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CHROMATOGRAPHIC PEAK SHAPE

II*. THE USE OF SHAPE MODELS FOR THE GENERATION OF MOMENTS

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SUMMARY

The calculation of the higher central moments of chromatographic peaks has been a long-time burden of the chromatographer. The calculation of these quantities experimentally is not often accomplished since the integration process is extremely sensitive to noise and the limits of integration, causing the results to vary over a large range. Owing to these discrepancies, the purpose of this work was to derive the moments of the predetermined eight-parameter peak shape model of Chesler and Cram after fitting the equation to experimental data, and to offer a comparison of the results to the direct integration of the profile. In some cases, the experimental moments are in close agreement with those predicted by the model, whereas in others the difference is quite substantial.

INTRODUCTION

The importance of statistical moments in the analysis of chromatographic peak shapes is well established¹⁻³. In addition to the characterization of solute peaks, the moments can yield information pertaining to processes occurring in the chromatographic column. Consequently, the moments can be used to identify the solutes on one hand and to obtain physicochemical parameters, such as rates of adsorption, on the other. The utilization of moments has been hampered by the fact that they are difficult to measure experimentally. With the exception of the data of very few workers, *viz.* Oberholtzer and Rogers⁴ and Petitclerc and Guiochon⁵, the reported values of the moments suffer from lack of accuracy and precision. Chesler and Cram⁶ as well as Petitclerc and Guiochon⁷ have shown the dependence of the measured moments on experimental variables such as the signal-to-noise ratio, digitizing rate, limits of integrations, etc. Since higher central moments, such as the third and fourth, tend to accentuate the contribution of points further away from the center of gravity (first moment) of the peak, any baseline noise will contribute significantly to the inaccuracy of the measurements.

The calculation of the second central moment, which is crucial to the evalua-

* For Part I see ref. 27.

tion of a chromatographic system, poses few problems in its calculation, provided the peak is not too broad and is reasonably symmetric. Sternberg⁸ discusses the various operating parameters that can contribute to the broadening of the zone, many of which can be controlled experimentally. If there is a large modification of the second moment by extra-column effects, the fourth moment which is used to calculate the excess of the profile, magnifies these effects which will not accurately describe the on-column processes. This is particularly important in determining the kinetic interactions between the solute and mobile phase (for diffusion studies) or stationary phase³.

The moments of chromatographic profiles have been related to the mass balance equations^{2,9-15}. Yamaoka and Nakagawa¹⁶ have shown the effect of the sample size on the moments. A detailed description of the moments have been reported in numerous works¹⁷⁻²² and will be omitted here.

Aside from the physical phenomena to which the moments are related, the moments can also be used to approximate the peak shape using the Gram-Charlier series^{12,23,24}. The coefficients of the terms in the series are functions of the higher order central moments. For example, the Gram-Charlier series was used by McQuarrie²⁵ to compare the peak shape generated with a Bessel function, whose derivation was based on the stochastic theory. In the work described here, the series was evaluated with the moments calculated from the model of Chesler and Cram²⁶.

Since the moments reflect the processes that occur in the column, they should be useful in characterizing the solutes and the stationary phase. More specifically, the moments should yield qualitative information about the solutes, thus allowing their identification. The moments should also be able to classify the "polarity" of the stationary phase. The present paper deals only with the solute identification.

Since routinely used gas chromatographs do not allow direct precise calculations of the moments, an alternative method is needed. If a mathematical model that describes the peak shape exists, then this model can be fitted to the experimental data and the moments calculated from the fitted equation. In a previous paper²⁷ we have described an eight-parameter equation suggested by Chesler and Cram²⁶ and we have shown that the equation can be utilized to evaluate chromatographic data. Here we describe the calculation of the moments from experimental data by the use of the Chesler and Cram²⁶ model.

EXPERIMENTAL

The data were collected as described previously²⁸. The column was 200 cm in length and 0.64 cm O.D. and packed with 10% Carbowax 1540 on Chromosorb W AW DMCS, 80-100 mesh. Preliminary data reduction from previous work²⁷ was done on a CDC 6400 computer while the moments calculations were run on a CDC Cyber 173.

THEORY

The eight-parameter equation of Chesler and Cram²⁶ was the model whose moments were investigated. The equation is of the form:

$$Y(t) = C_1 \left\{ \exp \left[\frac{-(t - C_4)^2}{2C_5} \right] + \left\{ 1 - 0.5 \{ 1 - \tanh[C_2(t - C_3)] \} \right\} \times \right. \\ \left. \times C_6 \exp [-0.5C_7(|t - C_8| + t - C_8)] \right\} \quad (1)$$

where \hat{y} = peak maximum; C_2 = slope of the hyperbolic tangent at $t=C_3$; C_3 = midpoint of the hyperbolic tangent; C_4 = position of the peak maximum; C_5 = variance of the Gaussian portion of the peak; C_6 = height ratio of the maximum of the exponential decay to C_1 at $t=C_8$; C_7 = rate of the exponential decay; and C_8 = position where the decay function originates.

The first term in eqn. 1 is the Gaussian contribution, the second term is the hyperbolic tangent function which is used to broaden, as well as to introduce smoothly the last term, an exponential decay. Various properties of this function have been discussed previously²⁷ and will therefore be omitted for the purpose of brevity.

Statistical moments of a population profile are defined as:

$$m_0 = \int_{-\infty}^{+\infty} f(t) dt \quad (2)$$

$$m_n = \frac{1}{m_0} \int_{-\infty}^{+\infty} t^n f(t) dt \quad n = 1, 2, 3, \dots \quad (3)$$

Eqn. 2 yields the area of the profile while eqn. 3 provides the non-central higher moments. Usually one is only concerned with the moments calculated about the center of gravity of the distribution, m_1 , since it is the central moments that contain the specific information concerning the peak shape and the physical properties of the solute zone.

The integration of $f(t)$ may not be straightforward. In such cases the Laplace transform of $f(t)$, $L[f(t)]$, can be used to generate the moments:

$$m_n = (-1)^{n+1} \lim_{s \rightarrow 0} \frac{d^n L[f(t)]}{ds^n} \quad n = 0, 1, \dots \quad (4)$$

where s is the Laplace variable.

