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A Comparison of Mobile-Phase Peak Dispersion in Gas and Liquid Chromatography*

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Summary

The field of axial and radial dispersion of unsorbed bands in columns or beds packed with spherical particles is reviewed and it is shown that there is broad agreement between various workers: at low reduced velocities both axial and radial dispersion occur by obstructed molecular diffusion. At higher velocities the processes are more complex but at very high velocities and at Reynolds numbers in excess of about 10 the reduced plate height becomes independent of velocity and has a value for axial dispersion of about 2 and for radial dispersion of about 0.2. In the intervening region the dispersion process is complex and shows dependence upon the column-to-particle-diameter ratio. The most inefficient columns appear to be formed when this ratio is between 10 and 30. It is therefore suggested that efforts be made to design and construct columns with greater trans-column uniformity. When trans-column packing inequalities are unimportant, the reduced plate height in the high-velocity region is only slightly affected by fluid velocity, in strong contrast to the situation in open tubes. With gases the reduced plate height does not rise much above 2 for well-constructed columns, whereas with liquids it rises to about 4 before turbulence becomes important and again limits the dispersion, so that it falls to about 2.

The dispersion of bands of solute during chromatography is generally measured by the plate height, H, defined as the rate of

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increase of variance of the Gaussian concentration profile per unit length of the column (*1*); that is,

$$H = d\sigma_z^2/dz \approx L(\sigma_t/T)^2 \tag{1}$$

The approximation is exact for liquids and almost exact for gases in columns with low pressure drop. H is a function of the fluid velocity and the structure of the column. Since contributions to H from many of the processes in the mobile phase are determined by the particle size, it is convenient to define a "reduced" plate height

$$h = H/d_p \tag{2}$$

h is a particularly useful parameter when treating unsorbed solutes. The dispersion rate may also be characterized by a dispersion coefficient, D, with the same units as a molecular diffusion coefficient, D_m, and defined by

$$D = \tfrac{1}{2} d\sigma_z^2/dt \tag{3}$$

D is related to H by

$$H = 2D/u_{\text{band}} \tag{4}$$

For unsorbed solutes u_{band} is equal to the interparticle fluid velocity averaged over any cross section of the column, u; for sorbed solutes it is uR, where R is the fraction of solute molecules in the mobile phase. The reduced plate height for unsorbed solutes is then

$$h = 2D/ud_p \tag{5}$$

Since dispersion results from a number of processes, many of which involve molecular diffusion, it is convenient to define a second reduced parameter, the reduced velocity, ν,

$$\nu = ud_p/\mathrm{D}_m \tag{6}$$

Thus

$$h = 2(D/D_m)/\nu \tag{7}$$

The reduced velocity may be pictured as twice the number of particles past which the mobile phase flows in the time taken for an average solute molecule to diffuse across one particle; it is a measure of the rate of flow relative to the rate of molecular diffusion.

At low fluid velocities $D = \gamma D_m$, and the dispersion occurs by obstructed molecular diffusion; the obstructive factor, γ, lies between 0.6 and 0.7 for spheres (*2,3*). At high reduced velocities the dispersion process is complex.

Many methods have been used to measure *H* or *D*. Chromatographers have almost exclusively employed the "pulse injection" method in which a small, preferably infinitesimal, sample of solute is injected sharply into the flowing solvent: the width of the emergent Gaussian band gives *H* (*1*). Chemical engineers have generally employed the "breakthrough" (*4,5*) or the "sinusoidal attenuation" (*6–8*) methods. In the former, solvent is sharply replaced by a solution or a second solvent miscible with the first: the spread of the overlap region on emergence from the column gives *H*. In the latter, a sinusoidal variation of solute concentration is imposed upon the steady flow of solution into the column or bed: the attenuation of the concentration fluctuation over the column length gives *H*. The sinusoidal attenuation method is particularly suitable for high flow rates. The appropriate equations and theory are fully described in the papers cited.

Since chemical engineers have generally aimed to approximate to infinite beds in their experiments, they have worked with short wide columns (typically $d_c = 5$ cm; $L = 50$ to 200 cm; $\rho = 50$ to 500), whereas chromatographers have used long narrow columns (typically $d_c = 0.5$ cm; $L = 200$ to 500 cm; $\rho = 5$ to 50). In chromatography attention has accordingly been drawn to the effect of the column-to-particle-diameter ratio, ρ, but in chemical engineering this factor has been largely ignored.

Previously one of us has shown (*10*) that the main cause of peak dispersion in chromatographic columns packed with glass beads and using liquid eluants is the existence of trans-column velocity variations and the slowness of trans-column equilibration. This has been emphasized by the experiments and theoretical calculations of Littlewood (*11*), based upon the nonequilibrium theory of chromatography developed by Giddings (*1*). The rate of radial mixing or radial dispersion is therefore of key importance in chromatography.

The radial dispersion rate has been measured as a function of fluid velocity for both liquids and gases (*4,6,9*). A stream of tracer material (for example, a dyestuff) is injected from a fine tube into the center of the packed bed, care being taken that the linear

