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REVIEW

The Effect of the Radial Velocity Profile on Band-Broadening in Preparative Scale Gas–Liquid Chromatography: A Critical Analysis

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Summary

The approximations necessary to compare theory and performance in large-scale chromatographic columns are critically analyzed. The existence of carrier gas velocity gradients across the column cross section is the major cause of band-broadening and inefficiency in large-scale columns. Estimates of these radial velocity gradients based on existing particle size and velocity measurements are shown to be too inexact to test the presently accepted theory. A radial velocity profile, which has the major features of profiles measured in somewhat similar systems, is proposed. The need for accurate measurements of velocity profiles is emphasized.

INTRODUCTION

Giddings has discussed and quantified the principles of column performance for large-scale gas chromatography (*1,2*). In his work, the generalized nonequilibrium theory of plate height, applicable to analytical columns, was extended to large-scale columns. The extended equation for plate height H may be expressed as (*3*):

$$H = A + B_0/u_0 + C_g^0 u_0 + C_l \bar{u} \tag{1}$$

A, B_0, C_l, and $\bar{u}$ have the same definition as for analytical columns. The gas-phase mass transfer term C_g^0 is the sum of five individual gas-phase contributions. C_{gI}, C_{gII}, C_{gIII}, and C_{gIV} are contributions from pore diffusion, interaction between unequal flow channels, the Golay effect, and solvent maldistribution. The major reason for peak spreading and low efficiencies in large columns is the existence of velocity profiles across the column cross section. Giddings developed the $C_{g\mathrm{V}}$ term to account for these radial variations of carrier gas velocity. Assuming that the axial velocity is a quadratic function of the radius,* and that the porosity (or fraction of volume occupied by the gas phase) is constant across the column cross section, the contribution to plate height (H_V) due to radial velocity variations in large columns was expressed as:

$$H_V = \frac{G_2^2 \bar{v} r_0^2}{96 \gamma D_g} \tag{2}$$

where G_2 = dimensionless constant from the quadratic velocity equation
$\bar{v}$ = average superficial carrier gas velocity
r_0 = tube radius
γD_g = effective gaseous diffusion coefficient

Since

$$H_V = C_{g\mathrm{V}} u_0$$

where u_0 = the interstitual gas velocity in the axial direction. Then $C_{g\mathrm{V}}$ can be expressed as:

$$C_{g\mathrm{V}} = \frac{p G_2^2 r_0^2}{96 \gamma D_g} \tag{3}$$

where p = porosity of the packed column.

Hargrove and Sawyer experimentally studied the performance of a typical analytical and a preparative column (*3*). For the preparative column, they compared experimental values of C_g^0, the total gas-phase mass transfer term, with C_g^0 calculated from theoretical expressions developed by Giddings. Since $C_{g\mathrm{V}}$ was the dominant contribution to C_g^0, Hargrove and Sawyer in effect tested Eq. (3). Their work is probably the most systematic effort yet to compare the theory for large-scale columns against actual column performance. A detailed examination of their analysis reveals—as others have suggested—the critical need for velocity distribution measurements.

Three topics are discussed in this paper. First, some difficulties in the analysis of large-scale columns are examined. The aim here is to point out what information would be necessary to minimize the approximations presently inherent in this type of study. Second, experimental measurements of velocity profiles in packed columns are re-

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* Giddings (*2*) also developed equations based on a more general velocity expression.

viewed. The aim here is to present a radial velocity profile that is more realistic than either the quadratic or "general" profile of Giddings. Third, an equation is suggested for the velocity profile of the preceding section.

ANALYSIS OF LARGE-COLUMN PERFORMANCE

Hargrove and Sawyer (*3*) very carefully measured the performance of an analytical and a 25-mm i.d. preparative column for similar systems. The liquid-phase mass transfer term C_l was the same for both columns. The predominant difference in the two columns was the gas-phase mass transfer term C_g^0. Nearly all of this difference was due to the C_{gV} contribution. As expected, C_{gV} was the major gas-phase term for the preparative column and was negligible for the analytical column. Qualitatively these results are very encouraging.

Calculated and experimental gas-phase mass transfer terms are presented in Table 1.*

TABLE 1

Calculated and Experimental Gas-Phase Mass Transfer Terms for 3-Pentanone

	Calculated × 10^3 (sec)		Experimental × 10^3 (sec)
	C_{gV}, Eq. (3)	$C_g^{0\,a}$	C_g^0
Analytical	0.06	0.76	0.5
Preparative	4.1	4.8	5.9

[a] Equations (2) and (3) of Ref. *3*.

