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PRACTICAL IMPLICATIONS OF MODERN LIQUID CHROMATOGRAPHIC COLUMN PERFORMANCE

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SUMMARY

A general equation relating column performance as a function of important experimental variables is described. Experimental data obtained from studies of effects of particle diameter (d_p) on efficiency, permeability, and shape of HETP *vs.* velocity curves for porous silica gel and alumina adsorbents of $5 \leqslant d_p \leqslant 40\,\mu m$ gave a better understanding of the role of new small d_p packings in high-performance liquid chromatography. Contrary to the belief that columns packed with porous particles of $d_p < 10\,\mu m$ require higher pressures, this study indicates that one may get faster separations with shorter columns at lower pressure with small d_p compared to larger d_p. Performance of columns packed with porous particles of $d_p < 20\,\mu m$ exceeds that of porous layer beads, often used in high-performance liquid–solid chromatography.

INTRODUCTION

Recent advances[1–5] in the preparation and packing of totally porous adsorbents of particle diameter (d_p) less than 20 μm for high-performance liquid chromatography (HPLC) have demonstrated column efficiencies of several orders of magnitude greater than classical open column chromatography employing particles of 100+ μm. Columns packed with these small particles give rise to low permeabilities (*i.e.*, higher pressure drops) and high-pressure pumps are required to make full use of them. As will be shown in this paper, small particles properly packed into short columns will always perform better separations in shorter analysis times than larger particles in long columns at the same pressure. Sometimes, tradeoffs between particle size of the packing, column length, and flow-rate are needed to achieve the required resolution in the shortest analysis time at the available system pressure. Because of the increasing use of columns packed with 5- and 10-μm particles, it is worthwhile to re-examine some of the basic chromatographic relationships in order to predict where such columns may offer the most utility.

Practical implication of columns packed with small particles on HPLC hardware will be discussed. As columns become more efficient, more care must be exercised in their use. Such factors as injection technique, extra column effects, detector response time, and detector cell volume now become even more important if full advantage of small particles is to be realized.

Currently, porous layer beads (PLB) are the most widely used of the HPLC packing materials. Compared to classical liquid chromatography packings, PLB offer reasonably high efficiency. They may be dry-packed easily and because of their relatively large particle size, typically 40 μm, give relatively high column permeability. However, due to low surface area, PLB suffer from reduced sample capacity.

Small porous packings offer high efficiency and have high sample capacity but the permeability is lower and the columns are more difficult to pack[1-5]. Sample capacity is most important for preparative HPLC and when using detectors of intermediate sensitivity, such as refractive index. Comparative performance of PLB and small porous packings, of considerable practical interest, is the subject of further discussion in this paper.

THEORETICAL

In HPLC we strive to achieve the most resolution in the shortest time. Resolution is governed by three factors —selectivity, capacity factor, and efficiency[6]. Selectivity is the hardest to optimize since it is governed by the adsorbent characteristics and mobile phase conditions. To change selectivity we must change one or the other and this requires time. For speed, the capacity factor should be in the range of 2 to 5 (ref. 7). This may usually be accomplished by adjustment of the mobile phase to optimize k' for those compounds of interest or by performing solvent programming (gradient elution) to lower k' values for strongly retained compounds. The easiest factor to optimize is efficiency since predictions from chromatographic theory may be utilized. Pressure drop is also important since it is limited by the HPLC hardware.

To obtain the highest number of plates in the shortest time at the lowest ΔP is our goal. Establishing the relationship of N, related to H by eqn. 1,

$$N = L/H \tag{1}$$

ΔP and t_r would help us to choose the chromatographic conditions to achieve optimum resolution in the shortest time. Comparison of different columns with regard to N, ΔP, and t_r allows us to make intelligent predictions on the column which should be used for best results.

