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GENERAL THEORY FOR CORRECTION FOR COMPRESSIBILITY EFFECTS IN BINARY COUPLED GAS CHROMATOGRAPHIC COLUMNS AND THE PROCEDURE FOR WINDOW DIAGRAM OPTIMISATION OF RELATIVE LENGTHS

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SUMMARY

Absolute and relative retentions observed in gas chromatography with serially coupled column pairs are significantly dependent on the sequence and relative lengths of the two columns on account of interplay between the capacity factors characterising each column unit and the compressibility effect of the carrier gas on local velocities. The general theory is presented for coupled columns of any type and shown to allow calculation of all necessary data for optimisation of relative lengths on the basis of readily determined practical quantities. Earlier approaches due to Hildebrand and Reilley and Buys and Smuts are shown to represent special cases of the general theory. The procedure for determining the relative column lengths needed to optimise separations via the window analysis technique is explained and shown to be very simple in application.

INTRODUCTION

We have dealt with the special case of binary coupled open tube columns in a previous publication[1] wherein we showed that it was possible to derive correction equations based solely on the basis of column section dimensions, *i.e.* length fractions and internal diameters, together with overall pressure drop. That approach was based on the Poiseuille equation which predicts for capillary columns a specific permeability, B_0, of $r^2/8$, where r is the internal radius of the column. A similar approach could be employed for packed columns based on the semi-empirical Kozeny–Carman equation[2–3] which yields a specific permeability, B_0, for packed beds as follows

$$B_0 = \frac{d_p^2 \, \varepsilon_0^3}{180 \, (1 - \varepsilon_0)^2} \tag{1}$$

where d_p is the effective particle diameter and ε_0 is the interparticle porosity, *i.e.* the fraction of the column internal volume available to moving gas. However, difficulties in the measurement of d_p and ε_0, coupled with the significant deviation of measured

permeability from the values predicted by this equation (*e.g.* refs. 4 and 5), effectively rule out routine usage of such an approach. To be of practical value any equation derived must be in terms of parameters that are easily and directly measurable with the individual column sections. We present such an empirical approach below.

Darcy's Law for fluid flow through a packed bed may be written in the form

$$u = -\frac{B_0}{\varepsilon \eta} \cdot \frac{\mathrm{d}p}{\mathrm{d}l} \tag{2}$$

where u is the local fluid velocity averaged over both interparticle and intraparticle free space, B_0 is the specific permeability of the bed, ε is the porosity of the bed, *i.e.* the sum of both interparticle and intraparticle fractional voidages, η is the fluid viscosity, and $\mathrm{d}p/\mathrm{d}l$ is the local pressure gradient. For a uniformly packed gas chromatographic column, integration over column length shows that the velocity at the outlet, u_0, is given by

$$u_0 = \frac{B_0}{2\varepsilon \eta \, L} \left[\frac{(p_i^2 - p_0^2)}{p_0} \right] \tag{3}$$

where p_i and p_0 are the pressures at the column inlet and outlet, respectively, and L is the column length. Hildebrand and Reilley[6] introduced the concept of resistance to gas flow, R_F, defined by

$$R_F = \frac{2\varepsilon \eta \, L}{B_0} = \left[\frac{(p_i^2 - p_0^2)}{p_0 u_0} \right] \tag{4}$$

It is also apparent that

$$R_F = \left[\frac{(p_i^2 - p_0^2)}{\bar{p}\bar{u}} \right] \tag{5}$$

where $\bar{p}$ and $\bar{u}$ correspond to the mean pressure and mean gas velocity within the column; $\bar{u}$ and $\bar{p}$ may, in turn, be replaced via

$$\bar{u} = L/t_d$$

and

$$\bar{p} = p_0/j$$

where t_d is the retention time for a non-sorbed substance (dead time), and j is the James–Martin pressure correction factor. On rearrangement and substitution for j we may then obtain the following relationship

$$t_d = \frac{2 \, L R_F}{3} \cdot \left[\frac{(p_i^3 - p_0^3)}{(p_i^2 - p_0^2)^2} \right] \tag{6}$$

