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THE GAS CHROMATOGRAPHIC DETERMINATION OF BINARY DIFFUSION COEFFICIENTS

I. A THEORETICAL DESIGN STUDY

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SUMMARY

A comprehensive theoretical error analysis of the factors involved in the chromatographic determination of binary diffusion coefficients shows that it is hardly possible to obtain a precision of better than 0.5% if conventional peak measurement techniques are employed.

INTRODUCTION

In a recent comprehensive survey of gaseous diffusion coefficients (D), Marrero and Mason¹ considered gas chromatography to give results of average reliability. At a temperature of 300 °K, comparisons with D obtained by other methods showed deviations of up to 4% with an average deviation of about 2%. The two-bulb method is considered to be the most reliable, yielding values within 2% of the actual value and, with exceptionally careful control², within 1%. In view of the convenience of the equipment, it is natural to consider whether it would be worth while trying to improve upon the reliability of the chromatographic method. A thorough theoretical analysis of the relevant design parameters is indicated. This study is seen as a contribution to this end, although the treatment is not exhaustive. Several variants of the method exist which differ mainly in the method by which end-effects are eliminated. A single variant, known in the literature as the peak arrest (PA) method, is concentrated on.

The original experiments of Knox and McLaren³ were used for the measurement of the tortuosity factor in packed columns. As far as we know, this method has not been applied to the systematic determination of diffusion coefficients *per se*. The fact that it is relatively unexplored was not, however, the sole motivation for its selection. It also appears to be more convenient and flexible and avoids the uncertainties related to the mass-transfer terms in the plate-height expression which are inherent in the other methods. These advantages have not been assessed quantitatively relative to the other methods; it is possible that with the necessary care, these methods

may be refined to the level of the PA method. The latter is expected, however, to be at least representative of the chromatographic methods.

The specific aim of this paper is to provide design data for the construction of an apparatus for measuring binary gaseous diffusion coefficients to a prescribed accuracy and precision. This implies a theoretical quantification of both systematic and random errors. This distinction is significant, as the deviations reported by individual workers usually refer to precision, while that of Marrero is an indication of the accuracy. The difference between the two is particularly important in chromatography, where gas chromatographers claim a 1–2% precision, in contrast to Marrero's values of up to 5% (up to 500 °K).

The various errors will be considered as arising from two sources: (i) the normal instrumentation errors and (ii) discrepancies between the theoretical model and experimental procedure. Elimination of the latter will require careful elaboration of the assumptions implicit in the mathematical model. A 1:1 correspondence between theory and experiment is ensured only if discrepancies are all either suitably quantified and incorporated in the theoretical model or if the experimental procedure can be refined so as to make this effect numerically negligible.

These two sources of error will now be considered separately. The latter is treated first as it is basic to the whole procedure.

THEORETICAL MODEL AND EXPERIMENTAL PROCEDURE

The apparatus consists of a pressure source that maintains a steady flow of carrier gas through an uncoated open-tubular column and past a detector. A gas sample, introduced as a trace at the column inlet, is carried through the column and its concentration is recorded as a function of time.

The differential equation describing the sample concentration distribution, C , as a function of the axial, Z , radial, r' , and time, t , coordinates is

$$\left(\frac{\partial C}{\partial t}\right)_z = -u(r') \frac{\partial C}{\partial Z} + D \left\{ \frac{\partial^2 C}{\partial Z^2} + \frac{1}{r'} \frac{\partial}{\partial r'} \left(r' \frac{\partial C}{\partial r'} \right) \right\} \quad (1)$$

where $u(r')$ is the linear carrier gas velocity and D has been assumed to be constant.

It is well known that, after a time interval of the order of the time required for radial equilibrium, eqn. 1 can be approximated by

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial Z} + D_e \frac{\partial^2 C}{\partial Z^2} \quad (2)$$

where

u = linear velocity averaged over the cross-section.

$D_e = D + u^2 a^2 / 48 D$, in which $u^2 a^2 / 48 D$ represents an effective longitudinal diffusion due to the coupling between the radial velocity distribution and the radial diffusion.

Application of the second moment operator

$$-\infty \int^{+\infty} (Z - \langle Z \rangle)^2 dZ / \int_{-\infty}^{+\infty} C dZ$$

to eqn. 2 yields⁴

$$\frac{d\sigma^2}{dt} = 2 D_e \quad (3)$$

so that for an initial variance σ_i^2 , the variance developed during a flow time t is given by

$$\sigma^2 = 2 D_e t + \sigma_i^2 \quad (4)$$

Eqn. 4 is the basic equation from which D can conveniently be obtained experimentally. It is interesting to note that eqn. 4 is valid irrespective of the form of the inlet, restricted only by the condition that C and its derivatives should tend to zero as $Z \rightarrow \pm \infty$. Some other features of its derivation which require comment are:

(i) The transient time necessary for the effective diffusion to become fully operative has already been mentioned. This time will be of the order of a^2/D (ref. 5).

