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CHROMATOGRAPHIC SOLUTE IDENTIFICATION USING PEAK SHAPE ANALYSIS

SANDRA D. MOTT and ELI GRUSHKA

Department of Chemistry, State University of New York at Buffalo, Buffalo, N.Y. 14214 (U.S.A.)

SUMMARY

Solute identification by retention data alone does not yield a positive identification for two or more solutes with approximately the same retention times. In such cases, two columns with two different stationary phases are needed for solute verification. For this reason, the concentration profiles of gas chromatographic peaks have been studied using the empirically derived eight-parameter model of Chesler and Cram. A non-linear least squares fit of the data to this model has made it possible to derive parameters which allow homologous class recognition and specific solute identification. Two methods for determining the initial estimates are presented. In one method the initial estimates were calculated from the data in a purely empirical manner, while the other is based mathematically on the model. The fitted values of the parameters from the two methods are compared for the purpose of illustrating the dependence of the fit on the choice of initial estimates. Some of the parameters are believed to have physical significance. For example, an almost linear relationship between one of the fitted parameters, C_2, and the diffusion coefficient, D_{AB}, of the solute in the carrier gas was found. Similar results were found for C_7 *versus* D_{AB}, the capacity ratio k' and C_2, and $k'/(1 + k')^2$ and C_2.

INTRODUCTION

The qualitative analysis of gas chromatographic peaks can be obtained from retention data. Such data are reported in terms of the Kováts indices[1], the Rohrschneider constants[2], etc. This approach works quite well[3] provided that there is enough of a difference between the retention data of the standards. If there can be no positive identification made for the specified column conditions from which the retention data are obtained, the stationary phase or temperature must be changed and the analyses re-evaluated[4].

Various port and pre-column devices have been utilized for solute identification (*cf.* ref. 3). While these devices are extremely useful, it is of basic interest to examine the relationship between the eluted peak shape and its nature, since this might also lead to a better understanding of column processes.

One approach to the identification procedure involves the use of moments and their derived parameters, skew and excess[5–10]. The correlation between skew and ex-

cess for various homologous families does not yield a positive identification of a solute according to its family, since there is a pronounced overlap for certain families[5]. Since moment analysis is very sensitive to noise, the use of the higher moments (*e.g.*, skew and excess) amplifies this noise[8] and the accuracy of this technique diminishes.

Slope analysis[5,7] may be employed by the use of second derivative plots as in the case of double peak recognition. This method is tedious as far as the mathematics are concerned but much simpler than moment analysis.

Curve fitting of the data to some predetermined model is still another alternative. For the application of this method, a mathematical model must be assumed. Throughout the literature various functions have been used such as the Poisson distribution[11], Bessel function[11], Gaussian[12,13], bi-Gaussian[12], exponentially modified Gaussian[5], a linear combination of the Cauchy function with a Gaussian[13], quadratic at the data closest to the maximum of the peak[14], Edgeworth series[12], Gram-Charlier series[9], a Gaussian with a triangular joining function to an exponentially weighted tail[8,10], and a Gaussian convoluted with a hyperbolic tangent joining function to an exponential decay[15]. The last function proposed is very similar in structure to the empirical equation developed by Gutknecht and Perone[16] for their work in polarography.

The models used for the description of chromatographic profiles have generally been based on phenomena associated with the chromatographic interactions of the solute[10,11]. Many of these functions assume a Gaussian leading edge from which valuable chromatographic data are readily obtainable. The shape of the tail of the peak presents the major problem that arises in the selection of a model for curve fitting analysis.

Sternberg[10] discusses the various parameters that affect the shape of the peak. These include the input function (sample injection), detector delay, and peak spreading in the connectors and tubing, as well as adsorption–desorption kinetics and diffusion in the carrier gas[11]. He proposes an approximation of the actual peak shape by Gaussian, triangular, and exponential portions. The "mirroring" of the front half of the peak to the back and compensating for the difference with his joining function is in close resemblance to the model suggested by Chesler and Cram[15]. In the latter instance, the hyperbolic tangent function joins smoothly with the Gaussian and decay portions.

Macnaughton *et al.*[17] monitored the shape of high-precision gas chromatographic peaks during principle component analysis of a homologous series, whereby changes in the chromatographic system were detectable along with sample composition. Anderson *et al.*[18] used computer analysis for resolving non-Gaussian peaks using a curve fitting procedure. They emphasize that it is known that the shape of the peak is a function of its position in the chromatogram, and sometimes due to its molecular structure if there is adsorption. As will be discussed in this work, it is the molecular structure that plays the more important role of the two, and the curve fitting procedure employed is feasible for qualitative analysis.

It was the aim of this study to determine the feasibility of classifying graphic peaks using the parameters of the function of Chesler and Cram[15] for three homologous families. It was thought that some of the parameters in the equation are characteristic of the solutes. Also, it is of interest to examine and see if functions such as suggested by Chesler and Cram can have physical significance. That is, if the parameters of the equation are a reflection of the column processes.

EXPERIMENTAL

Apparatus

The apparatus used for this work was similar to that used by Grushka and Maynard[19] and Grushka and Schnipelsky[20]. The column used was 200 cm in length and 0.64 cm O.D. The column packing consisted of Carbowax 1540 on Chromosorb W-AW-DMCS 80–100 mesh. The data were collected on paper tape, as described by Grushka and Schnipelsky[20], and converted to cards. All programs were run on a CDC 6400 computer.

