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Optimum Gas Chromatographic Conditions in Wall-Coated Capillary Columns

Extended and Simplified Forms of the Golay-Equation

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Systematic treatment of simplification effects on minimum plate height and optimum carrier gas velocity

Summary

Band broadening in capillary columns is satisfactorily described by the Golay-equation extended to situations of appreciable pressure drop by Giddings. In practice, however, several simplifications are often made. The effect of these simplifications on the calculated values of the minimum plate height and optimum carrier gas velocity are treated systematically.

Introduction

The broadening of a peak as it passes through an open tubular column is usually expressed through the number of theoretical plates, N , or plate height, H . With compressible media like in gas chromatography there exists a velocity gradient along the column and therefore the local plate height is a function of position x in the column. The local plate height $H(x)$ is defined as:

$$H(x) = \frac{d\sigma_x^2}{dx} \quad (1)$$

The variance is expressed in length² units. The local plate height equation for an open tubular column reads after Golay [1]:

$$H(x) = 2 \frac{D_{m,x}}{v(x)} + \frac{11k^2 + 6k + 1}{24(1+k)^2} \frac{r^2 v(x)}{D_{m,x}} + \frac{2}{3} \frac{k d_f^2 v(x)}{(k+1)^2 D_s} \quad (2)$$

In equation (2) the following symbols are used:

$v(x)$ is the local linear velocity at position x in the column.

$D_{m,x}$ is the diffusion coefficient of a solute in the mobile gas phase at the pressure of position x in the column.

D_s is the diffusion coefficient of a component in the stationary liquid phase.

r is the column radius.

k is the capacity ratio of a solute $= K \frac{V_s}{V_m} = K.a$

K is the partition coefficient of a solute.

a is the volumetric phase ratio of stationary and mobile phase.

d_f is the film thickness of the stationary liquid phase.

If a pressure gradient exists decompression of the carrier gas causes $H(x)$ to vary along the column. For an ideal gas both D_m and v vary inversely with pressure:

$$D_{m,o} P_o = D_{m,x} P(x) \quad (3)$$

$$v_o P_o = v(x) P(x) \quad (4)$$

As can be seen from eq.(2) the first two terms of the local plate height equation are independent of the pressure gradient in the column. Any pressure gradient effect on $v(x)$ is compensated by an equivalent effect on $D_{m,x}$. (Except for a small increase caused by factor f_1 , see eq. 8.) It is therefore convenient to use $D_{m,o}$ and v_o in the first two terms of eq.(2).

— $D_{m,o}$ is the diffusion coefficient of a component in the mobile phase at column outlet pressure.

— v_o is the linear velocity at the column outlet (obtained from the retention time t_o of an unretained component) or as already described by Martin and James [2].

$$v_o = \frac{\bar{v}}{f_2} = \frac{L}{t_o f_2} \quad (5)$$

$$f_2 = \frac{3}{2} \frac{P^2 - 1}{P^3 - 1} \quad (6)$$

By definition

$$P = \frac{P_i}{P_o} \quad (7)$$

is the ratio of inlet/outlet pressure.

As pointed out by Giddings [3, 4] and Sternberg [5] any gas packet within a column containing a significant pressure gradient will expand as it passes down the column. Taking into account the decompression effect as described by above mentioned authors, the measured or apparent plate height equation for open tubular columns reads:

$$H = \left[2 \frac{D_{m,o}}{v_o} + \frac{11k^2 + 6k + 1}{24(1+k)^2} \frac{r^2 v_o}{D_{m,o}} \right] f_1 + \frac{2}{3} \frac{k}{(1+k)^2} \frac{d_f^2 v_o f_2}{D_s} \quad (8)$$

This equation satisfactorily describes the effect of pressure gradient on the observed plate height, H .

