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INSTRUMENTAL CONTRIBUTIONS TO BAND BROADENING IN GAS CHROMATOGRAPHY

I. DEVELOPMENT OF A MODEL

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SUMMARY

The principles of superposition of the first and second moments are applied to a model gas chromatographic system in order to develop the equations necessary to describe the instrumental contributions to band broadening. The total first moment is obtained from an equation which gives a straight line when the pressure drop across a capillary column is small. The expression for the time-based second moment is given by a hyperbola with an inverse dependence on the carrier gas flow-rate. For the volume-based second moment, the hyperbolic equation predicts a direct dependence on the carrier gas flow-rate. For systems in which the mixing volumes and the detector-electrometer time constants are small, the equations are linearized to give the same slopes as the asymptotes of the hyperbola and nearly the same intercepts.

INTRODUCTION

Resolution on chromatographic columns is basically concerned with the width of the solute band, and the achievement of a differential rate of migration. Fundamental band-broadening processes in chromatographic columns have been reviewed¹ and treated theoretically by a number of workers^{2,3} and several models for these phenomena exist. Numerous studies in the literature have reported experimental measurements of the column band-broadening processes⁴ such as axial diffusion⁵. Knox and Salcem⁶ reported the independent contributions to the plate height from processes occurring in the mobile and stationary phases.

However, relatively little attention has been given to non-column or instrumental band-broadening processes. Instrumental band-broadening may be minimized through good experimental technique, although the measurement of the magnitude of these effects has not been previously reported. For high precision and accuracy in experimental gas chromatography (GC) these effects should be measured and taken

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into account. Their relative importance will be significantly increased in high-resolution GC. Therefore, this work is directed toward the examination of the effect of the experimental system on chromatographic measurements. Expressions are derived for these band-broadening effects in terms of the instrumental contributions to the observed first and second statistical moments.

Gel permeation chromatography (GPC) is an excellent example of the necessity of correcting for instrumental band-broadening effects in determining molecular weight averages. Various mathematical approaches have been used which treat the instrumental spreading function as a Gaussian operator⁷ and others have corrected for skewing⁸⁻¹⁰ and axial dispersion effects¹¹.

Sternberg's¹² statistical moment approach to instrumental band-broadening and peak shape analysis is the most comprehensive treatment of the topic which has appeared. While he does not develop the experimental verification of the methods for distinguishing the contributions of different broadening sources, the approach is sufficiently sound theoretically to be independent of the particular experiment.

As early as 1957, Giddings¹³ showed that the basic GC peak shape should be Gaussian when operating in the linear part of the distribution isotherm for a δ function input sample profile. Subsequently, the output response function for finite input sample volumes was calculated by Laplace transform techniques¹⁴ and by considering the input as a series of δ functions¹⁵. The concept of an equivalent Gaussian sample inlet profile was proposed in order to simplify the description of the column operators on the response curves¹⁶. Jacob and Guiochon¹⁷ extended the theory of GC at finite concentrations to the phenomena occurring during injection. Their work shows that the mobile phase velocity is changed while the sample is in the injection zone and secondly, treats the discontinuities associated with rectangular injection profiles. High-precision sampling methods have been developed for the work reported here in order to give sample input functions of well defined shape which could be treated mathematically^{18,19}.

Maynard and Grushka²⁰ reported a systematic experimental study of the effect of dead volume on the efficiency of a GC system. Their results showed that for GC, pre-column dead volume can be a greater contribution to the height equivalent to a theoretical plate (HETP) than post-column dead volume. Solutes with small capacity ratios (k') were shown to be more sensitive to dead volumes in the system than those with higher retention, while the effect of connecting tubing depended on the plate number generated internally. Other workers have evaluated the effects of mixing devices²¹ and turbulent flow²². Sternberg¹² differentiates between diffusion chamber and mixing chamber behavior and has proposed a new band-broadening mechanism based on laminar flow.

The influence of the geometry and volume of chromatographic detectors has been studied by a number of investigators for the thermal conductivity detector because its response time effects are larger than ionization detectors and therefore more easily measured²³.

