related to plate requirement for the most difficult to separate pair of components. A typical parameter is the relative adjusted retention (α), and the variation is almost invariably discontinuous, the discontinuities being due to changes in order of elution and changes in the identity of the most difficult pair.

Computer programs have been described for implementing the original window diagram technique^{6,7}, and the approach has been successively refined⁸⁻¹¹ such that readily measured retention parameters such as capacity factors are sufficient to implement the optimization, and even mixtures of unknown composition may be tackled. In addition, the approach to minimizing analysis time, developed by Purnell and Quinn¹², has been applied in conjunction with window diagram optimization in order that fastest analysis be the prime objective¹³⁻¹⁵.

Recently¹⁶⁻¹⁸ we have turned our attention to the optimization of relative lengths of serially coupled columns. Such operation is most convenient for combining retention characteristics of more than one stationary phase in open tubular chromatography, particularly where different surface treatments are required for each of the phases. The practice of coupling columns in series also has the advantage that lengths of pure phase column will usually be available after the initial measurement of retentions necessary for the production of a window diagram, and the sections may again be separated once an analysis has been achieved. Equations have been derived to correct for the effects of carrier gas compressibility within both open tubular^{16,17} and packed¹⁸ column sections. The equations are general in that column sections are not required to have identical internal diameters, and in the case of packed columns they need not have identical specific permeabilities or porosities.

The efficiency of coupled columns has been the topic of some discussion in the past (*e.g.* refs. 19 and 20), but here we are primarily concerned with optimizing speed of analysis. Consequently equations are derived below in terms of the ratio of theoretical plate height to mean carrier velocity, (H/\bar{u}) , since achievable time of analysis is directly related to this quantity rather than simply the plate height. For homogeneous columns we know¹² that optimum speed of analysis calls for operation at high carrier velocity thereby minimizing (H/\bar{u}) . This is shown to be equally valid for serially coupled columns. As we shall see, the overall (H/\bar{u}) for a binary coupled column of some effective composition is directly related to the (H/\bar{u}) for the individual sections. The overall value is, therefore, minimized when conditions dictate minimum (H/\bar{u}) in each of the two sections, *i.e.* mean carrier velocity must be high in both sections. Importantly, it follows that minimum (H/\bar{u}) may be predicted unambiguously for a coupled column of some desired effective composition from the minimum (H/\bar{u}) of the two individual sections. The question is, how?

THEORY

Efficiency of serially coupled columns

The observed theoretical plate height for a column of length L is defined by

$$H = L \left[\frac{\sigma_t}{t_R} \right]^2 \quad (1)$$

where t_R is the retention time of the solute band within the column and σ_t is the standard deviation of the solute band in units of time. Now suppose we have two column sections, A and B, coupled in series. Retention times within the sections will be additive, as will be the variances in retention due to each of the sections, *i.e.* for the coupled column,

$$t_R = t_{RA} + t_{RB}$$

and

$$\sigma_t^2 = \sigma_{tA}^2 + \sigma_{tB}^2$$

It follows from eqn. 1, and the above, that

$$\sigma_t^2 = t_{RA}^2 H_A / L_A + t_{RB}^2 H_B / L_B \quad (2)$$

where H_A and H_B are the plate heights for the column sections corresponding to conditions existing within them, and L_A and L_B are the section lengths. Therefore, the observed plate height for the coupled column is given by

$$H = (L_A + L_B) \left[\frac{(t_{RA}^2 H_A / L_A + t_{RB}^2 H_B / L_B)}{(t_{RA} + t_{RB})^2} \right] \quad (3)$$

which is equivalent to the expression for H derived by Giddings¹⁹.

