

## THEORETICAL PLATE HEIGHT IN HELICAL CHROMATOGRAPHIC COLUMNS

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Long columns for use in gas chromatography are usually coiled into a helix in order to conserve space, and there is some interest as to the extent such coiling should reduce the efficiency of the column. An earlier paper<sup>1</sup> attempted to analyze the situation and reached the conclusion that efficiency loss, or increase in plate height, would become serious with large tightly-coiled columns. This conclusion is certainly correct, but several questionable steps have been noted in the mathematical treatment which greatly reduce the significance of the analytical results obtained there.

In a coiled column, streamlines along the inside of the coil are shorter than those along the outside. The length distribution may be written in terms of the length  $l_0$  along the centerline:

$$l = l_0 \left( \frac{R_0 + r \sin \theta}{R_0} \right) \quad (1)$$

Nomenclature is shown in Fig. 1. Since the pressure drop along all streamlines is the same for a given change in angle  $\phi$  (*i.e.* no flow in  $r$  or  $\theta$  directions exists) the axial carrier gas velocity may be written in terms of the center line velocity  $v_0$ :

$$v = v_0 \left( \frac{R_0}{R_0 + r \sin \theta} \right) \quad (2)$$

In ref. 1 this velocity gradient was properly written, but then cylindrical coordinates, applicable only to straight columns, were used in the subsequent mathematical

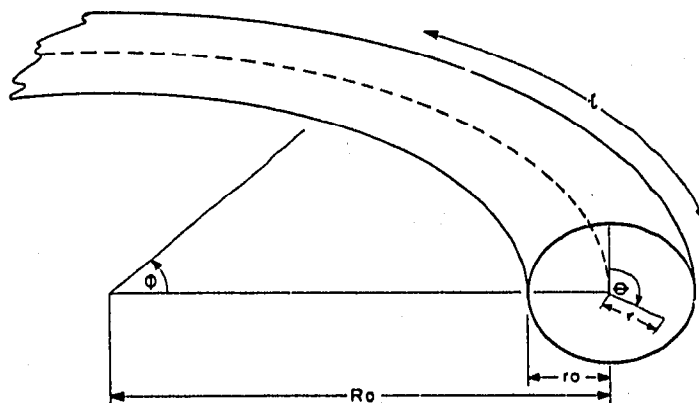


Fig. 1. Coordinate system.

treatment. This in effect said that a velocity gradient would exist but that all the streamlines were of equal length. A more realistic approach would be to use toroidal coordinates\*. In this case the rate of accumulation of solute would be written as

$$\frac{\partial c}{\partial t} = \frac{RD}{(r)(R_0 + r \sin \theta)} \left[ \frac{\partial}{\partial r} (r) (R_0 + r \sin \theta) \frac{\partial c}{\partial r} + \frac{\partial}{\partial \theta} \frac{(R_0 + r \sin \theta)}{r} \frac{\partial c}{\partial \theta} + \frac{r}{R_0 + r \sin \theta} \frac{\partial^2 c}{\partial \phi^2} \right] - \frac{v_0 R R_0}{(R_0 + r \sin \theta)^2} \frac{\partial c}{\partial \phi} \quad (3)$$

where  $c$  is overall concentration,  $t$  is time,  $R$  is fraction of component in mobile phase, and  $D$  is diffusivity (assumed constant here).

Assuming for the moment that the model actually used in ref. 1 (*i.e.* a straight column with the velocity distribution of a coiled column) is applicable to some physical system, two subsequent mathematical manipulations are questionable and lead to rather tenuous results. The first of these is the occasional elimination of the small term  $\varepsilon$ , defined by  $c = c^* (1 + \varepsilon)$ , where  $c^*$  is the concentration assuming lateral equilibrium. Although  $\varepsilon$  is small, so are the lateral diffusion effects which are sought, and any cancellation of small terms is more safely done in the final equation rather than in intermediate equations. The second is the use of incorrect averages in writing an overall material balance:

$$\frac{\partial c^*}{\partial t} = -v_0 R \frac{\partial c^*}{\partial z} + DR \frac{\partial^2 c^*}{\partial z^2} \quad (4)$$