(ii) The expression for the effective diffusion coefficients depends on the assumption of a parabolic flow profile with no slip along the column wall.

(iii) The flow is assumed to be perfectly laminar, *i.e.*, no convective eddies are present.

(iv) In the integration of eqn. 3, D was assumed to be independent of t . This is not true if conditions such as pressure and temperature vary along the column axis.

(v) The walls are assumed to be smooth and the possibility of the existence of a stationary phase is excluded, *i.e.*, the mass distribution coefficient $k = 0$.

(vi) Coiling and other geometrical effects may modify the diffusion coefficient.

(vii) Eqn. 4 is valid for an arbitrary shape of the input peak provided that actual second moments on a Z -coordinate basis are measured.

In the PA method, flow is arrested when the peak is about midway through the column and allowed to spread out for a time t_2 under molecular diffusion alone. This contribution to σ^2 is given by

$$\sigma_D^2 = 2 D t_2$$

and is simply added to the other terms in eqn. 4. Indeed, Sternberg⁶ has shown that extra-column effects also contribute additively so that the total variance of the peak after passing through the detector is given by

$$\sigma^2 = \sigma_i^2 + \sigma_C^2 + \sigma_D^2 + \sigma_0^2 \quad (5)$$

where σ_i^2 is the variance at the column inlet and $\sigma_C^2 = 2D_e(t_1 + t_3)$; t_1 is the time from the moment that the peak enters the column to arrest and t_3 is the time from after arrest to column outlet. σ_0^2 is considered to contain all additional contributions that arise from connections between outlet and detector and the detector itself.

If σ_D^2 is now varied while all other variables are held constant, D is obtained simply from the slope of the straight line σ^2 versus t_2 . Differences in pressure and temperature between the diffusion region and the position where σ^2 is actually measured can easily be accounted for in terms of the gas laws. Gradients over the diffusion region should be made negligible, however, as it will complicate the analysis unduly. Possible variances introduced by the stop and start of the peak should also be con-

stant, but this can easily be checked experimentally. Other sources of band spreading are collected as the straight line intersection and the uncertainties related to them become merely a matter of the reproducibility of the experimental procedure. Many of the difficulties mentioned above are thereby effectively eliminated.

Provided that the diffusion takes place in a tube of uniform cross-section, geometrical effects should be unimportant. Coiling effects are also expected to be negligible as the diameter is very large relative to the mean free path of the molecules. Non-elastic interactions with the column wall will reduce the molecular diffusion by a factor $1/(1+k)$, and adequate experimental preventive measures should be taken for its elimination.

The final feature (vii) contains two effects that merit a more detailed investigation. The first effect relates to the fact that chromatographic detectors measure peaks on a time and not a Z basis, and these are not, in general, simply related. For instance, in the case of a δ input, the solution of eqn. 2 is

$$C(Z,t) = \frac{m_0}{A (2\pi\sigma^2)^{\frac{1}{2}}} \exp \left[-\frac{(Z-ut)^2}{2\sigma^2} \right] \quad (6)$$

where $\sigma^2 = 2D_e t$. It has been shown by Levenspiel and Smith⁷ that it is only for $D_e/ul < 0.01$ that the relationship

$$\sigma^2(Z) = u^2\sigma^2(t) \quad (7)$$

becomes a valid approximation. In the present case, σ^2 is given by eqn. 5, which will be written as

$$\sigma^2 = 2D_e(t_1 + t_3) + \sigma_e^2 \quad (8)$$

in order to separate the term dependent on the time of flow and the other contributions, $\sigma_e^2 = \sigma_l^2 + \sigma_D^2 + \sigma_0^2$. A criterion for the quantification of the deviation from gaussian form can now be formulated by noting that the deviation is due to diffusion which takes place during the transit time, Δt , of the peak past the detector. In this time Δt , an extra $\Delta\sigma^2 = 2D_e\Delta t$ is added. A measure of Δt is the time interval for 2σ of the peak to move past the detector, *i.e.*, $\Delta t = 2\sigma/u$. The relative error in the variance should therefore be a function of $\Delta\sigma^2/\sigma^2$, which can be written as

$$\frac{\Delta\sigma^2}{\sigma^2} = \frac{4}{\left[2 \left(\frac{ul}{D_e} \right) + \left(\frac{\sigma_e}{l} \right)^2 \left(\frac{ul}{D_e} \right)^2 \right]^{\frac{1}{2}}} \quad (9)$$