The retention time of a substance within a column section is given by

$$t_R = t_d (1 + k') \quad (4)$$

where t_d is the retention time for a nonsorbed substance, *i.e.* the dead time for the column section, and k' is the capacity factor of the retained substance in the section. Now let us define, as we have previously¹⁶⁻¹⁸, a parameter P as the ratio of the column section dead times,

$$P = t_{dA} / t_{dB} \quad (5)$$

and a new parameter K as the ratio of $(1 + k')$ for the sections,

$$K = (1 + k'_A) / (1 + k'_B) \quad (6)$$

The product PK is then simply the ratio of the retention times within the two sections, that is, t_{RA} / t_{RB} . Eqn. 3 may now be expressed in the form

$$H = (L_A + L_B) \left[\frac{(P^2 K^2 H_A / L_A + H_B / L_B)}{(PK + 1)^2} \right] \quad (7)$$

It follows directly from eqn. 7 that, since $N = L/H$, the observed number of theoretical plates for the coupled column (N) is given by

$$\frac{1}{N} = \frac{(P^2 K^2 / N_A + 1 / N_B)}{(PK + 1)^2} \quad (8)$$

where N_A and N_B are the number of plates that would be observed for the individual sections for extant conditions. The above expression is equivalent to that derived by Kwok *et al.*²⁰ in terms of corrected retention volumes and mean column section pressures.

Now as mentioned earlier, analysis time is directly proportional to (H/\bar{u}) where mean carrier velocity, \bar{u} , is defined as L/t_d . Therefore, for the coupled column,

$$\bar{u} = (L_A + L_B) / (t_{dA} + t_{dB})$$

and it follows from eqn. 7 by substitution first for L_A and L_B separately, and then, for $(L_A + L_B)$, that

$$\frac{H}{\bar{u}} = \frac{(P + 1)}{(PK + 1)^2} \left[PK^2 \left(\frac{H_A}{\bar{u}_A} \right) + \left(\frac{H_B}{\bar{u}_B} \right) \right] \quad (9)$$

For fastest possible analysis, (H/\bar{u}) must be minimized for the most difficult to separate components. Since, for a given complex mixture, values of K are fixed and, as has been discussed previously^{17,18}, P is fixed by the window diagram optimization, it follows that both (H_A/\bar{u}_A) and (H_B/\bar{u}_B) must be minimized *i.e.*, the coupled column sections must be of sufficient length such that mean carrier velocity within each corresponds to points on their respective Van Deemter curves at which lines drawn from the origin are effectively asymptotic. For such conditions both (H_A/\bar{u}_A) and (H_B/\bar{u}_B) are themselves then constant and eqn. 9 gives us immediate access to minimum (H/\bar{u}) for the required coupled column. Eqn. 7 and 8 are not useful in predicting optimum analysis time.

In order to examine the dependence of minimum (H/\bar{u}) on the column section parameters it seems expedient to define, as before^{17,18}, a function f of true length fraction, l , such that the observed overall capacity factor for a coupled column is given by

$$k' = f_A k'_A + f_B k'_B \quad (10)$$

with $f_A + f_B = 1$. It was shown^{17,18} that f_A is related to P through

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

It is eqn. 10, or an equivalent, which forms the basis of window diagram optimization of f_A and, hence, of P ; the true length fractions, l_A and l_B , then being determined for some overall column length and pressure drop.

At this point it seems worth pointing out that although P is fixed for optimum separation, the value of K may be different for each component of the mixture, and indeed, there must be some variation of this quantity for the window diagram approach to be worth pursuing. It is evident from eqns. 7, 8 and 9 that there can be a variation in H , N and (H/\bar{u}) for the components eluted, a variation over and above that normally observed due to differing diffusivities. Therefore, for coupled column systems we would not generally expect to see the normal approximately linear variation of peak width with retention.

Returning to the relationship expressed in eqn. 9 we may now examine the variation of minimum (H/\bar{u}) with f_A over its full range of 0 to 1 (corresponding to P from 0 to ∞) for any K , $(H/\bar{u})_A$ and $(H/\bar{u})_B$. In Fig. 1 we show this variation for $(H/\bar{u})_A = (H/\bar{u})_B = 0.01$ sec and various K from 0.1 to 10. Differentiation of eqn. 9 with respect to P shows that for $K \neq 1$, (H/\bar{u}) reaches a maximum when $PK = 1.0$, *i.e.* when the solute band spends an equal time within each section. It may be seen that a short section of strongly retaining column can have a disastrous effect on (H/\bar{u}) . For example, with a K of 10, (H/\bar{u}) has a maximum of 0.03025 sec at $f_A = 0.0909$ (corresponding to $P = 0.1$), more than three times that for the individual

