The effect of column characteristics on the minimum analyte concentration and the minimum detectable amount in capillary gas chromatography. Part II: the stationary phase film thickness

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The Effect of Column Characteristics on the Minimum Analyte Concentration and the Minimum Detectable Amount in Capillary Gas Chromatography

Part II: The Stationary Phase Film Thickness

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Capillary gas chromatography
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Summary

For a typical narrow bore (50 μm) and wide bore (320 μm) capillary column the effects of increased stationary phase film thickness (d) on the minimum detectable amount, Q₀, as well as on the minimum analyte concentration, C₀, are described. In treating the effect of an increased film thickness, two approaches can be followed: either the separation temperature is kept constant, resulting in larger values of the capacity ratio, k, or the column temperature is increased such as to keep k constant. For normalized chromatographic conditions the effects of both approaches on the minimum plate height, optimum carrier gas velocity, and required plate number are described, finally yielding expressions for Q₀ and C₀ for both mass flow and concentration sensitive detectors. At constant temperature, C₀ always increases with the film thickness for mass flow sensitive detectors (e.g. FID). Wide bore thin film columns offer the lowest value of C₀ attainable. For concentration sensitive detectors (e.g. TCD), C₀ is affected neither by column diameter nor by film thickness. The Q₀-d plot for constant temperature shows a minimum, suggesting an optimum film thickness for mass flow sensitive as well as concentration sensitive detectors. The corresponding capacity ratio has a value between 0.5 and 1.5. At elevated temperatures (k constant) in combination with mass flow sensitive detectors, again an optimum film thickness exists, corresponding to a minimum value of C₀. For constant capacity ratio Q₀ always increases with the film thickness for both types of detectors. As indicated above, in some situations the lowest values of C₀ and Q₀ are obtained at an increased film thickness, the effect being marginal. As an initial guideline, for the daily practice of capillary gas chromatography with respect to minimum values of C₀ and Q₀, the use of thin film columns is to be preferred.

1 Introduction

Important new developments in column technology include the preparation of capillary columns with stable thick films of stationary phases [1–5]. Thick film capillary columns are advantageously used for the analysis of volatile compounds as the solute capacity ratios are increased without any need for sub-ambient oven temperatures. Moreover, large film thicknesses allow the introduction of larger sample volumes, thus decreasing C₀. On the other hand the separation efficiency is reduced, due to a larger minimum plate height, elevating Q₀ and this counterbalances the beneficial effects of the increased injection volume. Recently, comparative studies on the performance of capillary columns with various diameters and film thicknesses have been published by Ettre and co-workers [6–8].

In Part I of this work, we presented the theory of the effect of the column diameter on the minimum detectable amount and the minimum analyte concentration for thin film capillary columns [9]. For a mass flow sensitive detector like the FID it was shown that wide bore columns should be employed for the analysis of highly diluted samples unless an on-column enrichment technique is used.

So far the stationary phase film thickness has been left out of consideration because of the complexity of the related theoretical treatment. Defectiveness in the theoretical aspects of thick film columns presented in the cited literature might lead to erroneous conclusions concerning the detectability of trace compounds. In this paper, an attempt is made to provide a complete survey of the implications of an increased stationary phase film thickness (d) for the minimum detectable amount (Q₀) as well as for the minimum analyte concentration (C₀).

2 Basic Relationships

Unlike the theoretical treatment of thin film capillary columns, the resistance to mass transfer in the stationary phase can no longer be neglected. In this paper a factor “a”
is defined as the ratio between the pressure corrected $C_{m,o}$ and $C_s$ terms in the Golay-Giddings equation [10], i.e.:

$$ a = \frac{C_s}{C_{m,o}} f_2 $$

and so *):

$$ a = \frac{64k}{1 + 6k + 11k^2} \frac{d^2_s}{d^2_c} \frac{D_{m,o}}{D_s} \frac{f_2}{f_1} \frac{C_{m,o}}{f_1} \frac{f_2}{f_1} $$

where $k$ is the capacity ratio, $d_t$ the film thickness, $d_c$ the column inner diameter, and $D_{m,o}$ and $D_s$ the solute diffusion constants in the mobile respectively stationary phase.