Thus, a plot of t_d against $(p_i^2 - p_0^3)/(p_i^2 - p_0^2)^2$ should be a straight line passing through the origin and of slope $(2/3)LR_F$. The determination of R_F for a particular column is thus straightforward. It is also apparent from eqn. 4 that, for a uniform packing, R_F is directly proportional to column length and is, alone, sufficient to describe gas flow as a function of pressure drop, thus eliminating any need of specific knowledge of either B_0 or ε.

Consider now coupled column sections F followed by B (front and back), having lengths L_F and L_B, internal radii r_F and r_B, and porosities ε_F and ε_B, respectively. Suppose p_i, p and p_0 correspond to the pressures at the inlet, the junction and the outlet, respectively, and then let u_{Fi} and u_{FO} represent the gas velocities at the inlet and outlet of column F, and similarly u_{Bi} and, u_{BO} for column B. If F_c is the volumetric flow measured at outlet pressure, and corrected to column temperature, then the volumetric flow at a point where the pressure equals some value p is given by $F_c p_0/p$. Now, as mentioned earlier, the gas velocity at some point in the column, u, is defined as being averaged over the cross-section of all free space at that point (both inter- and intra-particle free space) so that $u = p_0 F_c/p\pi r^2 \varepsilon$, or

$$\frac{p_0 F_c}{\pi} = p\, u\, r^2 \varepsilon \tag{7}$$

where r and ε represent the column internal radius and porosity at that point. It follows that

$$\frac{p_0 F_c}{\pi} = p_i u_{Fi} r_F^2\, \varepsilon_F = p u_{FO} r_F^2\, \varepsilon_F = p u_{Bi} r_B^2\, \varepsilon_B = p_0 u_{Bo} r_B^2\, \varepsilon_B \tag{8}$$

Making appropriate substitutions from eqn. 4,, wherefrom

$$p u_{FO} = (p_i^2 - p^2)/R_{FF} \text{ and } p_0 u_{BO} = (p^2 - p_0^2)/R_{FB}$$

we find that

$$\frac{r_F^2 \varepsilon_F}{R_{FF}} (p_i^2 - p^2) = \frac{r_B^2 \varepsilon_B}{R_{FB}} (p^2 - p_0^2) \tag{9}$$

R_{FF} and R_{FB} referring to front and back column sections, respectively.

The mobile phase volume of a column (strictly, the sum of inter- and intra-particle free space), V_M, is relatively easily measured, being given by

$$V_M = j F_c\, t_d \tag{10}$$

It is also evident that

$$V_M = \pi r^2\, \varepsilon L \tag{11}$$

so that eqn. 9 may now be written in the form

$$\left[\frac{V_{MF}}{L_F R_{FF}}\right] (p_i^2 - p^2) = \left[\frac{V_{MB}}{L_B R_{FB}}\right] (p^2 - p_0^2) \tag{12}$$

Hence,

$$p^2 = \frac{p_i^2 - l_F[p_i^2 - (V_{MB}R_{FF}/V_{MF}R_{FB})p_0^2]}{1 - l_F[1 - V_{MB}R_{FF}/V_{MF}R_{FB}]} \tag{13}$$

where l_F is the length fraction of section F, *i.e.* $l_F = L_F/(L_F + L_B)$. We are now in a position to calculate the pressure at the junction of a coupled packed column.

Eqn. 13 is the general solution for coupled columns of any type and may for example be used when capillary column internal diameters are uncertain or unknown. The approach to optimisation described later is equally general.

