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

Glenn E. Spangler
Technispan LLC, 1133C Greenwood Road, Pikesville, MD 21208

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

$$HETP = \frac{2D_g}{\overline{u}} + C_S\overline{u} + C_M\overline{u}$$

where D_g is the diffusion coefficient in the gas phase, and C_S and C_M are the resistances to mass transfer in the gas and liquid phases, respectively. For a rectangular column, the average linear velocity $\overline{u}$ is given by

$$\overline{u} = \frac{1}{8bd}\int_{-b}^{+b}\int_{-d}^{+d}\left[\frac{\left(x^2-b^2\right)\left(y^2-d^2\right)}{\left(x^2-b^2\right)+\left(y^2-d^2\right)}\right]dxdy\,\frac{1}{h}\frac{dP}{dz}$$

where $2b$ and $2d$ are the width and height of the column, h is the viscosity of the carrier gas, and dP/dz is the pressure gradient along the column. Whenever $b>>d$, $\overline{u}$ can be approximated by

$$\overline{u} = -\left[A_1\frac{b^2d^2}{b^2+d^2} + A_2\frac{b^4d^4}{\left(b^2+d^2\right)^3} + \cdots + A_n\frac{b^{2n}d^{2n}}{\left(b^2+d^2\right)^{2n-1}} + \cdots\right]\frac{1}{h}\frac{dP}{dz}$$

where A_n are constants whose values depend on the type and level of approximation.

Keywords: Gas chromatography, resolution, HETP, flow mechanics, microfluidics.

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 $\overline{u}$ for the carrier gas flowing through the column

$$HETP = \frac{2D_g}{\overline{u}} + C_S\overline{u} + C_M\overline{u} \quad (1)$$

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]

$$C_S = \frac{2k}{3\left(1+k\right)^2}\frac{d_f^{\,2}}{D_S} \quad (2)$$

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 resistance to mass transfer in the gas phase C_M, on the other hand, is complexly related to the permeability of the column that is in turn dependent on column geometry. Additional work is needed before a simple expression can be written down for C_M.

Because the diffusion coefficient characterizing mass transfer in the gas phase is orders of magnitude greater than the diffusion coefficient characterizing mass transfer in the liquid phase, C_S is much greater than C_M. One attempt to fit data collected by Terry on a microfabricated rectangular column yielded a value of 13 milliseconds for C_S and a value of 12 microseconds for C_M [2,4]. Consequently, C_M is not needed to make a reasonable estimate of the *HETP* [5].

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.

THEORETICAL VELOCITY

The velocity profile for the linear flow of carrier gas through a rectangular column is given by [2,6]

$$\overline{u} = \frac{1}{8bd}\int_{-b}^{+b}\int_{-d}^{+d}\left[\frac{\left(x^2-b^2\right)\left(y^2-d^2\right)-d_1\left(l^2,x,y\right)}{\left(x^2-b^2\right)+\left(y^2-d^2\right)-d_2\left(l,x,y\right)}\right]dydx\,\frac{1}{h}\frac{dP}{dz} \quad (3)$$

$$= -\frac{1}{4bd}\int_{-b}^{+b}\int_{-d}^{+d}K_v(x,y)dydx\,\frac{1}{h}\frac{dP}{dz}$$

where $2b$ and $2d$ are the width and height of the column, h is the viscosity of the gas, dP/dz is the pressure gradient along the column, and $K_v(x,y)$ is the column permeability. d_1 and d_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)

$$\bar{u} = -\frac{1}{8bd}\frac{b^2d^2}{b^2+d^2}\int_{-b}^{+b}\int_{-d}^{+d}\left[\frac{\left(1-\frac{x^2}{b^2}\right)\left(1-\frac{y^2}{d^2}\right)}{1-\frac{x^2+y^2}{b^2+d^2}}\right]dydx\frac{1}{h}\frac{dP}{dz} \qquad (4)$$

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

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

for $b >> d$. Making this substitution, the second integration yields

$$\bar{u} = -\frac{1}{3}\frac{b^2d^2}{b^2+d^2}\frac{1}{h}\frac{dP}{dz} \qquad (6)$$