The ratio $a$ describes the influence of the stationary phase film thickness on the plate height relative to the $C_{m,o}$ term. It shows a quadratic dependence on the film thickness and is negligibly small for thin film columns (e.g. $a < 0.05$), whereas it should be accounted for when thick film columns are used (e.g. $a > 0.30$). Later the effect of the film thickness on $a$ will be shown in Figure 3 for a wide and a narrow bore column.

Cramers et al. [10] derived expressions for the optimum carrier gas velocity and the minimum plate height by differentiation of the Golay-Giddings equation. Their equations (20) and (21) can be rearranged to give:

$$ u_{o,opt} = \frac{8 D_{m,o}}{d_c} \sqrt{F(k)} \frac{1}{\sqrt{1 + ay}} $$

$$ H_{min} = \frac{1}{2} f_1 \frac{d_c}{d_c} \sqrt{F(k)} \frac{1 + \frac{3}{2}a + \frac{3}{2}ay}{\sqrt{1 + ay}} $$

where $y$ includes the carrier gas velocity dependence of $f_2$.

$$ y = \frac{1 + u_o}{f_2} \frac{\delta f_2}{\delta u_o} $$

It follows that:

$$ y = \frac{1}{2} + \frac{3}{2} \frac{p^2 + p + 1}{p^2 + p + 1} $$

while

$$ F(k) = \frac{1 + 6k + 11k^2}{3(1 + k)^2} $$

$$ f_1 = \frac{9}{8} \frac{p + 1}{(p + 1)^2} and \ f_2 = \frac{3}{2} \frac{p^2 - 1}{p^2 - 1} $$

where $P$ is defined as the ratio of the column inlet and outlet pressures.

When a fixed ratio b between the input band width and the chromatographic peak broadening is defined, i.e.

$$ b = \frac{a_o}{a_c} $$

and the "coating efficiency factor" (CE) accounts for all additional peak broadening processes except sample injection and by definition the stationary phase contribution, the actual total plate number ($N_t$) is related to the theoretically maximum plate number by [9]:

$$ N_t = N_{max} \frac{CE}{1 + b^2} \frac{C_{m,o}}{f_1} \frac{f_2}{f_1} $$

2.1 Expression for $t_r$, $Q_o$, and $C_o$

For a fixed actual plate number, required to separate a critical pair according to:

$$ N_t = 16 \frac{R^2}{S} \frac{1}{k} \frac{C_{m,o}}{D_s} \frac{f_2}{f_1} (1 + k) \frac{f_1}{f_2} $$

expressions for the retention time, the minimum detectable amount and the minimum analyte concentration can be derived.

2.2 Retention Time

$$ t_r = \frac{L}{u_{o,opt}} (1 + k) $$

$$ t_r = \frac{H_{min}}{f_2} \frac{N_{max}}{u_{o,opt}} (1 + k) $$

And using equations (3), (4), and (11):

$$ t_r = \frac{1}{16} \frac{d_c}{d_c} \frac{N_t}{1 + b^2} \frac{C_{m,o}}{D_s} \frac{f_2}{f_1} (1 + k) \frac{f_1}{f_2} (1 + \frac{3}{2}a + \frac{3}{2}ay) $$

2.3 Minimum Detectable Amount

For a mass flow sensitive detector:

$$ Q_o^m = \sqrt{2\pi} \frac{4R_n}{S} \frac{t_r}{\sqrt{N_t}} $$

and for a concentration sensitive detector:

$$ Q_o^c = \sqrt{2\pi} \frac{4R_n}{S} \frac{t_r}{\sqrt{N_t}} F_d $$

When the detector flow rate is equal to the column flow rate, i.e.