It follows that the deviations can be reduced by decreasing the dimensionless parameters $\bar{D}_e = D_e/ul$ and $l = l/\sigma_e$. The actual effect of these parameters can be assessed by incorporating them into the expression for C as

$$C(l,t) = \frac{m_0}{A \left\{ 2\pi l^2 \left[2 \left(\frac{D_e}{ul} \right) \left(\frac{ut}{l} \right) + \left(\frac{\sigma_e}{l} \right)^2 \right] \right\}^{\frac{1}{2}}} \exp \left\{ \frac{- \left(1 - \frac{ut}{l} \right)^2}{2 \left[2 \left(\frac{D_e}{ul} \right) \left(\frac{ut}{l} \right) + \left(\frac{\sigma_e}{l} \right)^2 \right]} \right\}$$

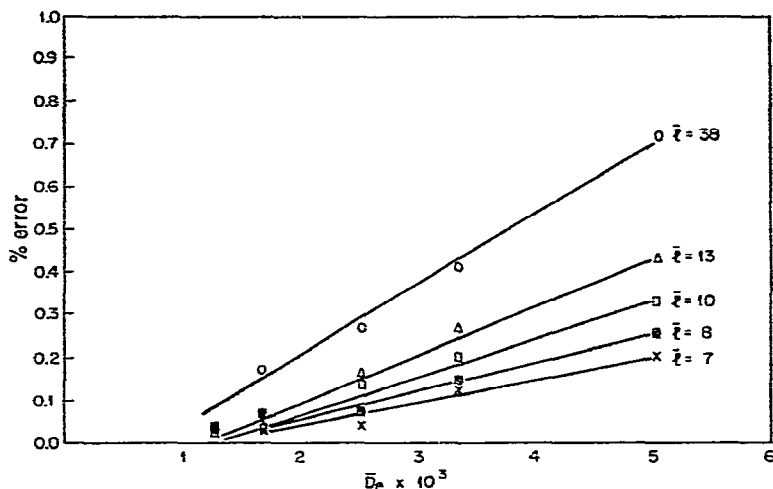


Fig. 1. Quantification of the effect of finite transit time past the detector. The percentage error in w_z is given as a function of De/ul for different values of $\bar{l} = l/\sigma_e$.

If C is plotted as a function of t , a comparison between the Z -based σ^2 (at $t = l/u$) and σ^2 measured in terms of the actual w_z can be made as a function of \bar{D}_e and \bar{l} . The results of such an analysis are summarized in Fig. 1. No effort was made to achieve precision and the straight lines are drawn merely as an indication of the trends. For a representative value of $\bar{l} \approx 30$, it can be seen that a value of $\bar{D}_e = D_e/ul \approx 10^{-3}$ will reduce the error to about 0.1%, which can usually be regarded as negligible.

The second effect is not inherent in the method but arises from a desire to keep the equipment as simple as possible. Provided that the facilities are available, the analogue output from the detector can be digitized and the variance evaluated directly on a digital computer. If not, the common procedure is to assume a gaussian peak form and evaluate σ^2 from the known relationship between σ^2 and the peak width at a certain fractional height. The gaussian assumption is critical in this instance. Deviations can be the result of two types of factors. The first group is associated with non-gaussian deviations of the Z distribution itself and can be caused by effects such as multi-site adsorption, pressure and temperature gradients across the peak during peak spreading and a non-gaussian inlet distribution. The necessity for eliminating the first two has already been stressed, while the relative contribution of the inlet, and thus its contribution to the non-gaussian deviation, can be reduced to an arbitrary level simply by increasing t_2 . This follows because σ_D^2 is known to be gaussian. The second group arises from detector effects. The first of these, *viz.* the measurement of the distribution on time basis, has already been discussed. Non-linear detector response constitutes the second. This is always a possibility which should be investigated separately for each specific mixture-detector combination. With digital analysis, numerical correction of the data is feasible provided that the concentration response is known. For the peak-width method, analysis is virtually precluded unless the sensitivity can be increased to admit analysis in a lower concentration range where the response becomes sufficiently linear. A third factor is the finite detector volume, which implies that the measurement is not a point measurement. Sternberg⁶ has shown

that this contributes $\sigma_e^2 = 1/12 \cdot (V_{eff}/\dot{V})^2$, which unfortunately occurs in the form of an exponential tail. The fact that it is a constant contribution is consequently no guarantee that the slope of the σ^2 versus t line remains unaffected, as the gaussian assumption is violated. The final consideration concerns the finite response time of servomechanisms in the recorder. This normally should not be a problem with modern equipment, but it is evident that elimination of the potential sources of error listed will require a careful study of detector specifications.