The effects of the transducers and read-out devices may be readily calculated. The servo recorder and analog-to-digital converter (ADC) cannot be treated as linear systems and are not treated in this work. The recorder becomes a non-linear element when its maximum slewing rate is exceeded, when its zero does not match that of the preceding equipment, or when its full scale deflection is exceeded²⁴. The band-

broadening contribution of the ADC cannot be considered to be limiting with any reasonable sampling rate and a digital data logger for this purpose has been previously described²⁵. The relative errors in band-broadening measurements introduced by digital data acquisition systems and the data reduction algorithms have been evaluated²⁶⁻²⁸. In their application of numerical Laplace transforms to chromatographic peak analysis for the calculation of statistical moments, Yamaoka and Nakagawa²⁹ showed that the ADC conversion error was negligible when the transform was defined in the form of Simpson's rule.

Reilley and co-workers^{14,30} used discrete convolution methods to calculate the profile resulting from the operation of a column (a Gaussian operator) on several input profiles. These calculations are complicated by the interdependence of some of the integral forms encountered. In a later paper³¹, they developed the use of the Laplace transform to calculate the response transform of a complex system and showed that the moments may be obtained directly from the response transform without inversion. Operational methods for linear systems were employed which were essential to the development of their discussion of chromatographic peak profiles and to Sternberg's¹² treatment of the instrumental band-broadening.

The power and high accuracy of using statistical moments for peak profile characterization has been widely demonstrated in the chromatographic literature as it represents an approach which is theoretically sound and can be related back to the basic mass-balance equations for linear and non-linear non-equilibrium systems. A basic understanding of this approach can be found in the literature^{29,32,33}. Statistical moments have been used to develop a dynamic gas adsorption theory³³, detect overlapping chromatographic peaks³⁴, analyze exponentially modified Gaussians³⁵, simulate non-linear^{36,37} and linear equilibrium³⁸ GC, develop the theory of multiple phase chromatography³⁹, deconvolve peak shape parameters from functions generated by curve fitting⁴⁰, and model skewing behavior⁴¹.

The work reported here concerns the development of a model for a chromatographic system in which equations are derived for the total first and second moments of the model using the techniques developed by Ashley and Reilley³¹ and Sternberg¹². The value of this approach is determined by the accuracy with which the model represents a real chromatographic system.

DISCUSSION

The chromatographic elution profile may be regarded as a composite distribution function which results from the interaction of several independent distributions or operators. One of these is the sorption column which is usually assumed to have the properties of a Gaussian operator. In order to treat only the extra-column effects and to avoid the complications of non-ideal sorption behavior, the sorption column will not be considered here. Then the output distribution function should be a true representation of the sample input profile modified by the instrumental contributions. Since the areas in which a knowledge of the instrumental contributions is desirable are also the areas in which these contributions must be kept to a minimum, the presence of broadening due to sorption would make the treatment of these instrumental contributions very difficult. Once the extra-column contributions have been determined, then on-column processes may be studied in detail with higher accuracy.

Moments of distribution functions

The reference point for the calculation of the moments of a distribution must be clearly specified to satisfactorily characterize that distribution. In GC the two reference points of interest are at $t = 0$, and the center of gravity of the peak of interest. The zero of the time scale is ordinarily defined as the time when the center of gravity of the sample profile enters the column. This is a convenient and well defined time, since the customary input profile is assumed to be a Dirac delta function. Therefore it is not necessary to account for the sample width. In high-speed chromatography, or in the absence of a sorption column, it will be seen that the input profile has a finite width and must be considered in the treatment of the experimental data.

The moments are calculated from the normalized defining integrals:

$$\text{zeroth moment: } A = \int S(t) dt \quad (1)$$

$$\text{first moment: } \bar{t} = \frac{\int t S(t) dt}{\int S(t) dt} \quad (2)$$

$$\text{second moment: } \sigma_0^2 = \frac{\int t^2 S(t) dt}{\int S(t) dt} \quad (3)$$

For the peak profile function, $y = S(t)$, A is the area of the peak profile, \bar{t} is the first moment or the location of the center of gravity of the peak profile, and σ_0^2 is the second moment with respect to time zero. Nothing is assumed about the shape of the peak profile at this point. The only requirement is that the integrals in eqns. 1–3 exist and that they may be evaluated either in closed form or numerically.