$$ F_d = F_c = \frac{\pi}{4} \frac{d_c}{u_{o,opt}} $$

it follows after elaboration:

$$ Q_o^m = \frac{1}{4} \sqrt{2\pi} \frac{R_n}{S} \frac{d_c}{d_c} \sqrt{N_t} \frac{1 + b^2}{C_{m,o}} \frac{F(k)}{D_s} \frac{f_2}{f_1} (1 + \frac{3}{2}a + \frac{3}{2}ay) $$

$$ Q_o^c = \frac{1}{2} \pi \sqrt{2\pi} \frac{R_n}{S} \frac{d_c}{d_c} \sqrt{N_t} \frac{1 + b^2}{C_{m,o}} \frac{F(k)}{(1 + k) \frac{f_1}{f_2}} $$

$$ (1 + \frac{3}{2}a + \frac{3}{2}ay) \sqrt{1 + ay} $$

*) The symbols used are listed at the end of this article.
2.4 Minimum Analyte Concentration

For both detector types the minimum analyte concentration is related to the minimum detectable amount by

\[ C_0 = \frac{Q_0}{V_{\text{inj}}} \]  

(21)

and for a Gaussian input band:

\[ V_{\text{inj}} = \sqrt{2\pi} \sigma_i F_c \]  

(22)

Together with the equations (18), (19), and (20) this yields for a mass flow sensitive detector:

\[ C_0^m = \frac{2}{\pi} \frac{C}{S} \frac{1}{d_o} \frac{1}{b} \frac{\sqrt{F(k)}}{D_{m,o}} \frac{1}{1 + ay} \]  

(23)

and for a concentration sensitive detector:

\[ C_0^c = \frac{4R_n}{S} \frac{1}{b} \]  

(24)

It should be noted that the right-hand parts of the above equations containing "a" and "y" express the stationary phase contributions. For thin film columns "a" approaches zero, converting each of the expressions into the corresponding one of Part I.

The pressure dependence of \( t_R \), \( Q_o \), and \( C_o \) at optimum carrier gas velocity is expressed by the quotient \( f_1/f_2 \) and also by "a" and "y", which are functions of \( P \) as well. At a minimum pressure drop (\( P=1 \)) both \( f_1/f_2 \) and \( y \) equal unity, while for \( P >> 1 \) \( f_1 \) equals 9/8 and \( f_2 \) approaches 3/2\( P \).

According to Darcy’s law the pressure ratio can be expressed as [11]:

\[ P = \frac{64\eta H_{\text{min}} N_{\text{max}} u_0}{d_c^2 P_0} + 1 \]  

(25)

with \( \eta \) the dynamic viscosity of the carrier gas and \( P_0 \) the column outlet pressure. So for \( P >> 1 \) using eq. (3), (4), and (11) this yields:

\[ \frac{f_1}{f_2} = \frac{9}{d_c} \sqrt{\frac{2\eta D_{m,o}}{P_0}} \frac{N_{1+b}^{1+b}}{\ln 1 + \frac{3a}{4} \frac{1}{a} \frac{CE}{1 + \frac{1}{2}a}} \]  

(26)

and \( y \) equals 1/2.

Because eq. (26) still contains the pressure dependent factor \((1 + \frac{3a}{4})/(1 + \frac{1}{2}a)\), and "a" itself is inversely proportional to \( f_1/f_2 \) (cf. eq. (2)), "a" and \( f_1/f_2 \) can only be determined by iteration.

3 Comparison of Thick and Thin Film Capillary Columns

The influence of the stationary phase film thickness on \( Q_o \) and \( C_o \) is comprehensively described by the equations (15), (19), (20), (23), and (24). By increasing the film thickness in a given column, two options occur: increasing \( d_f \) at constant temperature and hence increased capacity ratio (k), or increasing \( d_f \) at an elevated temperature in order to keep k constant. Whatever approach is selected, most of the parameters describing \( Q_o \) and \( C_o \) are affected. Moreover, the actual plate number required to establish a certain peak resolution also changes, both by changing the capacity ratio as well as by changing the temperature which affects the relative retention \( \alpha \). Figure 1 shows a schematic view of the mutual influences associated with either of both options.