INSTRUMENT ERRORS

The actual measurements made in the determination of D can be ordered as follows:

(i) The peak width, w_r , at fractional height r is measured. From w_r , σ_p^2 is calculated as

$$\sigma_p^2 = -w_r^2/8 \ln r \quad (11)$$

(ii) σ_p^2 is the variance as measured on the recorder paper. What is required is the actual variance, σ^2 , of the peak within the column. As time is invariant, this is given by

$$\sigma^2 = \sigma_p^2 (u_c^2/u_p^2) \quad (12)$$

where

u_p = linear paper velocity;

u_c = linear velocity of the carrier at the position of arrest within the column but at the time that the peak moves past the detector. Eqn. 12 assumes the validity of the simple relationship between the time and the Z -based second moment, as discussed in the previous section.

(iii) The measurement of σ^2 is repeated for different times, t_2 , and a straight line is fitted to the data by means of a least-squares analysis. The slope, b , of this line is related to D by

$$D = b/2 \quad (13)$$

Three stages in the error analysis can now be identified. Firstly, the uncertainty in D is derived in terms of the uncertainty of a single σ^2 measurement and the number (n) and spread ($\text{Var } t_2$) of the measurements (*cf.*, eqn. 15) so that a constraint set on the uncertainty of a single σ^2 depends on two factors, *viz.* the uncertainty in the coordinate transformation defined by eqn. 12 and the uncertainty in the actual measurement of the width, w_r , on the recorder paper. These two facets will be dealt with below under *Stage 2* and *Stage 3*, respectively. Random and systematic errors will be considered separately.

Random errors

Stage 1. According to Birge⁸, the variance, $\text{Var } b$, in the slope of a straight line is given by

$$\text{Var } b = r_e^2 (n/G) \quad (14)$$

where

$$r_e = [\Sigma d_j^2 / (n - 2)]^{\frac{1}{2}}$$

and

$$G = n \Sigma t_{2j}^2 - (\Sigma t_{2j})^2$$

where

$$d_j = \sigma_j^2 - \sigma_j^2 \text{ (calc.)}$$

σ_j^2 is an observed value and σ_j (calc.) the corresponding value predicted by the straight line. Eqn. 14 can be rewritten in terms of $\text{Var } t_2$, defined by

$$\text{Var } t_2 = \Sigma (t_{2j} - \langle t_2 \rangle)^2 / (n - 1)$$

as

$$\text{Var } b = \left(\frac{\Sigma d_j^2}{n - 1} \right) \cdot \left(\frac{1}{n - 2} \right) \cdot \left(\frac{1}{\text{Var } t_2} \right) \quad (15)$$

The factor $\Sigma d_j^2 / (n - 1)$, in the remainder of this discussion, will be regarded as equivalent to the variance defined by

$$\text{Var } \sigma^2 = \Sigma (\sigma_j^2 - \langle \sigma^2 \rangle)^2 / (n - 1) \quad (16)$$

Strictly, this is not correct, as $\text{Var } \sigma^2$ refers to measurements carried out at the same t_2 . On the other hand, $\text{Var } \sigma^2$ is expected to be virtually independent of t_2 so that the approximation should be valid. In addition, the above analysis implicitly assumes that deviations are due exclusively to variations in σ^2 , *i.e.*, that the variance in time measurements can be regarded as negligible.

For a given $\text{Var } \sigma^2$, eqn. 15 predicts $\text{Var } b$ to be inversely proportional to both $n - 2$ and $\text{Var } t_2$. As $(\text{Var } t_2)^{\frac{1}{2}}$ can be interpreted as a rough measure of the spread, Δt_2 , of the t_2 values, an increase in Δt_2 can be seen as an effective means of decreasing the variance in D . The theoretical predictions are shown in Figs. 2 and 3, from which it follows that little is gained by increasing Δt_2 and n beyond $n \approx 8$ and $\Delta t_2 \approx 10$ min. It also follows from an inspection of eqn. 15 and the definition of $\text{Var } t_2$ that the best sampling policy for a specific value of n is to repeat the measurements $n/2$ times each at the lower and the higher t_2 value instead of spreading them over the intermediate range. This assumes there is a constant statistical weight factor over this range.

Stage 2. It follows directly from eqn. 12 that

$$\frac{\text{Var } \sigma^2}{\sigma^4} = \frac{4 \text{Var } u}{u^2} + \frac{4 \text{Var } u_p}{u_p^2} + \frac{\text{Var } \sigma_p^2}{\sigma_p^4} \quad (17)$$

