Use of equations for the description of experimental dependence of the height equivalent to a theoretical plate on carrier gas velocity in capillary gas–liquid chromatography

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Abstract

Optimal equation for fitting the experimental data on the height equivalent to a theoretical plate (HETP) versus carrier gas velocity in GLC was determined. The data obtained by authors and the literary data by other investigators were used for the comparative study of Van Deemter, Golay and the little known Golay–Guiochon equations. The Golay–Guiochon equation takes into account instrumental contribution and other sources of additional band broadening. Correlation coefficient R and Pirson's criterion χ^2 were used as a criterion of the data correspondence to the equations. The Golay–Guiochon equation is the best for fitting of the experimental data in 71% considered examples, 19% experimental data may be fitted very precisely by the Van Deemter equation, the Golay equation is preferable for 7% experimental data only. Three percent experimental data may be fitted with the same precision by the Golay and the Van Deemter equations. The results obtained are of theoretical and practical interest. The Golay–Guiochon equation must be used more widely in analytical practice and physicochemical measurements. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The phenomenon of Band broadening in a chromatographic column is very complex. It is of great importance for analytical purposes because zones' broadening leads to falling off in separation. Hence, the phenomenon is widely covered in the literature (see, e.g., Refs. [1–5]).

Note that the determination of the optimal dependence (in reference to the experimental data) of height equivalent to a theoretical plate (HETP, H) on the carrier gas velocity (u) is a necessary and an important stage when studying the nature of the band broadening, interpreting the phenomenon, optimising the separation:

$$H = f(u) \tag{1}$$

In the modern scientific literature the Van Deemter equation for packed columns [6] and the Golay equation for capillary columns [7–9] are in common use. These remarkable equations published more than 40 years ago were the first to allow chromatographers to offer correct physicochemical explana-

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tion of the band broadening and to propose the fundamentals for separation optimisation. The equations are of great importance now.

In our opinion, the Golay–Guiochon [10] equation is promising. Unlike the Van Deemter and the Golay equations, the Golay–Guiochon equation takes into account extra-column band broadening (for example, the instrumental contributions). This equation is little known and discussed in some studies by Guiochon and co-workers [10–12].

It should be noted that, although the Van Deemter equation was proposed for packed columns only, we used it in the given study according to Desty and Goldup who applied the equation to capillary gas–liquid columns [13].

Let us consider the above-mentioned equations.

In the well-known studies by Golay [7–9] the band broadening due to the longitudinal diffusion in carrier gas flow and final rate of mass transfer in gas and liquid phases was considered. Golay's equation can be presented in the simple form as:

$$H = B_1/u + C_1 u \tag{2}$$

where

$$B_1 = 2D_g \tag{3}$$

$$C_1 = C_G + C_L \tag{4}$$

$$C_G = \frac{1 + 6k + 11k^2}{24(1 + k)^2} \cdot \frac{r^2}{D_G} \tag{5}$$

$$C_L = \frac{2k}{3(1 + k)^2} \cdot \frac{d_f^2}{D_L} \tag{6}$$

where D_G is the diffusion coefficient in the gas phase, k is the retention factor, r is the radius of capillary column, d_f is the film thickness of stationary liquid phase (SLP) in the column, D_L is the diffusion coefficient in SLP, B_1 is the longitudinal diffusion term, C_G and C_L are the coefficients of the resistance to mass transfer in the mobile and stationary phases, respectively.

The Golay equation bases on the distinct physical model of the band broadening and the observed regularities of the band broadening on the experimental parameters may be fitted very precisely by the equation. Unfortunately, only limited publications on this matter are available (see, e.g., Refs.

[14,15]) and this problem in capillary GLC does not appear to be discussed in the most excellent monographs [1–5].