3.1 Option 1: Increasing \( d_f \) at Constant T

When the film thickness is increased and the temperature is kept constant, the capacity ratio increases proportionally to the inverse of the phase ratio (\( \beta \)):

\[ k = \frac{1}{\beta} K \]  

(27)

where the distribution constant \( K \) remains unchanged at a fixed temperature:

\[ K = \exp(-\Delta G/RT) \]  

(28)

For open tubular columns with no extremely thick stationary phase film, the phase ratio can be approximated by:

\[ \beta = \frac{d_0}{4d_i} \]  

(29)

So, when the film thickness is increased by a factor \( DF \), it follows from eq. (27) and (29):

\[ k_{ki} = DF k_{tn} \]  

(30)

where

\[ DF = \frac{d_{fi}}{d_{tn}} \quad (DF > 1) \]  

(31)

Apart from the stationary phase influence on \( H_{\text{min}} \) and \( u_{\text{opt},0} \), expressed by "a", the increased capacity ratio itself also affects the minimum plate height as well as the optimum
carrier gas velocity by a factor \( \sqrt{F(k)} \) respectively \( 1/\sqrt{F(k)} \) (cf. eq. (3) and (4)). Since \( F(k) \) increases monotonously with \( k \) (cf. Figure 2), \( H_{\text{min}} \) will be larger, whereas \( u_{\text{o, opt}} \) will be smaller for a thick film column.

For a fixed demand on peak resolution the required actual plate number decreases according to (cf. eq. (12)):

\[
\frac{N_{t, tk}}{N_{t, tn}} = \frac{[1 + DF(k) k]}{DF(1 + k)}\]

where \( k \) is the capacity ratio for the thin film column. Changes in \( N_t \) and \( H_{\text{min}} \) affect the required column length, which, together with a different value of the optimum carrier gas velocity will alter the column pressure drop. This affects \( y \) and the pressure correction factors \( f_1 \) and \( f_2 \). The ratio \( f_1/f_2 \) influences "\( a_1 \)" and "\( a_2 \)" together with \( y \) affects \( u_{\text{o, opt}} \) and \( H_{\text{min}} \) again.

Finally, after rearrangement of the equations (15), (19), (20), (23), and (24), relationships between the thick film and thin film (\( a = 0 \)) values for \( t_R \), \( Q \), and \( C \), can be expressed explicitly:

\[
\begin{align*}
\frac{t_{R, tk}}{t_{R, tn}} &= \frac{F(DF,k)}{F(k)} \frac{[1 + DF(k) k]}{DF(1 + k)} (1 + a) \quad \text{for } P = 1 \\
\frac{t_{R, tk}}{t_{R, tn}} &= \frac{F(DF,k)}{F(k)} \frac{[1 + DF(k) k]}{DF(1 + k)} (1 + a)^{3/2} \quad \text{for } P >> 1 \\
\frac{Q_{m, tk}}{Q_{m, tn}} &= \frac{F(DF,k)}{F(k)} \frac{[1 + DF(k) k]}{DF(1 + k)} (1 + a) \quad \text{for } P = 1 \\
\frac{Q_{m, tk}}{Q_{m, tn}} &= \frac{F(DF,k)}{F(k)} \frac{[1 + DF(k) k]}{DF(1 + k)} (1 + a)^{3/2} \quad \text{for } P >> 1 \\
\frac{Q_{c, tk}}{Q_{c, tn}} &= \sqrt{\frac{F(DF,k)}{F(k)}} \frac{[1 + DF(k) k]}{DF(1 + k)} (1 + a) \quad \text{for } P = 1 \\
\frac{Q_{c, tk}}{Q_{c, tn}} &= \sqrt{\frac{F(DF,k)}{F(k)}} \frac{[1 + DF(k) k]}{DF(1 + k)} (1 + a)^{3/2} \quad \text{for } P >> 1
\end{align*}
\]