Since C_{gV} is the dominant term of C_g^0 for the large column, Eq. (3) could be tested against the experimental results. Unfortunately, several approximations were necessary before C_{gV} was able to be calculated. The authors concluded that (*3*): "the agreement between the calculated and experimental values for C_g^0 is surprisingly good and provides strong support for the general validity of Equation 3." They further concluded that the major band broadening factor for the large column was the radial distribution of carrier gas velocity and that Eq. (3) accounted for this effect reasonably well.

More perspective can be added to the above work by a closer look

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* Taken from Ref. *3*. A complete description of the experimental procedure is given there.

at the approximations necessary in using Eq. (3). The nature of these approximations suggest future experimentation directed at improving our ability to test the theoretical work. Two closely related aspects of this problem will be discussed:

(a) The relationship between the radial velocity distribution of the carrier gas and average particle diameter.

(b) The estimation of particle size variations across the column cross section.

For a quadratic radial velocity profile, v is given by (*2*):

$$v = \bar{v}\left[G_0 + G_2\left(\frac{r}{r_0}\right)^2\right] \tag{4}$$

where G_0 and G_2* = dimensionless constants
r_0 = the column radius
r = the variable distance from the column center
$\bar{v}$ = the average superficial carrier gas velocity
v = the superficial carrier gas velocity at a distance r from the column center

G_2 can be expressed as:

$$G_2 = \frac{2(v_w - v_c)}{v_w + v_c} = \frac{2\left(\frac{v_w}{v_c} - 1\right)}{\left(\frac{v_w}{v_c} + 1\right)} \tag{5}$$

where v_w = velocity at the wall
v_c = velocity at the column center

Approximations must now be made. Hargrove and Sawyer assumed that v is proportional to the square of the particle diameter (d_p). They further assumed that their particle size distribution was similar to that of Giddings and Fuller (*4*). In the absence of actual velocity data, this seemingly is not a bad estimation. Pypker (*5*) showed that differently sized particles do not form a homogeneous mixture in a packed column. Giddings and Fuller (*4*) accurately measured the radial distribution of particle sizes in columns packed with 80/100 mesh chromosorb W and 120/170 mesh glass beads. The particle size variations were correlated with radial velocity variations measured by Huyten. Nevertheless, they concluded that the square of the ratio of average particle

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* This is the same G_2 that appears in Eq. (3).

diameter near the wall to the average particle diameter at the column center $(\bar{d}_{pw}/\bar{d}_{pc})^2$ *roughly* correlated with the wall to center velocity ratios of Huyten (v_w/v_c). This result expressed in equation form is:

$$\frac{v_w}{v_c} = \left(\frac{\bar{d}_{pw}}{\bar{d}_{pc}}\right)^2 \tag{6}$$

Huyten measured velocities in four concentric areas of his 3-in. i.d. column. The outer annulus comprised 30% of the total cross-sectional area of the column. Thus, Huyten's "wall velocity" is not a point velocity, but an average velocity integrated over the outer 30% of the column. Effects due to high voidage areas near the wall or skin friction at the wall contributed to the velocity measured in the outer annulus. These, and possibly other local effects, cannot be determined individually without measurement of point velocities. Calculations based on our present knowledge of velocity profiles are necessarily very approximate.

Hargrove and Sawyer compared their systems with that of Giddings and Fuller, assumed that $(\bar{d}_{pw}/\bar{d}_{pc})$ was 1.12, and calculated v_w/v_c, G_2, and C_{gV} using the above equations.

Consider the accuracy of the particle size distributions of Giddings and Fuller. Although their individual measurements were very accurate,* a substantial variation in particle size was present at any radial position. The standard deviation for the average particle diameter at a given radius was about 20% of the diameter at that location. For a somewhat dissimilar system—such as that of Hargrove and Sawyer—the ratio $(\bar{d}_{pw}/\bar{d}_{pc})$ can only be roughly approximated. If Hargrove and Sawyer had assumed a diameter ratio of 1.07 instead of 1.12, the calculated value of C_{gV} would have been 1.5×10^{-3} sec. The experimental C_{gV} would then be 3½ times as great as the calculated C_{gV}. This comparison illustrates the high sensitivity of C_{gV} to the diameter ratio, which is an estimated quantity.

A better approach to the calculation of C_{gV} would be to use estimates of the velocity profile. This circumvents inaccuracies associated with using the diameter ratio. In addition to the sensitivity of C_{gV} to the diameter ratio, several related questions cannot be answered at the present time:

(a) What effect does the particle size distribution within a given region have on the carrier gas velocity?

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* Giddings and Fuller estimated the average error of a measurement at less than 0.005 mm or less than about 3% of a typical particle diameter.

(b) What is the effective diameter in a fluid dynamic sense of a highly irregular particle?