Procedure

Three solutes from each of three homologous series were introduced individually to the chromatograph via a Seiscor Model VIII injection valve (Seiscor, Tulsa, Okla., U.S.A.). The oven temperature was maintained at 60°, except for one study, where the temperature was 80°. The carrier velocity was kept at 10 cm/sec.

All of the solutes were obtained from various vendors and were of reagent grade.

THEORY

The function used in the curve fitting procedure is the eight-parameter function suggested by Chesler and Cram[15]. This model can be expressed as follows:

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

where

$Y(t)$ = value of the function at time t
C_1 = maximum of the peak
C_2 = slope of the hyperbolic tangent
C_3 = midpoint of the hyperbolic tangent
C_4 = position of the peak maximum
C_5 = variance of the peak at 0.61 of C_1
C_6 = ratio of the height of the exponential decay to C_1 at $t = C_8$
C_7 = rate of decay of the exponential
C_8 = position where the decay function originates.

The first term in the equation is the Gaussian which defines the front part of the peak. The remaining two terms are the hyperbolic tangent joining and exponential decay functions. As an approximating fucntion, more flexibility is allowed, due to the increased number of parameters that control the shape of the peak as opposed to other models, for example, the exponentially modified Gaussian[7,21]. Also these parameters, or a combination of such, may contain other chromatographic information.

The leading edge of the peak is assumed to be Gaussian from which estimates of C_1, C_4, and C_5 can be obtained directly from the digitized data. For the remaining parameters, C_2, C_3, C_6, C_7, and C_8, it is imperative that these values be estimated systematically from peak to peak to avoid any fluctuations in the fitted values. The al-

gorithm used for evaluating the initial estimates from the digitized data is straightforward and can be done within the computer program. It was found that the estimates for C_2, C_3, and C_8 are all directly related to τ, defined as the skewness factor by Roberts et al.[21]. This constant τ is evaluated by the difference between the width of the peak at $1/4$ C_1 on the tailing edge and the width of the peak at $1/2$ C_1 on the leading edge. Estimates for C_2 can be obtained from $(\tau)^{-\frac{1}{2}}$, but for cases where τ is small (less than 1.0) the estimate for C_2 is determined as $(\tau)^{-1}$. C_2 indicates the broadness or asymmetry of the peak; thus as τ increases, the estimate for C_2 decreases with increasing asymmetry. Estimated values for C_3 and C_8 are evaluated as $C_4 + \tau$ and $C_4 + 2\tau$, respectively. In this case, as τ increases C_3 and C_8 occur further from the peak maximum than for a peak with a small value of τ. The height ratio of the exponential decay C_6 is determined by the value of the data at approximately C_8 divided by the peak height. Likewise for C_7, the slope of the curve is calculated between C_8 and the next data point, divided by the peak height, since the decay function is assumed predominant at this point.

An alternative method was derived for the evaluation of the initial estimates. In this case the front half of the peak was subtracted from the back half. The remaining data resembled another peak which will be referred to as the difference peak. From this difference peak C_2, C_3, C_6, C_7, and C_8 are estimated.

The midpoint of the hyperbolic tangent function, i.e., C_3, is taken as the position of greatest slope of the increasing portion on the difference peak, while C_2 is this slope divided by the original peak height, C_1. Assuming that $C_8 \geqslant C_3$, C_6 is estimated as

$$C_6 \approx 2\, Y_d/C_1 \tag{2}$$

where Y_d is the value of the difference peak at the estimated value of C_3. The rate of the exponential decay C_7 is estimated by selecting two points along the tail of the difference peak such that the joining function would be approximately unity and the only function with significant influence would be the decay function. Thus, C_7 is calculated as

$$C_7 \approx \frac{\ln \dfrac{Y_{d1}}{Y_{d2}}}{t_2 - t_1} \tag{3}$$

where Y_{d1} and Y_{d2} are taken from the tail of the difference peak with t_1 and t_2 as their corresponding time values. The starting position of the exponential can be estimated by calculating C_8 at some point on the tail of either the difference peak or the main peak, far removed from C_3 such that the hyperbolic tangent is unity. Thus,

$$C_8 \approx t + \frac{1}{C_7} \ln \left(\frac{Y}{C_1 C_6} \right) \tag{4}$$

where t is the corresponding time of the data point Y.

It is interesting to note that the product of the joining function and exponential decay passes through a maximum which is not necessarily at $t = C_8$ as previously re-

ported[15]. Assuming that the maximum occurs at $t \geqslant C_8$, after differentiation of the remaining terms in eqn. 1, the position of the maximum can be evaluated at

$$t = C_3 + \frac{1}{2C_2} \ln \left[\frac{C_2}{C_7} + \sqrt{\left(\frac{C_2{}^2}{C_7{}^2} + 1 \right)} \right] \tag{5}$$

Since C_2 and C_7 are always greater than zero, the argument of the natural logarithm function is positive, thus only real values will exist for the position of the maximum. If the value of C_2 was to tend to infinity, i.e., for a very symmetrical peak, the second term would diminish to zero and the maximum would be very close to C_3, if C_3 were to exist at all.