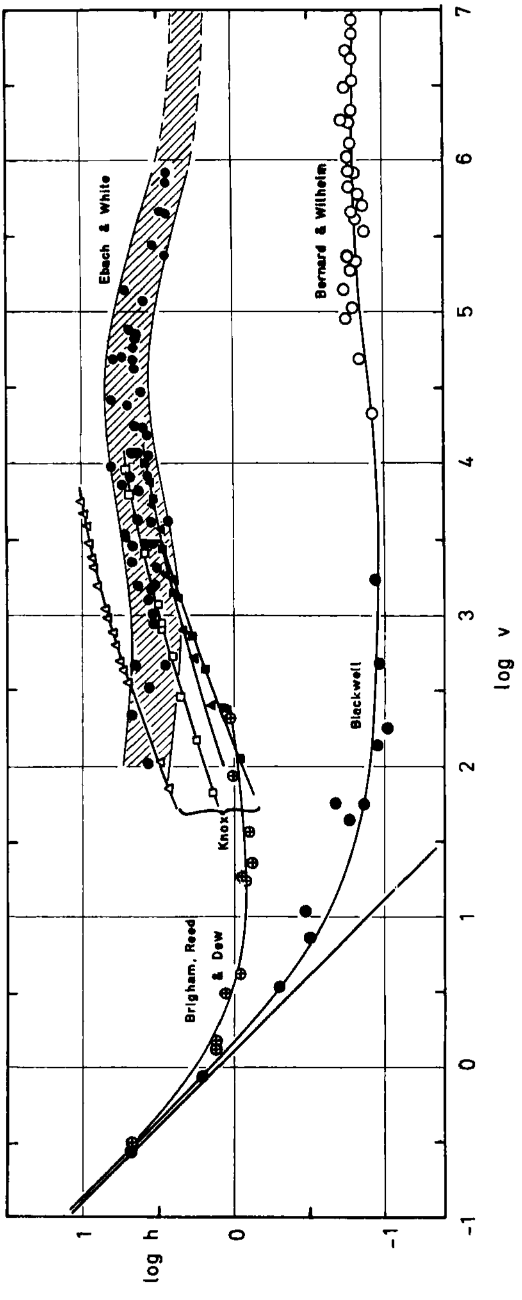

FIG. 1. Axial and radial plate heights as functions of reduced velocity for liquid eluants. (For references see the text.)

velocity of the main stream and tracer stream are the same. The radial concentration distribution at the end of the column is determined by a probe which can be moved radially.

The radial dispersion coefficient D_r is defined by

$$D_r = \tfrac{1}{2} d\sigma_r^2/dt \tag{8}$$

A corresponding "radial plate height" may be defined by Eq. (9) as the rate of increase of the *radial* variance per unit length of column:

$$H_r = d\sigma_r^2/dz = 2D_r/u \tag{9}$$

and a reduced radial plate height $h_r = H_r/d_p$.

The characterization of the radial dispersion by a radial plate height is particularly convenient, because it focuses attention upon the geometrically dependent part of the dispersion process rather than upon the more tractable time-dependent molecular diffusion. It must, however, be emphasized that the term "radial plate height" is not ideal and that the original concept of a theoretical plate as defined by Martin and Synge (*12*) has no relevance in connection with radial dispersion. The entire significance of the radial plate height is contained in Eqs. (8) and (9).

Experiments by a number of workers (*4–10*, *27*), summarized in

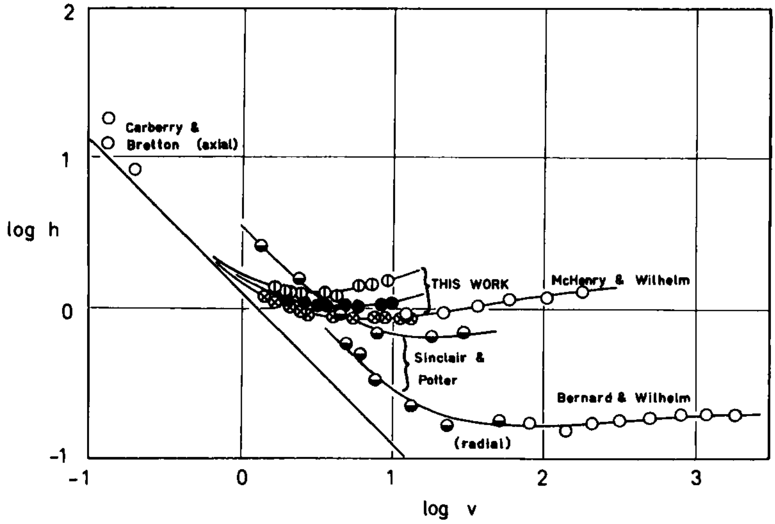

FIG. 2. Axial and radial plate heights as functions of reduced velocity for gaseous eluants. (For references see the text.)

Figs. 1 and 2, show that the radial plate height is always much less than the axial plate height except at low velocities, when both dispersion processes are dominated by molecular diffusion, and $H = H_r = 2\gamma D_m/u$ or $h = h_r = 2\gamma/\nu$.

At sufficiently high fluid velocities, turbulence becomes important and influences the rates of axial and radial dispersion. Under these conditions the Reynolds number, defined in Eq. (10), is more relevant than ν.

$$R_e = u\rho_m d_p/\eta = (D_m\rho_m/\eta)\nu \tag{10}$$

Flow is effectively laminar in a bed of packed spheres for $R_e < 1$ but is highly turbulent for $R_e > 100$. In the intervening region turbulence spreads as the velocity increases from the wider to the narrower spaces in the packing. With straight open tubes turbulence sets in suddenly when R_e exceeds about 2000.

With gases R_e and ν are roughly equal ($D_m = 10^{-1}$, $\eta = 10^{-4}$, $\rho_m = 10^{-3}$), but with liquids R_e is 1000 to 10,000 times smaller than ν ($D_m = 10^{-5}$ to 10^{-6}, $\eta = 10^{-2}$, $\rho_m = 1$). Thus with gases turbulence becomes important almost as soon as molecular diffusion ceases to dominate axial dispersion; but with liquids axial diffusion and turbulence can both be unimportant over a 100 to 1000-fold range of u. Peak dispersion then arises because of variations in the axial component of the fluid velocity over the column cross section. Bands fail to disperse completely (a) because an element in any stream path samples a wide variety of velocities in passing down the column, so that the average velocities of a number of elements fixed to stream lines deviate only slightly from the average velocity for the fluid as a whole; and (b) because molecules of solute in any stream can move into adjacent streams by radial molecular diffusion. These effects independently limit the dispersion of a band as it moves down the column: (a) alone gives a contribution $h = 2\lambda$ and (b) alone gives a contribution $h = \omega\nu$; the factor ν expresses the balance between the dispersive effect of axial transport and the cohesive effect of transverse diffusion of solute. It was originally believed that the total contribution to h when both factors were operating should be written

$$h = 2\lambda + \omega\nu \tag{11}$$

but it is clear that the two effects cooperate to reduce dispersion.