$$f_1 = \frac{9}{8} \frac{(P^4 - 1)(P^2 - 1)}{(P^3 - 1)^2} \quad (9)$$

$f_1 = 1$ for $P = 1$, for $P \rightarrow \infty$ f_1 approaches $\frac{9}{8}$

If in a first approximation (valid at not too high values of the average column pressure) the partition coefficient K is considered to be independent of pressure, eq.(8) can be written in a simplified form:

$$H = \left[\frac{B}{v_o} + C_{m,o} v_o \right] f_1 + C_s v_o f_2 \quad (10)$$

Using the relation (only valid for uniform film distributions)

$$k = K \frac{V_s}{V_m} = \frac{2K df}{r} \quad (11)$$

C_s can be written also as:

$$C_s = \frac{k^3}{6(1+k)^2} \frac{r^2}{K^2 D_s} \quad (12)$$

In most of the experimental conditions encountered in gas chromatography the gas flow can be considered laminar. The gas flow is proportional to the pressure gradient:

$$v(x) = \frac{-\kappa}{\eta} \frac{dp}{dx} \quad (13)$$

This is Darcy's equation; κ being the column permeability; η the dynamic viscosity of the carrier gas. As shown by *Martire et al.* [6] under practically all conditions the carrier gas can be considered as an ideal gas and therefore the dynamic viscosity is independent of pressure. Combining equation (4) and (13) yields on integration:

$$v_o = \frac{\kappa}{2\eta L P_o} (P_o^2 - P_i^2) \quad (14)$$

or

$$v_o = \frac{\kappa P_o}{2\eta L} (P^2 - 1) \quad (15)$$

Combination of equations (15), (5) and (6) gives:

$$\bar{v} = \frac{3}{4} \frac{\kappa P_o}{\eta L} \frac{(P^2 - 1)^2}{P^3 - 1} \quad (16)$$

For an open tubular column (column diameter d_c) the permeability is given by:

$$\kappa = \frac{d_c^2}{32} \quad (17)$$

Minimum plate height and optimum carrier gas velocity

By differentiating eq. (10) with respect to v_o , using equation (15) to give the relation of P and v_o , and setting the result equal to zero, the optimum value of v_o and the minimum value of H are found.

The results of this differentiation are:

$$v_{o,opt} = \sqrt{\frac{B_o (f_1 - y_1)}{C_{m,o} f_1 + C_{m,o} y_1 + C_s f_2 + C_s y_2}} \quad (18)$$

$$H_{min} = \left\{ \frac{f_1 (C_{m,o} f_1 + C_{m,o} y_1 + C_s f_2 + C_s y_2)}{f_1 - y_1} + C_{m,o} f_1 + C_s f_2 \right\}^* \sqrt{\frac{B_o (f_1 - y_1)}{C_{m,o} (f_1 + y_1) + C_s (f_2 + y_2)}} \quad (19)$$

Values of $y_1 = v_o \frac{\partial f_1}{\partial v_o}$ and $y_2 = v_o \frac{\partial f_2}{\partial v_o}$ are given in Table 1.

As can be seen from this table for all practical purposes $y_1 \ll f_1$. Thus eq. (18) and (19) reduce to:

$$v_{o,opt} = \sqrt{\frac{B_o f_1}{C_{m,o} f_1 + C_s (f_2 + y_2)}} \quad (20)$$

$$H_{min} = \left\{ 2 C_{m,o} f_1 + C_s (2 f_2 + y_2) \right\}^* \sqrt{\frac{B_o f_1}{C_{m,o} f_1 + C_s (f_2 + y_2)}} \quad (21)$$

Within the limits set by the assumptions made-ideal carrier gases, laminar flow - eqs. (20) and (21) completely describe the theoretical behaviour of wall-coated capillary columns. In the following part of this paper we will systematically

Table 1

Variation of f_1 (eq. 9), f_2 (eq. 6), $y_1 (v_o \frac{\partial f_1}{\partial v_o})$ and $y_2 (v_o \frac{\partial f_2}{\partial v_o})$

with the ratio, P , of inlet to outlet pressure.