The time of a chromatographic analysis is given by eqn. 2 in which t_r is proportional to the k' of the last chromatographic peak[8]

$$t_r = \frac{L}{v}(1 + k') \tag{2}$$

One way to compare HPLC columns is to plot H as a function of v. Columns which show low H and gradually rising H–v slopes are preferred. The lower the slope the higher the flow-rate that may be used to decrease analysis time without sacrificing column efficiency and resultant loss of resolution. Although theoretical expressions to explain the shape of H–v curves have been suggested[9-11], none correctly reproduce experimental data[10] and, at present, we must resort to an empirical equation rather than an exact one. The empirical eqn. 3 of Snyder[12]:

$$H = \mathrm{D}\, v^n \tag{3}$$

appears to fit a large number of HPLC data when used over a limited velocity range[12–18]. Unfortunately, the value of n may vary somewhat depending on the velocity range under consideration. At low values of v (less than 0.2 cm/sec) and small particles, the presence of longitudinal diffusion of solutes has a strong influence on H (ref. 18). The H–v curves show a rise in H with decreasing v (refs. 3, 4, 19) and eqn. 3 does not apply. At high velocities (greater than 10 cm/sec), the experimental inaccuracy in measuring t_r and w used to calculate H from the chromatogram affects the ability to determine reliable n values. Eqn. 3 appears to give the best "fit" in the $0.5 \leqslant v \leqslant 10$ cm/sec range. Values of n have ranged from 0.3 to 0.7 for liquid–solid chromatography[4,12,13] and liquid–liquid chromatography[14–17,20,21] to a maximum of 0.9 in ion-exchange chromatography[22]. Values of $n \geqslant 1$ imply that an increase in v will result in no further decrease in analysis time for a required constant resolution.

Column efficiency may also be related to d_p. From eqn. 3 at a velocity of 1 cm/sec, $H = \mathrm{D}$ and the relationship between H and d_p may be represented by:

$$H = \mathrm{D} = K_H\, d_p^{\,z} \tag{4}$$

Here $K_H = H$ for $d_p = 1\ \mu$m and $v = 1$ cm/sec .The exponent z has been found to be nearly constant (1.6 ± 0.2) for a given adsorbent system for $k' > 1$ and $v > 1$ cm/sec (refs. 4, 12, 23). Recently, Huber[19] has shown that at lower velocities and lower k' values, z may drop to values less than one, but for well retained compounds at typical HPLC flow-rates, eqn. 4 is a good approximation.

Since v, n, and d_p appear to have the strongest influence on H, we may combine eqns. 3 and 4 to obtain a more complete relationship:

$$H = K_H\, d_p^{\,z}\, v^n \tag{5}$$

Column pressure drop is a second most important and probably most limiting chromatographic parameter. For a liquid chromatograph, its maximum value influences column length and particle size as well as the mobile phase and its linear velocity. Pressure drop is related to these column parameters by:

$$\Delta P = \frac{v\,\eta\,L}{K_0} \tag{6}$$

Column permeability, K_0, may be related to d_p by use of eqn. 7 well discussed by Giddings[9].

$$K_0 = \frac{f_0\, d_p^{\,y}}{2\Phi'} = \frac{d_p^{\,y}}{K_p} \tag{7}$$

Although theoretically $y = 2$ for a regularly packed column[9], experimental values of $1.4 \leqslant y \leqslant 2$ have been reported[4,12,14,23,24]. These differences are maybe related to complex flow patterns resulting from bridging of particle aggregates in packed columns[9,24].

By substituting K_0 into eqn. 6 and solving for ΔP we obtain:

$$\Delta P = \frac{v\,\eta\,L\,K_p}{d_p^{\,y}} \tag{8}$$

Combining eqns. 1, 2, 5, and 8 and solving for t_r results in:

$$t_r = \frac{K_H^{2/(1+n)} (\eta K_p)^{(1-n)/(1+n)} N^{2/(1+n)} (1 + k')d_p \left\{z - \left(\frac{1-n}{1+n}\right)(y - z)\right\}}{\Delta P^{(1-n)/(1+n)}} \quad (9)$$

In eqn. 9, column length and mobile phase linear velocity have been eliminated in order to obtain the optimum relationship between t_r, ΔP, N, and d_p. If any one of the variables in eqn. 9 is changed, it is assumed that L and v will be changed in accordance with eqns. 1, 2, 5 and 8. By substitution of typical or actual experimental values, eqn. 9 permits us to evaluate the effects of column head pressure on analysis time for separations requiring a minimum number of plates for columns of different d_p.