(c) How does the orientation of the irregular chromosorb particles affect the carrier gas flow?

Velocity measurements in large-scale chromatographic columns are unfortunately rather scarce. The most comprehensive study of radial velocity profiles is still the classic work of Huyten (*6*). The theoretical basis developed by Giddings (*2*) can accommodate any radial velocity profile. The only limitation is the tractability of the mathematics. Renewed efforts to quantify carrier gas flow patterns seem to be the best approach to strengthening our understanding of large column behavior.

GAS FLOW IN PACKED BEDS

The need for research aimed at measuring radial velocity distributions has been discussed in the previous section. This need does not imply that we have no knowledge of the subject, but rather that our present understanding should be refined and extended. Huyten's measurements show some of the phenomena that must be present in all large columns (*6*). The carrier gas velocity is a minimum at the center and increases uniformly until it approaches the wall. The exact behavior near the wall is not known, but the average velocity in the annular region closest to the wall was higher than the velocity at any other cross-sectional location. Studies of beds packed with substantially different sized particles reveal some phenomena that no doubt occur in large-scale chromatographic columns (*7–10*). A radial velocity profile, based on these packed-bed studies, will be proposed.

Smith, Fahien, and co-workers (*7–9*) measured radial velocity profiles in packed beds using hot wire anemometers. Because they were primarily interested in applications to packed bed catalytic reactors, the geometries of their systems differed significantly from that of say a 2-in. i.d. chromatographic column. The ratio of tube diameter to particle diameter (D_t/d_p) varied from 5 to 32. Packing diameters varied from ⅛ to ½ in. Both spherical and cylindrical packings were studied. In contrast, D_t/d_p for a 2–3-in. chromatographic column would be 200–400, particle diameters for 60/80 mesh material would average about 0.008 in., and packing particles would have irregular shapes. Clearly, only qualitative application of the above studies to large-scale chromatographic columns is warranted.

Velocity profiles measured by the above investigators had the following characteristics: a flat central section with velocity increasing with distance from the center, a velocity maximum about 1–1.5 particle diameters from the wall, and a rapid velocity decrease between the maximum and the wall. Figure 1 is a sketch of a profile with this behavior. The velocities of Fahien and Smith (*8*) were explained on the basis of void fraction alone up to 81% of the tube radius. As D_t/d_p increases, the radial velocity gradients become less pronounced. But even at their highest D_t/d_p of 32, the maximum velocity was about 20% higher than the velocity at the tube center (*7*). The fact that 19% of the column cross section lies between $.9r_0$ and r_0 emphasizes the importance of knowing the flow patterns near the wall.

The velocity maximum that occurs at 1–1.5 particle diameters from

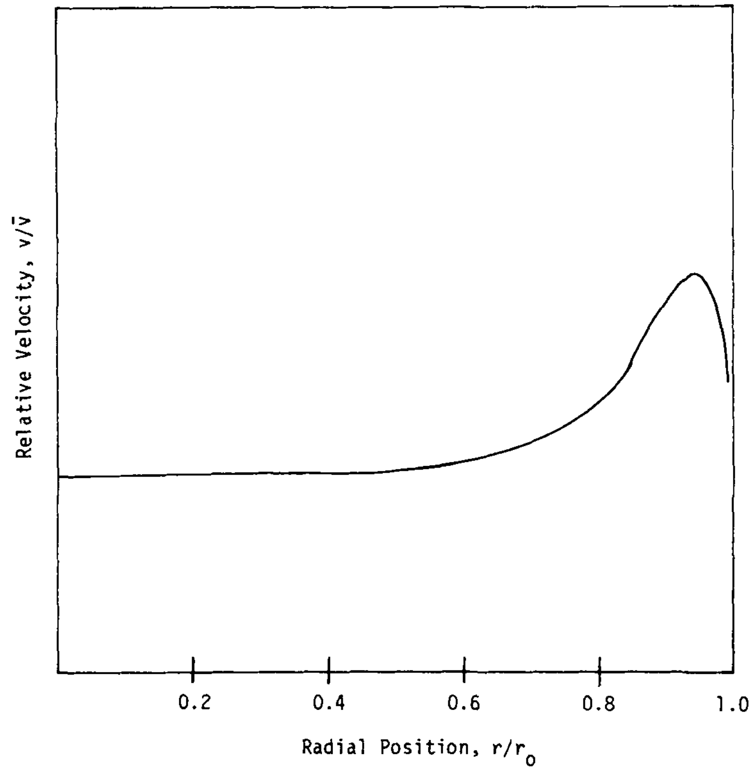

FIG. 1. General velocity profile for gas flowing through a packed bed.

the wall has usually been attributed to the high voidage there. Mickley et al. *(10)* have presented additional information concerning this point. A 1-ft square bed was packed with 1.5 in. diameter table tennis balls in a rhombohedral array. Half and quarter spheres were used at the walls to keep the voidage constant. A maximum velocity about 10% higher than the center velocity occurred 1.5 particle diameters from the wall. They concluded that "the wall effect is only partly due to the radial variation of voidage. Apparently the wall itself decreases the total resistance to flow in the wall region" *(10)*. These findings cast even more doubt on the advisability of correlating velocity with particle size in the region near the wall.