Applying a mathematical model to a physical system necessitates the implementation of constraints in the curve fitting program. One of the most crucial constraints is that none of the parameters are allowed to become negative. If they do, then the physical significance of the model will be lost. To alleviate this problem eqn. 1 was modified and supplied to the program in the following manner[22]

$$Y(t) = C_1^2 \left\{ \exp \left[\frac{[(t - C_{4*}^2)]^2}{2C_{5*}^2} \right] + \left[1 - 0.5 \left(1 - \tanh \left[C_{2*}^2 (t - C_{3*}^2) \right] \right) \right] \cdot C_{6*}^2 \exp \left[- 0.5 C_{7*}^2 \left(|t - C_{8*}^2| + t - C_{8*}^2 \right) \right] \right\} \tag{6}$$

where C_{1*}, C_{2*}, C_{3*}, C_{4*}, C_{5*}, C_{6*}, C_{7*}, and C_{8*} correspond to the square root of their respective parameters in the original equation. This revision of the equation allows the parameters to become negative during the iterative processes, but when substituted in the equation itself they are squared, thus resulting in positive values. It should also be noted that the modified form of the equation does not require any special software for checking the values of the parameters between iterations. Another constraint is that for the method to be internally consistent within a given set of experimental data, the same method of initial estimates must be utilized throughout, as well as the manner in which it is fitted.

By the application of the aforementioned modifications, it is possible to fit experimental data to the given model with the chances of false convergence being minimized. The method by which the data are supplied to the curve fitting program is entirely up to the user. The data can be fitted in two parts. The front part of the peak up to the peak maximum is fitted to the Gaussian portion of the equation, while the remaining part is fitted to the entire model, using the values of C_1, C_4, and C_5 from the first fitting and keeping them constant. Another alternative is to follow the above method and then proceed by fitting the entire set of data to the complete model using the values from the previous fits as initial estimates. Finally, one can follow the method used by Chesler and Cram[15], where the entire set of data is fit to the model holding C_1, C_4, and C_5 constant while the other parameters are being fitted. The choice of the method to fit the data should be consistent for a particular analysis.

The program for the non-linear least squares curve fitting used in this study, NLIN2, was written at E. I. du Pont de Nemours Company and modified by the computing center at this university[22]. The algorithm this routine was written from was developed by Marquardt[23]. It combines the Taylor series method with the method of steepest descent to interpolate the estimates of the parameters for a non-linear function.

RESULTS AND DISCUSSION

Qualitative analysis

The study of peak shapes via the non-linear least squares curve fitting technique was first investigated by visually estimating the parameters C_2, C_3, C_6, C_7, and C_8. This technique was not satisfactory because the parameters for different runs of the same solute did not converge consistently. With this problem a systematic method of initial estimates had to be followed for the duration of the study. The simplest method to implement was the empirical, τ based estimates. All of the data yielded parameters that were consistent, with the exception of hexane, as will be discussed shortly.

To test the validity of the model for symmetric profiles, a Gaussian peak was simulated by the computer, and was fitted to eqn. 6 by estimating the parameters according to the τ method. The values used for generating the Gaussian peak were: $C_1 = 100$, $C_4 = 1.50$, and $C_5 = 2.25$. Estimates for the eight parameters and their final fitted values are given in Table I. The least square fit was excellent: the "goodness" of the fit, Φ (sum of the squares of the residuals), was 7.2×10^{-18} for the front of the peak and 5.9×10^{-18} for the fitting of the back half to the entire equation.

As illustrated by Table I, the most significant parameter that caused such a good fit of the data is C_6. If C_6 is zero, the product of the joining function and exponential decay is also zero, resulting in a pure Gaussian peak. It was expected that C_2, since it controls the broadening of the peak, would tend to infinity, while C_3 and C_8 would approach C_4 for the Gaussian profile. As seen in Table I this did not occur. A possible explanation might lie in the nature of the model and in the fact that it has adjustable parameters. Nevertheless, it will be shown that useful information can be obtained from the procedure used.

TABLE I

LEAST SQUARES FIT OF A GAUSSIAN PEAK TO THE PROPOSED EQUATION BY CHESLER AND CRAM

Parameter	Initial estimate	Fitted value
C_1	100.0	100.0
C_2	1.11	0.973
C_3	5.40	9.88
C_4	4.50	4.50
C_5	1.82	2.25
C_6	0.430	3.93×10^{-8}
C_7	0.362	1.77
C_8	6.30	5.02

If one is to study carefully the model proposed by Chesler and Cram, the parameters that control the shape of the tail, C_2, C_3, C_6, C_7, and C_8, must be fully understood. Supposing a peak has a characteristically long tail, it should be intuitive that this implies a small value (<0.5) of C_2, a large value of C_6 (>0.5), a small value of C_7 (≈ 0.1), and that C_3 and C_8 have values that are far removed from the actual peak maximum. C_2 is extremely important, since it controls the broadness of the peak. Defining two new parameters, C_3' and C_8' as the distance C_3 and C_8 occur from C_4, respectively, the broadness of any peak may be studied in more detail. It is on the ratio

of these differences, C_3'/C_8', as well as on C_2 and C_7, that the identification process will be based.