RESULTS AND DISCUSSION

Efficiency as a function of particle diameter

Previous studies have evaluated the effect of d_p on column efficiency for three different porous chromatographic packings—silica gel[4], alumina[25], and a hydrocarbon-bonded phase[26]. All columns were packed by the high-pressure, balanced-density slurry procedure[2]. The results of these studies are summarized in Fig. 1, where H, at $v = 1$ cm/sec, is plotted as a function of d_p according to eqn. 4. Each value of H was determined from experimental H–v curves at $v = 1$ cm/sec since, according to eqn. 3, $H = D$ for any value of n. For small changes in v this equivalency should remain valid[12,13]. The value of d_p was calculated from scanning electron micrographs of the adsorbents as described previously[4].

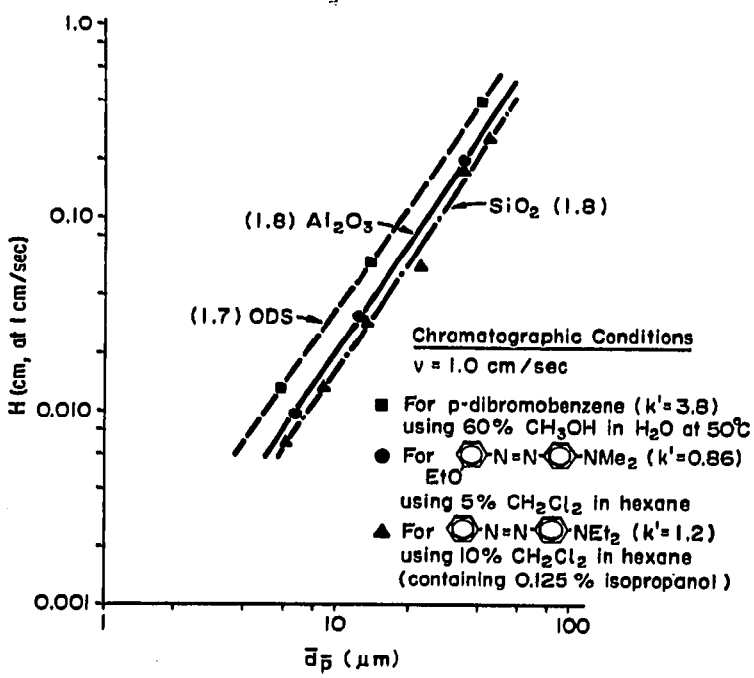

Fig. 1. Dependence of HETP on particle diameter for silica[4], alumina[25], and hydrocarbon-bonded (ODS) phase[26].

The data of Fig. 1 were not corrected for mobile phase viscosity differences which would affect their absolute positions on the H-axis. Mobile phases of higher viscosity, such as 60% methanol in water at 50° (η = 0.8 cP) used in evaluation of the hydrocarbon-bonded phase of Fig. 1, give lower values of solute diffusion coefficients compared to mobile phases of lower viscosity, such as those used to test silica and alumina (η = approx. 0.3 cP). The solute diffusion coefficient in the mobile phase is inversely proportional to H (ref. 15); hence, higher viscosity solvents give higher H values.

For all of the chromatographic packings of Fig. 1, H shows a marked dependence on d_p for the entire d_p range. The average slope of the three curves was 1.8 ± 0.1 and, therefore, z = 1.8 for eqn. 5.

Pressure as a function of particle diameter

Fig. 1 does not give any indication of the increased pressure requirements for columns of smaller particle sizes. Recall that eqn. 8 showed an inverse relationship between ΔP and d_p. In earlier studies[4,25], we found that experimental column permeabilities for silica gel and alumina varied with $d_p^{1.8}$ or y = 1.8 in eqn. 8.