In view of the above studies it can be concluded that:

(a) The carrier gas velocity profile for a large-scale chromatographic column should have the same general form as Fig. 1.

(b) Knowledge of the fluid dynamics of flow through packed beds does not allow quantitative predictions of velocity profiles in large-scale chromatographic columns.

(c) Detailed velocity measurements, especially in the region near the wall, are highly desirable.

MATHEMATICAL DESCRIPTION OF VELOCITY PROFILE

The velocity profile of Fig. 1 can be described by an empirical expression such as that suggested by Giddings *(2)*:

$$v = \bar{v}\Sigma G_n(r/r_0)^n \tag{7}$$

Giddings has mathematically incorporated this velocity distribution into an equation for its contribution to plate height. Thus, column performance can be predicted from a detailed knowledge of the velocity profile.

Alternatively, the velocity profile of Fig. 1 can be approximated by the profile of Fig. 2 and a discontinuous mathematical expression of the following form:

$$v = \bar{v}\left[G_0' + G_2'\left(\frac{r}{r_0}\right)^2\right] \qquad 0 \leq r \leq r_{\max} \tag{8}$$

and

$$v = v_{\max}\left[1 - \frac{r - r_{\max}}{r_0 - r_{\max}}\right] \qquad r_{\max} \leq r \leq r_0 \tag{9}$$

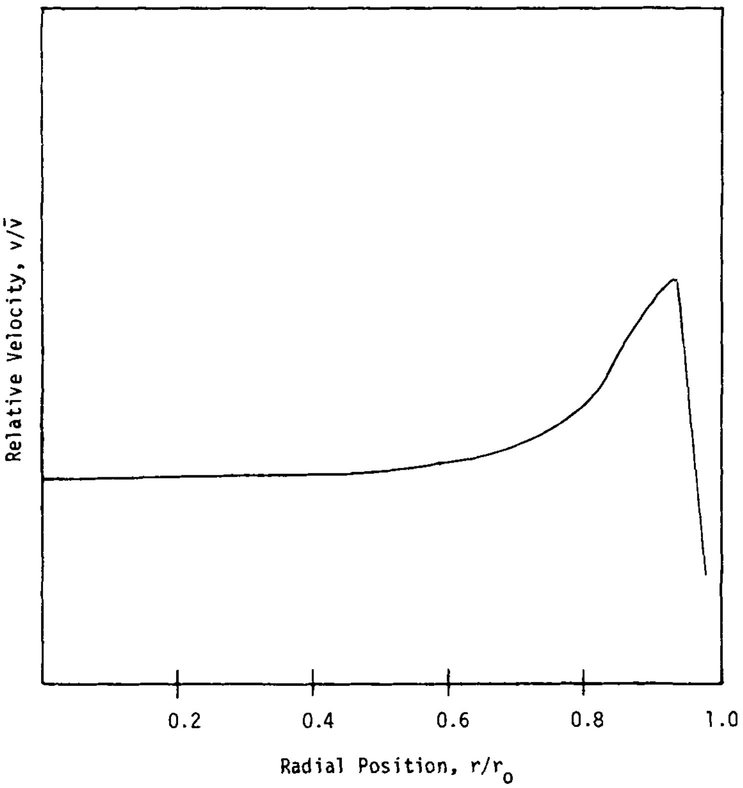

FIG. 2. Approximate velocity profile for carrier gas in a large-scale chromatographic column.

where v = the superficial carrier gas velocity at a distance r from the column center
$\bar{v}$ = the average superficial velocity integrated over the column cross section between $r = 0$ and r_{max}
G_0', G_2' = empirical dimensionless constants
r_0 = column radius
r = variable distance from the column center
r_{max} = radial position at which v is a maximum

Equations (8) and (9) imply that the velocity profile is quadratic between $r = 0$ and r_{max}, and that it is linear between r_{max} and the wall. The velocity at the wall is zero.

If Eqs. (8) and (9) can be adjusted to satisfactorily fit velocity data, then a plate height (or $C_g v$) expression can be derived. Presently, there is little incentive to do this since the required velocity data are unavailable.

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