It is important to bear in mind that eqn. 4 does not yield the central moments. The central moments, μ_n , are calculated using the following set of equations:

$$\mu_2 = m_2 - m_1^2 \quad (5)$$

$$\mu_3 = m_3 - 3m_1m_2 + 2m_1^3 \quad (6)$$

$$\mu_4 = m_4 - 4m_1m_3 + 6m_1^2m_2 - 3m_1^4 \quad (7)$$

$$\mu_5 = m_5 - 5m_1m_4 + 10m_1^2m_3 - 10m_1^3m_2 + 4m_1^5 \quad (8)$$

As mentioned, the moments of a chromatographic peak are important since they contain information regarding the chromatographic system. For example, a negative third central moment reflects a fronting peak which can be frequently cor-

rected by the injection of a smaller amount of solute. Conversely, a large positive third central moment is indicative of a tailing peak, where extra-column effects or adsorption-desorption kinetics may be responsible. The deviation from a Gaussian profile is readily seen in the higher moments and their derived quantities skew and excess. These quantities are calculated from the central moments by

$$\text{skew} = \frac{\mu_3}{\mu_2^{3/2}} \quad (9)$$

$$\text{excess} = \frac{\mu_4}{\mu_2^2} - 3 \quad (10)$$

The values of skew and excess for a Gaussian profile are zero. When these quantities vary drastically from their Gaussian values, in either direction, the chromatographic system may have to be changed to increase the efficiency of the system.

The application of the higher moments is useful when one is comparing the experimental profile to that of the theoretical Gram-Charlier series. The series is of the form

$$f(t) = \frac{g(t)}{\sqrt{2\pi\mu_2}} \left[1 + \sum_{i=3}^{+\infty} C_i H_i \left(\frac{t - m_1}{\sqrt{\mu_2}} \right) \right] \quad (11)$$

where $g(t) = \exp[-(t - m_1)^2/2\mu_2]$, $H_i = i$ th Hermite polynomial, and $C_i =$ coefficients of the i th Hermite polynomial.

The coefficients of the Hermite polynomials are functions of the moments of the profile. It is obvious that for a Gaussian profile the coefficients C_i are zero. Also, as a peak departs from a Gaussian profile, more terms are needed in the series of eqn. 11 to describe that profile. With the higher moments being more sensitive to any asymmetry present, the number of terms needed in the Gram-Charlier series for a relatively accurate description of the experimental data are not known.

The integration of eqn. 1 is by no means trivial, and a closed form solution may not be attainable. The first term of the equation can be integrated directly to obtain the moments of the Gaussian portion. The remaining terms must be treated in such a way as to introduce as small an error as possible since they cannot be integrated in closed form in the real plane. Considering the hyperbolic tangent joining function and the exponential decay function, their product is defined over two intervals in the plane:

$$f_1(t) = \frac{C_1 C_6}{2} [1 + \tanh C_2(t - C_3)] \quad t \leq C_8 \quad (12)$$

$$f_2(t) = \frac{C_1 C_6}{2} [1 + \tanh C_2(t - C_3)] \exp [-C_7(t - C_8)] \quad t > C_8 \quad (13)$$

The integrals for each portion can be expressed as:

$$\int_{-\infty}^{C_8} f_1(t) dt = \frac{C_1 C_6}{2} \int_{-\infty}^{C_8} [1 + \tanh C_2(t - C_3)] dt \quad (14)$$

$$\int_{C_8}^{+\infty} f_2(t) dt = \frac{C_1 C_6}{2} \int_{C_8}^{+\infty} [1 + \tanh C_2(t - C_3)] \exp [-C_7(t - C_8)] dt \quad (15)$$

Eqn. 14 can be rearranged to allow the evaluation of a proper definite integral of the form:

$$-\infty \int^{C_8} f_1(t) dt = \frac{C_1 C_6}{C_2} \int_0^{k_1} \frac{u_1}{u_1^2 + 1} du_1 \quad (16)$$

where $k_1 = \exp[C_2(C_8 - C_3)]$ and $u_1 = \exp[C_2(t - C_3)]$. The area contribution of this portion of the peak can be obtained directly:

$$m_0 = \frac{C_1 C_6}{2C_2} \ln \{1 + \exp [2C_2(C_8 - C_3)]\} \quad (17)$$

The remaining moments cannot be calculated as central moments, since $f_1(t)$ and $f_2(t)$ both contribute to the center of gravity of the peak. The remaining moments of $f_1(t)$, expressed in terms of u_1 are:

$$m_n = \frac{C_1 C_6}{C_2} \int_0^{k_1} \frac{u_1}{u_1^2 + 1} \left[\frac{1}{C_2} \ln u_1 + C_3 \right]^n du_1 \quad n = 1, 2, \dots \quad (18)$$

For computational purposes, for all solutes used in this study, the lower limit of integration can be changed from 0 to $e^{-C_2 C_3}$. This change of limits is a result of the following integral that was evaluated for each solute:

$$\frac{C_1 C_6}{2} \int_{-\infty}^0 [1 + \tanh C_2(t - C_3)] dt = 0 \quad (19)$$

This can be verified by the fact that the integrand, evaluated at both its upper and lower limits has a value of zero, provided that C_3 is sufficiently large. From the limitations imposed upon this model, the integral in eqn. 19 should be valid for all solutes since $t = 0$ is taken to be the time of injection.

The expression for the integral in eqn. 18 cannot be evaluated in closed form nor can a set of series with a reasonable number of terms be used to approximate it, the remaining alternative being the numerical Simpson's rule. If the intervals are taken to be small enough, the error can be controlled, and with the aid of a computer, the time used for such a calculation is barely significant.

The last integral of interest is eqn. 15. In this case, it is the number of arguments of the exponential that limit its evaluation. Taking the Laplace transform of eqn. 15 and changing variables:

$$L[f_2(t)] = \frac{C_1 C_6}{2C_2} \exp [C_1(C_8 - C_3)] \exp (-sC_3) \int_0^{k_2} \frac{u_2}{u_2 + 1} \left(\frac{C_1 + s}{2C_2} \right) du_2 \quad (20)$$

where $k_2 = \exp[-2C_2(C_8 - C_3)]$ and $u_2 = \exp[-2C_2(t - C_3)]$.

