
Limitations of the Assumption of Negligible Film Thickness in Capillary Chromatography

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Key Words

Capillary gas chromatography
Thick-film

Summary

The validity of Golay's assumption of a thin film in his theoretical development of capillary chromatography is evaluated by comparing it to Ari's theory which takes into account film curvature. The two solutions are compared using previously published capillary gas chromatography data. The results show that deviations between the theories are insignificant at conventional aspect ratios of 3 %, but can be important at 10 %.

Golay's theoretical treatment of capillary chromatography is considered to be the seminal work on the subject [1]. However, the limitations of his assumption that the stationary phase film is infinitely thin is more relevant today when many commercially available columns have films thicker than 3 μm . Aris [2] derived equations for retention and peak variance in capillary tubes without making any assumption as to the film thickness. In this note we compare the predictions of the Golay to the Aris solution to define those conditions under which the simpler Golay equations can be used without significant error. It is shown that although the two sets of equations diverge as the film thickens for all practical purposes the Golay solution can be used without substantial error for typical thick film capillary columns.

In 1958 Golay reported [1] the following equations for the retention time (t_R) and the peak variance (σ^2):

$$t_R = \frac{L}{u} (1 + 2K\Phi) = \frac{L}{u} (1 + k'_{\text{golay}}) \quad (1)$$

$$\sigma^2 = 2 \frac{G_g L}{u^3} (1 + k'_{\text{golay}}) + \frac{L}{u} \frac{r_i^2}{384D_g} (1 + 6k'_{\text{golay}} + 11k'^2_{\text{golay}} + \frac{2}{3} \frac{L}{u} \frac{w^2 k'_{\text{golay}}}{D_1}) \quad (2)$$

where the symbols are defined in the list given below. One year later Aris [2] solved the same problem as did Golay but he did not make any assumptions concerning the thickness of the film relative to the diameter of the capillary. The issue of film thickness became of some importance to us since we have been involved in the development of arrays of capillary fibers for preparative chromatography. In that work we use porous fibers which are quite thick relative to the radius of the lumen. Aris's results are summarized below:

$$t_R = \frac{L}{u} (1 + K(2\Phi + \Phi^2)) = \frac{L}{u} (1 + k'_{\text{aris}}) \quad (3)$$

$$\sigma^2 = 2 \frac{D_g L}{u^3} (1 + k'_{\text{aris}}) + \frac{L}{u} \frac{r_i^2}{384D_g} (1 + 6k'_{\text{aris}} + 11k'^2_{\text{aris}} + 2 \frac{L}{u} \frac{k'_{\text{aris}}}{D_1} f\left(\frac{r_0}{r_i}\right) (r_0^2 - r_i^2)) \quad (4)$$

where $f(p)$ is given by:

$$f(p) = \left(\frac{2p^4 \ln p^2}{p^2 - 1} - 3p^2 - 1 \right) / (8(p^2 - 1)) \quad (5)$$

The Φ^2 term in Eq. (3) represents the amount of stationary phase neglected in Golay's treatment. The function $f(p)$ accounts for the curved geometry of the stationary phase in the Aris treatment in contrast to the flat geometry assumed in the Golay thin-film approximation. As w approaches zero, or equivalently as r_i approaches r_0 , Eq. (3) and (4) become identical to Eq. (1) and (2) respectively.

In order to test whether the two approaches give significantly different results under practical conditions we compared the results for a well characterized system [3, 4]. Ettre studied the properties of a series of alkanes on an SE-30 column using helium as the carrier. A 50 meter column with inside radius of 160 μm was used in our calculations. Estimates of the diffusion coefficients and the solute partition coefficients for hexane, heptane and decane at 150 $^\circ\text{C}$ were taken from Ettre's paper. The film thickness was varied from 1 μm to 16 μm , a value much greater than will ever be encountered in practice. Based on the Golay equation and the above defined parameters the optimum linear velocity for hexane was found to be 52 cm/s for a 3 μm film. We rather arbitrarily decided to make the comparison at a velocity of 50 cm/s.