Subatmospheric outlet pressure P_o

P_i	P_o	P	f_1	f_2	y_1	y_2
1	10^{-4}	10^4	1.1250	15×10^{-5}	1.13×10^{-8}	-7.5×10^{-5}
1	10^{-2}	10^2	1.1249	0.0150	0.0001	-0.0075
1	10^{-1}	10	1.1157	0.1486	0.0080	-0.0723
1	0.9	1.11	1.0009	0.9465	0.0016	-0.0485

Atmospheric outlet pressure P_o

1.1	1.0	1.1	1.0008	0.9517	0.0014	-0.0446
1.5	1.0	1.5	1.0128	0.7895	0.0164	-0.1454
2.5	1.0	2.5	1.0510	0.5385	0.0335	-0.1864

Outlet pressure $P_o > 1$ bar

1.5	1.0	1.5	1.0128	0.7895	0.0164	-0.1454
10.5	10.0	1.05	1.0002	0.9754	0.0005	-0.0236
100.5	100.0	1.005	1.0000	0.9975	4×10^{-8}	-0.0025

Table 2Theoretical values of $H_{\min.}$ [cm] calculated by different equations.Conditions: 0.25 mm i.d. capillary column
 $C_{m,0}$ at $P_0 = 1$ bar: 0.0004 s

P _i	P _o	P	H _{min.} (I)	H _{min.} (II)	H _{min.} (III)	H _{min.} (IV)	H _{min.} (V)	
Subatmospheric outlet pressure P _o								
1.0	10 ⁻⁴	10 ⁴	0.099	0.099	0.094	7.10	0.017	C _s = 7x10 ⁻³ s
1.0	10 ⁻²	10 ²	0.099	0.099	0.094	0.71	0.017	
1.0	10 ⁻¹	10	0.098	0.098	0.093	0.23	0.017	
1.0	10 ⁻⁴	10 ⁴	0.030	0.030	0.029	1.70	0.017	C _s = 4x10 ⁻⁴ s
1.0	10 ⁻²	10 ²	0.030	0.030	0.029	0.17	0.017	
1.0	10 ⁻¹	10	0.029	0.029	0.029	0.056	0.017	
1.0	10 ⁻⁴	10 ⁴	0.020	0.020	0.020	0.380	0.017	C _s = 2x10 ⁻⁵ s
1.0	10 ⁻²	10 ²	0.020	0.020	0.020	0.042	0.017	
1.0	10 ⁻¹	10	0.020	0.019	0.020	0.021	0.017	
Atmospheric outlet pressure P _o								
1.1	1.0	1.1	0.071	0.071	0.071	0.073	0.017	C _s = 7x10 ⁻³ s
1.5	1.0	1.5	0.066	0.066	0.066	0.073	0.017	
2.5	1.0	2.5	0.057	0.057	0.056	0.073	0.017	
1.1	1.0	1.1	0.024	0.024	0.024	0.024	0.017	C _s = 4x10 ⁻⁴ s
1.5	1.0	1.5	0.023	0.023	0.023	0.023	0.017	
2.5	1.0	2.5	0.022	0.022	0.022	0.024	0.017	
1.1	1.0	1.1	0.017	0.017	0.017	0.017	0.017	C _s = 2x10 ⁻⁵ s
1.5	1.0	1.5	0.018	0.018	0.018	0.017	0.017	
2.5	1.0	2.5	0.018	0.018	0.018	0.017	0.017	
Outlet pressure P _o > 1 bar								
1.5	1.0	1.5	0.066	0.066	0.066	0.073	0.017	C _s = 7x10 ⁻³ s
10.5	10.0	1.05	0.028	0.028	0.028	0.028	0.017	
100.5	100.0	1.005	0.018	0.018	0.018	0.018	0.017	
1.5	1.0	1.5	0.023	0.023	0.023	0.024	0.017	C _s = 4x10 ⁻⁴ s
10.5	10.0	1.05	0.018	0.018	0.018	0.018	0.017	
100.5	100.0	1.005	0.017	0.017	0.017	0.017	0.017	
1.5	1.0	1.5	0.018	0.018	0.018	0.017	0.017	C _s = 2x10 ⁻⁵ s
10.5	10.0	1.05	0.017	0.017	0.017	0.017	0.017	
100.5	100.0	1.005	0.017	0.017	0.017	0.017	0.017	

treat the deviations that occur when more simplified equations than 20 and 21 are used to describe column performance.

A. Effect of the inlet to outlet pressure ratio $P = \frac{P_i}{P_0}$

As can be seen from Table 1 for values of $P > 1.5$ y_2 is not negligible compared to f_2 .