Pressure–time equation

Substituting the experimental values of z = y = 1.8 into eqn. 9 we obtain:

$$t_r = \frac{K_H^{2/(1+n)} (\eta K_P)^{(1-n)/(1+n)} N^{2/(1+n)} (1 + k') d_p^{1.8}}{\Delta P^{(1-n)/(1+n)}} \qquad (10)$$

Now we may evaluate the effect of experimental variables of eqn. 10 on pressure–time relationships. In these comparisons, we shall optimize the chromatography by varying L and v at constant d_p, N, k', and mobile phase. Experimentally, variation of v only is the most convenient since we merely change flow-rate. Variation of L is the least convenient since, to optimize a given separation one may have to pack a new column or columns each time.

Effect of n on analysis time

The slope of the H–v curve has a strong influence on analysis time. Substituting some typical experimental values of N = 2350 plates, η = 0.3 cP (hexane), k' = 1.3, and d_p = 10 μm into eqn. 10 we may vary n within the range of experimental values cited earlier. Values of K_H and K_P used for calculation are discussed in the List of symbols. Fig. 2 shows, as expected, that an increase in pressure (faster flow-rates) will decrease analysis time for all values of n less than one. As n increases from 0.2 to 0.7, the slope of the t_r–ΔP curve decreases. Thus, for highest values of n, increased pressures give only marginal savings in time. Within the valid velocity range, the value of n is influenced somewhat by the packing structure but mostly by the extent of contribution of mass transfer in the stationary phase or stagnant mobile phase[19]. Its value may be difficult to control for a given chromatographic system. For silica and alumina of $5 \leqslant d_p \leqslant 40$ μm, solutes of $k' > 1$, and $0.5 \leqslant v \leqslant 3.5$ cm/sec, n has been found to be equivalent to 0.6 ± 0.1 (refs. 4, 25).

In using eqn. 3, all H–v curves must pass through a common point at v = 1 cm/sec and H = D, irrespective of the value of n. This means that H–v curves below

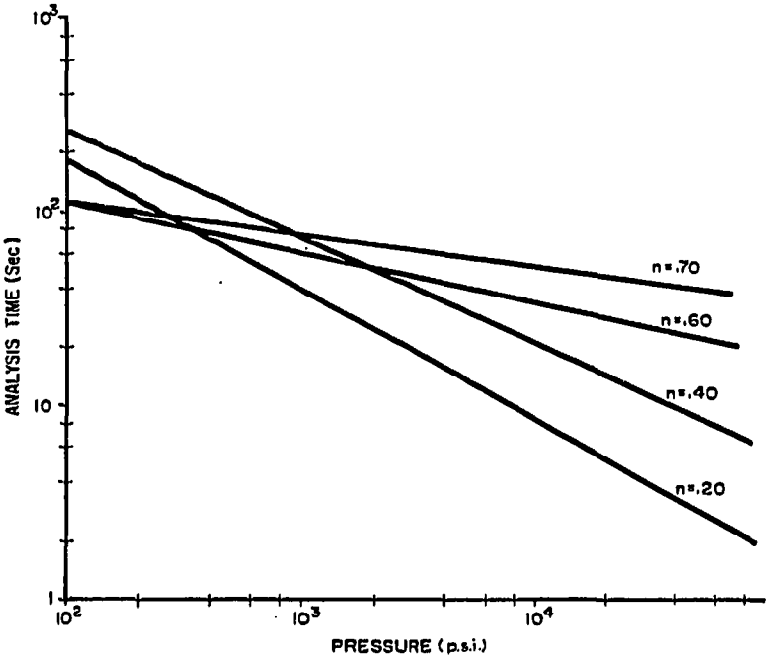

Fig. 2. Effect of velocity exponent n on pressure-time relationship. $H = Dv^n$; $N = 2350$; $\eta = 0.3$ cP; $d_p = 10\ \mu$m.