Giddings (*1*) has shown that a more realistic formulation which allows for this is

$$h = (1/2\lambda + 1/\omega\nu)^{-1} \tag{12}$$

In both Eqs. (11) and (12) λ and ω are purely geometric parameters characteristic of the packing structure. The idea that (a) and (b) are "coupled" introduces additional complications when any exact formulation is attempted, because it is necessary to consider separate contributions to h from processes occurring on different geometric scales in the column. Thus in a packing of nonporous particles, at least four contributions are distinguished by Giddings (*13*), those from trans-channel, short-range interchannel, long-range interchannel, and trans-column nonequilibrium. The full equation including the independent term for axial molecular diffusion becomes

$$h = 2\gamma/\nu + \sum_{1}^{4} (1/2\lambda_i + 1/\omega_i\nu)^{-1} \tag{13}$$

One of us (*10*) has already shown that even this equation is probably inadequate. With liquids the major contribution to the plate height arises from trans-column nonequilibrium, and on the basis of Giddings' analysis it would be expected that only a single term in the summation would be important. Experiment shows that the simple coupled form does not fit the data. The best fit was obtained by Eq. (14), which is based upon the idea of coupling but whose physical interpretation was not clear:

$$h = 2\lambda \ln \frac{1 + \omega_2\nu/2\lambda}{1 + \omega_1\nu/2\lambda} \Big/ \ln \frac{\omega_2}{\omega_1} \tag{14}$$

It could, however, be argued that in dealing with trans-column equilibration the molecular diffusion coefficient D_m, which is involved implicitly in the trans-column term through the reduced velocity, should be replaced by a radial dispersion coefficient, D_r. It is, therefore, relevant to consider briefly the mechanism of radial dispersion.

THE MECHANISM OF RADIAL DISPERSION

Figures 1 and 2 show that the radial plate height becomes almost constant when molecular diffusion becomes unimportant. In Fig. 1

the curve for $\nu < 1000$ has been drawn according to the equation

$$h_r = 0.10 + 1.20/\nu \qquad (15)$$

At higher reduced velocities h shows a slight rise with the onset of turbulence, reaching a value of about 2. With gases the effect of turbulence seems to be to sharpen the minimum, so that the curve of h_r versus ν breaks away from Eq. (15) at relatively low reduced velocities and settles down to a value of about 2.

The first term in Eq. (15) can be identified as arising from a "stream-splitting" mechanism dependent only upon the packing geometry, and the second from obstructed molecular diffusion with $\gamma = 0.6$. Figure 3(A) illustrates how stream splitting may occur. Several theoretical models for radial dispersion have been investigated. Saffman (*14*) carried out a rigorous random-walk treatment of a model consisting of randomly oriented capillaries. He obtained a high velocity value of $h_r = 0.375$. Littlewood (*15*) considered radial dispersion to be analogous to gaseous diffusion of light molecules in very heavy molecules and derived $h_r = 0.8$. Both values are several times too high. We give below a very simple treatment which gives a value close to that found experimentally.

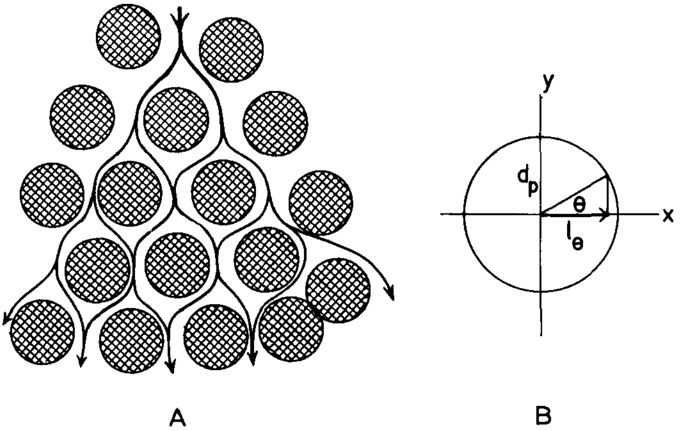

FIG. 3. The mechanism of radial dispersion: (A) the stream-splitting mechanism; (B) illustration of typical radial step

$$l_\theta = \tfrac{1}{2} d_p \cos\theta$$

Stream splitting occurs because streams of solution meet particles lower down the bed head on and are forced to divide and go around them. They then link up with other fragmented streams. Such fragmented streams suffer the same fate when they meet other particles, and so on. Each stream which impinges directly on the top of a sphere will be divided equally around the sphere, and thus a typical molecule of solute will suffer a step along a radial axis of $l_\theta = \frac{1}{2}d_p \cos \theta$ [Fig. 3(B)]. The average step length is readily shown to be d_p/π. The radial variance according to the random-walk treatment (*1*) is given as

$$\sigma_r^2 = (\text{number of steps}) \times (\text{step length})^2$$

Suppose that one lateral step is taken for every $\omega_3 d_p$ moved axially. The number of steps is $n = L/\omega_3 d_p$, and the radial plate height is

$$h_r = \sigma_r^2/Ld_p = 1/(\omega_3 \pi^2) \approx 0.1/\omega_3 \tag{16}$$

It is reasonable to suppose that ω_3 lies between 0.5 and 1.0 and therefore that h_r lies between 0.1 and 0.2, as found experimentally when molecular diffusion and turbulence are unimportant.