The data given in Table II show the results of fitting chromatographic peaks to eqn. 6 for three homologous families. The values of the parameters show consistency within a given family. All of the peaks were fitted in exactly the same manner, i.e., using the τ method of initial estimates and fitting first the front half of the peak to a Gaussian, then the remaining data to the entire equation using the values of C_1, C_4, and C_5 from the first fit. The precision of the data is quite good for most of the parameters. Hexane presented a special case. For a sample of over ten hexane peaks, fluctuations of the fitted parameters were very predominant. This was most noticeable for C_2. An explanation for this is the fact that the τ estimates varied between 0.40, 0.45, and 0.50 sec. Due to the 0.05 recorder digitization rate, and a very limited amount of data available for the narrow hexane peaks, this variation in τ was shown to be highly significant. Values of C_2 for hexane could be grouped into three categories: 4.31 ($\tau =$ 0.50 and 0.45), 2.72 ($\tau = 0.40$), and 2.17 ($\tau = 0.40$). The value of $C_2 = 4.31$ was eliminated by the use of eqn. 5 and locating the position of the maximum of the difference peak. Because of the experimental error involved in digitized data, the remaining values of C_2 were averaged and used for the identification analysis.

TABLE II

VALUES OF THE FITTED PARAMETERS FOR THREE HOMOLOGOUS FAMILIES PLUS STANDARD DEVIATIONS

Solute	C_2	C_3	C_4	C_5	C_6	C_7	C_8
n-Hexane	2.40	27.35	26.73	0.203	0.649	2.16	27.29
	± 0.30	± 0.06	± 0.01	± 0.0004	± 0.271	± 0.11	± 0.15
n-Heptane	1.68	33.32	32.14	0.537	0.425	1.18	32.81
	± 0.06	± 0.05	± 0.05	± 0.001	± 0.019	± 0.04	± 0.04
n-Octane	1.11	51.52	49.84	1.314	0.410	0.698	50.73
	± 0.01	± 0.02	± 0.03	± 0.003	± 0.001	± 0.012	± 0.02
Benzene	0.434	129.95	125.10	7.725	0.391	0.348	127.49
	± 0.007	± 0.10	± 0.89	± 0.022	± 0.007	± 0.001	± 0.09
p-Xylene	0.168	400.99	388.88	52.99	0.364	0.137	394.35
	± 0.002	± 0.46	± 0.16	± 0.14	± 0.013	± 0.004	± 0.33
Mesitylene	0.0892	729.45	770.40	171.66	0.376	0.0818	780.56
	± 0.0029	± 1.38	± 0.45	± 1.34	± 0.090	± 0.0104	± 0.49
Ethanol	0.739	134.43	132.65	5.480	0.334	0.209	137.20
	± 0.003	± 0.08	± 0.05	± 0.043	± 0.007	± 0.003	± 0.10
n-Propanol	0.391	256.00	252.50	21.75	0.194	0.0779	260.49
	± 0.002	± 0.18	± 0.08	± 0.16	± 0.004	± 0.0019	± 0.09
n-Butanol	0.196	515.55	508.24	75.34	0.227	0.039	524.66
	± 0.004	± 0.20	± 0.14	± 0.64	± 0.004	± 0.0005	± 0.25

For the identification procedure it was assumed that C_2 and C_3'/C_8' would be most beneficial. Fig. 1 shows the relationship between C_3'/C_8' and C_2. The three families studied here are grouped together in different regions on the plot. If one had two peaks of approximately the same retention time (C_4) (consider ethanol and benzene), normally the column conditions must be changed (stationary phase, temperature, etc.) to distinguish between these two solutes. With the use of the C_3'/C_8'
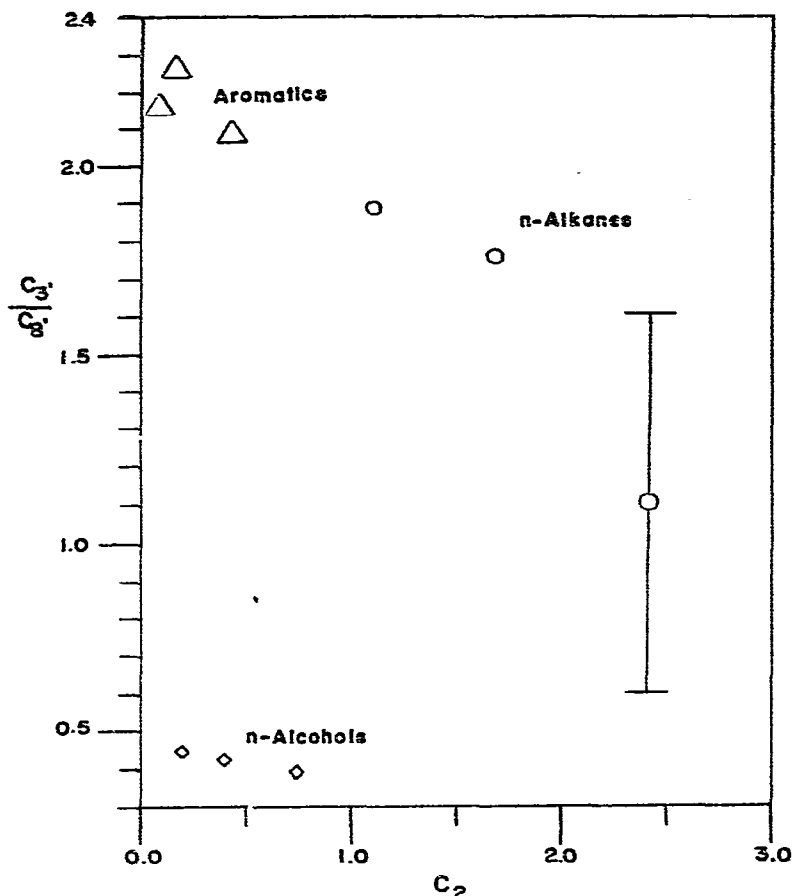
Fig. 1. C_3'/C_6' versus C_2 for three homologous families. Column temperature, 60°; carrier velocity, 10 cm/sec. The vertical bar represents the extremely large deviation for hexane in C_3'/C_8'. All other deviations are included.