In the present study the values of the upper limit of integration, k_2 , depending upon the solute, ranged from 0.1 to 9.3. For the cases when $k < 0.5$, a series expansion of $1/(1+u_2)$ was used, and the integral then evaluated term by term. Since the center of convergence is zero and the radius is $|u_2| < 1$, various series are needed for the cases when k exceeds 0.5. For this purpose, nine series, each with a different center and radius of convergence were employed. The integral was now of the form:

$$L[f_2(t)] = \frac{C_1 C_6}{2C_2} \exp [C_7(C_8 - C_3)] e^{-sC_3} \left\{ \int_0^{1/2} u_2^{\left(\frac{C_7+s}{2C_2}-1\right)} S_0 du_2 \right. \\ \left. + \int_{1/2}^{3/2} u_2^{\left(\frac{C_7+s}{2C_2}-1\right)} S_1 du_2 + \dots + \int_{\frac{2n-1}{2}}^k u_2^{\left(\frac{C_7+s}{2C_2}-1\right)} S_n du_2 \right\} \quad (21)$$

where the n th term is determined whenever the following condition is fulfilled: $2n-1/2 < k_2 \leq 2n+1/2$; S_n is the Taylor series expansion of $1/u_2 + 1$ around center n . The integration of the successive series is continued until k_2 is defined between the lower and upper limits of integration, at which point the upper limit becomes k_2 .

The non-central moments for the entire peak, *i.e.* the Gaussian portion, joining function and decay function were calculated and their sum was used to generate the central moments, using eqns. 5-8.

RESULTS AND DISCUSSION

Comparison of experimental moments to moments calculated from eqn. 1

The moments of chromatographic peaks that are obtained in most laboratories are from the direct integration of digitized data. Unless the chromatographic system is carefully designed and handled, and the data smoothed, these numerical moments may vary drastically. Table I gives the values of the first and second central moments and the skew and excess that were calculated from the digitized data and those calculated from the integration of the fitted peak shape model. The average values of $C_2 - C_8$ for each solute can be found in our earlier publication²⁷. For the majority of solutes investigated, the moments calculated from the model involved a smaller error than the moments obtained directly from the normalized digitized data. Since skew and excess are directly proportional to μ_3 and μ_4 , respectively, and are much more sensitive to peak shape variations, a large relative error in the precision is expected. This is observed in both cases of experimental and calculated moments. The relative error is much less for the moments obtained from the fitting equation and may be as much as 15 times smaller than obtained directly from digitized data.

The large relative error for the skew and excess for mesitylene calculated from the model was due to a considerable variation in the upper limit of integration. For one particular peak the value of this constant was 7.0, while the remaining peaks grouped around 8.2. The values for skew and excess with relative errors, for the set of mesitylene peaks neglecting the above mentioned peak are 0.485 (± 3.76) and 1.368 (± 7.35), respectively. Since the constant is an exponential function of C_7 , C_3 and C_8 , any variations in the fitted values will be seen in the moments more readily than in the fit of the equation itself.

It must be mentioned that the moments in Table I were calculated using the fitted values from Chesler and Cram's equation for individual peaks and not from the average values previously reported (Table II in ref. 27).

The values of the first moment calculated from the actual experimental data and from the model are in close agreement. Large variations between the experimental

TABLE I

VALUES OF THE MOMENTS OF EXPERIMENTAL PEAKS COMPARED TO VALUES OBTAINED FROM FITTED PEAKS

Values in parentheses are percent relative errors.

Compound	m_1 (<i>expt.</i>)	m_1 (<i>model</i>)	μ_2 (<i>expt.</i>)	μ_2 (<i>model</i>)	Skew (<i>expt.</i>)	Skew (<i>model</i>)	Excess (<i>expt.</i>)	Excess (<i>model</i>)
<i>n</i> -Hexane	26.94	26.91*	0.354	0.351*	0.725	0.679*	1.541	-1.51*
	±0.005	±0.003	±0.009	±0.002	±0.088	±0.007	±0.410	±0.03
	(±0.019)	(±0.011)	(±2.69)	(±0.570)	(±12.1)	(±1.03)	(±26.6)	(±1.99)
	26.91**		0.364**		0.791**		2.00**	
	±0.008		±0.003		±0.013		±0.05	
	(±0.030)		(±0.824)		(±1.64)		(±2.50)	
<i>n</i> -Heptane	36.34	35.34	0.788	0.891	0.584	0.920	0.848	2.81
	±1.16	±0.05	±0.034	±0.008	±0.028	±0.029	±0.098	±0.16
	(±3.19)	(±0.14)	(±4.31)	(±0.898)	(±4.79)	(±3.15)	(±11.6)	(±5.69)
<i>n</i> -Octane	50.98	50.16	2.62	2.25	1.76	1.01	8.585	3.32
	±1.62	±0.03	±0.20	±0.02	±0.46	±0.02	4.71	±0.10
	(±3.18)	(±0.06)	(±7.63)	(±0.89)	(±26.1)	(±1.98)	(±54.9)	(±3.01)
Benzene	125.70	125.60	11.95	11.10	1.10	0.711	4.66	2.12
	±0.09	±0.09	±0.10	±0.03	±0.72	±0.004	±0.54	±0.01
	(±0.07)	(±0.07)	(±0.84)	(±0.27)	(±65.5)	(±0.563)	(±11.6)	(±0.47)
<i>p</i> -Xylene	390.07	389.2	69.76	71.64	0.553	0.614	1.34	1.88
	±0.61	±0.09	±0.47	±0.94	±0.031	±0.026	±0.12	±0.12
	(±0.61)	(±0.02)	(±0.67)	(±1.31)	(±5.61)	(±4.23)	(±8.96)	(±6.38)
Mesitylene	772.25	772.24	214.20	223.96	0.417	0.543	0.843	1.67
	±0.40	±0.50	±5.66	±8.27	±0.080	±0.117	±0.374	±0.61
	(±0.05)	(±0.06)	(±2.64)	(±3.69)	(±19.18)	(±21.5)	(±44.4)	(±36.5)
Ethanol	136.57	134.75	82.03	21.55	3.15	1.80	11.38	6.08
	±0.07	±0.04	±4.74	±0.52	0.08	±0.03	±0.52	±0.11
	(±0.05)	(±0.03)	(±5.78)	(±2.41)	(±2.54)	(±1.67)	(±4.57)	(±1.81)
Propanol	258.81	256.25	263.19	103.73	3.26	2.55	12.88	11.23
	±0.19	±0.12	±21.61	±3.44	±0.12	±0.04	±1.06	±0.28
	(±0.07)	(±0.05)	(±8.21)	(±3.31)	(±3.68)	(±1.57)	(±8.23)	(±2.49)
<i>n</i> -Butanol	520.27	520.43	866.14	719.36	2.58	2.66	8.42	10.80
	±2.60	±0.21	±36.30	±16.79	±0.09	±0.02	±0.73	±0.11
	(±0.50)	(±0.04)	(±4.19)	(±2.33)	(±3.49)	(±0.75)	(±8.67)	(±1.02)

