CHANGES OCCURRING WITH THE IMMOBILE LIQUID PHASE IN GAS–LIQUID CHROMATOGRAPHY

III. THE EFFECT ON OBSERVED PLATE HEIGHT

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The resolution of mixtures by gas–liquid chromatography is achieved by taking advantage of the different migration rates of the components of a mixture through a particular column under conditions which minimize zone spreading. Having once established the conditions necessary for a particular separation, it is desirable that the system be sufficiently stable that resolution is reproducible upon repetition. Failing this, it is desirable to understand the sources of instability and the manner in which they affect the resolution so that corrective measures may be taken. In the first paper of this series, KELLER et al.[1] reviewed the reports of the effects of instability of chromatographic columns and presented experimental data for the effect on retention volumes of liquid partitioner redistribution which occurs with repeated use of columns or with use outside of the recommended temperature. The second paper of this series[2] presented a theoretical analysis of these changes as they affect retention volumes. This third communication considers how the various forms of column instability are reflected in the zone spreading as measured by the observed plate height, H_{obs}, determined from the record of the chromatogram.

It must be stressed that the two factors of resolution, peak position and peak spreading, are basically different. The retention volume is a thermodynamic quantity which is independent of the details of the distribution of the liquid partitioner and depends upon the average amount of liquid in the column[2]. Zone spreading, however, is controlled by the kinetics of the mass transport between and within phases, and this, in turn, depends upon geometries of the phases involved. These geometries will vary over the column length as a result of column use. This variation leads to different contributions to the observed zone dimensions by the various sections along the column length. The observed plate height expression must be developed by a composition of local plate heights, H_{local}, suited to the conditions existing at particular points within the column. These equations should predict the effect of the various changes which occur with the liquid phase on the observed plate height.

THEORY

While the original theoretical model which led to the concept of the height equivalent to a theoretical plate, HETP, is no longer accepted as adequate, the utility of this parameter has not been damaged in any way. Here it is taken as a measure of zone spreading expressed as the variance or the square of the standard deviation, σ^2, of a Gaussian concentration distribution divided by the length of column traversed by the zone, L.

$$H_{obs} = \sigma^2/L \qquad (1)$$

The variance can be analyzed into a sum of terms for diffusion-like processes which depend upon the properties of the system in the region of the zone. The variance at a particular column position depends upon the residence time of the zone at that location (i.e., $\sigma^2 = 2Dt$). Thus, observed plate height is a *time average* of local plate heights and measures the net amount of spreading which occurred during zone migration.

"Elution" effect

The observed plate height is routinely calculated from the variance in time of the elution diagram, τ^2, and the retention time, t_R, measured from the instant of sample injection, or some quantities equivalent to these. When the liquid partitioner has undergone macroscopic redistribution, this method of calculating plate height is not equivalent to equation (1). To distinguish it from the form of equation (1) an apparent plate height is defined as $H_{app} = L(\tau^2/t_R^2)$. The variance in time of the elution diagram is related to the zone variance in distance by the velocity of the zone at the time of elution, $u_0 = R_0 v_0$, where R_0 is the fraction of the solute molecules in the gas phase at the column outlet and v_0 is the linear gas velocity at the outlet. The latter is found by dividing the outlet gas volume rate of flow (at column temperature and outlet pressure) by the mobile phase cross-sectional area at the outlet. The retention time is related to the column length through the average zone velocity which is the product of the gas velocity and the R value averaged over the column length, $\bar{u} = \overline{Rv}$. This average must be such that $L = \bar{u} \, t_R$. The extra column contributions to retention time, i.e., detector and injector designs, etc., are here taken to be negligible which, in practice, may not be true at all. The observed plate height as defined in eqn. (1) is calculated from the measured quantities, H_{app}, by the following expression:

$$H_{obs} = L \frac{\sigma^2}{L^2} = L \frac{\tau^2}{t_R^2} \frac{(R_0 v_0)^2}{(\overline{Rv})^2} = H_{app} \frac{(R_0 v_0)^2}{(\overline{Rv})^2} \qquad (2)$$

The factor $(R_0 v_0/\overline{Rv})^2$ is generally neglected in plate height calculations. While this approximation is likely valid for cases of small pressure drop acros the column and a uniform distribution of partitioning liquid, it is not valid when the partitioning liquid is unevenly distributed along the column length. The neglect of changes in this velocity ratio with column ageing will lead to changes in the calculated plate height which are unrelated to the real efficiency of the column.