versus C_2 plot, one can readily distinguish between different solutes. Conversely, if two solutes have either the same C_3'/C_8' or C_2 value their retention times, most likely, would be different. Thus using the parameters in Fig. 1 and C_4 qualitative identification can be made. Similar results can be seen in Fig. 2. In this plot of C_3'/C_8' versus C_7 the solutes are grouped into families in a comparable fashion to Fig. 1. This can be taken to imply that even though the value of C_4 increases within a given family, the characteristics of the shape of the peak exhibited by the tail are consistent within that family.

The second method of initial estimates was used as the next step to study the dependence of initial estimates on convergence. It was found that this method breaks down for symmetrical peaks and for profiles due to overloaded columns. The reason for this is that the difference peak calculated is very sensitive to noise and is negative for the most part, therefore making initial estimation virtually impossible. This was
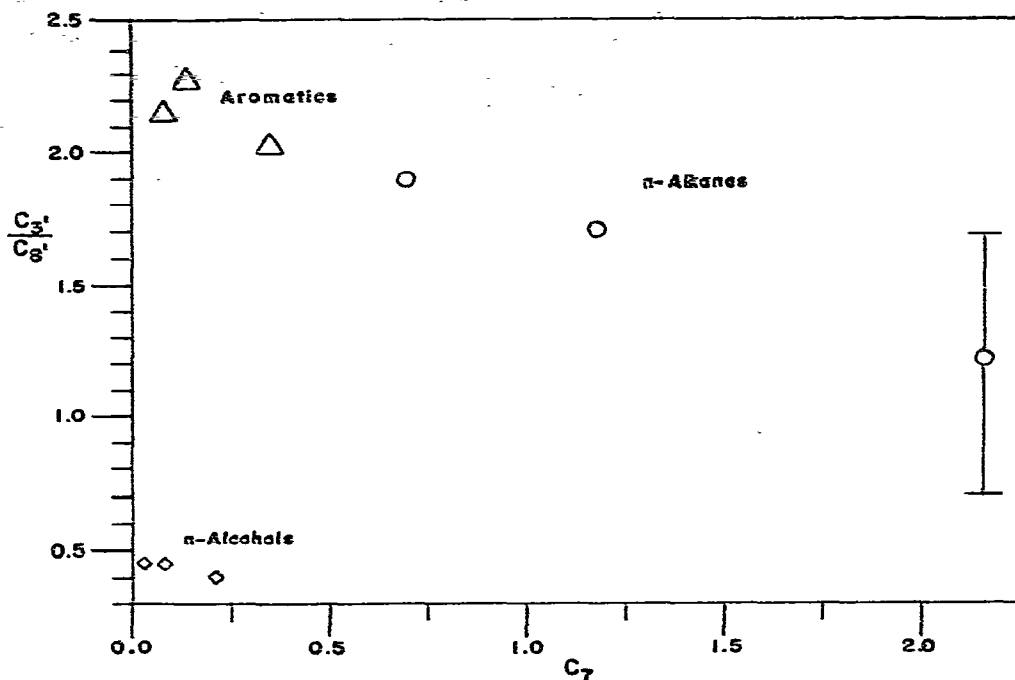
Fig. 2. C_3'/C_8' versus C_7 for three homologous families. Column temperature, 60°; carrier velocity, 10 cm/sec. The vertical bar presents the extremely large deviation in C_3'/C_8' for hexane.

the case for some of the solutes analyzed. Various conditions of column overloading are presently being studied in more detail. As an added note of interest, the τ method of estimates is not as sensitive to column overloading, and this may be the more versatile of the two methods of estimation.

Preliminary studies at 80° seem to indicate that the present method of solute identification is still valid. The dependence of the method on various operating conditions is now being studied.

It should be emphasized that the present study was done with individual solutes. In reality, the chromatogram can be quite complex and complete resolution of the various solute might not be complete. In such cases, the identification procedure is not as clear cut. However, for process control purposes, this method in conjunction with calibration curves, can be quite useful. While ancillary equipment such as a mass spectrometer is extremely beneficial, the peak shape allows solute identification with relative ease.