* $C_2 = 2.72$.** $C_2 = 2.17$.

data and the mathematical model start to become noticeable in μ_2 and the other higher moments. In order to justify the comparison of the experimental moments, to those using the Chesler and Cram model, the experimental profile must be compared with the calculated profile. Figs. 1 and 2 are two plots which show both the experimental and fitted profiles. Fig. 1 is for a typical heptane peak with a Φ value (sum of the squares of the residuals) of 9.20×10^{-5} for fitting the front half of the peak and 2.02×10^{-3} for fitting the back half. As can be seen, the calculated profile approximates the experimental profile very well. A plot of the digitized data and fitted data for propanol is given in Fig. 2. In this case, $\Phi = 7.4 \times 10^{-4}$ for the front portion of the peak and 0.02 for the back half. The fit is not as good as that for heptane. This is also reflected in the μ_2 values shown in Table I. The agreement in the experimental and calculated second central moments is much better for heptane than for propanol. The values of the skew

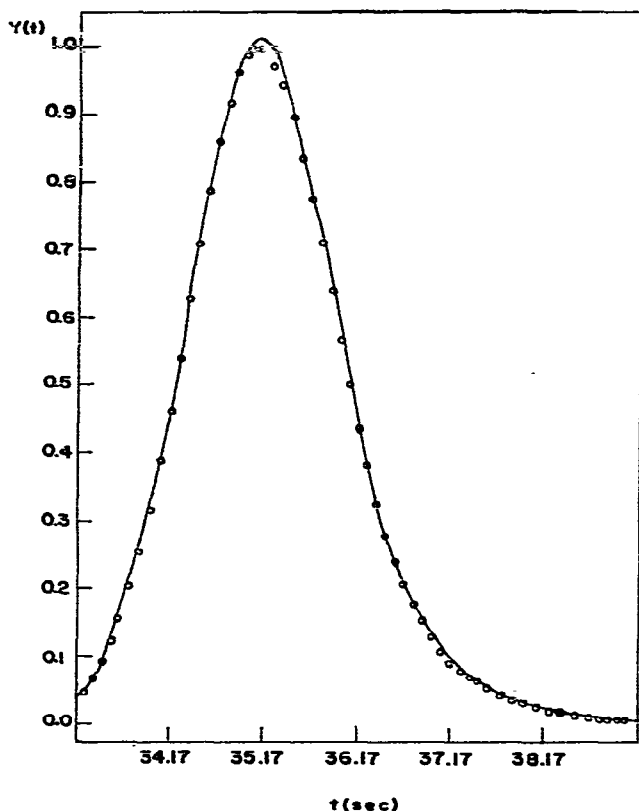


Fig. 1. Experimental (O) and fitted (—) data versus time for a typical heptane peak. Fitted parameters: $C_2 = 1.66$, $C_3 = 36.36$, $C_4 = 35.16$, $C_5 = 0.537$, $C_6 = 0.438$, $C_7 = 1.20$, $C_8 = 35.81$.

for propanol differ by 21% (experimental to model) while the excess calculated from the model is 13% less than the excess calculated from the experimental data. The values for heptane differ by approximately 50%. Although the experimental and calculated values of the skew and excess may not be in close agreement, the fit of the model to the data can be very good. Thus, the moments cannot be used as tool for determining the "goodness" of the fit, which is unfortunate.

Table I shows that the experimentally obtained μ_2 for the alcohols is much higher than the values calculated from eqn. 1. The reasons for this discrepancy are not known to us.

The moments calculated for the hexane peaks were grouped into two categories. The reason for this was evident by virtue of the fact that these values correspond to two distinct values of C_2 obtained while fitting eqn. 1 to experimental data. Originally, these two sets were classed together, for reasons discussed previously²⁷. This is necessary for the purpose of illustrating the dependence of the moments on the various parameters which will be discussed shortly.

Table I shows that, for a given family, increasing the number of carbons has a consistent effect on the values of the skew calculated via the model. This is not seen

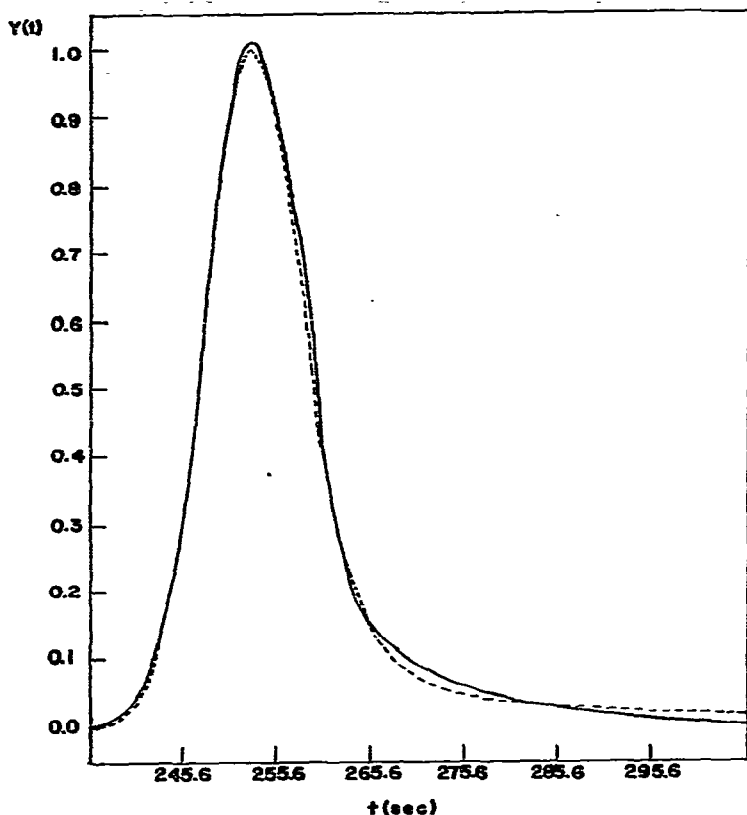


Fig. 2. Experimental (---) and fitted (—) data versus time for a typical propanol peak. Fitted parameters: $C_2 = 0.388$, $C_3 = 255.85$, $C_4 = 252.45$, $C_5 = 21.67$, $C_6 = 0.197$, $C_7 = 0.0796$, $C_8 = 260.43$.

experimentally for the alkanes and alcohols. Considering the excess obtained from the model, its value increases for the alkanes, decreases for the aromatics and propanol has the maximum value for the alcohols. From the experimental moments, propanol also has the maximum value. The variation for excess calculated directly from the data for the alkanes may be due to the fewer number of data points available for these solutes compared to those of other families; whereas the value for propanol cannot be explained since the same trend was observed when the excess was calculated from the experimental data.