The second moment is most readily interpreted if it is measured about the center of gravity of the profile rather than from the time zero point which is experimentally observed. The defining integral for the second moment may be re-written to give the second moment about the center of gravity of the peak profile as

$$\sigma^2 = \frac{\int (t - \bar{t})^2 S(t) dt}{\int S(t) dt} \quad (4)$$

where σ^2 designates the second moment about the center of gravity. Thus by using eqn. 3, the normalized second moment will be a measure of the width of the peak profile. By expanding the squared term in eqn. 4 and substituting eqns. 1–3 we have

$$\sigma^2 = \sigma_0^2 - \bar{t}^2 \quad (5)$$

which allows the calculation of the second moment for a single component distribution about the center of gravity from the second moment about $t = 0$ and the first moment of the peak. Sternberg¹² derived a similar equation by defining the profile function as a sum of several component profile functions.

Individual band broadening contributions

The general model of the chromatographic system which will be employed in this discussion is shown in Fig. 1. Some chromatographic systems will have contribu-

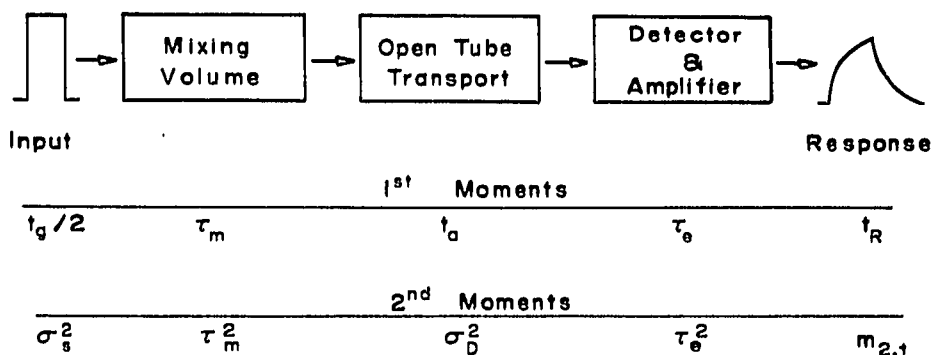


Fig. 1. Block diagram of a model GC system for obtaining the instrumental contributions to band broadening from the first and second moments.

tions which are not included in this model such as broadening due to sudden diameter changes in the gas flow path or slow vaporization of a liquid sample. However, such effects can generally be reduced or eliminated by improved design or experimental technique.

Sternberg¹² developed the superposition principle for a system operating on an input to produce the observed output from the linearity properties of the Laplace transform. However, it will be more desirable from an experimental point of view to develop the superposition principles for the first and second moments. These principles may also be stated as the additivity rules for independent first and second moments.

If we let $F(t)$ be a function composed of two linearly independent functions $F_1(t)$ and $F_2(t)$, then

$$F(t) = F_1(t) + F_2(t) \tag{6}$$

and the Laplace transform of $F(t)$ is given by $f(s)$.

$$f(s) = f_1(s) \cdot f_2(s) \tag{7}$$

The N th moment with respect to $t = 0$ may be obtained by taking the limit as the Laplace variable, s , approaches zero for the N th derivative of the characteristic function. This result is normalized by dividing by the area or by the limit as s approaches zero of the characteristic function. Thus, for the general case,

$$v_{N,t} = (-1)^N \frac{\lim_{s \rightarrow 0} f''^{(N)}(s)}{\lim_{s \rightarrow 0} f(s)} \tag{8}$$

where $f(s)$ is a composite function or a single distribution. Applying eqn. 8, for the case of $N = 1$, to eqn. 7

$$v_1 = v_{1,1} + v_{1,2} \tag{9}$$

so that the total first moment is the sum of the first moments of the independent contributions. Similarly, applying eqn. 8 for $N = 2$

$$v_2 = v_{2,1} + v_{2,2} \quad (10)$$

which gives the rule for the addition of second moments. These functions must be linear, independent components. This requires a thorough understanding of the physical interaction of the components of the instrument because complex situations may exist where several mechanisms which may not be independent in behavior are involved. Consequently, the functions describing their behavior will not be independent. For example, the flame ionization detector has a contribution due to the finite sensing volume and an exponential contribution due to its resistance and capacitance.