so that the coordinate transformation gives a contribution

$$\frac{4 \text{Var } u}{u^2} + \frac{4 \text{Var } u_p}{u_p^2} \quad (18)$$

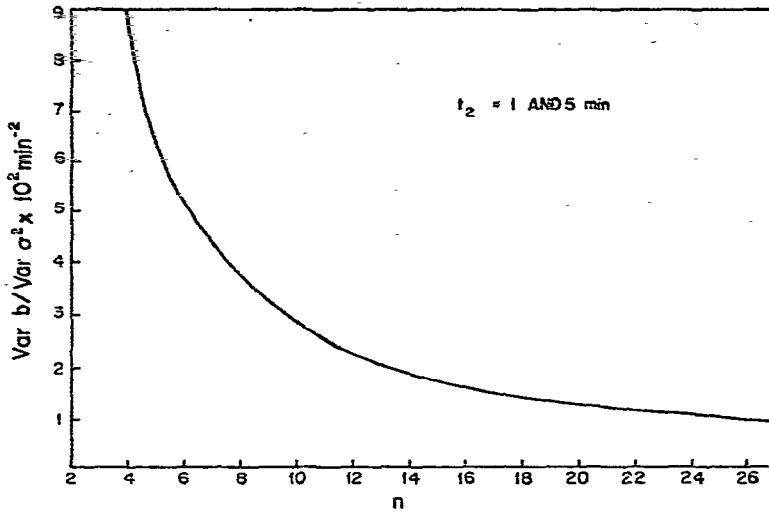


Fig. 2. Illustration of dependence of $\text{Var } b$ on the number of measurements, n (eqn. 15).

In modern equipment, the second term should be negligible so that the concern is actually to minimize the first. This will depend on the functional dependence of $\text{Var } u$ on u , which in turn will depend on the method used in measuring u . An increase in u will also have to be considered in conjunction with its effect on (i) the finite transit time effect at the outlet, (ii) the dependence of the arrest characteristics on u and (iii) the dependence of $\text{var } \sigma_c^2$ on u , as one requires σ_c^2 to be a constant for all measurements.

These questions can be more conveniently answered experimentally and a theoretical analysis will not be attempted here.

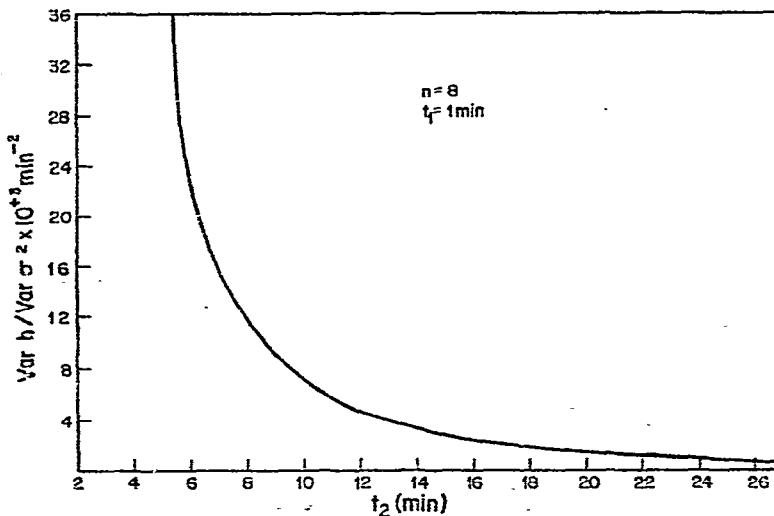


Fig. 3. Illustration of dependence of $\text{Var } b$ on t_2 (eqn. 15).

Stage 3. If $r = y/h$ is the fractional height at which the peak width, w_r , is measured, the variance σ_p^2 is related to w_r by eqn. 11, i.e.

$$\sigma_p^2 = w_r^2/8 \ln h/y \quad (19)$$

if a gaussian peak form is assumed. Calculation of σ_p^2 requires four independent measurements: (i) placement of the baseline, B , and measurement of (ii) peak height h , (iii) fractional height y and (iv) width w_r . Errors in each of these factors will give rise to an additive variance contribution in σ_p^2 . The general equation relating errors in σ_p^2 to errors in the measured quantities follows from eqn. 19 as

$$\frac{d\sigma_p^2}{\sigma_p^2} = \frac{2 dw_r}{w_r} + \frac{dy}{y \ln h/y} - \frac{dh}{h \ln h/y} \quad (20)$$

This equation will be applied to the evaluation of the contributions due to B , h , y and w_r . The analysis will follow closely that of Ball *et al.*⁹ for an analogous investigation.

(i) *Baseline.* Let the true baseline define the line of reference. If B is too low, ΔB will be negative; if B is too high, $\Delta B > 0$ and h will then be measured incorrectly as $h - \Delta B$. The placing of the y line relative to the incorrect baseline will then involve an additional error of $+\Delta B$ so that

$$\begin{aligned} y &= r(h - \Delta B) + \Delta B \\ &= rh + \Delta B(1 - r) \end{aligned} \quad (21)$$

and

$$\begin{aligned} dy &= y - rh (= \text{true } y) \\ &= \Delta B(1 - r) \end{aligned} \quad (22)$$