In 1978 Guiochon and co-workers proposed the equation taking into account the extra-column band broadening. We take this equation as the Golay–Guiochon equation.

$$H = B_2/u + C_2 u + D_{ex} u^2 \tag{7}$$

where

$$B_2 = 2D_g \tag{8}$$

$$C_2 = \frac{1 + 6k + 11k^2}{24(1 + k)^2} \cdot \frac{r_0^2}{D_g} + \frac{2k}{3(1 + k)^2} \cdot \frac{d_f^2}{D_\ell} \tag{9}$$

$$D_{ex} = \frac{\sigma_t^2}{(1 + k)^2 L} \tag{10}$$

where D_g is the diffusion coefficient in the gas phase, k is the retention factor, r_0 is the radius of capillary, d_f is the film thickness of SLP, D_1 is the diffusion coefficient in SLP, σ_t^2 is the dispersion characterizing the extra-column band broadening, L is the column length, D_{ex} is the main characteristic of the extra-column band broadening in Eq. (7) ($D_{ex} u^2$ is the extra-column band broadening expressed in H values.)

Unfortunately, there are only limited publications (see, e.g., Refs.[10–12]) where Eq. (7) was used in capillary GLC for the fitting the experimental data and the determination of B_2, C_2 and D_{ec} coefficients. But the Golay–Guiochon equation is very promising since the extra-column band broadening usually takes place at real experimental conditions, especially under high-speed conditions.

According to Guiochon and co-workers [10], who suggested introducing the additional term $D_{ex} u^2$ into the Golay's equation, this term is a result of time constants of the electronic components registering the chromatographic zones. But, it should be noted that the nature of the processes contributed to the extra-column band broadening is wider. It seems likely that the contribution of the band broadening due to the final width of the initial zone before the column is also of great importance along with the 'electronic reason'.

The equation proposed by Van Deemter et al. [6] can be given as follows:

Table 1
Characteristics of chromatographic systems used for the calculations

	Column	SLP	Carrier gas	Sorbate	T (°C)	Ref.
A1	30 m×0.25 mm	PEG-20M	SF$_6$	Hexanol-1	150	A[a]
A2		(d_f=0.25 μm)		Methylpelargonate		
A3				Octanol-1		
A4				Decanol-2		
A5				Nonanol-1		
A6				Decanol-1		
A7				Naphthalene		
A8				2,6-Dimethylaniline		
A9				Undecanol-1		
A10				2,6-Dimethylphenol		
A11				Dodecanol-1		
B1	20 m×0.32 mm	SE-52	He	n-Nonane	100	A
B2				n-Decane		
C1	22 m×0.32 mm	SE-52 (d_f=1.7 μm)	He	n-Decane	70	A
D1	30 m×0.25 mm	SE-30 (d_f=0.5 μm)	He	Phenol	100	A
E1	30 m×0.25 mm	SE-30 (d_f=0.25 μm)	He	Phenol	100	A
F1	30 m×0.25 mm	PEG-20Ì (d_f=0.25 μm)	He	Phenol	100	A
G1	30 m×0.25 mm	PEG-20Ì	He	Pentanol-1	100	A
G2		(d_f=0.25 μm)	He	m-Xylene		
H1	30 m×0.25 mm	PEC-20M	He	n-Decane	100	A
H2		(d_f=0.5 μm)		Pentanol-1		
H3				m-Xylene		
H4				Ethylacetate		
I1	75 m×0.14 mm	SE-30	H$_2$	n-Decanol	120	A
I2		(d_f=0.3 μm)		Octanol-1		
I3				2,6-Dimethylphenol		
I4				n-Undecane		
I5				2,6-Dimethylaniline		
I6				Naphthalene		
I7				n-Dodecanol		
J1	75 m×0.14 mm	SE-30	CO$_2$	n-Decanol	120	A
J2		(d_f=0.3 μm)		Octanol-1		
J3				2,6-Dimethylphenol		
J4				n-Undecane		
J5				2,6-Dimethylaniline		
J6				Naphthalene		
J7				n-Dodecanol		
K1	75 m×0.14 m	SE-30	N$_2$	n-Decanol	120	A
K2		(d_f=0.3 μm)		Octanol-1		
K3				2,6-Dimethylphenol		
K4				n-Undecane		
K5	75 m×0.14 m	SE-30	N$_2$	2,6-Dimethylaniline	120	A
K6		(d_f=0.3 μm)		Naphthalene		
K7				n-Dodecanol		

Table 1 (*continued*)