The correct equation would be

$$\frac{\partial c^*}{\partial t} = -\frac{R}{\pi r_0^2} \iint v \frac{\partial c}{\partial z} r dr d\theta + \frac{DR}{\pi r_0^2} \iint \frac{\partial^2 c}{\partial z^2} r dr d\theta \quad (5)$$

Equation (4) may not be substituted for eqn. (5) with desired accuracy except in trivial cases.

By taking the two steps above, some rather untenable results were obtained. For instance the rate of accumulation  $s$  of solute due to lateral diffusion was said to be

$$s = (v - v_0) R \frac{\partial c^*}{\partial z} \quad (6)$$

where  $z$  is axial distance. This would mean that  $s$  is independent of lateral diffusivity, being the same for  $D = 0$  as for  $D = \infty$ . Actually eqn. (6) is valid only for the case where lateral diffusivity is infinite. In that case, however, it may be easily shown that coiling the column has no effect on plate height. Later the average material flux was said to be

$$q = c^* R v_0 - \frac{7 v_0^2 r_0^4 R}{96 R_0^2 D} \frac{\partial c^*}{\partial z} \quad (7)$$

\* Helicoidal coordinates would be strictly correct, but the transformations involved become very messy, and the additional precision is negligible when the pitch of the helix is much smaller than its radius as is the case in chromatographic columns.

(Note that the term for longitudinal diffusion has been omitted here, since only the increase of plate height due to coiling was of interest.) If the use of average concentrations had been correct, as was assumed in eqn. (4), then it would also be correct to write merely

$$q = c^* R v_0 \quad (8)$$

Needless to say, eqns. (7) and (8) cannot both be right, and the equivalent of (8) was used at one step in deriving (7).

A correct solution for the general case seems to be unattainable by analytic means. Certain limiting situations may be solved, however. Consider what happens when diffusivity is zero. The time needed for a bit of solute to travel a distance  $l$  along a streamline is

$$t = \frac{l}{vR} \quad (9)$$

Using eqns. (1) and (2) for  $l$  and  $v$  and letting  $t_0 = l_0/v_0R$

$$t = \left( \frac{R_0 + r \sin \theta}{R_0} \right)^2 t_0 \quad (10)$$

With the solute introduced as a Dirac function at the column inlet (*i.e.*,  $M$  moles of solute are injected instantaneously) the outlet concentration averaged over the column cross section is

$$c^* = \frac{M}{\pi F} \left[ 1 - \left( \frac{R_0}{r_0} \left( \frac{t}{t_0} \right)^{1/2} - \frac{R_0}{r_0} \right)^2 \right]^{1/2} \frac{R_0}{r_0 t_0^{1/2} t^{1/2}}$$

where  $F$  is the volumetric flow rate of carrier gas. It is this concentration that the detector would see. This is an ellipse for very small values of  $r_0/R_0$  and becomes skewed as  $r_0/R_0 > 0.1$ . A very small but finite lateral diffusivity will not alter this curve significantly. The concentration peak will break through at  $t = (1 - r_0/R_0)^2 t_0$  and will end at  $t = (1 + r_0/R_0)^2 t_0$ . Its width  $w$  will be  $4 (r_0/R_0) t_0$ . Since the number,  $N$ , of apparent transfer units is, according to KEULEMANS<sup>2</sup>:

$$N = \left( \frac{4 t_0}{w} \right)^2 \quad (11)$$

we may write for the case of the coiled column

$$N = \left( \frac{R_0}{r_0} \right)^2 \quad (12)$$

The number of theoretical plates in such a case is therefore independent of column length. A column with  $R_0/r_0 = 10$  would have 100 theoretical plates, clearly an undesirable situation.