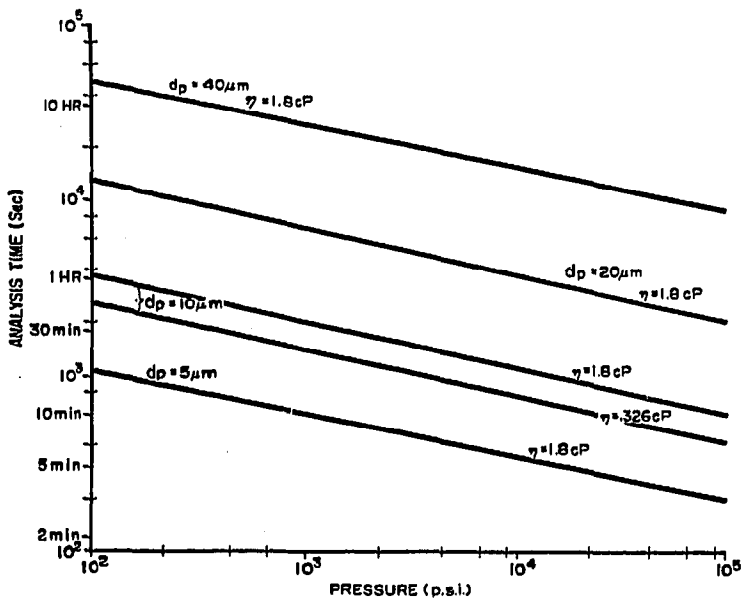

Fig. 3. Effect of particle size and viscosity on pressure-time relationship. $\alpha = 1.05$; $R = 1.0$; $N = 28{,}250$; $n = 0.60$.

$v = 1$ cm/sec with high n values are lower than those curves with low n values. The crossover points on Fig. 2 are a result of this assumption.

Effect of particle size and viscosity on analysis time

Using eqn. 10 with $n = 0.6$ and similar conditions used for Fig. 2, Fig. 3 shows pressure–time relationships as a function of particle size and viscosity for a very difficult separation requiring that $N = 28{,}250$ plates. When L and v were varied to maintain a fixed column head pressure, a decrease in d_p of the column packing gave decreased analysis times. For example on Fig. 3 consider the separation being performed at a constant 1000 p.s.i. Reduction of d_p from 40 μm (26,500 sec) to 5 μm (620 sec) decreased analysis time by a factor of almost 45.

The role of pressure in HPLC is more strongly emphasized on Fig. 3 by comparing the separation time required for the standard column chromatography on 40 μm porous particles at 100 p.s.i. (12.8 h) to the new liquid chromatography on 5 μm particles at 5000 p.s.i. (7 min).

For a fixed pressure and particle size, lower viscosity mobile phases will give decreased analysis times. Fig. 3 shows that, if, for a particular liquid–solid chromatographic separation, a non-polar hydrocarbon is called for, use of hexane ($\eta = 0.3$ cP) rather than cycloheptane ($\eta = 1.8$ cP) is suggested. Due to lack of defined quantitative studies in the literature, the effect of viscosity on efficiency was not included in Fig. 3. Only the effect of viscosity on permeability was included. If the η contribution to H was included, a lower viscosity solvent would give a further decrease in analysis time due to increased plate number for the reasons discussed earlier.

Contrary to the belief that columns packed with smaller particles require higher pressures, Fig. 3 shows that to accomplish the same separation requiring a fixed number of plates at a constant pressure, one may always get faster analyses with smaller particles or conversely with smaller particles one may obtain the same analysis time with less pressure. The decreased permeability of columns packed with smaller particles is more than compensated for by increased efficiency, allowing the use of shorter columns with lower flow-rates and pressures.

Rather than varying L (by adding and subtracting columns) and v in order to optimize a separation, practicing chromatographers developing analytical methods invariably prefer to work with a single column. In this case in order to maximize N, it is usually preferable to work with the longest column packed with the smallest particles with the experimental potential for high pressure and high flow-rates. Thus, higher pressure pumps are quite useful since one is not limited to low flow-rates. If sufficient effective plates are available from a column but are not required, they may always be sacrificed by decreasing k' through increasing mobile phase strength or by raising v once suitable resolution is obtained. Then, the flexibility of modern HPLC instrumentation with solvent programming and high-pressure capabilities is an important consideration. In the case of constant L, it has been shown that analysis time is inversely proportional to pressure[27]. A highly efficient column of small porous particles should also be preferable to recycle liquid chromatography[28] with larger particles and multiple passes since full advantage of increased plate number is realized with a single column.