The difference in the residence time, peak variance and HETP based on the two approaches are displayed in Figures 1-3 as a function of the aspect ratio, that is, the ratio of the film thickness to the radius of the capillary. The results for heptane at an aspect ratio of 0.05 are shown in Figure 4.

As expected, the difference between the two sets of equations increases as the ratio of the film thickness to the capillary radius increases. When the aspect ratio is 0.10, a value that far exceeds anything that will be

found in practice, the Golay equation underestimates the retention time by 3 % and the variance by 9 %. Since both terms are underestimated the HETP is quite insensitive to the choice of equations. In the range of k' values explored here (0.6 to 4.1) the results are not very sensitive to the amount of retention, the data in Figure 4 show that the deviations approach an asymptotic limit vs. linear velocity.

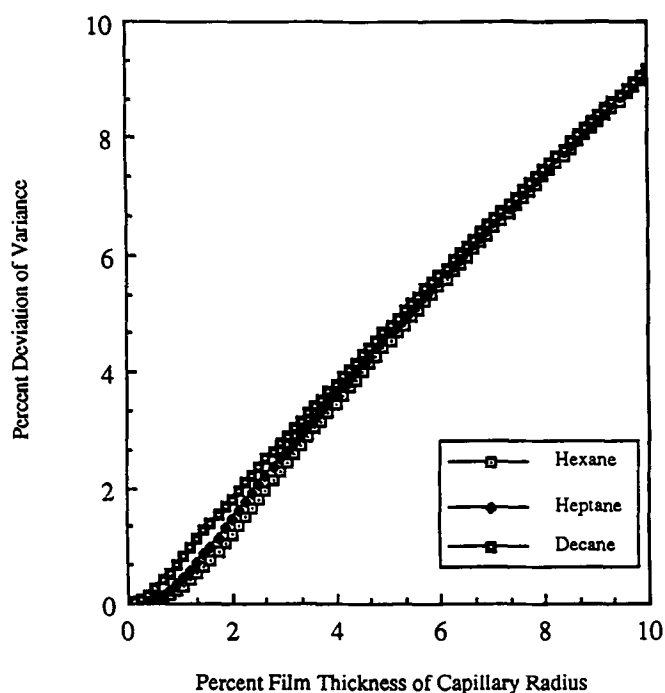


Figure 2
Effect of the Thin Film Assumption on Variance

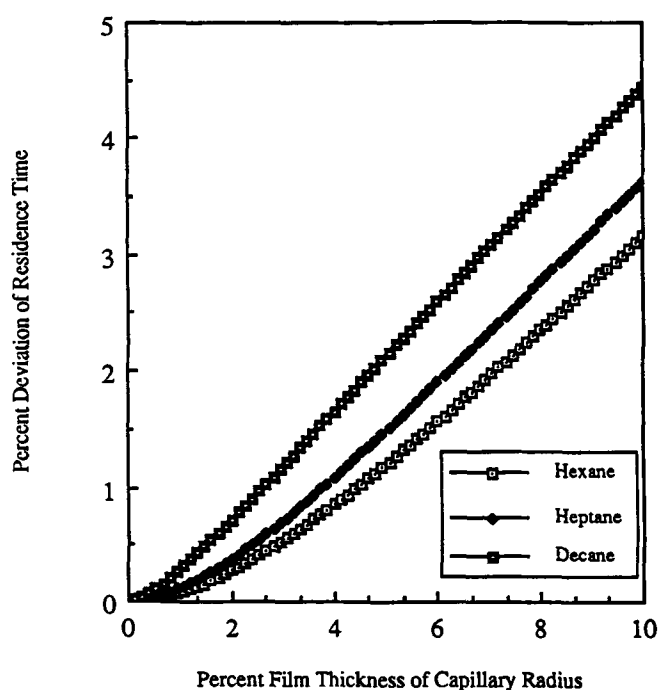


Figure 1
Effect of the Thin Film Assumption on Residence Time

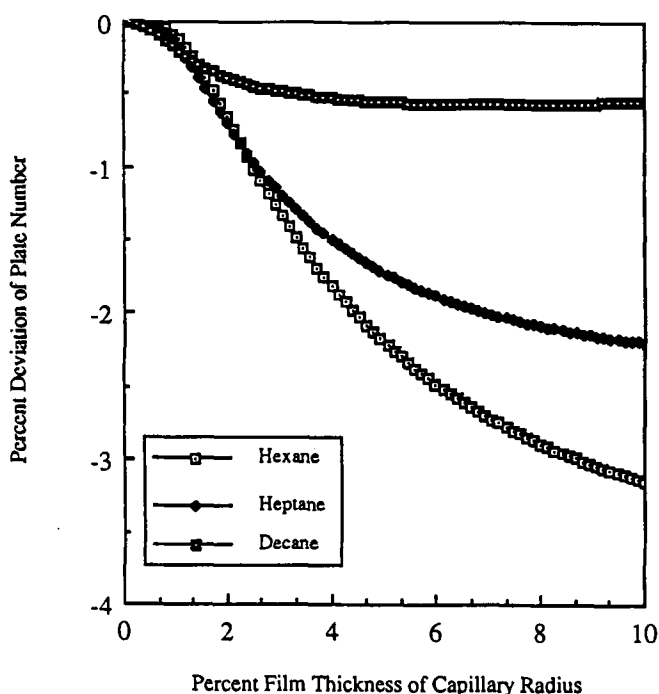


Figure 3