Relation of parameters to chromatographic data

The parameter C_2, as discussed previously, controls the broadness of the back portion of the peak which may contain valuable chromatographic information. Similarly, the parameters C_3'/C_8' and C_7, also used for the qualitative analysis study, were thought to contain such data. By examination of the processes that occur within the column and correlating them with various parameters of the equation of Chesler and Cram, much more information may be readily obtainable by the chromatographer.
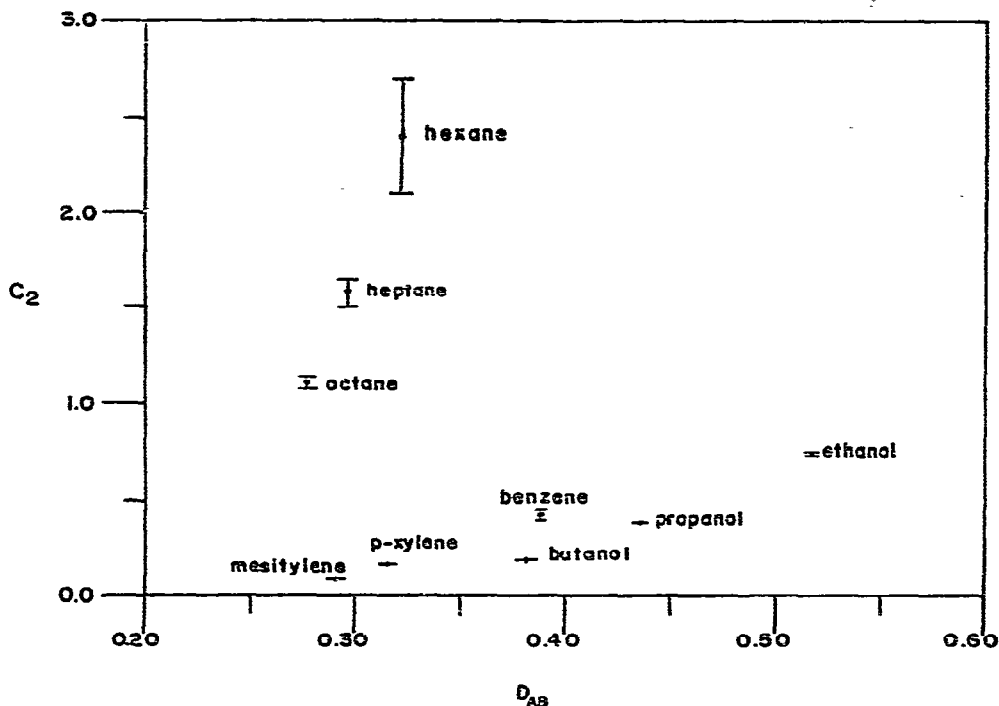
Fig. 3. Relationship between C_2 and the diffusion coefficients of the solutes in helium. The vertical bars indicate the standard deviation in C_2. The horizontal bars indicate that the errors involved were so small that they could not be shown on this scale.

The first process investigated was the diffusion of the solute in the mobile phase. If diffusion was to play an important role in the shape of the profile, it should be reflected in the various parameters. Fig. 3 shows a plot of C_2 versus D_{AB}, the diffusion coefficient of the solute in helium at 60°, calculated from the equation of Fuller et al.[24]. All of the solutes seem to be reflecting the same behavior according to their family, namely, an almost linear dependence of C_2 on the diffusion coefficient D_{AB} exists. If indeed this is the case, such graphs could be used to estimate diffusion coefficients with relative ease. This is an exciting extension of the fitting procedure. The trend that occurs when plotting C_7 versus D_{AB} (Fig. 4) is not as linear, but again a reasonable estimate of D_{AB} may still be possible to obtain. It is interesting to note that for the $C_3'/C_8'-D_{AB}$ coordinate system (Fig. 5) the aromatics retained the configuration that they had exhibited in the $C_3'/C_8'-C_2$ coordinate system. Figs. 3–5 seem to imply that the diffusion in the mobile phase plays a singificant role in the shape of the profile. A more extensive study into the dependence of C_2, C_7, C_8, and C_3 on D_{AB} is now being carried out in this laboratory.

The next chromatographic parameter that was examined was the capacity ratio k'. Since this parameter reflects the amount of the solute in the stationary and mobile phases, it is characteristic of the solute for a given combination of stationary
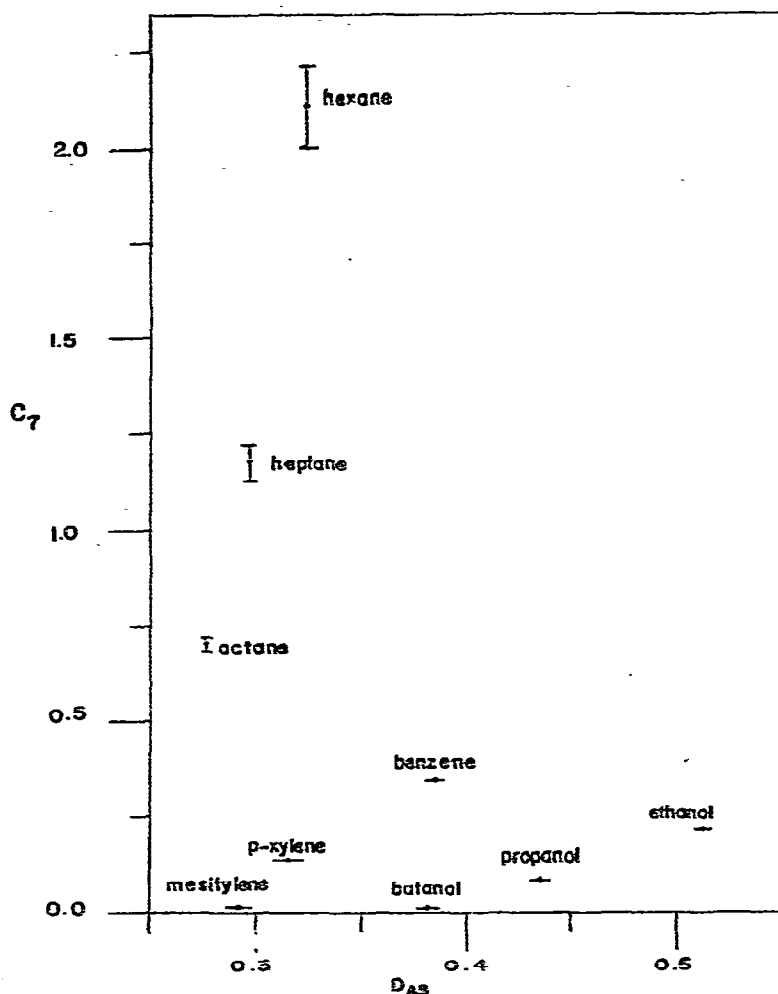
Fig. 4. Relationship between C_7 and D_{AB} of the solutes in helium. The vertical bars indicate the standard deviation in C_7. The horizontal bars denote small errors that could not be shown to scale.