If $P < 1.5$ eqs. (20) and (21) for all practical purposes further reduce to:

$$v_{0,opt} = \sqrt{\frac{B_0 f_1}{C_{m,0} f_1 + C_s f_2}} \quad (22)$$

and:

$$H_{\min} = 2 \sqrt{B_0 f_1 (C_{m,0} f_1 + C_s f_2)} \quad (23)$$

It is clear that only if P approaches 1 (low pressure drop in normal operation, or operation at elevated outlet pressures) (22) and (23) further simplify to:

Table 3Theoretical values of $v_{0,opt}$ [cm/s] calculated by different equations.Conditions: 0.25 mm i.d. capillary column
 $C_{m,0}$ at $P_0 = 1$ bar: 0.0004 s

P _i	P ₀	P	V _{0,opt} (I)	V _{0,opt} (II)	V _{0,opt} (III)	V _{0,opt} (IV)	V _{0,opt} (V)	
Subatmospheric outlet pressure P ₀								
1.0	10 ⁻⁴	10 ⁴	59603	59604	43004	507	212132	C _s = 7x10 ⁻³ s
1.0	10 ⁻²	10 ²	596	596	430	51	2121	
1.0	10 ⁻¹	10	59	59	43	16	212	
1.0	10 ⁻⁴	10 ⁴	164317	164317	138873	2121	212132	C _s = 4x10 ⁻⁴ s
1.0	10 ⁻²	10 ²	1643	1643	1389	211	2121	
1.0	10 ⁻¹	10	163	164	139	64	212	
1.0	10 ⁻⁴	10 ⁴	208683	208683	205396	9477	212132	C _s = 2x10 ⁻⁵ s
1.0	10 ⁻²	10 ²	2087	2087	2054	866	2121	
1.0	10 ⁻¹	10	207	209	205	173	212	
Atmospheric outlet pressure P ₀								
1.1	1.0	1.1	5.16	5.17	5.05	4.93	21.2	C _s = 7x10 ⁻³ s
1.5	1.0	1.5	6.04	6.09	5.54	4.93	21.2	
2.5	1.0	2.5	7.94	8.09	6.72	4.93	21.2	
1.1	1.0	1.1	15.4	15.4	15.2	15.0	21.2	C _s = 4x10 ⁻⁴ s
1.5	1.0	1.5	16.4	16.6	15.9	15.0	21.2	
2.5	1.0	2.5	17.9	18.4	17.3	15.0	21.2	
1.1	1.0	1.1	20.7	20.7	20.7	20.7	21.2	C _s = 2x10 ⁻⁵ s
1.5	1.0	1.5	20.6	20.9	20.8	20.7	21.2	
2.5	1.0	2.5	20.4	21.0	21.0	20.7	21.2	
Outlet pressure P ₀ > 1 bar								
1.5	1.0	1.5	6.04	6.09	5.54	4.93	21.2	C _s = 7x10 ⁻³ s
10.5	10.0	1.05	1.30	1.30	1.29	1.28	2.12	
100.5	100.0	1.005	0.20	0.20	0.20	0.20	0.21	
1.5	1.0	1.5	16.4	16.6	15.9	15.0	21.2	C _s = 4x10 ⁻⁴ s
10.5	10.0	1.05	2.03	2.02	2.02	2.02	2.12	
100.5	100.0	1.005	0.21	0.21	0.21	0.21	0.21	
1.5	1.0	1.5	20.6	20.9	20.8	20.7	21.2	C _s = 2x10 ⁻⁵ s
10.5	10.0	1.05	2.12	2.11	2.12	2.12	2.12	
100.5	100.0	1.005	0.21	0.21	0.21	0.21	0.21	

$$v_{0,opt} = \sqrt{\frac{B_0}{C_{m,0} + C_s}} \quad (24)$$

and:

$$H_{\min} = 2 \sqrt{B_0 (C_{m,0} + C_s)} \quad (25)$$

In Tables 2 & 3 values of $H_{\min}$ and $v_{0,opt}$ are given calculated by means of the sets of equations (18), (19); (20), (21); (22), (23); (24), (25) and (26), (27) (deduced later) respectively. Calculations are carried out for 0.25 mm i.d. columns with varying $C_s/C_{m,0}$ ratios for sub-atmospheric, atmospheric, atmospheric and elevated column outlet pressures. As can be concluded from the numerical results eqs. (18) (19) and the more simplified eqs. (20), (21) give almost similar results in all situations.