This error in y also introduces an error in w_r :

$$dw_r = \left(\frac{\partial w_r}{\partial y} \right) dy = - \left\{ 2^{\frac{1}{2}} \sigma_p / \left[y (\ln h/y)^{\frac{3}{2}} \right] \right\} dy \quad (23)$$

so that from eqns. 22 and 20, with

$$\begin{aligned} dw_r &= - 2^{\frac{1}{2}} \sigma_p (1 - r) \Delta B / [y (\ln h/y)^{\frac{3}{2}}] \\ dy &= (1 - r) \Delta B \end{aligned}$$

and

$$dh = - \Delta B$$

it follows that

$$\frac{d\sigma_{pB}^2}{\sigma_{pB}^2} = \frac{-(1 - r) \Delta B}{y \ln h/y} + \frac{(1 - r) \Delta B}{y \ln h/y} + \frac{\Delta B}{h \ln h/y} = \Delta B / (h \ln h/y) \quad (24)$$

It is interesting to note that the errors in w_r and y cancel each other. This will also be seen to apply in (ii) and (iii) below.

(ii) *Height, h.* An error, Δh , in the height will affect the y value even if the baseline is correct:

$$\begin{aligned} y_{\text{incorrect}} &= r(h + \Delta h) \\ dy &= r\Delta h \end{aligned} \quad (25)$$

Also, from eqn. 23,

$$dw_r = -\frac{2^{\frac{1}{2}} \sigma_p r \Delta h}{y (\ln h/y)^{\frac{3}{2}}} \quad (26)$$

Thus

$$\begin{aligned} dy &= r\Delta h \\ dh &= \Delta h \end{aligned}$$

so that

$$\frac{d\sigma_{ph}^2}{\sigma_p^2} = -\Delta h / (h \ln h/y) \quad (27)$$

(iii) *Intermediate height, y.* Here

$$\begin{aligned} dh &= 0 \\ dy &= \Delta y \end{aligned}$$

and

$$dw_r = -\frac{2^{\frac{1}{2}} \sigma_p \Delta y}{y (\ln h/y)^{\frac{3}{2}}}$$

so that

$$\frac{d\sigma_{py}^2}{\sigma_p^2} = 0 \quad (28)$$

(iv) *Width.* Here

$$\begin{aligned} dh &= 0 \\ dy &= 0 \\ dw_r &= \Delta w_r \end{aligned}$$

Therefore

$$\frac{d\sigma_{pw}^2}{\sigma_p^2} = \frac{2\Delta w_r}{w_r} \quad (29)$$

Because the measurements are statistically independent, the total variance is the sum of the individual variances:

$$\frac{\text{Var } \sigma_p^2}{\sigma_p^4} = \frac{1}{\sigma_p^4} (\text{Var } \sigma_{pB}^2 + \text{Var } \sigma_{py}^2 + \text{Var } \sigma_{ph}^2 + \text{Var } \sigma_{pw}^2) = \frac{(\Delta B)^2}{h^2 (\ln h/y)^2} + \frac{(\Delta h)^2}{h^2 (\ln h/y)^2} + \frac{(\Delta w_r)^2}{2 \sigma_p^2 \ln h/y} \quad (30)$$

According to Ball *et al.*¹⁰, Δw_r can be formulated semi-empirically by

$$\Delta w_r = \Delta m \left[1 + \frac{\sigma_p}{y (2 \ln h/y)^{\frac{1}{2}}} \right] \quad (31)$$

substitution of which into eqn. 30 gives

$$\frac{\text{Var } \sigma_p^2}{\sigma_p^4} = \frac{(\Delta B)^2 + (\Delta h)^2}{h^2 (\ln h/y)^2} + \frac{4 (\Delta m)^2 \left(1 + \frac{w_r}{4 r h \ln h/y} \right)}{w_r^2} \quad (32)$$

In Fig. 4, the relative variance in σ_p^2 is plotted as a function of the peak shape factor $h/w_{0.5}$ for different $r = y/h$. Typical values of ΔB , Δh and Δm were taken to be 0.010, 0.012 and 0.008 cm, respectively¹⁰, and h was taken to be 20 cm (the typical width of a recorder paper). Fig. 5 is a similar plot of $\text{Var } \sigma_p^2 / \sigma_p^4$ as a function of r for various shape factors. Peaks can be regarded as normal for a shape factor $s = h/w_{0.5} = 1$. Values of s greater than unity represent sharper peaks, while broad peaks are characterized by s values smaller than unity. A number of general observations follow from an inspection of the figures: (i) sharp peaks give rise to excessive variances in the width measurement and should be avoided; (ii) little is gained by decreasing s below 1; and (iii) for $s = 1$, the optimum r is about 0.2.