Solute identification by the use of moments

Fig. 3 is a plot of skew versus excess calculated for each solute from the parameters of eqn. 1. The alkanes vary with a positive slope for increasing carbon number while the aromatics correlate with a positive slope for decreasing carbon number. The corresponding plot for the alcohols cannot be explained since propanol lies to the right of butanol. Also, no correlation is seen in the excess values obtained from the experimental data directly.

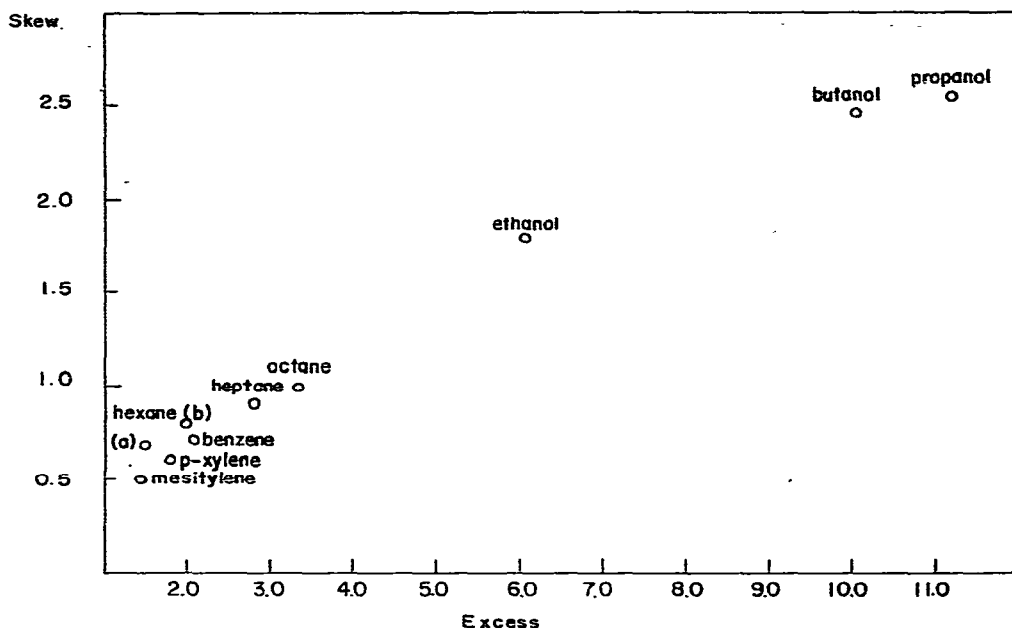


Fig. 3. Skew versus excess calculated from the moments of eqn. 1. The two points for hexane represent the two sets of data obtained from calculations (see text). Error bars are omitted for simplicity. (a) $C_2 = 2.72$, (b) $C_2 = 2.17$.

Due to the reverse correlation of the alkanes and aromatics on the skew versus excess plot, skew versus carbon number was plotted. Fig. 4 illustrates the differences between these two families. Although the trend of these families is in the opposite direction, they lie in a similar region of the plot. The alcohols, which represent a polar homologous series, lie in a region of the plot isolated from the alkanes and aromatics. It is intuitively obvious that the reason for the separation of families is a result of their molecular interactions with the stationary phase, which is a polar one (McReynolds' constants: $x' = 371$, $y' = 639$, $z' = 453$, $u' = 666$ and $s' = 641$, see ref. 29).

The value of the skew of a concentration profile, as previously mentioned, reflects the asymmetry of the peak, thus, as the tailing of the peak increases so does the skew. Considering the family of aromatics, the value of the skew decreases with increasing carbon number, which is not in accordance with an increase of the first moment. This may be indicative of kinetic processes unique to this particular stationary phase-solute system. If this is the case, then the polarity and/or specific family of the solute for a given stationary phase may be approximated. For such a study, a thorough investigation cannot be attempted with the minimal amount of data available at the present time.

Effect of various parameters to the theoretical moments

The use of the eight-parameter model which does not yield analytical expressions for the statistical moments implies that a numerical procedure must be used to

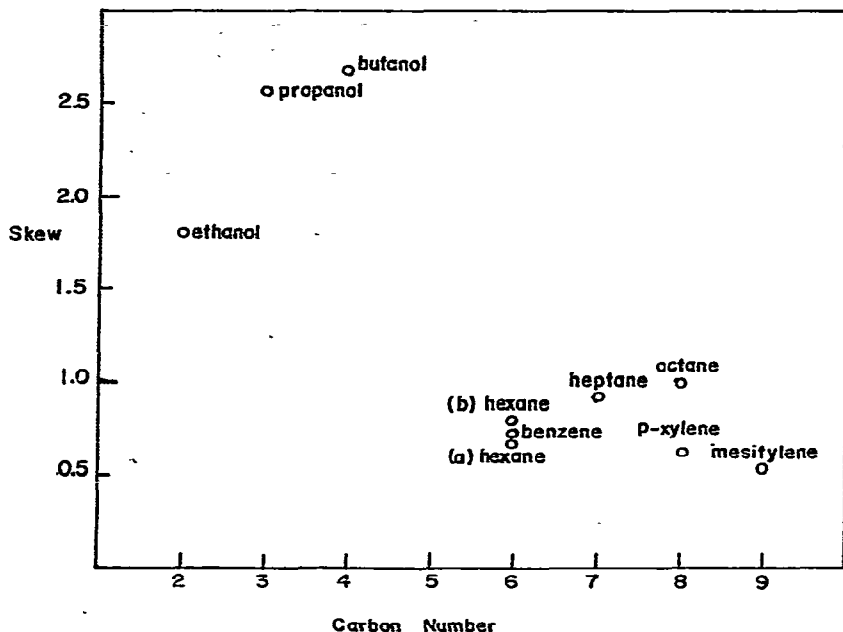


Fig. 4. Skew versus carbon number. The values for skew are taken from Table I calculated via the curve fitting model. For the two points representing hexane: (a) $C_2 = 2.72$, (b) $C_2 = 2.17$ (see text).

determine the dependence of the moments on the various constants. To accomplish this, a select parameter was varied while all of the remaining parameters were held constant for each of the nine solutes. The peak height, C_1 , was not changed since this would only affect the area and not the higher moments.