The contributions of the components of this model are of three types: a rectangular distribution, an exponential distribution, and a Gaussian distribution. Each of these may arise from several different physical mechanisms and will be considered in light of the model used. The functional form of these contributions and their first two moments are listed in Table I.

TABLE I
MOMENTS OF INDIVIDUAL DISTRIBUTIONS

Type of distribution	Functional form	1st Moment	2nd Moment
Rectangular	$s(t) = s_0$ $0 < t < t_1$	$\frac{t_1}{2}$	$\frac{t_1^2}{12}$
Exponential	$s(t) = s_0 \exp(-t/\tau)$	τ	τ^2
Gaussian	$s(t) = s_0 \exp\left\{-\frac{(t - \bar{t})^2}{2\sigma^2}\right\}$	\bar{t}	σ^2

A rectangular component distribution approaches the ideal injection profile because it may be regarded as the limiting form of a Dirac delta function. Although difficult to obtain in practice, a profile whose width is small with respect to other broadening factors is an excellent approximation to a Dirac delta function.

Said¹² and Sternberg¹² pointed out that a detector with a finite detector sensing volume will introduce additional broadening as a rectangular operator. If the sensitive volume of the detector is designated by V_d and the flow-rate through this volume by F_d , then the time t_d , associated with this volume is given by,

$$t_d = \frac{V_d}{F_d} \quad (11)$$

for conditions of laminar flow. The second moment contribution of this component is given by

$$\tau^2 = \frac{t_d^2}{12} = \frac{V_d^2}{12F_d^2} \quad (12)$$

The most important sources of an exponential contribution to band broadening in a well designed chromatographic system are the mixing chambers, diffusion chambers, slow sample vaporization, and resistor-capacitor networks in the electrical circuits. The exponential time constant of the mixing chambers, τ , depends on the volume of the chambers, V , and the flow-rate, F :

$$\tau = \frac{V}{F} \quad (13)$$

Hence it is desirable to maintain large flow-rates through sections of the experimental system which behave as mixing chambers. Similarly, the electrical effects may be treated collectively and discussed in terms of their equivalent circuit. Sample vaporization contributions can be eliminated by limiting such studies to gas samples, and diffusion chambers may be similarly neglected by careful design of the instrumentation.

For the case treated here, no sorption is assumed in order to measure only the instrumental band broadening. The only Gaussian operator may then be assumed to be due to the longitudinal diffusion in the capillary tubing. From Golay's⁴³ equation for a non-sorbed species,

$$\frac{d\sigma_L^2}{dz} = \frac{2 D_u}{u_o} + \frac{r^2 u_o}{24 D_u} \quad (14)$$

where r is the radius of the tube, u_o the outlet carrier-gas velocity, and D_u the interdiffusion coefficient for the sample in the carrier gas, the time-based second moment may be obtained by multiplying the length-based second moment by the square of the ratio of the cross-sectional area of the column, A , to the volumetric flow-rate, F

$$\sigma_t^2 = \sigma_L^2 \left(\frac{A}{F} \right)^2 \quad (15)$$

By correcting for the pressure drop through the capillary by means of the average column pressure, \bar{p} , then for a uniform tube of length L , eqn. 14 becomes

$$\sigma_t^2 = \left(\frac{A \bar{p}}{F_0 p_0} \right) \left(\frac{2 D_u}{u_o} + \frac{r^2 u_o}{24 D_u} \right) \quad (16)$$

This expression may be simplified by expressing the volumetric flow-rate in terms of the linear gas velocity:

$$\sigma_t^2 = \left(\frac{\bar{p}}{p_0 u_o} \right)^2 \left(\frac{2 D_u}{u_o} + \frac{r^2 u_o}{24 D_u} \right) \quad (17)$$

This equation permits the calculation of the contribution of a capillary column to band broadening from the dimensions of the tube, the interdiffusion coefficient, and the pressure drop throughout the tube.