	Column	SLP	Carrier gas	Sorbate	T (°C)	Ref.
L1	25 m×0.16 mm	SE-30 ($d_f = 0.25$ μm)	N_2O	Naphthalene	130	A
M1	85 cm×65 μm	Squalane	H_2	n-Heptane	20	[10]
M2			H_2	n-Octane	20	
M3	100 cm×65 μm	–	H_2	Methane	20	
M4			H_2	n-Hexane	20	
M5			N_2	Methane	20	
M6			N_2	n-Hexane	20	
N1	30 m×0.32 mm	SPB-1 ($d_f = 0.25$ μm) WAX-10	He	Naphthalene	160	[17]
N2	–	($d_f = 0.25$ μm)	He	Naphthalene	160	
O1	20 m×0.27 mm	Dimethyl	N_2	n-Tridecane	100	[15]
O2		siloxane	He	n-Tridecane		
O3		($d_f = 0.22$ μm)	H_2	n-Tridecane		
P1	37 m×0.18 mm	Dimethyl	H_2		100	[15]
P2	60 m×0.27 mm	siloxane	H_2	n-Dodecane	100	
P3	58 m×0.51 mm		H_2	n-Dodecane	100	
P4	50 m×0.70 mm		H_2	n-Dodecane	100	
P5	49 m×0.88 mm		H_2	n-Dodecane	100	
Q1	25 m×0.32 mm	Dimethyl siloxane ($d_f = 3$ μm)	H_2	Compound with $k = 10$	85	[15]
Q2	25 m×0.53 mm	As Q1	H_2	Compound with $k = 10$		
Q3	25 m×0.32 mm	Diphenyl dimethyl siloxane ($d_f = 3$ μm)	H_2	Compound with $k = 10$		
Q4	25 m×0.53 mm	As Q3	H_2	Compound with $k = 10$		
R1	3 m×0.15 mm	CP-Sil 5CB ($d_f = 0.12$ μm)	H_2	n-Octane	40	[11]
R2	3.8 m×0.15 mm	As R1	H_2	n-Octane		
S1	25 m×0.53 mm	5-Phenyl– 95%methyl polysiloxane ($d_f = 3$ μm)	–	n-Dodecane	125	[4]
T1	25 m×0.25 mm	OV-1 ($d_f = 0.4$ μm)	H_2	n-Heptadecane	175	[2]
T2			He			
T3			N_2			

[a] Authors experimental data.

$$H = A + B_3/u + C_3 u \qquad (11)$$

where A is the eddy diffusion term, B_3 is the longitudinal diffusion term, C_3 is the coefficient of resistance to mass transfer. All the constants of the equations used in the present study were determined using experimental values (H, u) for the given dependence. A criterion is a minimisation of standard deviation value of HETP for all experimental data HETP=$f(u)$ fitted by the given equation.

Note, each equation from those considered above reflects an individual physicochemical concept. The