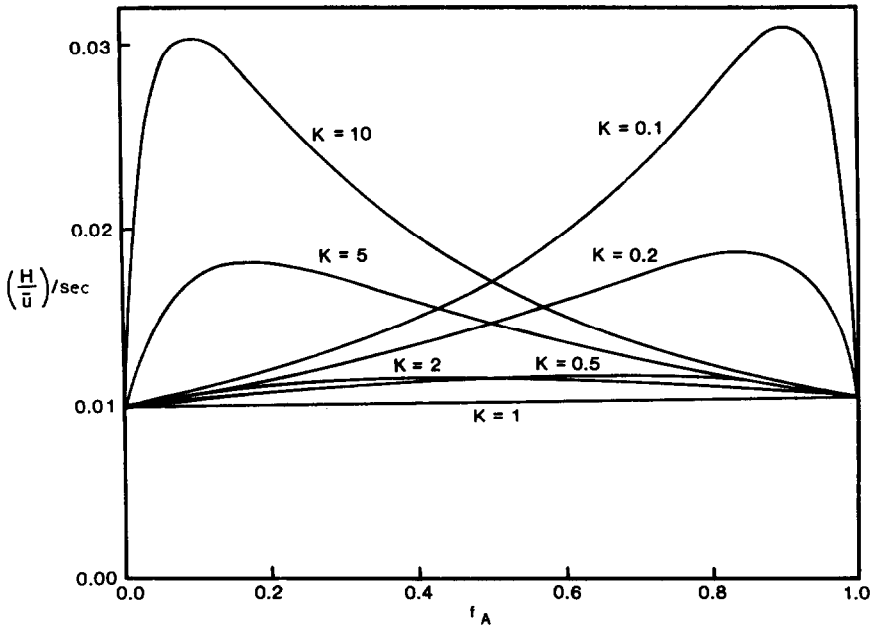


Fig. 1. Variation of (H/\bar{u}) with f_A for $(H/\bar{u})_A = (H/\bar{u})_B = 0.01$ sec and $K = 10, 5, 2, 1, 0.5, 0.2$ and 0.1 .

sections. The same column materials reversed would have a K of 0.1 , (H/\bar{u}) again reaching a maximum of 0.03025 sec now with $f_A = 0.9091$. The column section order has no effect on minimum (H/\bar{u}) for a particular overall effective composition, even though length fractions for the two configurations must differ for finite pressure drop. Not surprisingly, if $K = 1$, then (H/\bar{u}) is independent of column composition, and within the range $\frac{1}{2} < K < 2$ the effect is not significant, giving rise to at most a 12.5% increase in minimum (H/\bar{u}) .

Fig. 2 shows the variation of (H/\bar{u}) with f_A for the same range of K (0.1 to 10) but with a 10-fold difference in minimum (H/\bar{u}) i.e. $(H/\bar{u})_A = 0.05$ sec and $(H/\bar{u})_B = 0.005$ sec. Here we see that when $K = 1$, (H/\bar{u}) varies linearly with f_A ; $K > 1$ gives rise to positive deviation from linearity whilst, with $K < 1$ negative deviations result. Differentiation of eqn. 9 with respect to P reveals that (H/\bar{u}) reaches a maximum when

$$P = (2K - K^2E - 1)/K(2KE - K^2E - 1)$$

with the restriction that $P > 0$, and where $E = (H/\bar{u})_A/(H/\bar{u})_B$. Again taking a fairly extreme example of $K = 10$ with E here also equal to 10 , (H/\bar{u}) has a maximum at $P = 0.1224$ or $f_A = 0.1091$. At this effective composition minimum $(H/\bar{u}) = 0.1400$ sec, a 28-fold increase in minimum (H/\bar{u}) on change of f_A from 0.0 to 0.1091 . We see that the deleterious effect on (H/\bar{u}) of a short section of strongly retaining column may be enormously exacerbated if this section is also relatively inefficient.