For $H_{\min}$ further simplification to eqs. (22) and (23) is possible in most cases except for situations where a high value of $C_s/C_{m,0}$ is combined with a large value of P , but even then the deviations are small. In these cases the theoretical value of $H_{\min}$ calculated by the most extended equation is larger than predicted by the more simplified equations.

Figure 1 (a & b)

Calculated values of $H_{\min}$ and $v_{o,\text{opt}}$ in dependence on P using different sets of extended and simplified Golay equations. Conditions: $P_o = 1$ bar, $C_{m,o} = 0.0004$ s.

For $v_{o,\text{opt}}$ the same conclusions are valid: Only for large values of P combined with an appreciable C_s term eqs. (20) and (21) can be used. In this case the most complete equations yield the highest values of the optimum carrier gas velocity $v_{o,\text{opt}}$.

Figure 2

Theoretically anticipated dependence of $\frac{k}{11k^2 + 6k + 1}$ on k . This plot represents the expected variation of $C_s/C_{m,o}$ with k at constant $\frac{D_{m,o}}{D_s}$ and constant phase ratio a .

As is clearly shown by the data in tables 2 and 3 the use of eqs. (24) and (25) is limited strictly to situations where C_s is small compared to $C_{m,o}$ and the value of P approaches 1. Using eqs. (24), (25) results in too high values of $H_{\min}$ and in too small values of the optimum carrier gas velocity $v_{o,\text{opt}}$.

B. The effect of the relative magnitude of C_s and $C_{m,o}$ terms

In addition to the assumptions made in deriving eqs. (24) and (25) very often in literature it is stated that for capillary columns $C_{m,o} \gg C_s$. This then leads to the most simplified expressions for optimum gas chromatographic conditions:

$$v_{o,\text{opt}} = \sqrt{\frac{B_o}{C_{m,o}}} \quad (26)$$

$$H_{\min} = 2 \sqrt{B_o C_{m,o}} \quad (27)$$

In the following the relative magnitude of C_s and $C_{m,o}$ will be discussed. From the numerical values given in tables 2 and 3 it can be concluded that simplification to equations (26) and (27) is indeed only allowed if $C_s \ll C_{m,o}$. In this situation the sets of equations I, II, III, IV and V yield similar results, except for large values of P (sub-atmospheric outlet pressure). For the situation of atmospheric outlet pressure the optimum values of H and v_o following from the different equations are plotted in dependence on P for three different values of $C_s/C_{m,o}$ in Figs. 1a and b. The problem in anticipating the role of the contributions of the $C_{m,o}$ and C_s terms to the optimum conditions is that of having the precise mode of liquid distribution in a column.

Table 4

Variation of $C_s/C_{m,o}$ with phase ratio a , and K for capillary columns of different radius (true film distribution).

Values of $D_{m,o}$ and D_s are obtained from Desty [7]. Conditions: Carrier gas N_2 , outlet pressure 1 bar, stat. phase squalane, column temperature 50°C .

r μ	d_f μ	a	$g(k) = C_s/C_{m,o}$				
			K = 10	K = 100	K = 1000	$g_{\max}$	at $K_{\max}$
250	1	0.008	0.66	0.79	0.134	1.01	37.7
	0.5	0.004	0.13	0.25	0.064	0.25	75.4
	0.25	0.002	0.016	0.006	0.028	0.06	150
	0.1	0.0008	0.001	0.007	0.008	0.01	375
125	1	0.016	3.64	2.10	0.29	4.04	18.8
	0.5	0.008	0.66	0.79	0.134	1.01	37.6
	0.25	0.004	0.13	0.25	0.064	0.25	76
	0.1	0.0016	0.008	0.03	0.02	0.04	190
50	1	0.04	25.0	6.4	0.35	25.3	7.5
	0.5	0.02	6.08	2.8	0.36	6.3	15
	0.25	0.01	1.16	1.1	0.17	1.6	30
	0.1	0.004	0.13	0.25	0.064	0.25	75
25	1	0.08	79.4	14.1	3.84	101	3.8
	0.5	0.04	25.0	6.4	0.35	25.3	7.6
	0.25	0.02	6.08	2.8	0.36	6.3	15
	0.1	0.008	0.66	0.79	0.134	1.01	37.5