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

$$\bar{u} = -\frac{1}{8bd}\frac{b^2d^2}{b^2+d^2}\int_{-b}^{+b}\int_{-d}^{+d}\left(1-\frac{x^2}{b^2}\right)\left(1-\frac{y^2}{d^2}\right)\left(\begin{array}{c}1+\frac{x^2+y^2}{b^2+d^2}+\cdots \\ \left(\frac{x^2+y^2}{b^2+d^2}\right)^n+\cdots\end{array}\right)dydx\frac{1}{h}\frac{dP}{dz} \qquad (7)$$

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

$$\bar{u} = -\left[\begin{array}{l}A_1\frac{b^2d^2}{b^2+d^2}+A_2\frac{b^4d^4}{\left(b^2+d^2\right)^3}+ \\ \cdots+A_n\frac{b^{2n}d^{2n}}{\left(b^2+d^2\right)^{2n-1}}+\cdots\end{array}\right]\frac{1}{h}\frac{dP}{dz} \qquad (8)$$

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

$$\frac{dP}{dz} = \frac{P_o^2 - P_i^2}{2lP_o} \qquad (9)$$

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.

This research was sponsored by the Defense Sciences Office of the Defense Advanced Research Projects Agency (DARPA) issued by the U.S. Army Missile Command as Contract DAAH01-97-C-R129.

REFERENCES

[1] Golay, M.J.E. In *Gas Chromatography 1958*; Desty, D.H., Ed.; Academic Press: NY, 1958; pp. 36-55.

[2] Spangler, G.E. *Anal. Chem.* **1998**, *70*, 4805-4816.

[3] Ettre, L.S.; Hinshaw, J.V. *Basic Relationships in Gas Chromatography*, Advanstar Communications: Cleveland OH, 1993.

[4] Terry, S.C. Ph.D. Dissertation, Stanford University, 1975.

[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.

[6] Harley, J.C.; Huang, Y.; Bau, H.H.; Zemel, J.N. *J. Fluid Mech.* **1995,** *284*, 257-274.

[7] *CRC Standard Mathematical Tables and Formulae*, D. Zwillinger, Ed.; CRC Press: Boca Raton, FL, 1996, section 5.4.5, formulae 61 to 64.

[8] Kolesar, E.S., Jr., private communication, 1996.

[9] Hudson, M.L.; Kottenstette, R.; Matzke, C.M.; Frye-Mason, G.C.; Shollenberger, K.A.; Adkins, D.R. and Wong, C.C. Proceedings of ASME 1998, DSC-Vol. 66, pp. 207-214, 1998.

Table 1: Constants for equation 8 (expressed as fractions).

Approximation	**A_1**	**A_2**	**A_3**	**A_4**	**% Error**
Equation 6	1/3				+2.6
Equation 8, 1st	2/9				-32
Equation 8, 2nd	4/15				-18
Equation 8, 3rd	2/7	-32/1575			-12
Equation 8, 4th	8/27	-64/1575			-9.2
Equation 8, 5th	10/33	-1024/17325	256/40425		-7.3
Equation 8, 6th	4/13	-51136/675675	9728/525525		-6.1
Equation 8, 7th	14/45	-61216/675675	18688/525525	-8192/2837835	-5.3
Equation 8, 8th	16/51	-1195904/11486475	38912/687225	-16384/1461915	-4.6

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 $\bar{u}$ through $Q_c = 4bd\bar{u}$.