The above discussion describes certain sets of conditions which must be avoided if overall efficiency is to be observed for serially coupled columns. However, if we

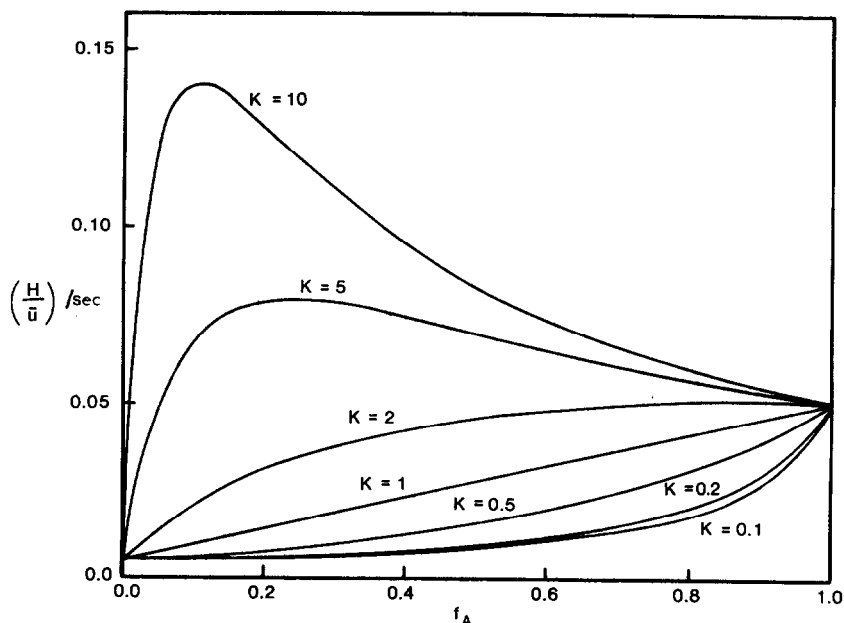


Fig. 2. Variation of (H/\bar{u}) with f_A for $(H/\bar{u})_A = 0.05$ sec, $(H/\bar{u})_B = 0.005$ sec and $K = 10, 5, 2, 1, 0.5, 0.2$ and 0.1.

consider fast analysis to be the primary objective then (H/\bar{u}) is but one of the governing factors. The effect of serial column operation on analysis time will now be discussed.

Optimized speed of analysis with serially coupled columns

For the sake of simplicity we shall confine our study to the minimization of the time for baseline separation of a two-component mixture, a situation applying also for a more complex mixture where the most difficult pair to separate corresponds to the last eluted components. The analysis time is then given by¹²

$$t_R = N_{\text{req}} \left[\frac{H}{\bar{u}} \right] (1 + k') \quad (11)$$

where k' is the capacity factor of the second eluted of the pair.

Assuming that we are concerned with optimizing length fractions of given packed column materials or open tubular columns, and we are therefore unable to alter solute capacity factors for the individual columns, N_{req} is most suitably substituted by $36 [\alpha' / (\alpha' - 1)]^2$, where α' is the relative uncorrected (for dead time) retention of the most difficult to separate pair. As explained previously^{14,15}, a window diagram may be used to maximize α' and thereby minimize N_{req} . Furthermore, for complex mixtures, since N_{req} is so sensitive to small changes in α' in the usual regions of interest, the proper application of a window diagram fixes the optimum f_A and P as well as the minimum N_{req} .

From eqn. 10 it may be shown, following substitution for f_B and k'_B , or for f_A and k'_A , that for some intermediate P or f_A ,

$$(1 + k') = \left[\frac{(PK + 1)}{K(P + 1)} \right] (1 + k'_A) = \left[\frac{(PK + 1)}{(P + 1)} \right] (1 + k'_B) \quad (12)$$

Also, from eqn. 9

$$\frac{H}{\bar{u}} = \left[\frac{(P + 1)(PK^2E + 1)}{E(PK + 1)^2} \right] \left[\frac{H}{\bar{u}} \right]_A = \left[\frac{(P + 1)(PK^2E + 1)}{(PK + 1)^2} \right] \left[\frac{H}{\bar{u}} \right]_B \quad (13)$$

Our expression for analysis time (eqn. 11) then becomes

$$t_R = N_{\text{req}} \left[\frac{(PK^2E + 1)}{KE(PK + 1)} \right] \left[\frac{H}{\bar{u}} \right]_A (1 + k'_A) \quad (14a)$$

or

$$t_R = N_{\text{req}} \left[\frac{(PK^2E + 1)}{(PK + 1)} \right] \left[\frac{H}{\bar{u}} \right]_B (1 + k'_B) \quad (14b)$$

From eqns. 14a and 14b we are able to make some simple deductions concerning analysis time.