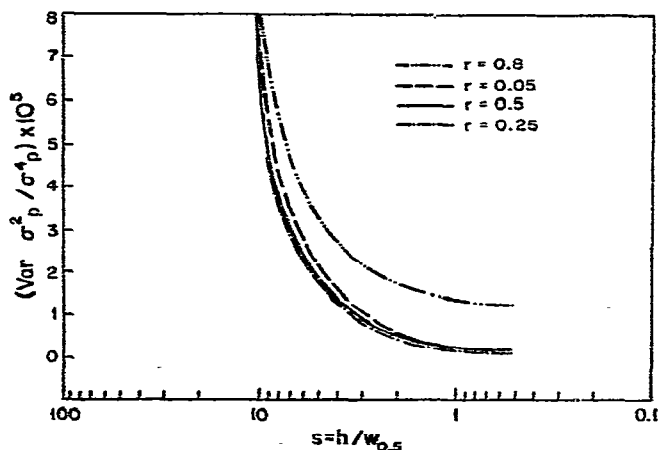


Fig. 4. Dependence of $(\text{Var } \sigma_p^2) / \sigma_p^4$ on shape, s , of peak.

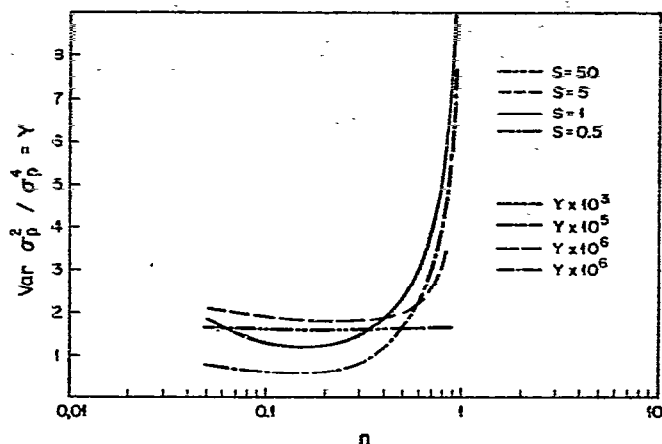


Fig. 5. Dependence of $(\text{Var } \sigma_p^2)/\sigma_p^4$ on fractional height, r , at which the width is measured.

These results should not be taken too literally, as they are based on a numerical model that may not be generally valid. They also rest on the assumption of gaussian peak shape. What they do indicate, however, is that the choice of peak shape and fractional height is not trivial, and that an effort should be made to optimize the measurements with respect to them.

Systematic errors. The systematic errors that arise from instrumentation can be simply systematized by listing all of the measuring instruments employed. Their relative contributions are assessed in terms of the general expression relating D via b and the coordinate transformation to w_r . The time axis can be distorted owing to inaccurate time measurement, which can be attributed to either the device used, the operator or both. Serious errors can be introduced if the absolute measurements of u and u_p are in error. This is quantified by writing eqn. 12 in differential form:

$$\frac{d\sigma^2}{\sigma^2} = 2 \frac{du}{u} - 2 \frac{du_p}{u_p} + \frac{d\sigma_p^2}{\sigma_p^2} \quad (33)$$

Other major potential sources of error are as follows.

- (i) The detector response, which has already been discussed.
- (ii) Absolute errors in recorder response.
- (iii) Absolute errors in the measurements of distances on the recording paper.

In most instances, e.g., with a ruler, these errors are due to both the instrument and operator.

(iv) The conditions for which D are reported may be inaccurate. These include temperature, pressure, purity of the gases used and the validity of the assumption of trace conditions for the sample (concentration dependence of D).

DISCUSSION

It is evident that compliance with an extensive list of conditions is prerequisite to the chromatographic peak arrest method for the determination of diffusion co-

efficients. On the other hand, these demands invariably involve the refinement of relatively simple measurements and standard precautionary measures, so that there appears to be no inherent limitation to the development of the method to the level of the best existing techniques.

It has been pointed out that many of the crucial issues can be decided only by actual experiments so that quantitative predictions are premature at this stage. An indication of the demands made on the measurements, however, can be given in terms of the preceding analysis. Two specifications in D will be considered, *viz.*, 1 and 0.1%. These approximately represent the state of art and an order of magnitude improvement, respectively.

Typically, values of D range from 0.1 to 1.0 $\text{cm}^2\text{sec}^{-1}$. Consider the case when $D = 0.1 \text{ cm}^2\text{sec}^{-1}$ and $\text{Var } D/D^2 = 10^{-4}$ (*i.e.*, the relative standard deviation of D is 1%). From

$$b = b_p u^2/u_p^2 \quad (34)$$

it follows that

$$\frac{\text{Var } b_p}{b_p^2} = \frac{\text{Var } b}{b^2} - 4 \frac{\text{Var } u}{u^2} - 4 \frac{\text{Var } u_p}{u_p^2} \quad (35)$$

If the reasonable assumption is made that the last term is negligible, it follows with the use of eqns. 13 and 34 that

$$\text{Var } b_p = 4 \left(\frac{u_p}{u}\right)^4 D^2 \left(\frac{\text{Var } D}{D^2} - 4 \frac{\text{Var } u}{u^2}\right) \quad (36)$$

Remembering that D is not a variable but dependent on the physical system, $\text{Var } b_p$ is seen to exhibit an optimum with respect to u if $\text{Var } u$ is assumed to be constant. By differentiating eqn. 36 and equating the result to zero, u_{opt} is obtained as

$$u_{\text{opt}} = [b \text{Var } u / (\text{Var } D/D^2)]^{1/2} \quad (37)$$

Some numerical results are summarized in Table I (the velocities are in cm/sec).