and mobile phases. In Fig. 6, a plot of k' *versus* C_2 illustrates the relationship between these two parameters. As the size of the molecule increases within a given family, its capacity ratio increases as C_2 decreases. This was found to be the case for the three families studied. It was this relationship that prompted the correlation of C_2 to the resistance to mass transfer in the stationary phase.

The dependence of the resistance to mass transfer in the stationary phase on the capacity ratio is via the term $k'/(1 + k')^2$ (ref. 11). By plotting C_2 against this term (Fig. 7), it is shown that, again, nearly a linear relationship exists for a specific family. It is of interest to note that while the aromatics and alcohols correlate with a positive slope, the alkanes follow a negative slope. This can be explained by virtue of the fact that the capacity ratios for the alkanes range from 0.3–1.5 while the remaining families have k' values with a minimum of 5.2. It is well known that the resistance to mass
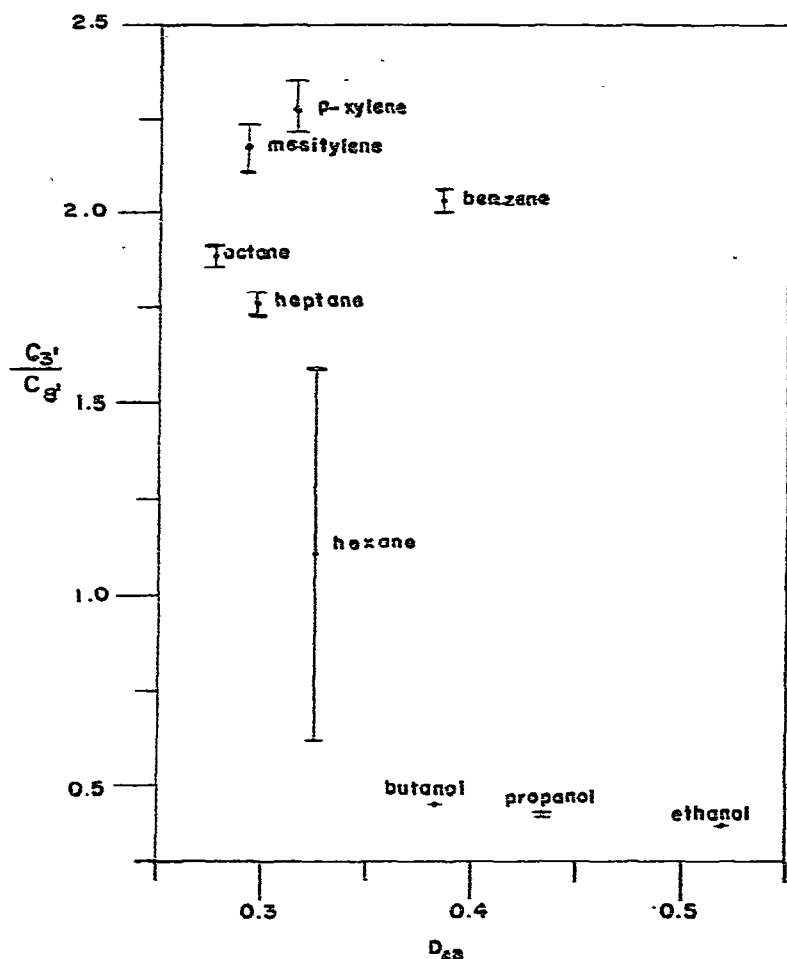
Fig. 5. Relationship between C_3'/C_8' and D_{AB} of the solutes. The vertical bars indicate the standard deviation in C_3'/C_8'. The errors denoted by the horizontal bars were too small to be drawn on this scale.

transfer in the stationary phase shows a maximum at $k' = 1$. Thus it is possible that C_2 is related to the plate height. Further work is being done to test the validity of the correlation of C_2 to the resistance to mass transfer term. If a definite correlation can be established, then rates of adsorption–desorption, diffusivity of the solute in the stationary phase, and the thickness of the film of stationary phase on the solid support may become easily evaluated v_: C_2 and other parameters of the equation of Chesler and Cram. Similarly, surface activity coefficients and other related thermodynamic data[25] may be correlated to these parameters.