Composition of experimentally observed moments

In order to develop equations which represent the contributions of the experi-

mental system, the principles of superposition of the first and second moments will be applied to the elements of the model in Fig. 1. These equations are exact for the model, but will fit the experimental data only as well as the model describes the actual apparatus.

The experimentally measured first moment corresponds to the uncorrected retention time of the system. It includes the transport time for a non-sorbed species through the column, t_A , which may be calculated by

$$t_A = \frac{\pi r^2 L}{J F_0} \quad (18)$$

where J is the compressibility correction factor. The experimentally observed first moment also includes contributions from the finite sample size, the time constant of the detector and associated electronics, τ_e , mixing chambers, τ_m , and the sensitive volume of the detector, t_d . Since there is no way of distinguishing between mixing chambers located in different parts of the apparatus, the mixing volumes are treated together for the conditions which prevail at the outlet of the column.

Adding the first moments of the contributions of the model we obtain

$$t_R = t_A + \frac{t_g}{2} + \tau_m + t_d + \tau_e \quad (19)$$

By substituting eqns. 12, 13 and 18 and equations from Table I in terms of the physical constants, eqn. 19 may be given by

$$t_R = \frac{\pi r^2 L}{J F_0} + \frac{t_g}{2} + \frac{V_m}{F_0} + \frac{V_d}{2 F_0} + \tau_e \quad (20)$$

for the case where the hydrogen flow-rate to the detector is always held equal to the carrier gas flow-rate so that $F_d = 2F_0$. By rearranging eqn. 20 into flow-dependent and flow-independent terms, an analytically useful form is obtained.

$$t_R = \frac{1}{F_0} \left(\frac{\pi r^2 L}{J} + V_m + \frac{V_d}{2} \right) + \left(\tau_e + \frac{t_g}{2} \right) \quad (21)$$

Eqn. 21 is the equation of a straight line and assumes that J is not a function of the outlet flow-rate. Only under conditions of a small pressure drop across the column will this be true. For a column with a small pressure drop, J may be taken as a constant and assigned a value equal to its mean value over the range of experimental conditions. By plotting the experimental first moment over a wide range of flow-rates, this variation in J will introduce a small error in the slope, but a larger error will appear in the intercept due to the extrapolation.

Another difficulty with eqn. 21 results from the great difference in magnitude of the volume of the column and the other volume terms in the slope expression. The volume of the capillary column should be in the order of several millilitres while the mixing volume and the sensitive volume of the detector will be only a few microlitres. The error in measuring the length and diameter of the capillary column can easily be

equal to or larger than the other volume terms. The magnitude of the transport time resulting from this column is such that its variation due to carrier gas flow-rate fluctuations may exceed the first moment contributions of the detector and the mixing chambers. Therefore, the relative magnitudes of the numbers involved, combined with the conditions of the extrapolation, makes the calculation of the exponential time constant and the sample width from the intercept very dubious.

The problems of the large differences in the magnitudes of the volumes and the difficulty with the compressibility correction in the analysis of the first moments may be avoided by applying the principle of superposition of variances to the model in Fig. 1.

$$m_{2,t} = \sigma_D^2 + \sigma_s^2 + \tau_m^2 + \tau_e^2 + \sigma_d^2 \quad (22)$$

In this equation, σ_D^2 represents the time-based second moment contribution of longitudinal diffusion and the velocity profile within the capillary column. It can be seen from eqn. 17 that this contribution is very small at large carrier gas velocities and can be neglected by proper design of the experiment. Substitution of eqns. 12 and 13 and equations from Table I into eqn. 22 gives

$$m_{2,t} \approx \frac{1}{F_0^2} \left(V_m^2 + \frac{V_d^2}{48} \right) + (\tau_e^2 + \sigma_s^2) \quad (23)$$