Table 2
Results of calculation for various equations

	$H = A + B_3/u + C_3u$ (11)				$H = B_1/u + C_1u$ (2)			$H = B_2/u + C_2u + D_{ex}^2$ (7)				Optimal equation
	A (cm)	B_3 (cm^2/s)	C_3 (s)	χ^2 ($\times 10^6$)	B_1 (cm^2/s)	C_1 (s)	χ^2	B_2 (cm^2/s)	$C_2 \times 10^4$ (s)	$D_{ex} \times 10^6$	χ^2	
A1	−0.106	0.428	0.0071	6.02	0.019	0.0042	16.96	0.153	−10.0	13.80	0.60	7
A2	−0.022	0.129	0.0030	0.80	0.043	0.0024	6.00	0.065	15.0	2.34	1.50	11
A3	−0.031	0.182	0.0038	1.40	0.069	0.0027	9.40	0.096	15.0	4.25	4.40	11
A4	−0.043	0.200	0.0047	5.40	0.034	0.0036	24.10	0.070	22.0	3.70	14.80	11
A5	−0.034	0.248	0.0038	5.30	0.120	0.29	17.00	0.145	17.0	3.12	10.30	11
A6	−0.012	0.219	0.0026	0.60	0.171	0.0022	1.90	0.185	18.0	1.25	0.70	11
A7	−0.040	0.196	0.0035	15.50	0.042	0.0024	29.90	0.095	3.0	5.48	5.00	7
A8	−0.041	0.318	0.0042	6.90	0.170	0.0028	19.40	0.218	7.0	7.28	2.80	7
A9	−0.021	0.160	0.0026	11.40	0.079	0.0021	14.20	0.111	8.0	3.24	6.20	7
A10	−0.016	0.148	0.0026	1.10	0.086	0.0021	3.60	0.104	14.0	1.86	0.80	7
A11	−0.141	0.1020	0.0070	1.50	0.055	0.0038	7.91	0.355	−3.0	10.10	10.00	11
B1	−0.057	1.040	0.0024	1.10	0.400	0.0015	0.78	0.581	5.0	1.77	0.09	7
B2	−0.035	0.815	0.0017	0.30	0.421	0.0012	0.28	0.530	6.0	1.04	0.40	11
C1	−0.029	0.715	0.0013	0.20	0.369	0.0008	0.11	0.486	2.0	1.19	0.02	7
D1	−0.073	1.420	0.0021	0.50	0.811	0.0009	1.51	0.997	−10.0	4.13	0.23	7
	−0.055	1.152	0.0028	12.00	0.803	0.0014	16.80	0.926	−5.0	5.54	7.00	7
F1	−0.057	1.320	0.0014	0.10	0.779	0.0003	0.68	0.964	−11.0	3.08	0.05	7
G1	−0.070	1.111	0.0030	0.30	0.681	0.0010	1.17	0.810	−13.0	7.54	0.17	7
G2	−0.061	0.927	0.0034	4.30	0.550	0.0016	12.10	0.673	−5.0	6.79	4.00	7
H1	−0.024	0.502	0.0021	3.30	0.360	0.0014	4.30	0.422	2.0	4.19	2.10	7
H2	−0.011	0.585	0.0003	2.60	0.649	0.0059	2.30	0.645	7.0	0.28	2.90	2
H3	−0.027	0.720	0.0017	1.30	0.561	0.0009	2.60	0.610	0	3.30	1.20	7
H4	−0.019	0.795	0.0019	2.30	0.680	0.0014	2.60	0.721	6.0	2.65	1.90	7
I1	−0.052	1.029	0.0010	0.60	−0.074	0.0006	0.63	0.277	0.6	0.50	0.20	7
I2	−0.052	1.130	0.0011	0.20	0.011	0.0007	0.60	0.349	1.6	0.48	0.05	7
I3	−0.057	1.241	0.0010	0.40	0.019	0.0006	0.73	0.402	0.4	0.55	0.20	7
I4	−0.072	1.311	0.0014	0.70	−0.231	0.0008	1.19	0.258	0.7	0.70	0.20	7
I5	−0.065	1.348	0.0012	0.50	−0.029	0.0007	0.95	0.409	0.5	0.62	0.10	7
I6	−0.069	1.430	0.0012	1.00	−0.038	0.0007	1.11	0.438	1.0	0.68	0.01	7
I7	−0.099	1.742	0.0019	2.90	−0.382	0.0010	2.38	0.316	2.9	0.99	0.40	7
J1	−0.093	0.621	0.0041	3.80	−0.200	0.0025	4.00	0.059	3.0	3.98	0.70	7
J2	−0.109	0.737	0.0049	5.50	−0.221	0.0029	5.54	0.078	3.0	4.69	0.90	7
J3	−0.099	0.676	0.0044	6.20	−0.199	0.0026	4.75	0.079	2.0	4.33	0.11	7
J4	−0.110	0.688	0.0052	3.20	−0.283	0.0033	5.37	0.090	8.0	4.46	0.47	7
J5	−0.115	0.772	0.0051	5.80	−0.241	0.0030	6.09	0.079	3.0	4.93	0.60	7
J6	−0.124	0.840	0.0054	7.80	−0.250	0.0032	7.25	0.091	2.0	5.39	0.60	7
J7	−0.170	1.071	0.0074	16.40	−0.419	0.0044	13.65	0.058	3.0	7.40	0.60	7
K1	−0.070	0.476	0.0032	2.50	−0.087	0.0020	2.24	0.075	1.8	3.30	0.30	7
K2	−0.079	0.570	0.0037	5.70	−0.067	0.0023	3.08	0.124	2.4	3.89	0.20	7
K3	−0.079	0.577	0.0035	5.10	−0.063	0.0021	3.50	0.127	0.4	3.91	0.30	7
K4	−0.113	0.729	0.0049	7.70	−0.180	0.0032	5.98	0.083	0.8	5.42	0.80	7
K5	−0.090	0.649	0.0040	5.80	−0.076	0.0024	3.86	0.138	0.5	4.40	1.00	7
K6	−0.096	0.691	0.0042	7.80	−0.084	0.0025	4.51	0.147	0.8	4.71	1.00	7
K7	−0.047	0.283	0.0036	9.20	−0.097	0.0028	17.30	0.098	2.1	6.30	1.00	7