In summary, the use of the mathematical model proposed by Chesler and Cram for non-linear least squares curve fitting can allow the identification of two solutes with approximately the same retention times without alteration of the column conditions. Also, the relation of these fitted parameters to the physical processes associ-
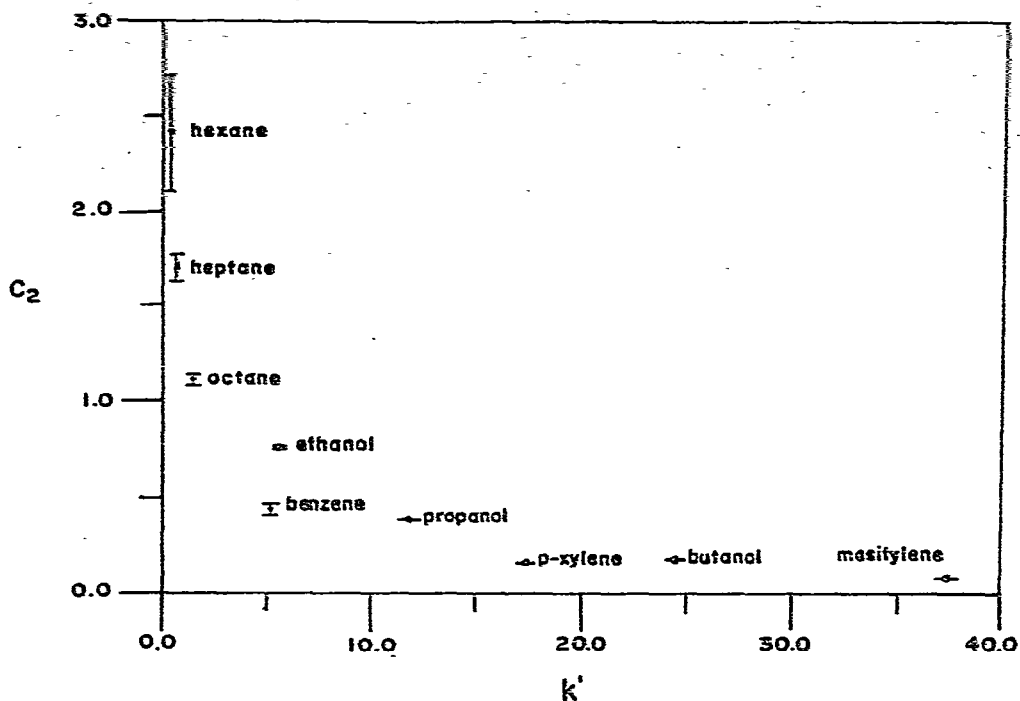
Fig. 6. Relationship between C_2 and the capacity ratio, k', of the solutes. The vertical bars indicate that the errors involved could not be shown on this scale.
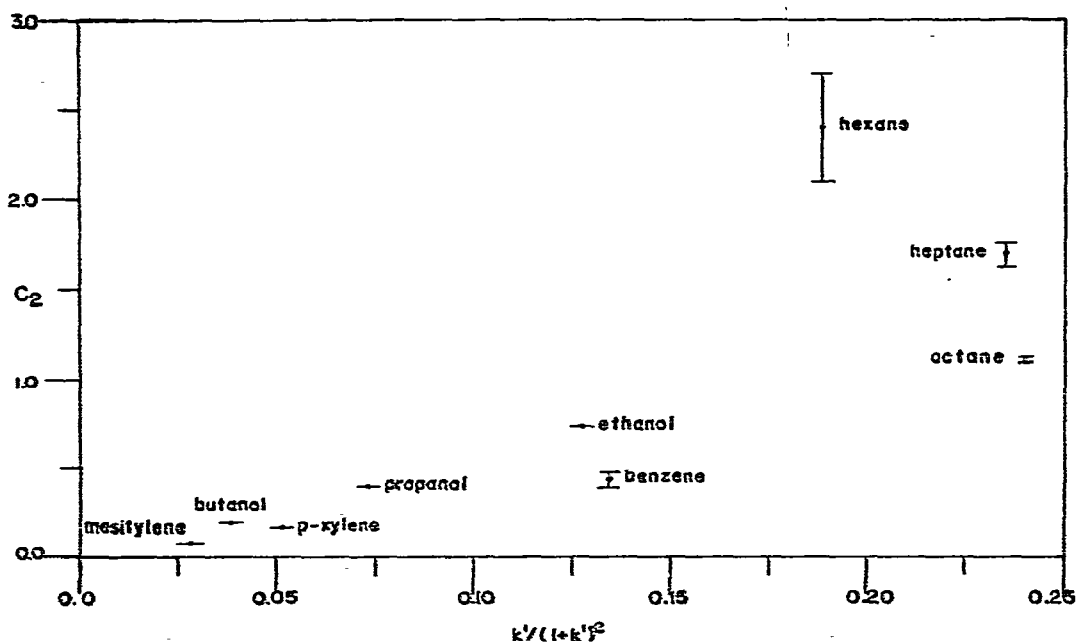

Fig. 7. Relationship between C_2 and $k'/(1 + k')^2$ for the various solutes. The vertical bars indicate the standard deviation in C_2. All horizontal bars indicate an error too small to be shown on this scale.

ated with the chromatographic analysis may produce a deeper insight into column processes. For both qualitative analysis and relating the parameters to chromatographic data, this method is much simpler and easier to use than the previous method of moment analysis. By expanding this study to various other families and column conditions, it is the goal of the authors to provide sufficient physical data for the support of the empirical model employed in this work.

ACKNOWLEDGEMENT

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