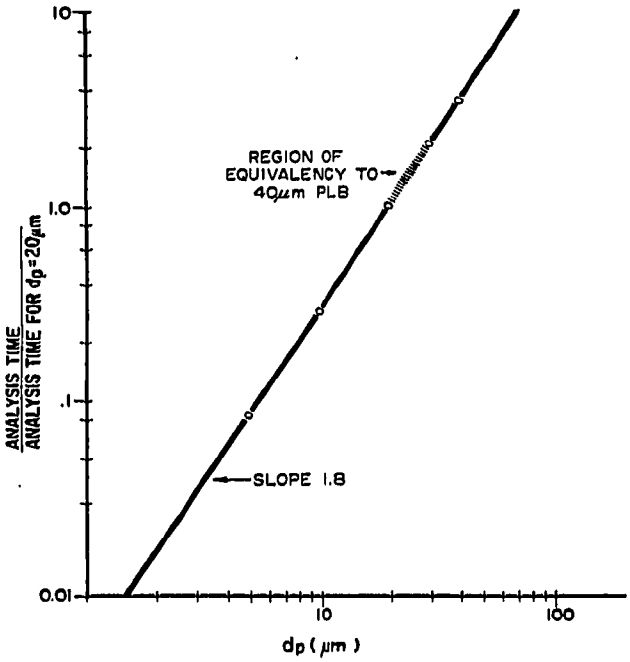

Fig. 4. Effect of porous particle diameter on analysis time. ΔP, N, and k' are constant; L and v vary with d_p.

Comparative performance between PLB and small porous particles

The success of modern HPLC during the last five years has been largely due to the porous layer bead packings which decreased analysis times to roughly one-tenth those of classical chromatography on 100 μm porous particles. As will be shown later, columns of porous particles in the range of 20 to 30 μm appear to have similar performance characteristics to columns of porous layer beads of 40 μm size. Now with increasing use of 5 μm (and possibly lower d_p) particles, an additional ten-fold increase in speed is possible without further increase in pressure. This is depicted diagrammatically on Fig. 4, which shows analysis time for $5 \leqslant d_p \leqslant 40\,\mu$m relative to porous particles of $d_p = 20\,\mu$m as a function of d_p. The region of performance equivalency between PLB and 20 to 30 μm porous particles is designated on the plot.

To semi-quantitatively compare column performance, eqn. 10 may be rearranged and solved for N_{eff} to provide the useful relation between plate number and the particle size at constant ΔP and t_r:

$$N_{eff} = \frac{\Delta P^{(1-n)/2}\, t_r^{(1+n)/2}\, k'^2}{K_H\,(\eta\, K_p)^{(1-n)/2}\, d_p^{\,1.8\,(1+n)/2}\,(1+k')^{(5+n)/2}} \tag{11}$$

This equation has the same form as eqn. 4a of ref. 13 and has been suggested by Snyder as a measure of relative column performance. Isolation of all experimentally dependent variables of eqn. 11, namely N_{eff}, ΔP, t_r, k', and η, on the left hand side and particle diameter on the right, we may define the function:

$$F \equiv 1/K_H K_p^{\,(1-n)/2}\, d_p^{\,1.8\,(1+n)/2} \tag{12}$$

which, by combining it with eqns. 4 and 7 with y = z = 1.8, can be equated to the