### 3.2 Option 2: Increasing \( d_f \) at Constant \( k \)

In order to keep the capacity ratio constant when the film thickness is increased, the GC oven temperature has to be elevated. Combination of the equations (27)-(29) yields for constant \( k \) and equal column inner diameter:

\[
\frac{1}{T_{tk}} = \frac{1}{T_{tn}} + \frac{\Delta(S) + R \ln DF}{\Delta H}
\]

Within a limited temperature range \( \Delta H \) is constant, and thus after elaboration of eq. (41) and (42) it follows:

\[
t = \frac{T_{tk}}{T_{tn}} \quad \text{it follows from eq. (43), that}
\]

\[
t = \frac{1}{1 + \frac{RT_{tn} \ln DF}{\Delta H}}
\]

The influence on the binary gas diffusion constant is given by Fuller et al. [12]:

\[
D_{m, tk} = D_{m, tn} \times (1.75)
\]

and thus the temperature considerably affects the optimum carrier gas velocity (cf. eq. (3)). Very few data are available concerning the diffusion constant in the stationary phase. Hawkess and co-workers expressed empirical relationships for \( n \)-alkanes in various stationary phases [13,14]. For a methyl silicone phase (SE-30) it reads:

\[
D_{m, tk} = D_{m, tn} \exp \left[ (225-250C) \left( \frac{1}{T_{tk}} - \frac{1}{T_{tn}} \right) \right]
\]

where \( C \) is the \( n \)-alkane carbon number.

By increasing the temperature, the relative retention (\( \alpha \)) decreases. Considering the separation of a critical pair (solutes "1" and "2"), with solute "2" being the second eluting compound, the relative retention is

\[
\alpha = k_2/k_1
\]

According to the option of constant \( k \), i.e. \( k_{2, tk} = k_{2, tn} \), it follows:

\[
\frac{C_{m, tk}}{C_{m, tn}} = \sqrt{\frac{F(DF,k)}{F(k)}} \frac{1}{\sqrt{1 + ay}}
\]

\[
\frac{C_{c, tk}}{C_{c, tn}} = 1
\]
Minimum Analyte Concentration/Minimum Detectable Amount

\[
\frac{a_k}{a_n} = \frac{k_{1:n}}{k_{1:k}} \tag{51}
\]

and in analogy with eq. (41)

\[
\frac{a_k}{a_n} = \frac{1}{DF} \exp \left[\left(\frac{\Delta G_1}{RT} - \frac{\Delta G_1}{RT}\right)_{h_k} \right] \tag{52}
\]

Finally, when \(\Delta H_1\) is constant too and \(\Delta (\Delta S_1) << R \ln DF\), this yields

\[
\frac{a_k}{a_n} = \frac{DF}{\Delta H_2} \tag{53}
\]

At a reduced relative retention the required plate number increases by a factor \(n\) according to

\[
n = \left(\frac{a_k}{a_n} \left(\frac{a_n}{a_n-1}\right)^2\right) \tag{54}
\]

Apart from the effect of the temperature on diffusion and separation, the dynamic viscosity of the carrier gas is changed as well. Its value at the thick film temperature can best be approximated by [15]:

\[
\eta_k = \eta_n \times 10^7 \tag{55}
\]