A $\pm 5\%$ variation in C_2 , the slope of the hyperbolic tangent at its midpoint, C_3 , shows little change in the values of m_1 , μ_2 , skew and excess. Changing C_5 by 10% resulted in a change close to 2% for m_1 , μ_2 , skew and excess. While C_2 and C_5 have little effect on the moments, a small variation in C_7 results in large changes in the magnitude of the moments. By increasing C_7 all of the moments decrease. For example, the second central moment for butanol decreases by 16% when increasing C_7 by 10%, and increases by 21% when decreasing C_7 by 10%. This is an expected result since C_7 , the rate of decay of the exponential, controls the shape of the tail of the peak. For this model, C_7 can be compared to $1/\tau$, where τ is the time constant of the decay, in the exponentially modified Gaussian³⁰; as C_7 ($1/\tau$) increases, the tailing of the peak decreases, and so does its width. The moments obtained from the exponentially modified Gaussian expressions³⁰, which were fitted to the data, are a good approximation of the moments calculated from eqn. 1. This is quite surprising since the exponentially modified Gaussian does not fit our peaks as well as eqn. 1. Incidentally, the first moment of the peaks can be also approximated from eqn. 1 by $C_4 + 1/C_7$ and the second moment by $C_5 + (1/C_7)^2$.

Considering the form of the integrals used to calculate the moments, both from $-\infty$ to C_8 and C_2 to $+\infty$, the moments are proportional to $1/C_2$ and $1/(C_7 + nC_2)$, respectively. If the model was composed of a pure exponential decay

the moments would be proportional to $1/C_7$ (τ). Even though a hyperbolic tangent function is used to join the Gaussian to the exponential decay, the analogy is still valid. Consequently, by altering the height of the decay function, e.g. an increase of C_6 , will correspond to broadening the peak and the tail will become more predominant.

When C_6 was varied between -10% and $+10\%$ of its original value for all of the alcohols, skew and excess decreased. The variation in the skew was approximately 2.5% while for the excess it was closer to 6% . The aromatics behaved in a different manner since the values of skew and excess increased when increasing C_6 from -10% to $+10\%$. For this case, benzene reflected the smallest variation in skew and excess, mesitylene had the largest and *p*-xylene was between these two extremes. Considering the last family, the alkanes, no consistent results were observed. Depending upon the solute, either skew or excess may decrease. If the change in C_6 is restricted to $\pm 10\%$, heptane and octane yield an increase of about 2% in the skew and 1% decrease in the excess. The excess for hexane decreased by 3% while the skew also decreased but was considerably less (ca. 0.5%).

The next parameter investigated was C_3 . An attempt was made to vary C_3 by 1% but due to the nature of the model and its moments, C_3 as well as C_8 , could not be changed independent of the other. Referring to eqn. 21, the moments for the backhalf of the peak are related to C_3 and C_8 exponentially. A re-evaluation of the data showed for the majority of experimental peaks as C_3 increased, so did C_8 and *vice versa*. It was then decided that these two parameters must be changed simultaneously in the same direction approximating the experimental variations as close as possible.

The alkanes all gave an increase in the value of skew when C_3 and C_8 were changed $\pm 5\%$. Heptane and octane showed an increase in their values for excess while a maximum around -2% occurred for hexane. The values for skew and excess increased for all of the aromatics. A maximum was observed near a -4% change in C_3 and C_8 of the skew for all of the alcohols. Propanol and butanol behaved in a similar manner since their values of excess steadily decreased. Ethanol was the unique member in this family.

Fig. 5 shows a plot of skew and excess *versus* a 1% change in C_3 and C_8 simultaneously for ethanol. In this case, both skew and excess have a maximum around -4% . It is important to mention that as C_3 and C_8 increase, μ_2 increases. This is due to the movement of the product of the joining and decay functions simultaneously along the time axis in the positive time direction, which results in broadening the peak. The 1% changes in C_3 and C_8 were close approximations to what was observed experimentally. Also, since the difference between C_8 and C_3 is an exponential function, these parameters had to be varied in such a way that their difference was relatively constant.

The maximum in the skew *versus* C_3 and C_8 plot is due to the fact that the third moment initially increases faster than $\mu^{3/2}$. This is also the case for the excess with respect to μ_4 . For this plot it is evident that a 1% change in C_3 and C_8 can cause vastly different values of the moments for ethanol. This was also observed experimentally. For the experimental ethanol peak, the second moment was the largest for the largest values of C_3 and C_8 . If one desires to use the curve fitting technique to obtain the constants of eqn. 1, care must be taken so that the variations in the parameters from peak to peak are kept minimal.