LONGITUDINAL DISPERSION

The mechanism of longitudinal dispersion can be considered to be simple only when molecular diffusion or turbulence dominate the process. Under the former condition $h = 2\gamma/\nu$; under turbulent conditions the column is most simply regarded as a series of mixing chambers (*16*) connected by narrow channels; a molecule thus moves jerkwise from one mixing chamber to the next. This model is very similar to that originally postulated by Martin and Synge (*12*) in the development of the theoretical plate concept. Each mixing chamber may be regarded as equivalent to a theoretical plate and the reduced plate height becomes equal to the average distance between mixing chambers measured in particle diameter units. If the mixing chambers are identified with the relatively wide voids in the packing, the reduced plate height in the turbulent region should be of the order of unity. Experiment (Figs. 1 and 2) shows that h is indeed roughly independent of reduced velocity at high Reynolds numbers and is about 2.

When neither molecular diffusion nor turbulence is dominant, the slowness of trans-column equilibration appears to be the major factor producing peak dispersion. Inserting the expression (15) for radial dispersion into the trans-column term of Eq. (13) yields

$$h = (1/2\lambda + (0.6 + 0.05\nu)/\omega\nu)^{-1}$$

$$= (1/2\lambda' + 0.6/\omega\nu)^{-1} \qquad (17)$$

where $1/\lambda' = 1/\lambda + 0.1/\omega$.

Equation (17) is identical in form to the original single-term-coupled equation (12). Thus the incorporation of a realistic radial dispersion coefficient into the last term of Eq. (13), as suggested earlier, makes no difference to the predicted form of the dependence of h upon ν. The discrepancies between theory and experiment still remain as far as axial dispersion is concerned.

The previous experiments (*10*) on the effect of column-to-particle-diameter ratio were conducted with columns of fixed diameter, 0.30 cm, using particles ranging from 0.0048 to 0.097 cm in diameter. Different batches of particles were used for different values of ν, and it is not certain whether the trans-column contributions to h were genuinely due to the effect of the wall on packing regularity or whether they were due to differences in particle-size distribution and packing density. The fact that a batch of particularly uniform particles gave a column of unusually high efficiency suggested that particle-size distribution might be of great importance. In the present experiments we have, therefore, varied the column diameter while keeping the particle size constant at 0.047 cm, and we have studied the effects of particle-size range and method of packing.

Previous work with gases has emphasized the importance of column-to-particle-diameter ratio (*17*) but has generally left unsolved the question of whether the dependence of h upon ν can better be represented by the linear or coupled form of equation (*18,19*). The discussion on this topic has recently been reopened by Klinkenberg (*20*) and Giddings (*21*).

Although the theoretical foundation of the concept of coupling seems unassailable, the summed form (13) can be reduced to a linear form under special conditions, and the question of which form best represents the data is therefore not purely academic. Furthermore, turbulence must become important with gases at quite low reduced velocities and must add further to the difficulties of interpreting the data. The first requirement, therefore, is more precise and more extensive data on peak spreading in gaseous and liquid systems.

EXPERIMENTAL

Liquids

0.5 to 1 μl samples of 40% acetone in water were injected from a Hamilton microsyringe a few millimeters below the top of the packing and eluted with water. The columns were packed with glass beads (English Glass Co. Ltd.) by adding wet beads to columns already filled with deaerated water. Columns were from 0.48 to 1.5 cm in diameter and about 135-cm long. The concentration profiles of the emergent bands were determined by the membrane detector illustrated in Fig. 4. Liquid from the column passes through a narrow tube and over a thin (0.0019-cm thick) dialysis membrane mounted perpendicular to the tube and about 0.025 cm

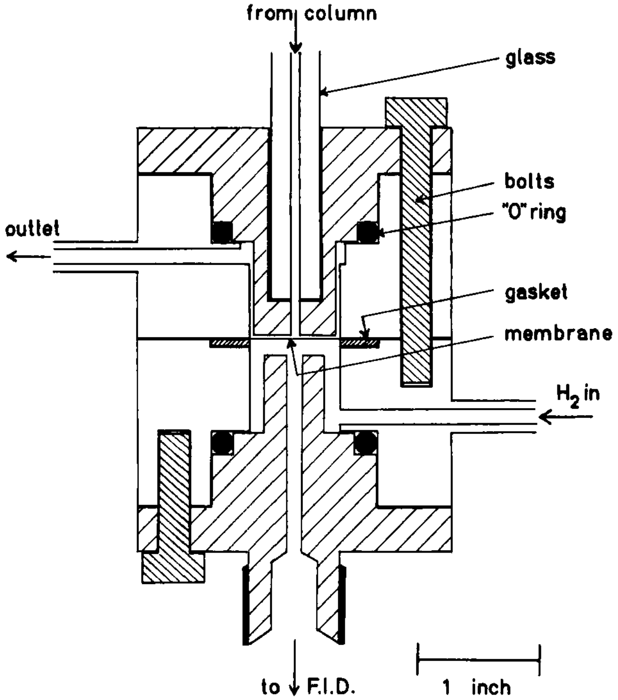

FIG. 4. Membrane detector. Body of brass of stainless steel.

TABLE 1
Bead Sizes

Code	Size range, ASTM	Sieve opening range, cm	Mean diameter by direct measurement, cm
A	25–30	0.071–0.059	0.0598
B	30–40	0.059–0.042	0.0469
C	40–50	0.042–0.030	0.0397

away from the end. Acetone and water from the emergent band diffuse through the membrane with a time constant of about 1 sec, and pass into a stream of hydrogen which leads to a hydrogen flame ionization detector as conventionally used in gas chromatography. The signal is amplified in the usual way and recorded on a Kent 1-sec potentiometric recorder. The detector proved stable and could detect 1 ppm of acetone in the solution above the membrane. Since the response is proportional to the partial vapor pressure of the organic material in the water, the membrane is only sensitive to rather volatile substances, or substances showing strong positive deviations from Raoult's law.

TABLE 2
Synthetic Mixtures of Beads

Code	Number composition			Mean diameter, cm
	A	B	C	
I	1	5	0	0.0489
II	1	2	1	0.0483
III	1	1	1	0.0488
Over-all mean				0.0487

The column was thermostated at 25°C. Peak shapes as determined by the detector were symmetrical within the limits of measurement at heights above 20% of the peak maximum; below this level there was slight tailing on the trailing edge of the bands.