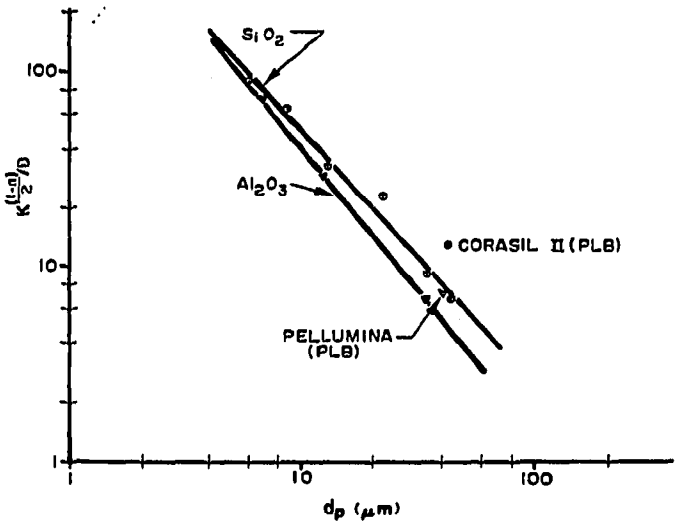

Fig. 5. Column performance factor, $F = K_0^{(1-n)/2}/D$, as a function of adsorbent particle diameter. ⊙, Silica, LiChrosorb® Si 60; a product of E. Merck (Darmstadt). ▼, Alumina, LiChrosorb Alox T; a product of E. Merck (Darmstadt). ●, Corasil® II, a silica PLB; a product of Waters Associates, Framingham, Mass. ▽, Pellumina, an alumina PLB; a product of Reeve Angel, Clifton, N.J.

Snyder performance factor, $F = K_0^{(1-n)/2}/D$ of ref. 13. This relative factor is significant in that it, in itself, is not directly a function of column length or mobile phase velocity and may be used to compare the performance of most columns in terms of their effective plates normalized for pressure drop and separation time.

Use of performance factor

To illustrate the use of the Snyder performance factor we shall compare two types of adsorbents of different d_p. Fig. 5 shows a plot of performance factors as a function of d_p for porous silicas and aluminas. Both types of absorbents show increasing F values with decreasing d_p. This observation further illustrates the advantages of use of smallest particles for maximum column performance. Although porous adsorbents of $d_p < 5\,\mu$m are not, at present, commercially available, extrapolation on Fig. 5 predicts that columns of such particles would offer even greater performance.

Eqn. 12 predicts for $n = 0.6$, the average value of n in eqn. 5 for silica and alumina, that F should be proportional to $d_p^{-1.44}$. From Fig. 5 the average value of the exponents for silica and alumina was −1.40. This dependence was higher than previously noted by Snyder[13], who predicted that F was proportional to d_p^{-2n} or an exponent of −1.2.

The F values for Corasil® II, a silica PLB, and Pellumina®, an alumina PLB, are also included on Fig. 5. For both adsorbents, a well packed column of porous particles approximately 30 μm gave equivalent performance to the PLB's in terms of plates normalized for pressure and time. It would be safe to say that, in liquid–solid chromatography, columns of porous particles 20 μm or less with narrow particle size distribution packed by the balanced-density slurry technique[2] will give consistently superior performance over columns packed with PLB adsorbents.

Choice of packing type

The question naturally arises concerning choice of column packing —small porous particles *vs.* PLB. If, from an historical point of view, the separation has already been developed in the literature using PLB by all means use them to save development time. In analytical chromatography for simple separations with widely varying k' values, the convenience of packing PLB materials suggests their use. Small porous particles generally require more complex packing techniques. As samples become more complex, with similar k' values, then the higher capacity and efficiency of 20 μm or less porous particle columns would be called for. For difficult separations requiring several thousand or more plates, the longest column with the smallest porous particles (5 μm) should be used. If detector sensitivity is a problem, the higher capacity of the porous packings permits larger sample sizes without significant loss of resolution. Certainly, for preparative work, the higher capacity of porous packings dictates their use. On a capacity basis, the smaller porous packings are more economical than PLB. For both PLB and small porous particles, high-performance liquid chromatographs with small extra column volumes and small detector cells should be used. Since the maximum number of plates attainable is dependent on maximum chromatographic pressure as depicted in eqn. 11, high-pressure pumps are advisable.