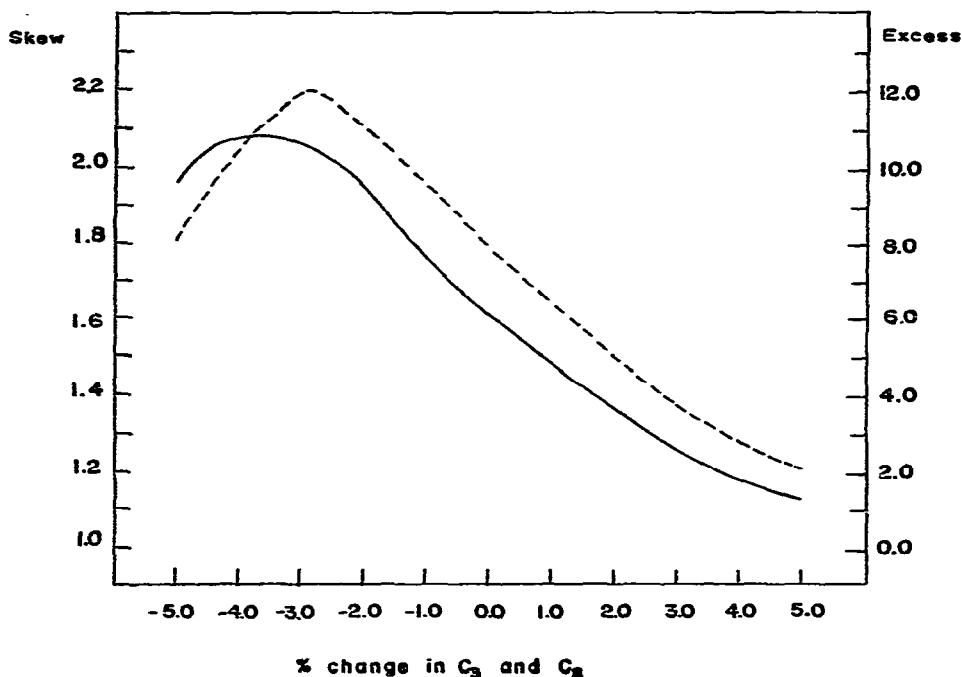


Fig. 5. Skew (---) and excess (—) for ethanol versus percent change in C_3 and C_8 simultaneously. Original values of parameters: $C_3 = 134.43$, $C_8 = 137.20$.

Comparison of the Chesler and Cram equation to the Gram-Charlier series

The Gram-Charlier series, whose coefficients are functions of the central moments of a concentration profile is commonly used with only the first two terms of the summation in eqn. 11. The first two terms are proportional to the skew and excess. If the next term in the series is generated, it is a function of μ_5 and the skew. In the limiting form of the series when the skew and excess are zero (along with the remaining coefficients of the higher terms in the series) only one term, the Gaussian, remains.

A major problem with using the Gram-Charlier series is that at the extremes of the peak there tend to be oscillations. This is illustrated in Fig. 6a for ethanol. The moments used to generate the Gram-Charlier series were taken from the integration of eqn. 1. The height of the simulated peak from eqn. 1, C_1 was taken to be unity. The peaks generated via the Gram-Charlier series were not normalized to unit height. By avoiding the normalization of the peak height, the oscillations at the beginning and end of the profile appear more pronounced. Also, it is easier to detect the shift in the maximum of the peaks. The time scale used is relative to C_4 in eqn. 1.

The peak corresponding to the Gram-Charlier series of three terms in Fig. 6a is much less distorted than the peak calculated using four terms of the series. The next term in the series whose Hermite polynomial will be a function of the odd powers of $t - m_1/\sqrt{\mu_2}$ will probably reduce the oscillating at the beginning of the peak considerably; what will happen at the tail of the peak is not known since the sixth central moment, μ_6 , was not calculated.

Fig. 6b is a set of profiles for mesitylene. It is important to mention that the

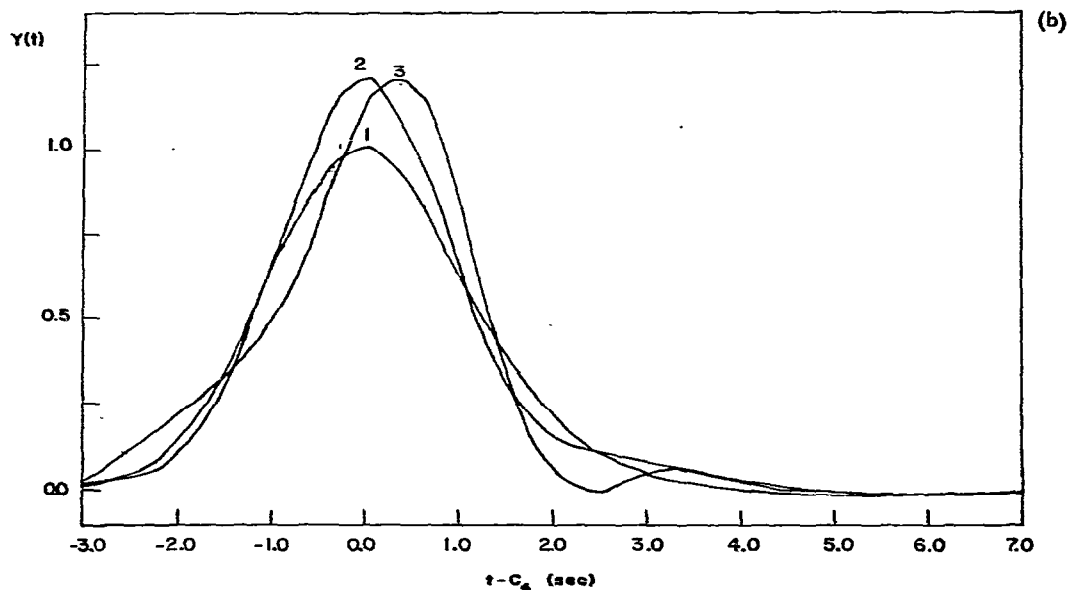
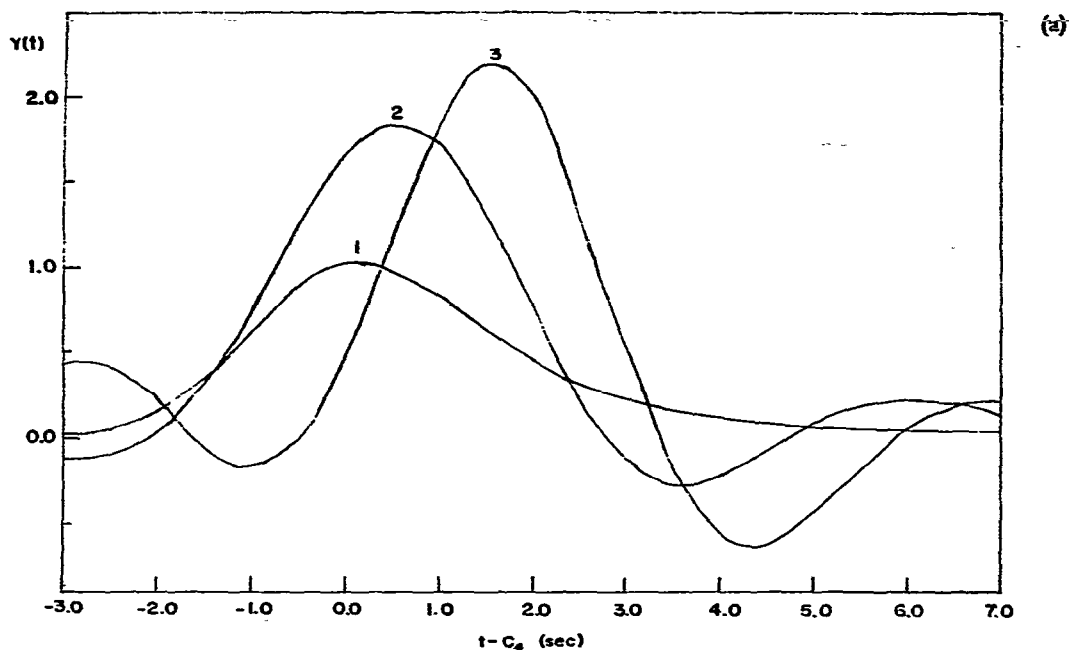