The diffusion coefficient of acetone in water, required for the evaluation of the reduced velocity, was determined experimentally by Knox and McLaren's method (3) as $(1.3 \pm 0.1) \times 10^{-5}$ cm^2/sec, and calculated by the Wilke-Chang equation (22) as 1.15×10^{-5} cm^2/sec. The latter value was used in the calculation of ν.

Three batches of beads were used in the experiments: details are given in Table 1. For the experiments on the effect of particle-size range synthetic mixtures were made from these three batches on a number basis as detailed in Table 2. Mean bead diameters were determined by aligning a given number of beads in a right-angled groove and measuring the length of the row.

Gases

The system for determining the spread of peaks in gaseous eluants has already been described (2,3). In this work, straight stainless-steel columns about 350 cm in length at ambient temperature were used. The carrier gas was nitrogen and the sample gas ethylene. The diffusion coefficient of ethylene in nitrogen was taken as 0.165 cm^2/sec (3).

RESULTS

Liquids

To determine if particle-size distribution had a significant influence on plate height the three mixtures of beads detailed in Table 2 were packed in water in 0.48-cm-diameter columns, with tapping endwise until no more settling occurred. Figure 5 shows

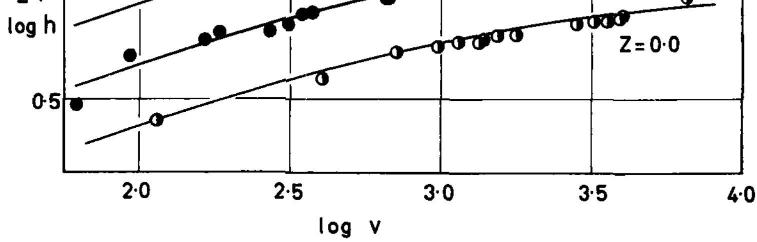

FIG. 5. Effect of particle-size distribution on h versus ν curves for liquid eluants. Lines are parallel and displaced exactly 0.2 and 0.4 $\log_{10}$ units. ◑, mixture I (Table 2); ●, mixture II; ○, mixture III.

that there is only slight decline in efficiency as the particle-size range is widened; the lines have been drawn parallel and displaced vertically exactly 0.2 and 0.4 log units, respectively. With the possible exception of extremely narrowly graded beads (see later) the size range is relatively unimportant.

The method of packing is apparently more important. As shown in the upper two curves of Fig. 6, a more efficient column is obtained when beads are packed into the column dry and the air subsequently dissolved out by passage of deaerated water than when wet beads are packed into a column already filled with water.

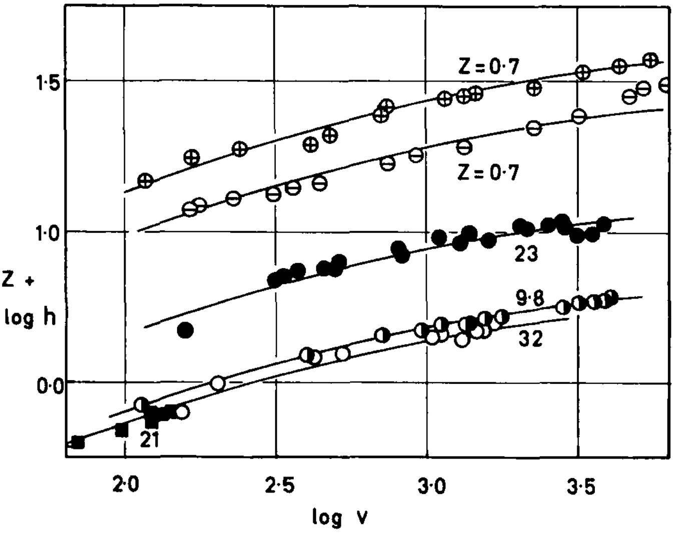

FIG. 6. Effect of packing method and column-to-particle-diameter ratio. ⊕, packed with water present; ⊖, packed dry. ●, ◑, ○, this work; ■, Gordon et al. (*23*); values of ρ marked on individual lines.

The effect of column-to-particle-diameter ratio was examined with columns 0.48, 1.08, and 1.50 cm in diameter packed with beads of batch B (mean diameter, 0.0469 cm). The data are shown in the lower three curves of Fig. 6 and compared with some of those obtained by Gordon et al. (*23*). They examined the dispersion of butanol samples in *n*-heptane using 0.925-mm-diameter columns packed with 0.045 ± 0.001-cm and 0.0195 ± 0.0005-cm-diameter beads, the ranges being the standard deviations of the bead diameters. Their original values of *H* and *u* have been converted to reduced values, using 3.75 × 10^{-5} cm^2/sec for the diffusion coefficient of *n*-butanol in heptane calculated from the Wilke-Chang equation (22).

The data from the present work and those of Gordon et al. lie on parallel curves. Our 1.08-cm-diameter column proved to be much less efficient than the other two columns and also less efficient than the 0.925-cm-diameter column of Gordon et al. This re-emphasises the importance of column to particle diameter while suggesting that enhanced performance can be obtained by using particularly well graded beads. It appears then that the regularity of packing is strongly influenced by the column-to-particle-diameter ratio.

The effect of the column-to-particle-diameter ratio on h can conveniently be summarized by plotting log h against log ρ for $\nu = 300$. Figure 7 compares the data obtained in this work with that obtained elsewhere. The points obtained from the data of Gordon et al., who used very closely graded beads, are consistently below ours. Thus while we found that particle-size distribution had little effect on performance when the particle-size range was widened, this present comparison suggests that with really uniform particles considerable improvements may be expected.