(i) If $KE = 1$ then t_R/N_{req} is constant throughout the range of effective composition. For such cases, improvement in N_{req} achieved through application of the window diagram approach would be reflected by a directly proportional improvement in analysis time.

(ii) If $K = 1$, the expressions for analysis time reduce to

$$t_R = N_{\text{req}} \left[\frac{(PE + 1)}{(P + 1)} \right] \left[\frac{H}{\bar{u}} \right]_B (1 + k')$$

where $k' = k'_A = k'_B$. This in turn may be reduced to

$$t_R = N_{\text{req}} [f_A(H/\bar{u})_A + f_B(H/\bar{u})_B](1 + k')$$

Therefore, if the two column sections are equally retentive then (H/\bar{u}) , and hence t_R/N_{req} , will be linearly dependent on f_A . For column sections of very different minimum (H/\bar{u}) this may influence the choice of window.

(iii) Finally, it is simple to show that when $KE > 1$

$$(H/\bar{u})_B(1 + k'_B) < (H/\bar{u})(1 + k') < (H/\bar{u})_A(1 + k'_A)$$

and when $KE < 1$

$$(H/\bar{u})_B(1 + k'_B) > (H/\bar{u})(1 + k') > (H/\bar{u})_A(1 + k'_A)$$

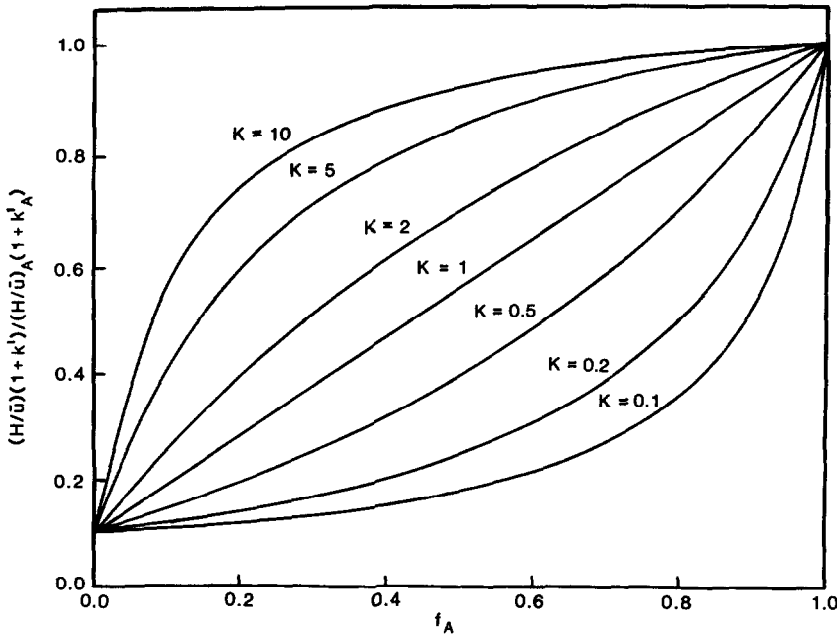


Fig. 3. Variation of $(H/\bar{u})(1+k')/(H/\bar{u})_A(1+k'_A)$ with f_A for $K = 10, 5, 2, 1, 0.5, 0.2$ and 0.1 with KE held constant at 10 .

This is important since it tells us that even though (H/\bar{u}) may, as illustrated earlier, pass through a maximum at some intermediate composition, t_R/N_{req} will never exceed the larger of $(H/\bar{u})_A(1+k'_A)$ and $(H/\bar{u})_B(1+k'_B)$. It also follows that t_R/N_{req} will never be less than the smaller of these two extrema.