If we now define a parameter P as

$$P = t_{dF}/t_{dB} \tag{14}$$

then it follows that the capacity factor k' for a coupled column is given[7] by

$$k' = \left[\frac{P\,k_F' + k_B'}{P + 1}\right] \tag{15}$$

Now, from eqn. 6

$$t_{dF} = \frac{2L_F R_{FF}}{3}\left[\frac{(p_i^3 - p^3)}{(p_i^2 - p^2)^2}\right] \tag{16}$$

which on substituting for $(p_i^2 - p^2)$ from eqn. 12 results in

$$t_{dF} = \frac{2}{3}\frac{(L_B R_{FB})^2}{L_F R_{FF}}\left(\frac{V_{MF}}{V_{MB}}\right)^2\left[\frac{(p_i^3 - p^3)}{(p^2 - p_0^2)^2}\right] \tag{17}$$

and since

$$t_{dB} = \frac{2L_B R_{FB}}{3}\left[\frac{(p^3 - p_0^3)}{(p^2 - p_0^2)^2}\right] \tag{18}$$

then

$$P = \frac{L_B R_{FB}}{L_F R_{FF}}\left(\frac{V_{MF}}{V_{MB}}\right)^2\left[\frac{(p_i^3 - p^3)}{(p^3 - p_0^3)}\right] \tag{19}$$

Eqn. 19 reduces to the solution put forward by Hildebrand and Reilley[6] only when V_M/L is the same for the two column sections, *i.e.* when they have equal $r^2\varepsilon$. This is understandable since they neglected the effect on carrier velocity of a change in porosity at the junction (see eqn. 8). Buys and Smuts[8], on the other hand, considered column sections not only of equal ε but also of equal ε/B_0, *i.e.* equal R_F/L.

Having solved the problem of predicting solute retention for coupled columns in terms of readily measurable practical quantities, we may now turn to the implementation of optimising the relative lengths of coupled columns required for given analyses.

As for our approach for optimising coupled capillary lengths[1], let us define a function, f, of true length fraction, l, such that

$$k' = f_F k'_F + f_B k'_B \tag{20}$$

where $f_F + f_B = 1$ and, as is evident from a consideration of eqn. 15,

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

Rearrangement of eqn. 19 gives us a solution for p in terms of P, i.e.

$$p^3 = \left[\frac{p_i^3 + P\gamma p_0^3}{1 + P\gamma} \right] \tag{21}$$

where

$$\gamma = \frac{L_F R_{FF}}{L_B R_{FB}} \left(\frac{V_{MB}}{V_{MF}} \right)^2 = \frac{\bar{R}_{FF}}{\bar{R}_{FB}} \left(\frac{\bar{V}_{MB}}{\bar{V}_{MF}} \right)^2$$

and $\bar{R}_{5F}$ and $\bar{V}_M$ are the respective quantities per unit length of each column and should be, ideally, constant. It follows, therefore, that γ is also a constant, being independent of the individual column lengths comprising the whole column. Substituting for P in eqn. 21 then gives the result

$$p^3 = \frac{p_i^3 - f_F(p_i^3 - \gamma p_0^3)}{1 - f_F(1 - \gamma)} \tag{22}$$

Finally, from eqn. 12 it is possible to derive an equation for l_F:

$$l_F = \left[\frac{\bar{R}_{FF}\bar{V}_{MB}}{\bar{R}_{FB}\bar{V}_{MF}} \left(\frac{(p^2 - p_0^2)}{(p_i^2 - p^2)} \right) + 1 \right]^{-1} \tag{23}$$

As developed for coupled capillaries[1], the route to true optimisation of length fraction is now apparent. Based on the linear relationships expressed by eqn. 20 a window diagram[9–12] produced from capacity factor data for the various components of the mixture measured on individual column sections would indicate the optimum f_F. Hence the pressure at the junction of such a coupled column operated at some overall pressure drop $(p_i - p_0)$ may be calculated via eqn. 22 since γ is also known. The optimum true length fractions may then be determined by application of eqn. 23 and the total length required from a knowledge of the theoretical plate requirement.

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