Fig. 6. (a) Various peak shape models for ethanol. (1) Calculated via Cram model $C_2 = 0.739$, $C_3 = 134.43$, $C_4 = 132.65$, $C_5 = 5.48$, $C_6 = 0.334$, $C_7 = 0.209$, $C_8 = 137.20$; (2) Gram-Charlier series using three terms, values of the moments, skew and excess are given in Table I calculated from the theoretical model; (3) Gram-Charlier series using four terms, $\mu_5 = 9.60 \times 10^4 \pm 7.57 \times 10^3$ calculated from theoretical model of Chesler and Cram. (b) Various peak shape models for mesitylene. (1) Cram equation $C_2 = 0.0892$, $C_3 = 792.45$, $C_4 = 770.40$, $C_5 = 171.66$, $C_6 = 0.376$, $C_7 = 0.0818$, $C_8 = 780.56$; (2) Gram-Charlier series using three terms, values of moments taken from Table I calculated from the theoretical model; (3) Gram-Charlier series using four terms, $\mu_5 = 9.44 \times 10^6 \pm 4.67 \times 10^6$, calculated from the theoretical model of Chesler and Cram.

oscillating at the extremes of the peak is not as prominent as it is for ethanol. The excess for mesitylene is 1.67 while for ethanol it is 6.08. As the excess of the peak increases, the tendency to oscillate at the extremes increases. This was also noted in the work of Grubner³¹ using the series with the three terms. There is also a shift in the maximum of the peak toward higher values as the excess increases. The plots in Fig. 6 show the profiles simulated from -3σ to $+7\sigma$. In previous work^{25,31} with this equation the data was plotted to $+3\sigma$, and it is beyond this region that the oscillations occur. On the other hand, the peak generated by the equation of Chesler and Cram²⁶ remains smooth. The oscillations and the need for the higher moments, which are sensitive to noise, make the Gram-Charlier series an undesirable peak shape model.

In general, the use of a curve-fitting model will generate a more consistent set of moments than the calculation of the moments directly from the chromatogram. The limiting factor in this approach is how well the model approximates the experimental peak. For this work the Gram-Charlier series is not a reliable model nor is the exponentially modified Gaussian.

The use of statistical moments from a chromatographic profile can be a viable aid in the identification analysis of an unknown solute. For example, two compounds with values of skew and/or excess that are in close resemblance can be identified by coupling these quantities with the first moment, and the converse holds. Since the moments reflect column processes, they may become valuable in the use of characterizing stationary phases, via the skew.

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REFERENCES

- 1 O. Grubner, *Advan. Chromatogr.*, 6 (1968) 173.
- 2 E. Grushka, *J. Phys. Chem.*, 76 (1972) 2586.
- 3 M. Suzuki and J. M. Smith, *Advan. Chromatogr.*, 13 (1975) 213.
- 4 J. E. Oberholtzer and L. B. Rogers, *Anal. Chem.*, 41 (1969) 1234.
- 5 T. Petitclerc and G. Guiochon, *Chromatographia*, 8 (1975) 185.
- 6 S. N. Chesler and S. P. Cram, *Anal. Chem.*, 43 (1971) 1922.
- 7 T. Petitclerc and G. Guiochon, *J. Chromatogr. Sci.*, 14 (1976) 531.
- 8 J. C. Sternberg, *Advan. Chromatogr.*, 2 (1966) 205.
- 9 O. Grubner, A. Zikánová and M. Rálek, *J. Chromatogr.*, 28 (1967) 209.
- 10 K. Yamaoka and T. Nakagawa, *J. Chromatogr.*, 105 (1975) 225.
- 11 O. Grubner and D. Underhill, *J. Chromatogr.*, 73 (1972) 1.
- 12 E. Kučera, *J. Chromatogr.*, 19 (1965) 237.
- 13 K. Yamaoka and T. Nakagawa, *J. Phys. Chem.*, 79 (1975) 522.
- 14 K. Yamaoka and T. Nakagawa, *J. Phys. Chem.*, 79 (1975) 2515.
- 15 K. Yamaoka and T. Nakagawa, *J. Chromatogr.*, 93 (1974) 1.
- 16 K. Yamaoka and T. Nakagawa, *Anal. Chem.*, 47 (1975) 2050.
- 17 J. E. Funk and P. R. Rony, *Separ. Sci.*, 6 (1971) 365.
- 18 P. R. Rony and J. E. Funk, *Separ. Sci.*, 6 (1971) 383.
- 19 K. De Clerk and T. S. Buys, *J. Chromatogr.*, 63 (1971) 193.
- 20 T. S. Buys and K. De Clerk, *J. Chromatogr.*, 67 (1972) 1.
- 21 T. S. Buys and K. De Clerk, *J. Chromatogr.*, 67 (1972) 13.
- 22 T. S. Buys and K. De Clerk, *Separ. Sci.*, 7 (1972) 441.

- 23 K. Yamaoka and T. Nakagawa, *J. Chromatogr.*, 92 (1974) 213.
- 24 R. V. Mehta, R. L. Merson and B. J. McCoy, *J. Chromatogr.*, 88 (1974) 1.
- 25 D. A. McQuarrie, *J. Chem. Phys.*, 38 (1963) 437.
- 26 S. N. Chesler and S. P. Cram, *Anal. Chem.*, 45 (1973) 1354.
- 27 S. D. Mott and E. Grushka, *J. Chromatogr.*, 126 (1976) 191.
- 28 E. Grushka and P. Schnipelsky, *J. Phys. Chem.*, 78 (1974) 1428.
- 29 R. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
- 30 E. Grushka, *Anal. Chem.*, 44 (1972) 1733.
- 31 O. Grubner, *Anal. Chem.*, 43 (1971) 1934.