Consider two columns which are of the same length, L, and which contain the same amounts of partitioning liquid but where this liquid is uniformly distributed throughout the first column, e.g., c g per unit length, in the second there is a greater

solvent load near the outlet and a smaller load near the inlet, e.g., $(3/2)c$ for the last half of the column and $(1/2)c$ for the first half. In Parts I and II[1,2] of this series it was concluded that the retention times would be the same for the two columns at equal flow rates. For the sake of simplicity of the immediate argument let it be assumed that the zone spreading is directly proportional to the average partitioner load, which, in this case, is the same in both columns and that a solute zone occupies j cm of column at the outlet for both columns. We later show that this cannot be true. As a further assumption, let the inlet and outlet pressures be the same for both columns and their difference be small enough that the carrier gas velocity at the outlet, v_0, is essentially the same as the average carrier velocity, $\bar{v}$. For the first column, the solute velocity at the outlet is $u_0(1) = R_0(1)v_0$ and the zone requires $j/[R_0(1)v_0]$ seconds to emerge; for the second column $u_0(2) = R_0(2)v_0$ and the elution time is $j/[R_0(2)v_0]$. But, $u_0(2) < u_0(1)$ by virtue of $R_0(2) < R_0(1)$ because of the higher solvent load at the outlet. Hence, at the outlet, the elution times are different and one observes a broader band in terms of time (larger τ^2) for the nonuniform column and a larger H_{app} than for the uniform column since the retention times are identical. By hypothesis, this difference does not exist in H_{obs}. The argument is equally valid for plate heights based on (1/4 peak width)^2/(peak retention)^2 as determined from distances measured on the record. Another way of expressing this result is to state that $R_0v_0/\overline{Rv} \neq 1$ for the nonuniform column even though $v_0 \cong \bar{v}$. For the first column $R_0 = \bar{R}$. If one reverses the second column so that the heavier load is at the inlet, the directions of the inequalities are reversed and one ought to observe a more efficient behavior if this effect is the only one to be considered.

"R-gradient" effect

However, for the situation of macroscopic redistribution without loss, resulting in a nonuniform liquid load, the real variances of the two zones referred to in the previous section will not be the same. A positive longitudinal gradient of the cross-sectional area of partitioning liquid, i.e., a greater liquid load at the outlet end, will exert a zone sharpening effect because the velocity of the front of the zone will be less than that at the tail. The difference in velocity of the front and the tail of a zone separated by one standard deviation, σ_i, may be approximated as

$$\left(\frac{dR}{dL}\right)_i v_i \sigma_i \tag{3}$$

where the index i indicates a particular location along the column. This expression assumes that the trans-zone zone-velocity gradient is independent of the local spreading rate and that the gradient is linear across the zone. The amount of contraction or expansion of the zone, $\delta\sigma$, is this difference multiplied by the retention time in the ith segment of the column, $dL/R_i v_i$. The total change in zone width due to the R-gradient is given by the integral:

$$\Delta\sigma = \int_0^L \left(\frac{dR}{dL}\right) \frac{\sigma}{R} \, dL \tag{4}$$

Evaluation of this integral requires a detailed knowledge of the liquid distribution.

