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Note

Approximate approach to correction for carrier compressibility effects in coupled packed gas chromatographic columns

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We have recently presented[1,2] an approach to correction for carrier gas compressibility effects in serially coupled open tubular columns which requires knowledge of only column section internal diameters and overall pressure drop. Such correction is essential when optimising relative section lengths by the window diagram technique. We have since extended the approach to include packed columns[3]. It was shown that if capacity factors (k') were assumed to have a linear dependence on some function (f) of true length fraction (l) *i.e.*

$$k' = f_F k'_F + f_B k'_B \tag{1}$$

where $f_F + f_B = 1$, and F and B refer to front and back column sections, then the pressure at the junction of the two sections (p) is given by

$$p^3 = \left[\frac{p_i^3 - f_F(p_i^3 - \gamma p_o^3)}{1 - f_F (1 - \gamma)} \right] \tag{2}$$

where

$$\gamma = \frac{\bar{R}_{FF}}{\bar{R}_{FB}} \left[\frac{\bar{V}_{MB}}{\bar{V}_{MF}} \right]^2$$

and p_i and p_o are the inlet and outlet pressures of the column respectively. $\bar{R}_F$ is the resistance to gas flow per unit length of column, defined by

$$\bar{R}_F = \left[\frac{2\varepsilon\eta}{B_o} \right] \tag{3}$$

where ε is the total porosity of the column packing, η is the carrier gas viscosity and B_o is the specific permeability of the packing. $\bar{V}_M$ is the mobile phase volume per unit length of column, so that

$$\bar{V}_M = \pi r^2 \varepsilon \tag{4}$$

where r is the column internal radius.

The window diagram technique may be employed to determine optimum f_F for separation of a given mixture, and the true length fraction of section F corresponding to this is given by

$$l_F = \left[\frac{\bar{R}_{FF}\, \bar{V}_{MB}\, (p^2 - p_o^2)}{\bar{R}_{FB}\, \bar{V}_{MF}\, (p_i^2 - p^2)} + 1 \right]^{-1} \tag{5}$$

The measurement of $\bar{V}_M$ is relatively easy. A method was proposed[3] for determining $\bar{R}_F$ which involves measurement of dead time over a range of inlet pressures. We hope to show here that such measurements may be unnecessary.

Eqn. 3 shows that $\bar{R}_F$ is dependent upon B_o. Now the Kozeny-Carman equation[4,5] yields a specific permeability, B_o, for packed beds as follows:

$$B_o = \frac{d_p^2\, \varepsilon_o^3}{180\, (1 - \varepsilon_o)^2} \tag{6}$$

where d_p is the mean packing particle diameter and ε_o is the interparticle porosity. When substituted into eqn. 3 for $\bar{R}_F$ this results in

$$\bar{R}_F = \frac{360\, (1 - \varepsilon_o)^2 \varepsilon \eta}{d_p^2\, \varepsilon_o^3} \tag{7}$$

The interparticle porosity (ε_o) of well-packed columns has been shown to be, to a good approximation, independent of both particle mesh size and intraparticle porosity (e.g. refs. 6 and 7). It follows from eqns. 4 and 7 that

$$\frac{\bar{R}_{FF}\, \bar{V}_{MB}}{\bar{R}_{FB}\, \bar{V}_{MF}} = \frac{d_{pB}^2}{d_{pF}^2} \tag{8}$$

The expected deviations in B_o from that predicted by the Kozeny-Carman equation would largely cancel on consideration of relative $\bar{R}_F$ as above.

On introducing the approximate relationship of eqn. 8 into eqn. 5,

$$l_F = \left[\frac{d_{pB}^2\, (p^2 - p_o^2)}{d_{pF}^2\, (p_i^2 - p^2)} + 1 \right]^{-1} \tag{9}$$

The factor γ of eqn. 2 similarly reduces to

$$\gamma = \frac{d_{pB}^2\, \bar{V}_{MB}}{d_{pF}^2\, \bar{V}_{MF}} \tag{10}$$

We therefore need to know only the mesh sizes of the packings, and to measure the relative mobile phase volumes per unit length of the column sections. If volumetric flow-rates are measured under identical conditions, i.e. same pressure drop and column and flow-meter temperatures, then

$$\frac{\bar{V}_{MB}}{\bar{V}_{MF}} = \frac{t_{dB}\ F_{FM(B)}\ L_F}{t_{dF}\ F_{FM(F)}\ L_B} \tag{11}$$

where $F_{FM(i)}$ is the flow-rate measured by the flow-meter for column section i.

EXPERIMENTAL

The approximate approach developed relies on the validity of the relationship expressed by eqn. 8, *i.e.* that for well-packed columns $\bar{R}_F\ d_p^2/\bar{V}_M$, or $R_F d_p^2/V_M$, is constant. We have determined R_F and V_M for four 3 m × 3.2 mm O.D. columns of Chromosorb G (AW-DMCS) coated with squalane. Mesh sizes of 60–80 and 100–120, and liquid loadings of 5 and 0.5 wt.% were considered. Measurements were carried out at 90.0°C on a Perkin-Elmer F-33 gas chromatograph, and the results are listed in Table I.

TABLE I

V_M AND R_F FOR 3-m COLUMNS STUDIED

Column	Mesh size	Liquid loading/wt.%	V_M (ml)	R_F (atm sec cm^{-1})
1	100–120	0.5	7.79	0.894
2	100–120	5.0	7.71	0.844
3	60–80	0.5	7.74	0.354
4	60–80	5.0	7.91	0.374

In the U.S. Sieve Series, mesh sizes of 60, 80, 100 and 120 correspond to openings of 0.250, 0.177, 0.149 and 0.125 mm, respectively. Taking the simple mean of the extremes of respective mesh openings gives us mean particle diameters of 0.2135 mm for 60–80 mesh, and 0.137 mm for 100–120 mesh. We are now in a position to calculate $R_F d_p^2/V_M$ for each of the four columns. These are listed in Table II.

TABLE II

$R_F\ d_p^2/V_M$ FOR 3-m COLUMNS STUDIED

Column	$R_F\ d_p^2/V_M$ (atm sec cm^{-2})
1	$2.15 \cdot 10^{-5}$
2	$2.05 \cdot 10^{-5}$
3	$2.08 \cdot 10^{-5}$
4	$2.16 \cdot 10^{-5}$

RESULTS

We may see from Table II that $R_F\ d_p^2/V_M$ appears to be remarkably constant equal to $2.11 \cdot 10^{-5} \pm 0.05 \cdot 10^{-5}$ atm sec cm^{-2} in spite of the approximations in both the theory and the assessment of mean particle diameter.

The sample of columns studied is admittedly small. Nevertheless, the results obtained suggest that our approximate approach to correction for compressibility

effects may be sufficient for analytical purposes. The use of this approach is certainly better than ignoring the effects of compressibility.

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