Once again, in combination with changed \(H_{min}, u_{o, opt}\), and \(\eta\) values, the column length, the column pressure drop, and the pressure correction factors \(f_1, f_2\) and \(y\) also change. Introduction of these temperature effects in the equations (15), (19), (20), (23), and (24) finally yields:

\[
\frac{t_{R,k}}{t_{R,n}} = n^{1.75} (1 + a) \quad \text{for } P = 1 \tag{56}
\]

\[
\frac{t_{R,k}}{t_{R,n}} = n^{3/2} \left(1 + \frac{3}{2} a\right)^{3/2} \quad \text{for } P >> 1 \tag{57}
\]

\[
\frac{Q_{o,k}}{Q_{o,n}} = \sqrt{n} \left(1 + a\right) \quad \text{for } P = 1 \tag{58}
\]

\[
\frac{Q_{o,k}}{Q_{o,n}} = n^{1/2} \left(1 + \frac{3}{2} a\right)^{3/2} \quad \text{for } P >> 1 \tag{59}
\]

\[
\frac{Q_{o,k}}{Q_{o,n}} = \sqrt{n} \left(1 + a\right) \quad \text{for } P = 1 \tag{60}
\]

\[
\frac{Q_{o,k}}{Q_{o,n}} = n^{1/2} \left(1 + \frac{3}{2} a\right)^{3/2} \quad \text{for } P >> 1 \tag{61}
\]

\[
\frac{C_{o,k}}{C_{o,n}} = \left(1 + \frac{3}{2} a\right)^{3/2} \quad \text{for } P = 1 \tag{62}
\]

Note that the condition \(P = 1\) or \(P >> 1\) in the equations (33)-(38) and (56)-(61) refers to the column pressure drops across both the thick film and the thin film column. However, it might occur that by increasing the film thickness the pressure drop no longer meets the thin film condition. In such cases a correction should be introduced. In the figures presented below the relationships are corrected for this phenomenon.

4 Discussion

The theoretical relationships presented are visualized by several graphs showing the influence of the film thickness on \(Q_o\) and \(C_o\) using realistic values for the various parameters for \(n\)-C10 hydrocarbon. The point of departure (DF = 1) is a thin film column with \(\beta = 800\). This phase ratio corresponds to a film thickness of 0.1 \(\mu\)m in a 320 \(\mu\)m i.d. column or 0.016 \(\mu\)m in a 50 \(\mu\)m i.d. column. Wide and narrow bore columns are distinguished and the effect of different compounds is studied.

Options 1 and 2 are compared with DF = 20 being their joint analytical condition. The changes according to option 1 are calculated at a constant temperature of 110 \(^\circ\)C and increasing \(k\)-values (\(k = 0.2\) at DF = 1 and \(k = 4\) at DF = 20), whereas for option 2 the capacity ratio is maintained at a value of 4 and the temperature is increased (\(T = 40\) \(^\circ\)C at DF = 1 and \(T = 110\) \(^\circ\)C at DF = 20).

4.1 Influence of Stationary Phase

Accounting for the resistance to mass transfer in the stationary phase, the optimum carrier gas velocity as well as the minimum plate height are affected (cf. eq. (2) and (3)).
The "a"-factor describing the stationary phase influence (eq. (1) and (2)) not only depends quadratically on the film thickness, but "a" is also determined by the column pressure drop, the temperature and the solute capacity ratio. For narrow bore columns "a" is smaller because of a reduced f2/f1 value at a large pressure ratio. Figure 3 shows a difference by a factor of about 5 when a 50 µm i.d. and a 320 µm i.d. column are compared under the specified conditions. The temperature effect is included in the ratio D_{m,0}/D_y, which decreases on elevation of the temperature. This results in a reduced "a"-factor. Finally "a" rapidly falls with increasing k-values after passage of a maximum value at k = 0.3 (Figure 2). So it can be concluded that the detrimental effect of the stationary phase film thickness on the chromatographic performance is smallest for high pressure ratios, high temperatures, and large capacity ratios.

4.2 Minimum Detectable Amount
Replacement of a thin film column by one with a thick film will drastically affect Q_o, as is shown in Figure 4. When the film thickness is increased in agreement with option 2 (constant k), Q_o gradually increases, while for option 1 (constant T) a minimum Q_o value is observed. The corresponding optimum film thickness is hardly affected by the column inner diameter, but is largely determined by the specific compound. The influence of different compounds on Q_o as well as on C_o will be discussed in more detail elsewhere [16].