This equation may be more readily handled if a change of variable is made

$$\mu_t^2 = m_{2,t} \quad (24)$$

so that eqn. 23 becomes

$$\mu_t^2 = \frac{1}{F_0^2} \left(V_m^2 + \frac{V_d^2}{48} \right) + (\tau_e^2 + \sigma_s^2) \quad (25)$$

By rearranging eqn. 25, it may be recognized as the equation of a hyperbola of the form

$$y^2 - cx^2 = b^2 \quad (26)$$

so that

$$\mu_t^2 - \frac{1}{F_0^2} \left(V_m^2 + \frac{V_d^2}{48} \right) = \tau_e^2 + \sigma_s^2 \quad (27)$$

From the resulting expression

$$\left[\mu_t - \frac{1}{F_0} \left(V_m^2 + \frac{V_d^2}{48} \right)^{\frac{1}{2}} \right] \left[\mu_t + \frac{1}{F_0} \left(V_m^2 + \frac{V_d^2}{48} \right)^{\frac{1}{2}} \right] = 0 \quad (28)$$

the equations of the asymptotes are obtained by setting the constant term to zero and factoring the resulting equation:

$$\mu_t - \frac{1}{F_0} \left(V_m^2 + \frac{V_d^2}{48} \right)^{\frac{1}{2}} = 0 \quad (29)$$

$$\mu_t + \frac{1}{F_0} \left(V_m^2 + \frac{V_d^2}{48} \right)^{\frac{1}{2}} = 0 \quad (30)$$

Eqs. 29 and 30 are the equations of two straight lines which pass through the origin and have slopes of plus and minus $(V_m^2 + V_d^2/48)^{\frac{1}{2}}$. These lines pass through the first and third quadrant for eqn. 29 and through the second and fourth quadrant for eqn. 30. Since negative values have no physical significance for the variables in these equations, only eqn. 29, for positive F_0 , is of interest.

In order to retain the interpretation of the intercept as the quadratic sum of the exponential time constant and the sample width in this linearization, the square root of the constant term of the hyperbola (eqn. 25) is added to eqn. 29. This equation will produce a line with the same slope as the asymptote of the hyperbolic form and the same intercept as the hyperbola:

$$\mu_t = \frac{1}{F_0} \left(V_m^2 + \frac{V_d^2}{48} \right)^{\frac{1}{2}} + (\tau_c^2 + \sigma_s^2)^{\frac{1}{2}} \quad (31)$$

Eqn. 23 may be converted to the volume-based second moment by

$$m_{2,v} = F_0^2 m_{2,t} \quad (32)$$

in order to change the flow dependence of the terms of eqn. 31

$$m_{2,v} = \left(V_m^2 + \frac{V_d^2}{48} \right) + F_0^2 (\sigma_s^2 + \tau_c^2) \quad (33)$$

By making a change of variable as in eqn. 24,

$$\mu_v^2 = m_{2,v} \quad (34)$$

we obtain the resulting equation

$$\mu_v^2 - F_0^2 (\sigma_s^2 + \tau_c^2) = V_m^2 + \frac{V_d^2}{48} \quad (35)$$

which is also the equation of a hyperbola. It should be noted that in this case the second-moment contribution of the gas sampling valve is not a function of the carrier gas flow-rate.

By a procedure analogous to that applied to eqn. 25, an approximation may be developed for eqn. 35:

$$\mu_v = F_0 (\sigma_s^2 + \tau_c^2)^{\frac{1}{2}} + \left(V_m^2 + \frac{V_d^2}{48} \right)^{\frac{1}{2}} \quad (36)$$

TABLE II
COMPARISON OF HYPERBOLIC EQUATION WITH LINEAR APPROXIMATION

F_0 (ml/sec)	Hyperbolic form u_v (μ l)	Linear form u_v (μ l)	Relative error (%)
0	10.0	10.0	0
0.1	10.4	12.9	24.0
1.0	30.5	38.9	27.5
2.0	58.5	67.8	15.9
3.0	87.1	96.6	10.9
4.0	116.0	126.0	9.5
10.0	289.0	299.0	3.5

This conversion allows the constants which appeared in the intercept term in eqn. 31 to be obtained from the slope of a least squares fit to the experimental data. Thus the large errors which could appear in the intercept due to a small error in the slope of the line are avoided.