Table 2 (*continued*)

	$H = A + B_3/u + C_3u$ (11)				$H = B_1/u + C_1u$ (2)			$H = B_2/u + C_2u + D_{ex}^2$ (7)				Optimal equation
	A (cm)	B_3 (cm^2/s)	C_3 (s)	χ^2 ($\times 10^6$)	B_1 (cm^2/s)	C_1 (s)	χ^2	B_2 (cm^2/s)	$C_2 \times 10^4$ (s)	$D_{ex} \times 10^6$	χ^2	
L1	−0.048	0.843	0.0023	9.50	0.570	0.0008	12.80	6.73	−13.0	7.70	0.69	7
M1	−0.003	0.634	0.0002	0.62	0.550	0.0002	5.00	0.607	1.3	0.04	0.35	7
M2	−0.009	0.729	0.0002	0.38	0.449	0.0001	2.00	0.541	0.5	0.06	3.70	7
M3	−0.071	2.490	0.0010	6.90	−0.220	0.0007	152.00	0.738	2.0	0.26	3.70	7
M4	−0.028	1.951	0.0002	2.90	0.573	0.0001	2.70	0.924	0.2	0.05	4.40	2
M5	−0.43	1.479	0.0006	2.80	−0.170	0.0004	5.90	0.425	0.7	0.16	0.28	7
M6	−0.09	−0.253	0.0001	3.40	0.182	0.0001	1.80	0.90	1.9	0.02	0.17	7
N1	−0.098	2.660	0.0018	1.00	0.860	0.0006	51.00	1.461	−7.0	1.85	0.40	7
N2	−0.089	2.390	0.0015	0.90	0.761	0.0005	43.00	1.319	−7.0	1.71	0.30	7
O1	−0.026	0.303	0.0022	2.40	0.095	0.0018	84.00	0.164	12.0	0.88	2.00	7
O2	−0.013	0.478	0.0008	0.09	0.239	0.0007	4.00	0.318	5.0	0.18	1.00	11
O3	−0.017	0.956	0.0006	1.00	0.590	0.0004	5.00	0.696	3.0	0.16	2.00	11
P1	−0.001	0.280	0.0004	0.50	0.260	0.0004	0.40	0.244	4.0	−0.01	0.50	2
P2	−0.018	0.502	0.0009	0.30	0.064	0.0007	7.00	0.179	6.0	0.12	0.40	11
P3	−0.013	0.617	0.0016	4.30	0.339	0.0014	4.30	0.377	14.0	0.05	4.90	11.2
P4	−0.002	0.417	0.0003	2.50	0.441	0.0025	2.20	0.451	25.0	0.07	2.50	2
P5	−0.010	0.548	0.0041	2.60	0.420	0.0039	2.20	0.433	38.0	0.11	2.70	2
Q1	−0.002	0.213	0.0026	0.30	0.210	0.0026	0.30	0.208	26.0	−0.01	0.40	11.2
Q2	−0.005	0.237	0.0046	0.20	0.211	0.0045	4.00	0.221	42.0	0.67	2.00	11
Q3	0.006	0.175	0.0137	1.00	0.190	0.0140	13.00	0.191	141.0	−0.45	1.40	11
Q4	0.014	0.173	0.0150	4.90	0.223	0.0160	50.00	0.212	161.0	−2.15	53.00	11
R1	−0.028	0.638	0.0008	6.70	0.351	0.0005	14.00	0.429	1.0	0.37	2.30	7
R2	−0.022	0.579	0.0006	2.50	0.349	0.0005	7.80	0.427	1.0	0.25	1.10	7
S1	−0.027	0.869	0.0026	24.2	0.480	0.0024	61.00	0.595	20.0	3.28	8.16	7
T1	−0.018	0.813	0.0006	0.47	0.650	0.0003	15.50	0.690	−0.3	5.99	2.68	11
T2	−0.021	0.582	0.0010	3.01	0.450	0.0006	35.10	0.479	1.8	7.36	4.07	11
T3	−0.029	0.252	0.0023	5.72	0.096	0.0017	63.90	0.136	8.4	18.8	1.63	7