Using a concentration sensitive detector, graphs shaped similarly to Figure 4 are obtained. For option 1, the Q_o-DF plot has a minimum too, however, at a slightly larger DF value.

In part I, it was concluded that for a fixed actual plate number the capacity ratio should be selected as small as possible. For the concept of a fixed resolution demand as it is worked out in this paper, the most favorable Q_o value according to option 1 is found for a capacity ratio between 0.5 and 1.5, dependent on column pressure drop as well as on the kind of detector used.

4.3 Minimum Analyte Concentration
For option 2 (constant k) the increased temperature competes the stationary phase influence on C_o (cf. eq. (62)), resulting in a minimum C_o value. As is shown by Figure 5 for narrow bore columns is achieved at a larger DF value, because the "a" factor is smaller due to a reduced f2/f1 ratio at high pressure drops. The optimum DF value is a complex function of t and "a", including ΔH, D_{m,0}, D_y, and P, so no general guidelines can be given here. If df is increased in accordance with option 1 (constant T) C_o increases continuously.

For a concentration sensitive detector the minimum analyte concentration, C_o is not affected by any of the varying parameters in either options.
In all cases where \( C \_o \) can be minimized the gain is only moderate and consequently thin film columns are the best choice.

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References


Symbols

\( a \) = ratio of the \( C \_e \) - and \( C \_m \)-term
\( b \) = ratio of the input band width and the chromatographic peak broadening

\( .c \) = for concentration sensitive detectors
\( C \) = solute carbon number
\( C \_o \) = minimum analyte concentration
\( C \_E \) = coating efficiency factor
\( C \_m.o \) = term of the Golay-Giddings equation describing the resistance to mass transfer in the mobile phase at column outlet conditions.
\( C \_s \) = term of the Golay-Giddings equation describing the resistance to mass transfer in the stationary phase.
\( d \_c \) = column inner diameter
\( d \_t \) = stationary phase film thickness
\( D \_m.o \) = solute diffusion constant in the mobile phase at column outlet conditions
\( D \_s \) = solute diffusion constant in the stationary phase
\( D \_F \) = ratio of the thick and thin film \( D \_r \)-values
\( f \_p \) = pressure correction factor after Giddings
\( f \_q \) = pressure correction factor after James & Martin
\( F \_c \) = volumetric column flow at outlet conditions
\( F \_d \) = volumetric detector flow
\( F(k) \) = capacity ratio function
\( \Delta G \) = Gibb’s free energy of retention
\( H \_mn \) = minimum plate height
\( \Delta H \) = enthalpy of retention
\( k \) = solute capacity ratio
\( K \) = solute distribution constant
\( L \) = column length
\( m \) = for mass flow sensitive detectors
\( n \) = ratio of the required actual plate number for the thick and thin film columns
\( N \_max \) = theoretical maximum plate number
\( N \_t \) = actual total plate number
\( P \) = ratio of the column inlet and outlet pressures
\( Q \_a \) = minimum detectable amount
\( R \) = gas constant
\( R \_n \) = detector noise
\( R \_s \) = peak resolution
\( S \) = detector sensitivity
\( \Delta S \) = entropy of retention
\( t \) = ratio of the thick and thin film column temperatures
\( t \_t \) = solute retention time
\( t \_k \) = for the thick film column
\( t \_n \) = for the thin film column
\( T \) = column temperature
\( V \_a.opt \) = optimum carrier gas velocity at column outlet conditions
\( V \_i \) = injected sample volume
\( y \) = correction factor describing the carrier gas velocity dependence of \( f \_2 \)
\( \alpha \) = relative retention
\( \beta \) = column phase ratio
\( \eta \) = dynamic viscosity of the carrier gas
\( \nu \_c \) = standard deviation of the chromatographic peak broadening process
\( \sigma \_1 \) = standard deviation of the input band
\( \sigma \_2 \) = for the first eluting solute of the critical pair
\( \sigma \_2 \) = for the second eluting solute of the critical pair