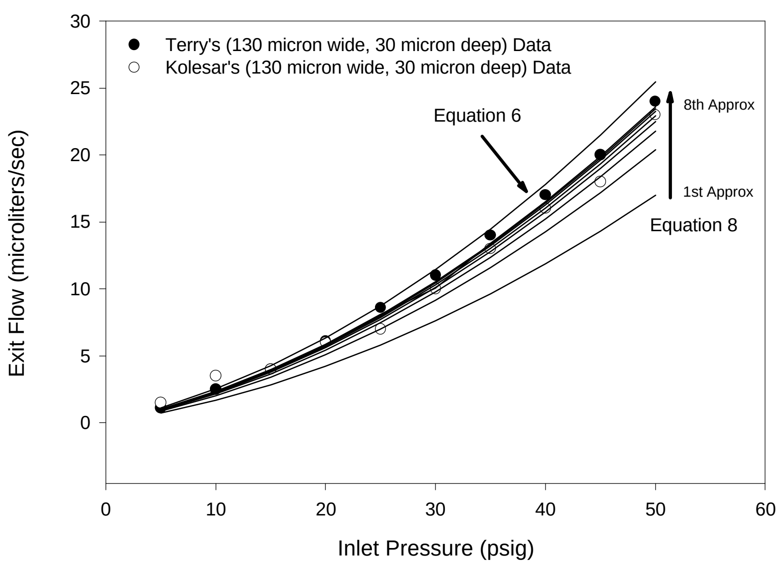

Figure 1: Fitting Terry's and Kolesar's 0.5 m long column data for helium at 23 ^{o}C [4,8].

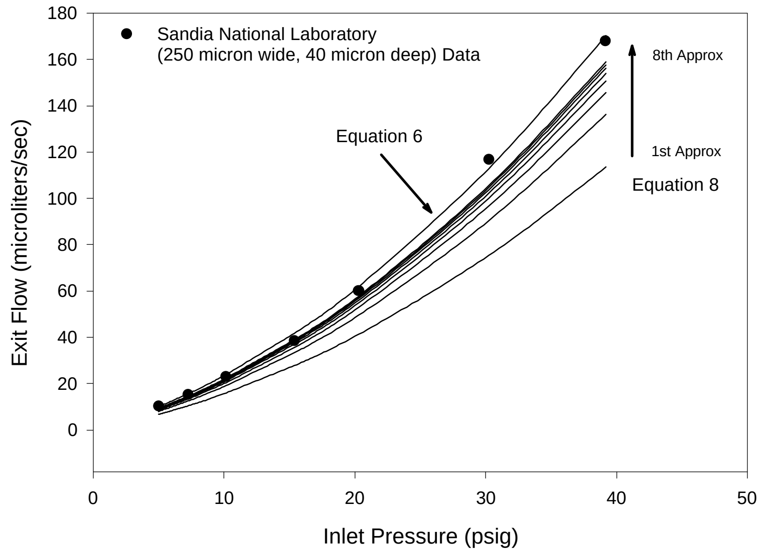

Figure 2: Fitting Sandia National Laboratory's 30 cm long column data for air at 23^o C [9].

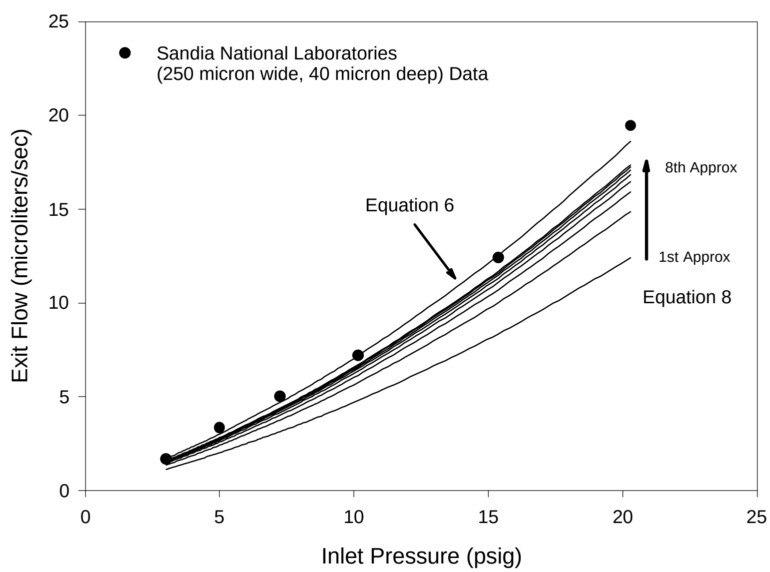

Figure 3: Fitting Sandia National Laboratory's 100 cm long column data for air at 23 ^{o}C [9].