LIST OF SYMBOLS

α = selectivity; $(t_{r_2} - t_{r_1})/t_0 = k_2'/k_1'$
D = constant defined in eqns. 3 and 4
d_p = particle diameter
η = mobile phase viscosity
F = Snyder performance factor = $K_0^{(1-n)/2}/\mathrm{D}$; defined in ref. 13. Equivalent to eqn. 12
f_0 = interparticle porosity; discussed in ref. 9
H = height equivalent to a theoretical plate; measure of efficiency
k' = capacity factor = $(t_r - t_0)/t_0$
K_0 = specific column permeability
K_{II} = H for $d_p = 1$ μm and $v = 1$ cm/sec; extrapolated from H (at $v = 1$ cm/sec) *vs.* d_p plot such as Fig. 1
K_p = permeability parameter = $2\Phi'/f_0$
Φ' = dimensionless flow resistance factor; ranges from 250–300 with an average experimental value of 300 for most packings
L = column length
N = number of theoretical plates = $16\,(t_r/w)^2$
N_{eff} = number of effective plates = $N\,(k'/1+k')^2$
n = average slope of log H–log v curve; defined over specific velocity range
ΔP = column pressure drop
t_0 = retention time of unretained component
t_{r_i} = retention time of component i
v = linear velocity = L/t_0
w = peak width
y = constant defined in eqn. 7
z = constant defined in eqn. 4

REFERENCES

1 J. F. K. Huber, *Chimia, Suppl.*, (1970) 24.
2 R. E. Majors, *Anal. Chem.*, 44 (1972) 1722.
3 J. J. Kirkland, *J. Chromatogr. Sci.*, 10 (1972) 593.
4 R. E. Majors, *J. Chromatogr. Sci.*, 11 (1973) 88.
5 R. M. Cassidy, D. S. LeGau and R. W. Frei, *Anal. Chem.*, submitted for publication.
6 F. Baumann, in N. Hadden and F. Baumann (Editors), *Basic Liquid Chromatography*, Varian Aerograph, Walnut Creek, 1971, p. 3–2.
7 L. R. Snyder and D. L. Saunders, *J. Chromatogr. Sci.*, 7 (1969) 195.
8 B. L. Karger, in J. J. Kirkland (Editor), *Modern Practice of Liquid Chromatography*, Wiley-Interscience, New York, 1971, p. 11.
9 J. C. Giddings, *Dynamics of Chromatography*, Part I, Marcel Dekker, New York, 1965.
10 J. H. Knox, *Anal. Chem.*, 38 (1966) 253.
11 J. F. K. Huber, *J. Chromatogr. Sci.*, 7 (1969) 86.
12 L. R. Snyder, *J. Chromatogr. Sci.*, 7 (1969) 352.
13 L. R. Snyder, in R. Stock and S. G. Perry (Editors), *Gas Chromatography 1970*, Institute of Petroleum, London, 1971, p. 81.
14 J. J. Kirkland, *J. Chromatogr. Sci.*, 10 (1972) 129.
15 G. J. Kennedy and J. H. Knox, *J. Chromatogr. Sci.*, 10 (1972) 549.
16 H. C. Beachell and J. J. De Stefano, *J. Chromatogr. Sci.*, 10 (1972) 481.
17 J. J. DeStefano and H. C. Beachell, *J. Chromatogr. Sci.*, 10 (1972) 654.
18 L. R. Snyder, *J. Chromatogr. Sci.*, 10 (1972) 369.
19 J. F. K. Huber, *Diskussionstagung der Deutschen Bunsen-Gesellschaft, Saarbrücken, October, 1972.*
20 J. F. K. Huber and J. A. R. Hulsman, *Anal. Chim. Acta*, 38 (1967) 305.
21 R. E. Jentoft and T. H. Gouw, *Anal. Chem.*, 40 (1968) 1787.
22 A. Jardy and R. Rosset, *J. Chromatogr.*, 83 (1973) 195.
23 I. Halasz and M. Naefe, *Anal. Chem.*, 44 (1972) 76.
24 L. R. Snyder, *Anal. Chem.*, 39 (1967) 698.
25 R. E. Majors, *J. Chromatogr. Sci.*, submitted for publication.
26 R. E. Majors, *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March, 1973*, paper No. 232.
27 B. L. Karger, in J. J. Kirkland (Editor), *Modern Practice of Liquid Chromatography*, Wiley-Interscience, New York, 1971, p. 35.
28 K. J. Bombaugh, in J. J. Kirkland (Editor), *Modern Practice of Liquid Chromatography*, Wiley-Interscience, New York, 1971, pp. 272–279.