THEORETICAL APPROXIMATIONS FOR THE LINEAR FLOW OF CARRIER GAS THROUGH A RECTANGULAR GC COLUMN

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ABSTRACT

The ability of a gas chromatographic (GC) column to separate two compounds is determined by its analytical resolution. The height equivalent to a theoretical plate (HETP) is given by

$$HETP = \frac{2D_g}{\bar{u}} + C_S \bar{u} + C_M \bar{u}$$  \hspace{1cm} (1)

where $D_g$ is the diffusion coefficient for the solute in the gas phase, and $C_S$ and $C_M$ are the resistances to mass transfer in the liquid and gas phases respectively. For rectangular columns, the resistance to mass transfer in the liquid phase $C_S$ is the same as for open tubular columns, namely [3]

$$C_S = \frac{2k}{3(1+k)^2} \frac{d_f^2}{D_S}$$  \hspace{1cm} (2)

where $d_f$ is the thickness (assumed to be uniform) of the liquid film applied to the inner walls of the column, $D_S$ is the diffusion coefficient for the solute in the film, and $k$ is the retention factor.

The purpose of this work is to derive a simpler expression for the average linear velocity so that the HETP can be more easily calculated.

INTRODUCTION

The ability of a gas chromatographic (GC) column to separate two compounds determines its analytical resolution. In 1958, Golay developed a plate theory to describe the resolution for open tubular columns [1]. Recently, that theory has been extended to rectangular gas chromatographic (GC) columns [2].

The height equivalent to a theoretical plate ($HETP$) is a function of the average linear velocity $\bar{u}$ for the carrier gas flowing through the column

$$\bar{u} = \frac{1}{8bd} \int_{-d}^{+d} \int_{-b}^{+b} \left[ \frac{(x^2 - b^2)(y^2 - d^2)}{(x^2 - b^2) + (y^2 - d^2)} \right] dy dx \frac{1}{\eta} \frac{dP}{dz}$$

$$= -\frac{1}{4bd} \int_{-d}^{+d} \int_{-b}^{+b} \frac{1}{K_{1}(x,y)} dy dx \frac{1}{\eta} \frac{dP}{dz}$$  \hspace{1cm} (3)

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Keywords: Gas chromatography, resolution, HETP, flow mechanics, microfluidics.
where \(2b\) and \(2d\) are the width and height of the column, \(\eta\) is the viscosity of the gas, \(dP/dz\) is the pressure gradient along the column, and \(K(x,y)\) is the column permeability. \(\delta_1\) and \(\delta_2\) are zero for continuum flow, and a function of the Knudsen number for slip flow.

Two approaches to simplifying equation 3 are described. The first is to write the relationship as (neglecting \(d_1\) and \(d_2\))

\[
\begin{align*}
\frac{d}{dz} & \left[ \left( \frac{1 - x^2}{b^2} + \frac{1 - y^2}{d^2} \right) dydx \frac{1}{\eta} dP dz \right] \\
& = -\left( \frac{b^2 d^2}{8bd} \right) \int_{b-d}^{b+d} \left( 1 - \frac{x^2}{b^2} - \frac{y^2}{d^2} \right) dydx \frac{1}{\eta} dP dz \tag{4}
\end{align*}
\]

and perform a direct integration [7]. When the first integration is performed over the wide (i.e., \(x\)-direction) dimension of the channel, a logarithmic term is obtained that can be approximated by

\[
\log \left[ \frac{b^2 + d^2 - y^2 + x \left( d^2 + b^2 - y^2 \right)}{b^2 + d^2 - x \left( d^2 + b^2 - y^2 \right)} \right] = \frac{2x}{b^2 + d^2} \sqrt{b^2 + d^2 - y^2} \tag{5}
\]

for \(b > d\). Making this substitution, the second integration yields

\[
\bar{u} = \frac{1}{3b^2 + d^2} \frac{dP}{\eta dz} \tag{6}
\]

The second approach is to perform a Taylor expansion on the integrand of equation 4 so that

\[
\begin{align*}
\frac{d}{dz} & \left[ \left( \frac{1 - x^2}{b^2} + \frac{1 - y^2}{d^2} \right) dydx \frac{1}{\eta} dP dz \right] \\
& = -\left( \frac{b^2 d^2}{8bd} \right) \int_{b-d}^{b+d} \left( 1 - \frac{x^2}{b^2} + \frac{y^2}{d^2} \right) dydx \frac{1}{\eta} dP dz \tag{7}
\end{align*}
\]

When equation 7 is integrated term-by-term, a series approximation for \(\bar{u}\) is obtained that increases in accuracy as higher order terms are included. This approximation is

\[
\begin{align*}
\bar{u} = - & \left[ A_0 \frac{b^2 d^2}{b^2 + d^2} + A_1 \frac{b^2 d^4}{(b^2 + d^2)^3} + \cdots \right] \frac{1}{\eta} \frac{dP}{dz} \\
& \cdots + A_n \frac{b^2 d^{2n}}{(b^2 + d^2)^{2n-1}} + \cdots \tag{8}
\end{align*}
\]

where the values of \(A_n\) are recorded in Table 1 for various levels of approximation.

**EXPERIMENTAL VELOCITY**

Terry [4], Kolesar [8] and Hudson, et al. [9] have measured the flow for various gases through microfabricated rectangular GC columns. The measured exit flows are shown in Figures 1 to 3. Also plotted in Figures 1 to 3 are curves calculated from equations 6 and 8. The calculations were performed assuming that the pressure gradient along the column is given by

\[
\frac{dP}{dz} = \frac{P_o^2 - P_i^2}{2lP_o} \tag{9}
\]

where \(P_i\) and \(P_o\) are the inlet and outlet pressures, and \(l\) is the length of the column. Equation 8 consistently underestimates the exit flow, and equation 6 consistently overestimates the exit flow. The percent errors associated with each are given in Table 1. Each reported error corresponds to an average of at least forty data points.

It is clear from Figures 1 to 3 that equation 6 provides a better fit to the data than equation 8. On the other hand, the fit with equation 8 improves as more terms are included in the expansion. The convergence is slow.

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**REFERENCES**

[5] This conclusion does not apply to liquid chromatography where the diffusion coefficient in the mobile phase is similar to that in the stationary phase.
Table 1: Constants for equation 8 (expressed as fractions).

<table>
<thead>
<tr>
<th>Approximation</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_4$</th>
<th>Error</th>
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<td>Equation 6</td>
<td>1/3</td>
<td></td>
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Note that the constant $A_1$ approaches one-third consistent with equation 6. The volumetric flow of carrier gas through the column $Q_c$ is related to $\pi$ through $Q_c = 4bdu$.

Figure 1: Fitting Terry’s and Kolesar’s 0.5 m long column data for helium at 23 °C [4,8].
Figure 2: Fitting Sandia National Laboratory’s 30 cm long column data for air at 23° C [9].

Figure 3: Fitting Sandia National Laboratory’s 100 cm long column data for air at 23° C [9].