The behavior of eqn. 36 may be evaluated by assuming a rectangular input function of 100-msec width ($\sigma_s^2 = 8.34 \cdot 10^2 \text{ msec}^2$), the sensitive detector volume and the mixing volumes to be 10 μ l together, and a total time constant of 10 msec. Substituting these values into eqn. 36 gives

$$\mu_v^2 = 8.35 \cdot 10^{-4} F_0^2 + 1 \cdot 10^{-10} \quad (37)$$

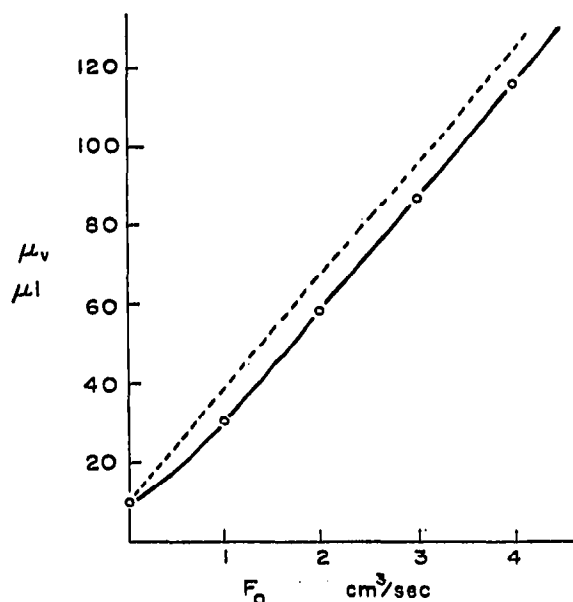


Fig. 2. Comparison of the hyperbolic form of the equation for the volume-based second moment (solid line) with the linearization form of the equation (broken line) as a function of carrier gas volumetric flow-rate, F_0 .

where F_0 is in liters/sec and μ_v^2 is in (liters)². The values for the volume-based second moment were calculated as a function of carrier gas flow-rate and are tabulated in Table II. These data are plotted in Fig. 2 with the line which is derived from the linearization approximation:

$$\mu_v = 2.89 \cdot 10^{-2} F_0 + 1 \cdot 10^{-5} \quad (38)$$

This line is seen to have the same slope as the asymptote and the same intercept as the hyperbola. The hyperbolic form of the equation departs from a straight line only in the region of very small flow-rates. Similarly, the linear form differs significantly from the hyperbolic form only at low rates. Since the parameters of interest are the physical constants of the system, the restriction of the linear form to large flow-rates is not detrimental.

The constants which characterize the instrumental contributions to band broadening should be evaluated from the slopes of the linear form of the equation because the hyperbolic forms asymptotically approach these slopes. After these constants have been evaluated at high flow-rates, they may be used to calculate the band broadening at normal flow-rates.