If it is recognized that the R-gradient always has the opposite sign to the gradient in the cross-sectional area of the liquid load, A_1, then it follows that $\Delta\sigma < 0$ for a liquid distribution that increases from inlet to outlet and that $\Delta\sigma > 0$ for a liquid distribution which decreases from inlet to outlet. For the usual case of a decreased load at the inlet resulting from column bleeding, the change in zone variance arising out of the R-effect operates in the opposite sense to the change due to the elution-effect discussed earlier (eqn. 2). It will be illustrated by the experimental section that the two effects may very nearly compensate each other. This seems to argue against using nonuniform columns as a way of improving column efficiency.

If dR/dL is constant (independent of column position), eqn. (4) can be written

$$\Delta\sigma = \sigma \int_{R_{in}}^{R_0} \frac{dR}{R} = \sigma \ln \frac{R_0}{R_{in}} \tag{5}$$

where R_{in} is the R-value at the column inlet.

Now, reconsider the two columns proposed earlier. For the uniform column $dR/dL = 0$, so $\Delta\sigma = 0$. This calls attention to the oversimplification of the present discussion since there is always a change in band width due to diffusion processes. For the discontinuous column, where there is a sudden stepwise change of concentration, σ remains constant up to the discontinuity. At this point the front of the band changes velocity from $R_{in}v_0$ to R_0v_0. The tail undergoes the same change when it reaches the discontinuity. For a band of width σ the change in width is

$$\Delta\sigma = (R_0 - R_{in})v_0\sigma \tag{6}$$

From this point on the band proceeds with width $(\delta + \Delta\sigma)$. The bands in the two columns do not reach the outlet with the same width. The experimentally determined partitioner distributions reported in the first paper of this series are intermediate between the extremes represented by these two columns. The apparent zone expansion discussed in relation to eqn. (2) will also have a numerical value between these same limiting values.

"Chromatodiffusion" effect

The changes which occur in the observed (time average) plate height arising from mass transfer and diffusion are far more subtle than those due to the elution- and the R-gradient effects. They have their origin in the changes in effective film thickness of columns with nonuniform load distributions. The observed variance of an eluting zone is the sum of contributions by each increment of column. Each incremental variance is corrected for the expansion of the carrier gas which occurs therein by virtue of the pressure gradient along the column.

$$\sigma^2 = \int_0^L \frac{p_i^2}{p_0^2} d(\sigma^2) \tag{7}$$

This integral, in which p_i and p_0 are zone position pressure and outlet pressure, respectively, is the sum of the variances obtained from all spreading mechanisms operating at each position and expanded by the pressure ratio between the point and the position of observation. Since it is the sum of a sum, its value is independent of the order of summation.

Considerable effort has been put forth in developing the theory of how various column parameters contribute to zone spreading. The most widely used of these expressions is the van Deemter, Zuiderweg and Klinkenberg equation[3]

$$H_{local} = 2\lambda d_p + \frac{2\gamma D_1'}{p_i v_i} + \frac{8}{\pi^2} R(1 - R) v_i \frac{d_f}{D_2} \tag{8}$$

where d_p is particle diameter, λ is the eddy diffusivity factor, D_1' is molecular diffusivity of a solute in the mobile phase times the pressure at column position i, γ is the labyrinth factor, d_f is the effective film thickness, and D_2 is the molecular diffusivity of the solute in the immobile liquid phase. Rigorously, this, and related expressions, give the local plate height or the variance for an infinitesimal segment of specific geometry. Equation (9) defines the local plate height in terms of the variance for the column segment between L_i and $L_i + dL$.

$$H_{local} = d(\sigma^2)/dL \tag{9}$$

A combination of eqns. (1), (7) and (9) gives the relationship between the observed and local plate heights.

$$H_{obs} = \frac{1}{L} \int H_{local} \frac{p_i^2}{p_o^2} dL \tag{10}$$

Both the mobile phase velocity, v_i, and the local pressure, p_i, which occur in the union of eqns. (8) and (10) are non-linear functions of the column position, L_i[4]. Very little error is introduced into calculations for systems where there is a small pressure drop across the column and where v_i is assumed to be constant and $p_i/p_o = 1$.