Golay Eq. (2) takes into account the longitudinal band broadening in the gas phase and the limited rate of mass transfer between the gas and stationary phases. The Golay–Guiochon Eq. (7) additionally takes into account the extra-column band broadening. The Van Deemter Eq. (11) additionally takes into account the band broadening due to the eddy diffusion as compared with the Golay equation.

Thus, the fitting of the experimental data with the Eqs. (2), (7), (9) is simultaneously the checking of the physicochemical concept used for their derivation.

Unfortunately, firstly, the experimental fundamentals of the above-mentioned equations are limited (see, e.g., Refs. [1–5,10–12]). Secondly, there is no

publication on capillary GLC where comparative study of several equations of the type of Eq. (1) has been performed for the experimental data obtained by various research on the various columns coated with different stationary phases under different experimental conditions. Thirdly, quantitative criteria for fitting the data by the equation are not in use in the published studies.

In this paper we perform the comparative study of fitting the experimental data from various research by Eqs. (2), (7) and (11). As noted above, the various physicochemical concepts of band broadening were checked simultaneously.

The correlation coefficient R and Pirson's criterion χ^2 [16] were used as the quantitative criteria of the

correlation between the experimental data and Eqs. (2), (7) and (11). Pirson's criterion is usually used for the estimation of the correlation between observed (experimental) and expected (theoretical) data distribution. The lower the χ^2 value, the better the correlation observed.

2. Experimental

Chromatographic measurements were made on a modified gas chromatograph LKhM-MD (Model 5; 'Khromatograf' Factory, Moscow, Russia) equipped with a flame ionization detection (FID) system.

The characteristics of the systems studied (columns, stationary liquid phases, temperature, carrier gas and compounds chromatographed) are presented in Table 1. Each HETP value was determined as an average of five experiments.

Calculations were performed using standard programme Origin (Version 2.88) for Microsoft Windows.

3. Results and discussion

Calculation results are presented in Table 2 and Fig. 1. As can be seen, the Golay equation is preferable for the fitting of the experimental data only in five of 67 considered examples (7%), the Van

Table 3
Frequency of observed negative values of coefficients of Eqs. (2), (7) and (11))

Equation	Frequency (%)	Negative values of the coefficients
Van Deemter	100	Coefficient A in Eq. (11)
Golay	31	Coefficient B in Eq. (2)
Golay–Guiochon	15	Coefficient C in Eq. (7)
	6	Coefficient D in Eq. (7)

Deemter equation in 13 (19%), and the Golay–Guiochon equation in 47 cases (71%). For two considered systems (3%) the Van Deemter and the Golay equations may fit both the experimental data.

In the present work authors used the results they obtained (45 examples, 63%) and the literary data (26 examples, 37%) published.

As follows from the data the Golay–Guiochon equation gives the best fit. Thus, the extra-column band broadening makes a significant contribution into retention since only the Golay–Guiochon equation takes this factor into consideration. Hence, it is expedient to use the Golay–Guiochon equation more widely.