To illustrate the effect more clearly, Fig. 3 shows plots of $(H/\bar{u})(1+k')/(H/\bar{u})_A(1+k'_A)$ for various K , with KE held constant at 10 . So when $K = 10$ then $E = 1$ and we can make a comparison with the plot of (H/\bar{u}) for $K = 10$ shown in Fig. 1. The improvement in (H/\bar{u}) to the right of the maximum in Fig. 1 is seen to be more than compensated by the increase in $(1+k')$. We see also confirmation of point (ii) above in that, when $K = 1$ then t_R/N_{req} is linearly dependent on f_A . In addition, for the examples of $KE = 10$ illustrated, we may deduce that when $K > 1$, $(H/\bar{u})(1+k')$ is more strongly influenced by $(H/\bar{u})_A(1+k'_A)$, and when $K < 1$ section B exerts the stronger influence, *i.e.* $(H/\bar{u})(1+k')$ is dominated by the more strongly retaining section. We can show that this is more generally true simply by holding E constant and varying K . Fig. 4 shows plots of $(H/\bar{u})(1+k')/(H/\bar{u})_A(1+k'_A)$ for several values of K between 0.1 and 5 with E held at 5 . For $K = 0.1, 0.125, 0.3$ and 0.5 , $(H/\bar{u})(1+k')$ is dominated by section B, and when $K = 2$ and 5 section A dominates, supporting the assertion. It will be noted that when $K = 1$, the variation in $(H/\bar{u})(1+k')$ is again linear [see point (ii)]. Also when $K = 0.2$ the variation is linear and constant. This is because $KE = 1$ and we can expect no change in the product $(H/\bar{u})(1+k')$ [see point (i)].

Finally, to return to Fig. 3, all plots correspond to t_R/N_{req} for elution of some mixture on section A being 10 times greater than for elution on B. If we assume that

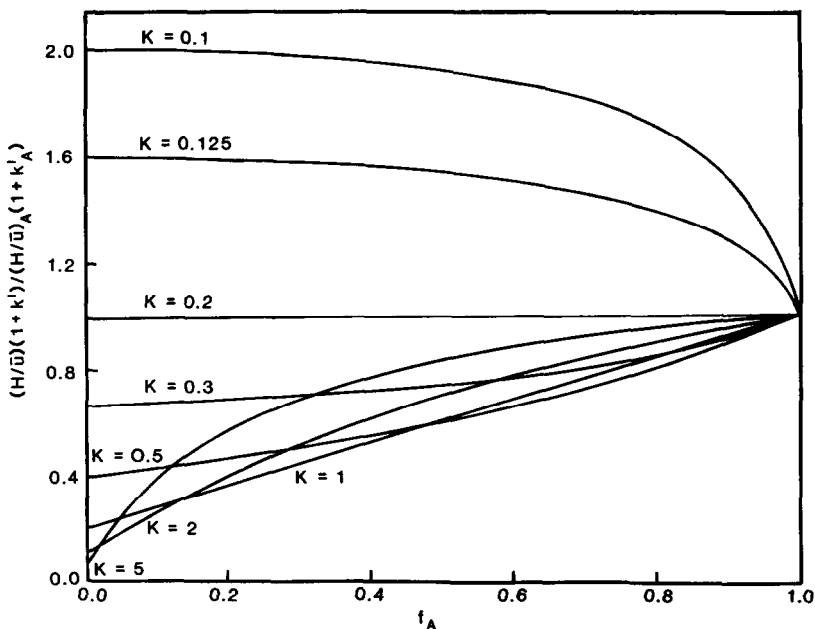


Fig. 4. Variation of $(H/\bar{u})(1+k)/(H/\bar{u})_A(1+k'_A)$ with f_A for $K = 5, 2, 1, 0.5, 0.3, 0.2, 0.125$ and 0.1 with E held constant at 5.

a window diagram indicates an optimum at some intermediate f_A then it is immediately obvious that we would rather this difference be due to relatively poor efficiency with A (see plots for $K = 10, 5, 2$ and 1 , corresponding to $E = 1, 2, 5$ and 10 , respectively). If the efficiency of A is particularly poor, but partially compensated by low retention, so much the better (see plots for $K = 0.5, 0.2$ and 0.1 , corresponding to $E = 20, 50$ and 100 , respectively). To sum up, fast analysis with coupled columns is favoured when the section exhibiting the lower $(H/\bar{u})(1+k')$ has the stronger retention, *i.e.* when $KE > 1$ and $K < 1$, or when $KE < 1$ and $K > 1$.