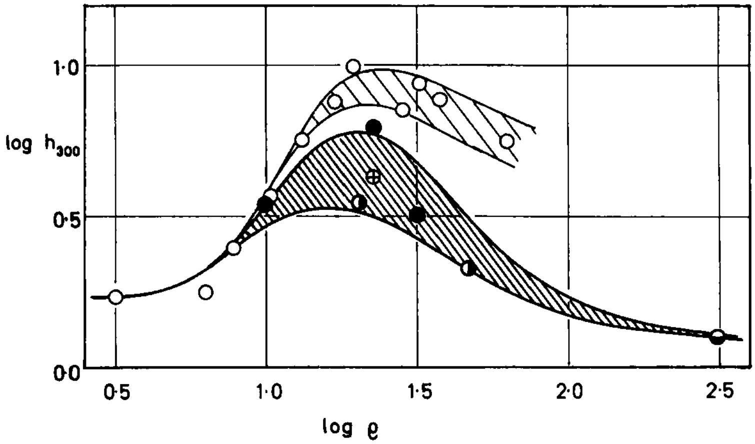

FIG. 7. Effect of ρ on h for liquid eluants at $\nu = 300$. ○, previous work (*10*); ⊕, previous work with narrowly graded beads (*10*); ●, this work; ◑, Gordon et al. (23); ◒, Brigham et al. (5).

The point for $\rho = 320$ was obtained by Brigham et al. (5) using a 3.2-cm-diameter column containing 0.0100-cm-diameter beads and the breakthrough method for determining *h*. They report that with a 14.0-cm-diameter column there was little difference in plate height, although with a 1.30-cm-diameter column *h* was significantly larger at any given velocity.

Comparison with our previous data (*10*) suggests that at least part of the rise in h_{300} with ρ then observed was due to changes in the regularity of packing as the particle size decreased rather than to true wall effects, although the agreement at lower values of ρ is good. There is general agreement that particularly inefficient columns are obtained with ρ between 10 and 30, but there still remains a considerable uncertainty as to the precise importance of particle-size range. More work is clearly required on methods of packing to obtain a method which is reproducible for different particle sizes and gives columns of maximum efficiency.

The difficulty of packing columns reproducibly for values of ρ in the region of 30 shows that wall effects are particularly important in this region. This conclusion is supported by Gratton and Fraser (*24*), who studied the two-dimensional packing of spheres in areas of different shapes. They showed that circular walls prevented regular packing and produced packing defects well away from the walls. A better column cross section would almost certainly be hexagonal, and it would be interesting to investigate the efficiency of such columns.

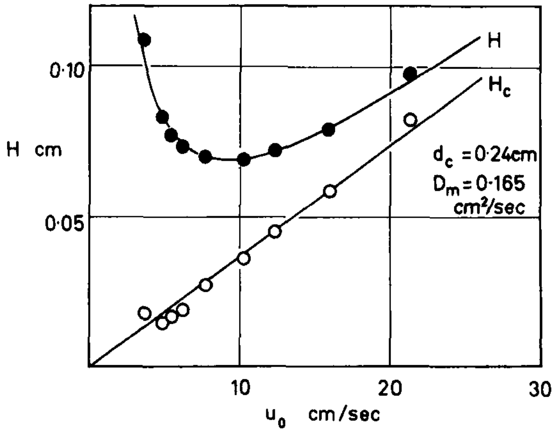

FIG. 8. Variation of H (●) and H_c (○) with u_0 for an open tube for nitrogen + ethylene. Lines calculated from Eq. (18).

Gases

Since γ for spheres lies between 0.6 and 0.7 (3) and is 1.00 for open tubes, the mobile-phase contribution to H, H_c, can be obtained simply by subtracting $2\gamma D_m/u$ from H. Figure 8 shows how this may be done for an open tube; the curves have been drawn according to Eq. (18), derived by Taylor (25).

$$H = 2D_m/u + d_c^2u/96D_m \qquad H_c = d_c^2u/96D_m \tag{18}$$

Figures 9 and 10 show data for two packed columns; the two curves

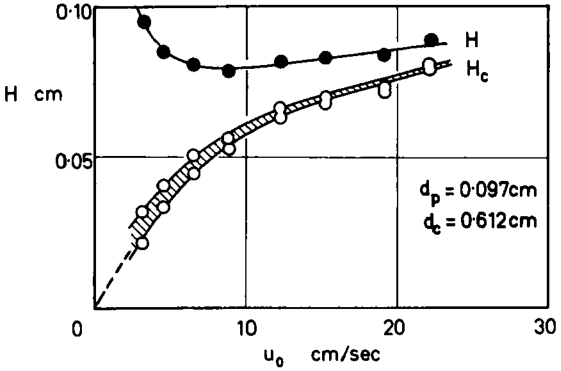

FIG. 9. Variation of H (●) and H_c (○) with u_0 for a packed column. Upper curve for H_c calculated for $\gamma = 0.60$, lower curve $\gamma = 0.70$.

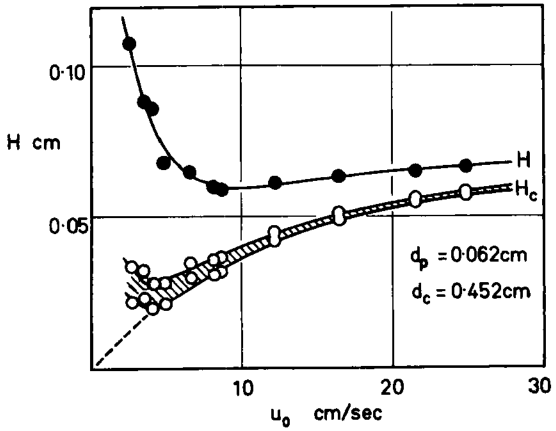

FIG. 10. Variation of H (●) and H_c (○) with u_0 for a packed column. Upper curve for H_c calculated for $\gamma = 0.60$, lower curve $\gamma = 0.70$.

for H_c in each figure are calculated with $\gamma = 0.6$ (upper) and $\gamma = 0.7$ (lower). Except at low velocities, when $2\gamma D_m/u$ is a large part of H, the precise value of γ is unimportant. For some columns there was a tendency at low u for the curve of H_c against u to turn upward, as shown in Fig. 10. The reason for this is not clear, but since the tendency was not universal and occurred only when the contribution of H_c to H was small, it is believed to be due to experimental error. For the majority of columns the plots of H_c against u could be extrapolated smoothly through the origin if $\gamma = 0.65$. This value is in satisfactory agreement with 0.61 ± 0.02, obtained by the static method (*3*).