Uniform film distribution

If first the possibility of true film distribution is considered it follows from equations (12) and (8) that

$$\frac{C_s}{C_{m,o}} = \frac{k}{11k^2 + 6k + 1} \cdot 4a^2 \frac{D_{m,o}}{D_s} \quad (28)$$

In Fig. 2

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

is plotted against k . As k increases $f(k)$ rises, passes through a maximum and then falls continuously. The position of this maximum can readily be calculated by differentiation of $f(k)$. The maximum value of $f(k) = 0.0791$ for $k = 0.3015$ (or $K_{\max} = \frac{0.3015}{a}$). The ratio $C_s/C_{m,o}$ depends besides on $f(k)$ on

the phase ratio a and the ratio of $D_{m,o}/D_s$. Of course no general calculation can be carried out. In Table 4 values of $C_s/C_{m,o}$ are given for capillary columns of different radius, varying the film thickness d_f . The value of $D_{m,o}/D_s$ is valid for $n-C_4$ to $n-C_9$ hydrocarbons separated at 50°C on squalane as the stationary phase, with N_2 as the carrier gas. The outlet pressure $P_o = 1$ bar. From data of Desty [7] it

appears that in this case $\frac{D_{m,o}}{D_s} \approx 5 \times 10^4$ for all six hydrocarbons.

From table 4 it can be concluded that even for true film distribution, the contribution of C_s can seldom be neglected. In practice for narrow bore columns the coefficient of resistance to mass transfer in the liquid phase will even control the efficiency. The results of table 4 are plotted in Figures 3 & 4.

Non-uniform films

From the C_s term as originally deduced by Golay (eq. 2) we see that C_s depends on d_f^2 . If there is no uniform film, C_s will be determined mainly by the spots in the column with the largest values of $\langle d_f \rangle$. If there is a droplet distribution of the stationary phase or if most liquid is situated in pores of the column wall the values of $\langle d_f \rangle$ will be appreciably larger than d_f calculated from k , K and r (according to eq. 11). $\langle d_f \rangle$ is unlikely to depend heavily on the phase ratio a , and will primarily be determined by such things as the extent of wetting of the support and the surface structure of the column wall. It is not unreasonable to suppose that, if pores exist, at low phase ratios first all pores are occupied.

Figure 3

Calculated dependence of $C_s/C_{m,0}$ on K for columns having the stationary phase distributed as a uniform film (Conditions as in table 4).

Increasing the phase ratio further will lead to the development of a film. The effect of the foregoing is that the ratio of $C_s/C_{m,0}$ will always be larger than given by equation (28) if the liquid film is non-uniform. Especially for steel capillary columns, etched glass columns, whisker columns etc. C_s will seldom be negligible compared to $C_{m,0}$.

Conclusions

Even under extreme conditions: large pressure gradients and for $C_s \gg C_{m,0}$ the set of equations II may be used. Equations (22) and (23) (III) can be used in all situations except when $C_s > C_{m,0}$ and P is large. Further simplification to (24) and (25) (IV) is only allowed if P approaches 1, the deviations being larger with increasing $C_s/C_{m,0}$ ratios.

The equation very often used in practice for $H_{\min}$ (26) is permitted only if $C_s \ll C_{m,0}$.

Equation (27) for $v_{0,opt}$ is allowed if $C_s \ll C_{m,0}$ except when P is very large, as with subatmospheric outlet pressures.

Figure 4

Calculated dependence of $C_s/C_{m,0}$ on K for columns having the stationary phase distributed as a uniform film (Conditions as in table 4).

The often made assumption $C_s \ll C_{m,0}$ is certainly more an exception than a rule, especially for narrow bore columns.

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