Comparison of speed of analysis obtainable with serially coupled columns and with mechanically mixed packed columns

In order to make the comparison in terms of attainable analysis time we have to make an assumption concerning the efficiency of columns containing mechanically mixed packings. It has been our experience that for such columns the best attainable (H/\bar{u}) has proved to have been no better than that predicted from a linear dependence of (H/\bar{u}) on composition by weight for packing materials of equal bulk density, mesh size and porosity (to all intents and purposes, for stationary phases coated on identical support). We shall therefore assume such a dependence. For such columns we can also assume linear dependence of k' on composition by weight^{14,15}. It follows that $(H/\bar{u})(1+k')$ and t_R/N_{req} are quadratic functions of composition.

The comparison of achievable analysis times must be made between a mechanically mixed column with weight fraction w_A of packing A, and a coupled column with an identical effective composition f_A of column section A. To this end, an expres-

sion for analysis time for a mixed column may be derived in terms of P for an equivalent coupled column:

$$t_R = N_{\text{req}} \left[\frac{(PK + 1)(PE + 1)}{KE(P + 1)^2} \right] \left[\frac{H}{\bar{u}} \right]_A (1 + k'_A) \quad (15)$$

where $w_A = P/(P + 1)$. It follows from eqns. 14a and 15 that the ratio of minimum analysis time with coupled columns, t_{RC} , to minimum analysis time with an equivalent mixed column, t_{RM} , is given by

$$\frac{t_{RC}}{t_{RM}} = \left[\frac{(PK^2E + 1)}{(PK + 1)} \right] \left[\frac{(P + 1)^2}{(PK + 1)(PE + 1)} \right] \quad (16)$$

Assuming $P > 0$, $t_{RC}/t_{RM} < 1$ when either

$$K < 1 \text{ and } E > \left[\frac{2 + P + PK}{1 + K + 2PK} \right]$$

or,

$$K > 1 \text{ and } E < \left[\frac{2 + P + PK}{1 + K + 2PK} \right]$$

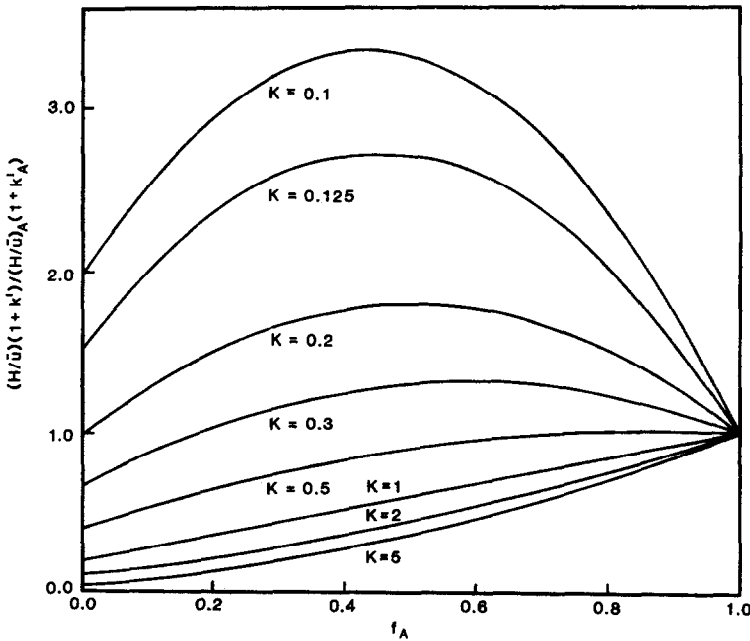


Fig. 5. Variation of $(H/\bar{u})(1 + k')/(H/\bar{u})_A(1 + k'_A)$ with f_A for mechanically mixed packings with $K = 5, 2, 1, 0.5, 0.3, 0.2, 0.125$ and 0.1 with E held constant at 5 ; linearity of (H/\bar{u}) with w_A assumed.