Figures 11 and 12 show plots of h_c, the reduced-mobile-phase plate height, against ν for a variety of column-to-particle-diameter ratios using a 366-cm-long 0.612-cm-diameter stainless-steel column. For $\rho \geqslant 2.95$ the plots show concave curvature toward the velocity axis, but for lower values of ρ the curves are apparently linear and resemble those obtained with an open tube. By choosing $\gamma = 0.65$, all the curves can be extrapolated through the origin. For $\rho \geqslant 2.95$ it is thus clear that a linear form of equation for the dependence of h_c on ν is incorrect. The simple-coupled form of equation [Eq. (12)] gives a better, although by no means perfect, fit.

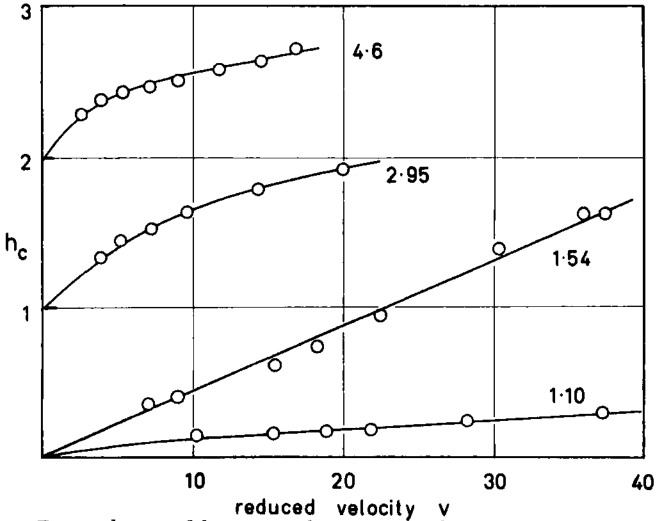

FIG. 11. Dependence of h_c upon ν for various values of ρ using nitrogen + ethylene. Values of ρ are given on curves which are displaced vertically for convenience. All lines drawn to pass through the origins.

Figures 11 and 12 also show that the profound effect of column-to-particle-diameter ratio is noticeable even at the lowest velocities at which h_c can be measured. This is more clearly shown in Fig. 13

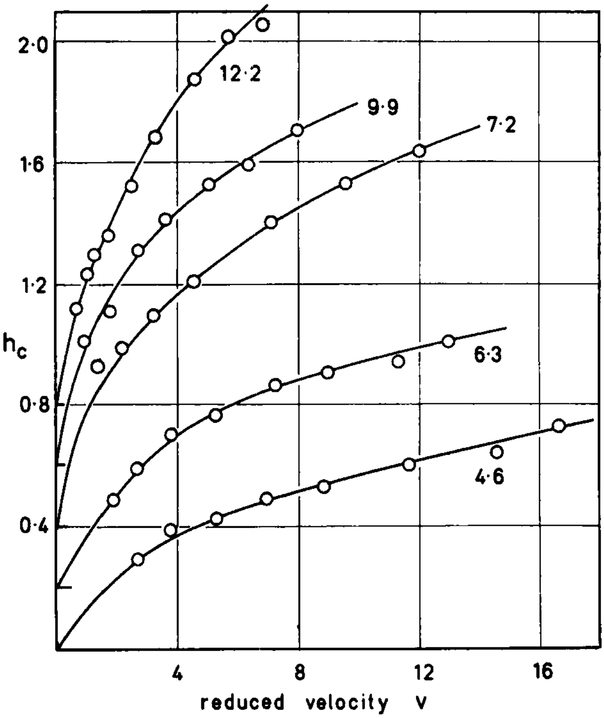

FIG. 12. Dependence of h_c upon ν for various values of ρ using nitrogen + ethylene. Values of ρ are given on curves which are displaced vertically for convenience. All lines drawn to pass through the origins.

by the logarithmic plot of $dh_c/d\nu$ at $\nu = 0$ against ρ. Data are included for the 0.612-cm and 0.452-cm-diameter columns. Although the scatter is wide, the general trend is clear, and similar to that observed in h_{300} with liquid eluants. There is some evidence that the decline in efficiency as ρ rises becomes less above $\rho = 10$, and that at higher values of ρ the efficiency may even increase again as it does with liquids. There is no evidence from the current experiments that turbulence is becoming important, but as Sternberg and Poulson (*17*) have pointed out, it is difficult to distinguish between the effects of coupling and turbulence.

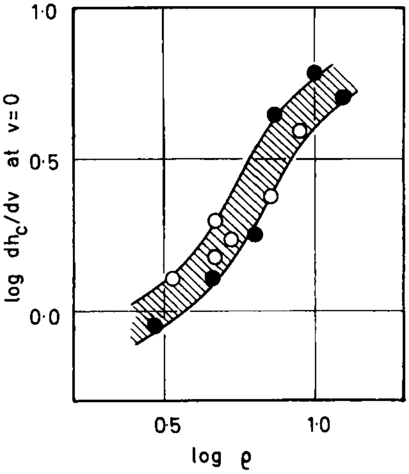

FIG. 13. The dependence of $dh_c/d\nu$ at $\nu = 0$ on ρ. ●, $d_c = 0.612$ cm; ○, $d_c = 0.452$ cm.