Effect of the Thin Film Assumption on Plate Number.

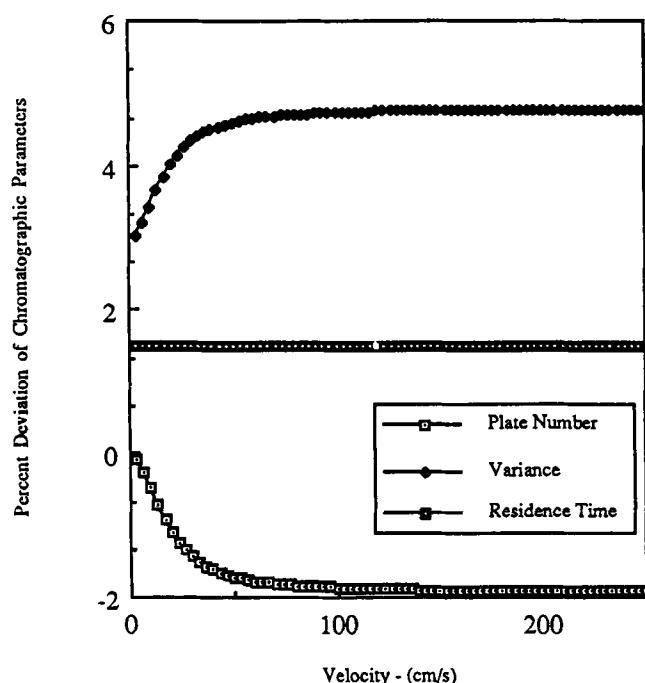


Figure 4
Sensitivity of the Thin Film Assumption to Velocity for the solute Heptane.

Under most practical circumstances the ratio of film thickness to tube radius does not exceed about 0.03. Consequently the Golay results do not differ from the Aris results by more than 1 %. Thus the difference would not be measureable or significant except in very careful theoretical studies, for example, those in which diffusion rates in the stationary phase are being measured by inverse gas chromatography.

Symbols

t_R = retention time
 σ^2 = peak variance
 L = column length
 u = average linear velocity
 w = stationary phase film thickness
 r_i = inner radius of capillary from axis to the gas liquid surface
 r_o = outer radius of the capillary from axis to solid wall
 K = partition coefficient
 k'_{golay} = capacity factor from Golay theory
 k'_{aris} = capacity factor from Aris theory
 D_g = gas phase diffusion coefficient
 D_l = liquid phase diffusion coefficient
 p = ratio of outer radius to inner radius of the capillary
 Φ = w/r_i , the phase ratio

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