That is to say, for certain sets of conditions a coupled column configuration is likely to carry out an analysis faster than an equivalent mechanically mixed column. Fig. 5 shows the variation of $(H/\bar{u})(1 + k')/(H/\bar{u})_A(1 + k'_A)$ for mechanically mixed columns with $E = 5$ and various K from 0.1 to 5, exactly the conditions considered for coupled columns in Fig. 4. We see that $(H/\bar{u})(1 + k')$ may pass through a true maximum at an intermediate composition, unlike with coupled column systems.

As an example of comparison between mixed and coupled columns, consider $K = 2$. Then for $t_{RC}/t_{RM} < 1$, $E > (2 + 3P)/(3 + 4P)$. Therefore, if $E < 2/3$ we can expect $t_{RC} < t_{RM}$ over the full intermediate composition range (P : 0 to ∞). Conversely, if $E > 3/4$ then $t_{RC} > t_{RM}$ over the full intermediate range. If $2/3 < E < 3/4$ then $t_{RC} < t_{RM}$ for part of the range and $t_{RC} > t_{RM}$ for the remainder of the range. Fig. 6 illustrates just such an occurrence wherein t_{RC} and t_{RM} are plotted for $K = 2$ and $E = 0.6, 0.7$ and 0.8 .

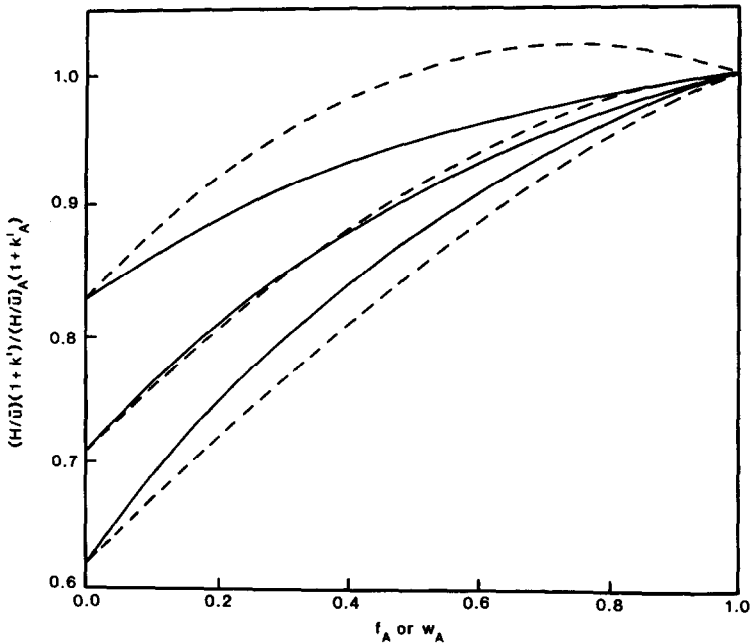


Fig. 6. Variation of $(H/\bar{u})(1 + k')/(H/\bar{u})_A(1 + k'_A)$ with composition for serially connected columns (—) and mechanically mixed columns (-----) with $K = 2$ and $E = 0.6, 0.7$ and 0.8 (upper, middle and lower pairs, respectively).

Finally, it is interesting to note that the conditions which favour coupled column operation (either $K < 1$ with $KE > 1$, or $K > 1$ with $KE < 1$) are more restrictive than, and are enclosed within, the conditions for $t_{RC} < t_{RM}$. Also when $K = 1$ then $t_{RC} = t_{RM}$ for all values of E .

CONCLUSIONS

The equations derived for minimum (H/\bar{u}) and for fastest time of analysis are essential to our approach to optimization of speed of analysis with binary coupled

columns via the window diagram technique. The general conditions disadvantageous to serial column operation are characterised, and for the first time we are in a position to determine the optimized time of analysis for serial column operation and compare it to the best time of analysis expected for mechanically mixed packed columns.

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