Finite lateral diffusivity would tend to make the outlet peak sharper so that the very sad case of eqn. (12) would only be approximated in an ordinary packed column, although it would apply to a bundle of capillary tubes which is coiled, unless special precautions are taken to make all capillaries the same length. As lateral diffusivity approaches infinity the effect of coiling becomes very small.

Using the model of ref. 1 and the same approach as given above, the number of plates for the case of zero diffusivity would be

$$N = 4 \left( \frac{R_0}{r_0} \right)^2 \quad (13)$$

and the theoretical plate height would be

$$H = l_0/N = \frac{1}{4} l_0 (r_0/R_0)^2 \quad (14)$$

Compare this to the value obtained in ref. 1:

$$H = \frac{7 v_0 r_0^4}{48 R_0^2 D} \quad (15)$$

There is almost no agreement between eqns. (14) and (15).

Fig. 2 shows qualitatively the number of theoretical plates as a function of column length for various combinations of column shape and longitudinal and lateral diffusivity. The slope of curve 4 decreases as diffusivity increases. Curve 6 is tangent to 4 at length = 0 and becomes asymptotic to 3 as length increases. Curve 5 will lie between 4 and 6. Curve 2 will be between 1 and 3.

It should be kept in mind that the phenomena due to column coiling are not

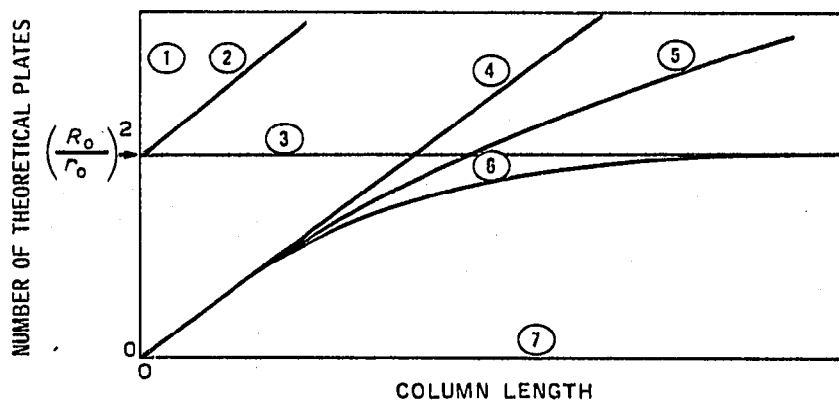


Fig. 2. Effect of diffusivity and configuration.

Curve	Longitudinal diffusivity	Lateral diffusivity	Column shape
1.	0	any	straight
	0	infinite	coiled
2.	0	finite	coiled
3.	0	0	coiled
4.	finite	any	straight
	finite	infinite	coiled
5.	finite	finite	coiled
6.	finite	0	coiled
7.	infinite	any	straight
	infinite	any	coiled

explained by analogy to a theoretical plate model. When a number of theoretical plates is assigned to a coiled column it merely refers to the amount of spreading of peaks which occurs and does not imply that a plate *mechanism* is actually applicable.

It is apparent that coiling of chromatographic column does have effects on the efficiency of the column. It seems likely, however, that an even greater loss may be caused by macroscopic disruption of the packing during coiling.

#### SUMMARY

The effect of column coiling upon theoretical plate height has been analyzed mathematically. A previous analysis<sup>1</sup> was found to employ untenable approximations. A new solution is presented for the case of zero diffusivity of solute which shows that the number of theoretical plates is:

$$N = \left( \frac{R_0}{r_0} \right)^2$$

irrespective of column length, where  $R_0$  is radius of the coil and  $r_0$  is radius of the column. Qualitative relationships between column length and configuration, lateral and longitudinal diffusivity, and number of theoretical plates are also shown.

#### REFERENCES

- <sup>1</sup> J. C. GIDDINGS, *J. Chromatog.*, 3 (1960) 520.
- <sup>2</sup> A. I. M. KEULEMANS, *Gas Chromatography*, Reinhold, New York, 1957.

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