DISCUSSION

Liquids

Figure 1 summarizes the existing data on dispersion of unsorbed bands using liquid eluants in columns containing spheres. Both radial and axial dispersion have been investigated over wide ranges of reduced velocity. The low-velocity data of Brigham et al. (*5*) on axial dispersion confirms that molecular diffusion is dominant at $\nu \leqslant 1$. These data link up well with our own data, if those results with particularly unfavorable column-to-particle-diameter ratios are ignored. At much higher velocities, when turbulence sets in, our data (*10*) are in good agreement with those of Ebach and White (*8*), who covered a wide range of velocities bridging the region between laminar and fully turbulent conditions. Their data at the lower end of their velocity range appear to give rather high values of h, but the fit in the region of $\nu = 10^4$ is good. It is clear that for $\nu > 10$ the reduced plate height in well-packed columns, where wall effects are minimized, never exceeds about four. This has important implications for the development of high-speed liquid chromatography, for which the earlier theories, and in particular the linear plate-height theories, predicted that slow mass transfer in the mobile phase would be the most serious limiting factor. With nonporous particles there is great scope for the development of this form of chromatography using long narrow columns operated at high inlet pressures.

The experiments on radial dispersion by Blackwell (9) at low velocities and by Bernard and Wilhelm (4) at high velocities show that the radial plate height is almost independent of velocity once molecular diffusion has ceased to be important. Turbulence has only very slight beneficial effects. In this respect packed columns differ greatly from open tubes, where the sudden onset of turbulence causes a dramatic increase in the rate of radial mixing. Since there is probably no way of increasing the rate of radial mixing without at the same time increasing longitudinal dispersion, the future for more efficient liquid columns lies in the elimination of the adverse effects of the walls.

The key to the improvement in chromatographic performance is therefore the design of nonporous column structure with regular properties over the column cross section. These structures must be of regular geometry and of high strength. They must be highly permeable to flow but must make full use of the capacity of random

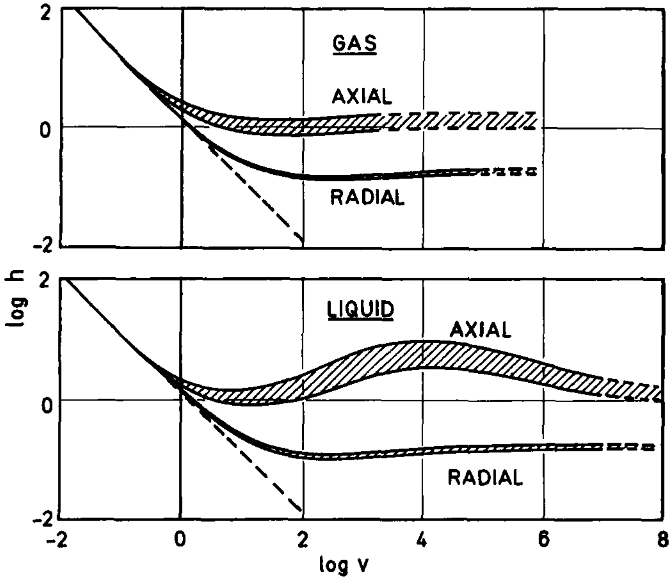

FIG. 14. Summary of the dependence of h upon ν for gaseous and liquid eluants.

packings to limit peak dispersion. They must also offer a uniform surface of sorbent which is readily accessible to the flowing fluid, be the flow laminar or turbulent.

The present status of measurements of radial and axial dispersion in liquid systems is shown in Fig. 14.

Gases

Figure 2 summarizes the existing data for dispersion in gases. Data from the present work, some of which are shown, agree well with those of McHenry and Wilhelm (7), who used very much larger scale equipment. The recent data of Sinclair and Potter (6), who employed mercury vapor as tracer, would be in excellent agreement with ours if their reduced velocities were a factor of 2 lower. The reason for the discrepancy is not clear, but could be that their assumed value of the diffusion coefficient of mercury (26) in air (0.11 cm^2/sec) is low by a factor of 2. The earlier experiments of Carberry and Bretton (27) confirm independently of gas chromatography that dispersion at low reduced velocities is caused by obstructed molecular diffusion.

Radial-dispersion measurements show that the radial plate height is constant at reduced velocities above about 30. The value is similar to that found with liquids in the turbulent region. The onset of turbulence at quite low reduced velocities with gases appears to eliminate the slight rise in the axial plate height with velocity observed with liquids for ν between 30 and 3000. Thus h is much more constant in gaseous systems using columns which minimize wall effects. Once more this has important implications for high-speed chromatography. It seems likely that very much faster analyses can be achieved than has previously been thought, provided the stationary-phase contribution to h can be sufficiently reduced.

For both liquid and gas chromatography the most important single improvement in column technology will be the development of a regular nonporous structure which minimizes trans-column variations in geometry and which can support a thin layer of sorbent material.

The present status of measurements of radial and axial plate height in gaseous columns packed with spheres is summarized in Fig. 14.

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Nomenclature

d_c, d_p	column and particle diameters, cm
D, D_r	axial and radial dispersion coefficients, cm²/sec
D_m	molecular diffusion coefficient, cm²/sec
h, h_r	axial and radial reduced plate heights $h = H/d_p$
H, H_r	axial and radial plate heights, cm
l_θ	typical radial step length
L	column length, cm
n	number of steps in random-walk treatment
r	radial distance, cm
R	fraction of solute in mobile phase
R_e	Reynolds number
t	time, sec
T	elution time, sec
u, u_0	average interstitial fluid velocity at any cross section in the column, and at column outlet, cm/sec
u_{band}	band velocity, cm/sec
z	axial distance from start of column, cm
γ	obstructive factor
η	viscosity, g/cm sec
λ, λ_i, λ'	geometric parameters
ν	reduced velocity
ρ	column-to-particle-diameter ratio d_c/d_p
ρ_m	density of mobile phase, g/cm³
σ_z, σ_L	standard deviations of Gaussian profiles at axial distances z and L, cm
σ_t	standard deviation as a time, sec
σ_r	standard deviation or radial concentration profile, cm
θ	angle in random-walk treatment
ω, ω_i, ω_1, ω_2	geometric parameters connected with radial mass transfer
ω_3	geometric parameter in random-walk treatment

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