We also estimated the frequency of the observed negative values of the coefficients of Eqs. (2), (7) and (11) when using the same experimental data (see Table 3). It is difficult to get the physicochemical explanation of the phenomenon. As seen from the data listed, the least number of the examples char-
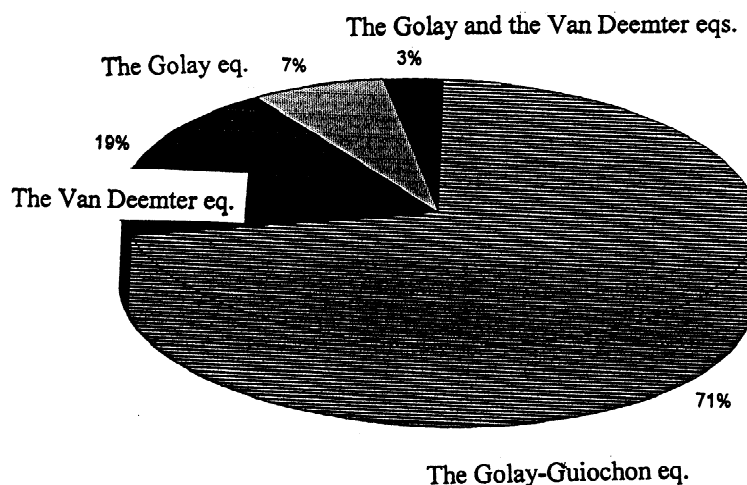

Fig. 1. Distribution of the best fit to the various equations.

acterised by negative value of the coefficients observed for the Golay–Guiochon equation.

In our opinion, the results obtained are of interest both for the theory, optimisation of experimental conditions and physicochemical measurements deal with the determination of the values involved in Eq. (7). In our opinion, an analogous equation taking into consideration the extra-column band broadening may be of great importance for liquid chromatography as well.

4. Conclusion

The comparative study of three equations (Golay, Golay–Guiochon, and Van Deemter) was originally performed for a great number of experimental data obtained by the authors and found in the scientific literature. It was shown that the Golay–Guiochon equation gives the best fit to the experiment. This justifies that the extra-column contribution is significant since only the Golay–Guiochon equation takes into account this factor.

The Golay–Guiochon equation may be recommended for common use in analytical practice and physicochemical measurements.

References

[1] B. Ravindranath, in: Principles and Practice of Chromatography, Ellis Horwood, Chichester, 1989.

[2] K.J. Hyver (Ed.), High Resolution Gas Chromatography, Hewlett-Packard, 1989.

[3] R.L. Grob (Ed.), Modern Practice of Gas Chromatography, Wiley-Interscience, New York, 1995.

[4] J.V. Hinshaw, L.S. Ettre, in: Introduction to Open-Tubular Column Gas Chromatography, Advanstar, Cleveland, 1994, p. 57.

[5] W. Jennings, in: Gas Chromatography with Glass Capillary Columns, Academic Press, New York, 1980.

[6] J.S. van Deemter, F.J. Zuiderweg, A. Klinkenberg, Chem. Eng. Sci. 5 (1956) 271.

[7] M.J.E. Golay, in: D.H. Desty (Ed.), Gas Chromatography 1958, Butterworths, London, 1958, p. 36.

[8] M.J.E. Golay, in: M. Van Swaay (Ed.), Gas Chromatography 1962, Butterworths, London, 1962.

[9] M.J.E. Golay, in: V.J. Coates, H.S. Noebels, I.S. Fagerson (Eds.), Gas Chromatography 1958, Academic Press, New York, 1958, p. 1.

[10] G. Gaspar, R. Annino, C. Vidal-Madjar, G. Guiochon, Anal. Chem. 50 (1978) 1512.

[11] G. Gaspar, J. High Resolut. Chromatogr. 15 (1992) 295.

[12] C.P.M. Schutjes, C.A. Cramers, C. Vidal-Madjar, G. Guiochon, J. Chromatogr. 279 (1983) 269.

[13] D.H. Desty, A. Goldup, in: R.P.W. Scott (Ed.), Gas Chromatography 1960, Butteworths, London, 1962, p. 162.

[14] F. David, M. Proot, P. Sandra, J. High Resolut. Chromatogr. 8 (1985) 551.

[15] P. Sandra, J. High Resolut. Chromatogr. 12 (1989) 273.

[16] A.J. Gordon, R.A. Ford, in: A Handbook of Practical Data, Techniques and References, Wiley-Interscience, New York, London, 1972.

[17] G. Gastello, S. Vezzani, P. Moretti, J. High Resolut. Chromatogr. 17 (1994) 31.