From eqn. 37 in eqn. 36:

$$(\text{Var } b_p)_{u_{\text{opt}}} = \frac{1}{27} \left(\frac{\text{Var } D}{D^2}\right)^3 \frac{u_p^4 D^2}{(\text{Var } u)^2} \quad (38)$$

TABLE I

VALUES OF u_{opt} (EQN. 37) FOR VARIOUS COMBINATIONS OF $(\text{Var } D)/D^2$ AND $\text{Var } u$.

$\text{Var } u$ (cm^2/sec^2)	$\frac{\text{Var } D}{D^2}$	
	10^{-4}	10^{-6}
10^{-4}	2.45	24.5
10^{-6}	0.245	2.45

An order of magnitude calculation of σ_p^2 can now be based on eqn. 38. Let $n = 8$, $\text{Var } t_2 = 10^4$ (corresponding to $t \approx 600$ sec), $D = 0.5 \text{ cm}^2\text{sec}^{-1}$, $\text{Var } u = 10^{-5} \text{ cm}^2\text{sec}^{-2}$ and $u_p = 0.5 \text{ cmsec}^{-1}$. For a 1% precision in D , the corresponding $\text{Var } \sigma_p^2 \approx 0.3 \text{ cm}^4$ while for 0.1% $\text{Var } \sigma_p^2 \approx 0.3 \cdot 10^{-6} \text{ cm}^4$. A representative value for σ_p is ca. 5 cm. As

$$\frac{\text{Var } \sigma_p^2}{\sigma_p^4} = 4 \frac{\text{Var } \sigma_p}{\sigma_p^2} \quad (39)$$

the standard deviations in σ_p are obtained as $\Delta\sigma_p \approx 5 \cdot 10^{-2} \text{ cm}$ and $\Delta\sigma_p \approx 5 \cdot 10^{-5} \text{ cm}$ for 1% and 0.1% precision, respectively. These are the upper limits as the errors, regarded as additive, may cancel each other to a certain extent in practice. Nevertheless, it can be seen that it would hardly be possible to surpass a precision of 0.5% if conventional peak measurement techniques are employed. If a precision of 0.1% is required, the use of electronic data processing equipment appears to become imperative.

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LIST OF SYMBOLS

- a = inner column radius;
- A = πa^2 ;
- b = slope of straight line: σ^2 vs. t_2 ;
- b_p = slope of straight line: σ_p^2 vs. t_2 ;
- B = baseline;
- C = solute concentration;
- d_j = residual of j th measurement,
defined as $d_j = \sigma_j^2(\text{obs.}) - \sigma_j^2(\text{calc.})$;
- D_e = effective molecular diffusion coefficient;
- \bar{D}_e = dimensionless parameter, defined as $\bar{D}_e = D_e/lu$;
- D = binary molecular diffusion coefficient;
- G = parameter defined in eqn. 14;
- σ = standard deviation;
- h = peak height;
- k = mass distribution coefficient;
- l = column length;
- l = dimensionless parameter, defined as $l = l/\sigma_e$;
- Δm = parameter in eqn. 31;
- m_0 = total sample mass;
- n = number of measurements;
- r = fractional height, y/h ;
- r' = radial coordinate;

- r_e = parameter defined as $[\sum d_j/(n-2)]^{\frac{1}{2}}$;
 s = peak shape factor, defined as $s = h/w_{0.5}$;
 σ^2 = total peak variance in column coordinates;
 σ_C = variance produced during time of flow through column;
 σ_D^2 = variance produced by diffusion alone, *i.e.*, during t_2 ;
 σ_i^2 = variance at column inlet;
 σ^2 = variance produced by extra-column effects at outlet, including detector;
 σ_p^2 = total peak variance on recorder paper;
 t = time;
 t_1 = time from moment peak enters column to arrest;
 t_2 = arrest time (time of spreading);
 t_3 = time from after arrest to column outlet;
 $u(r')$ = linear carrier gas velocity at r' ;
 u = linear carrier gas velocity averaged over cross-section;
 u_p = linear chart paper speed;
 \dot{V} = volume rate of flow;
 V_{eff} = effective detector volume;
 w = peak width;
 w_r = peak width at fractional height r ;
 y = intermediate height at which peak width is measured;
 Z = axial coordinate.

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