REFERENCES

- 1 E. Grushka, *Anal. Chem.*, 46 (1974) 511A.
- 2 E. Grushka, L. R. Snyder and J. H. Knox, *J. Chromatogr. Sci.*, 13 (1975) 25.
- 3 J. C. Giddings, *Dynamics of Chromatography*, Part I, Marcel Dekker, New York, 1965.
- 4 B. E. Bowen, *Ph.D. Dissertation*, University of Florida, Gainesville, Fla., 1973.
- 5 D. D. Chilcotte and C. D. Scott, *J. Chromatogr.*, 87 (1973) 315.
- 6 J. H. Knox and M. Saleem, *J. Chromatogr. Sci.*, 10 (1972) 80.
- 7 L. H. Tung, *Separ. Sci.*, 5 (1970) 429.
- 8 M. Hess and R. F. Kratz, *J. Polym. Sci., Part A-2*, 4 (1966) 731.
- 9 W. N. Smith, *J. Appl. Polym. Sci.*, 11 (1967) 639.
- 10 H. E. Puckett, M. J. R. Cantow and J. F. Johnson, *J. Polym. Sci., Part C*, 21 (1968) 67.
- 11 T. Provder and E. M. Rosen, *Separ. Sci.*, 5 (1970) 437.
- 12 J. C. Sternberg, *Advan. Chromatogr.*, 2 (1964) 205.
- 13 J. C. Giddings, *J. Chem. Phys.*, 26 (1957) 1755.
- 14 C. N. Reilley, G. P. Hildebrand and J. W. Ashley, Jr., *Anal. Chem.*, 34 (1962) 1198.
- 15 P. C. Haarkoff, P. C. van Berge and V. Pretorius, *J. S. Afr. Chem. Inst.*, 14 (1961) 82.
- 16 K. DeClerk, T. S. Buys and V. Pretorius, *Separ. Sci.*, 6 (1971) 733.
- 17 L. Jacob and G. Guiochon, *J. Chromatogr. Sci.*, 13 (1975) 18.
- 18 B. E. Bowen, S. P. Cram, J. E. Leitner and R. L. Wade, *Anal. Chem.*, 45 (1973) 2185.
- 19 R. L. Wade and S. P. Cram, *Anal. Chem.*, 44 (1972) 131.
- 20 V. Maynard and E. Grushka, *Anal. Chem.*, 44 (1972) 1427.
- 21 L. Mir, *J. Chromatogr. Sci.*, 9 (1971) 436.
- 22 H. Kaizuma, M. N. Myers and J. C. Giddings, *J. Chromatogr. Sci.*, 8 (1970) 630.
- 23 H. Oster and E. Ecker, *Chromatographia*, 3 (1970) 220.
- 24 I. G. McWilliam and H. C. Bolton, *Anal. Chem.*, 41 (1969) 1762.
- 25 T. H. Glenn and S. P. Cram, *J. Chromatogr. Sci.*, 8 (1970) 46.
- 26 S. N. Chesler and S. P. Cram, *Anal. Chem.*, 43 (1971) 1922.
- 27 S. N. Chesler and S. P. Cram, *Anal. Chem.*, 44 (1972) 2240.
- 28 M. Goerdert and G. Guiochon, *Chromatographia*, 6 (1973) 76.
- 29 K. Yamaoka and T. Nakagawa, *J. Chromatogr.*, 92 (1974) 213.
- 30 J. W. Ashley, G. P. Hildebrand and C. N. Reilley, *Anal. Chem.*, 36 (1964) 1369.
- 31 J. W. Ashley and C. N. Reilley, *Anal. Chem.*, 37 (1965) 626.

- 32 O. Grubner, *Advan. Chromatogr.*, 6 (1968) 173.
- 33 O. Grubner and D. W. Underhill, *Separ. Sci.*, 5 (1970) 555.
- 34 E. Grushka, M. N. Myers and J. C. Giddings, *Anal. Chem.*, 42 (1970) 21.
- 35 E. Grushka, *Anal. Chem.*, 44 (1972) 1733.
- 36 K. Yamaoka and T. Nakagawa, *J. Chromatogr.*, 103 (1975) 221.
- 37 T. S. Buys and K. DeClerk, *Separ. Sci.*, 5 (1972) 543.
- 38 K. Yamaoka and T. Nakagawa, *J. Chromatogr.*, 93 (1974) 1.
- 39 K. Yamaoka and T. Nakagawa, *J. Chromatogr.*, 105 (1975) 225.
- 40 S. N. Chesler and S. P. Cram, *Anal. Chem.*, 45 (1973) 1354.
- 41 T. S. Buys and K. DeClerk, *Separ. Sci.*, 7 (1972) 441.
- 42 A. Said, *AIChE J.*, 5 (1959) 69.
- 43 M. J. E. Golay, in D. H. Desty (Editor), *Gas Chromatography 1958*, Academic Press, New York, 1958, p. 36.