The conditions for the application of the Van Deemter equation are that lateral diffusion, i.e., into and out of the liquid normal to the carrier flow, is rate controlling and that the eddy diffusion term, $2\lambda d_p$, is independent of velocity. Substitution of the Van Deemter expression into the numerator of eqn. (10) yields a sum of three terms describing contributions to the plate height, eddy diffusion, molecular diffusion and chromatodiffusion, respectively.

$$H_{obs} = 2\lambda d_p + \frac{2\gamma D_1'}{pv} + \frac{8}{\pi^2 L} \frac{R_i(1 - R_i) v_i d_f^2}{D_2} dL \tag{11}$$

Only the last term depends upon the details of the liquid distribution. In addition to d_f, the liquid film thickness, the R_i is subject to change with loss of partitioning agent and with macroscopic redistribution. The film depth can also change when there is a microscopic redistribution.

The relationship between film thickness and cross-section is quite dependent on the geometry. For Giddings' sawtooth model of the support surface[5] and for uniform impenetrable spheres, the film thickness is directly proportional to the liquid cross-section. With the approximation made so far, eqn. (11) may be written:

$$H_{obs} = S + \frac{T}{L} \int_0^L R_i(1 - R_i) d_f^2 dL \tag{12}$$

where S and T are constants made up of parameters which are not functions of L. If it is assumed that the distribution coefficient in the expression for R is constant and that macroscopic redistribution of partitioner does not alter the cross-section of the mobile phase to any significant extent, then

$$R = \frac{1}{1 + k_1 A_L} \qquad (13)$$

where k_1 is a constant. In order to examine the influence of the liquid distribution on H_{obs}, assume that the column packing consists of impenetrable uniform spheres of radius r, uniformly coated with liquid to a depth d_f. GIDDINGS'[6] root-mean-square film thickness is the equivalent of this uniform film. The volume of liquid on a single particle V_p, is given by

$$V_p = \tfrac{4}{3}\pi[(r + d_f)^3 - r^3] \qquad (14)$$

If this expression is expanded and only first order terms in the film thickness are retained, then

$$V_p = 4\pi r^2 d_f \qquad (15)$$

If the number of particles in a unit length of column is ρ, then the volume of liquid per unit length of column, A_L, is

$$V_L = 4\pi r^2 \rho d_f = k_2 d_f = A_L \qquad (16)$$

where k_2 is a constant for a uniformly packed column. Equation (13) becomes

$$R = \frac{1}{1 + k d_f} \qquad (17)$$

where $k = k_1 k_2 =$ constant. Equation (12) becomes

$$H_{obs} = S + \frac{Tk}{L} \int_0^L \frac{d_f^3}{(1 + k d_f)^2} \, dL \qquad (18)$$

This equation may be used to predict the change in band width in a semiquantitative manner. In doing this, it will be assumed that S is insensitive to solute identity.

First assume a uniform partitioner distribution so that d_f is a constant. Equation (18) integrates to

$$H_{obs} = S + \frac{Tk d_f^2}{(1 + k d_f)^2} \qquad (19)$$

For solutes which have a retention volume nearly the same as the air peak, $i.e.$, $R \doteq 1$ or $k d_f \ll 1$, then

$$H_{obs} = S + Tk d_f^3 \qquad (20)$$

For solutes of a very large retention volume, $i.e.$, $k d_f \gg 1$

$$H_{obs} = S + \frac{T}{k} d_f \qquad (21)$$

The observed plate height is more dependent on the film thickness for very fast solute peaks than it is for very slow peaks.

For the situation of constant but different liquid distributions in two sections of the column, eqn. (18) becomes

$$H_{\mathrm{obs}} = S + \frac{Tkd_{f1}^3}{L(1 + kd_{f1})^2} \int_0^{L_1} dL + \frac{Tkd_{f2}^3}{L(1 + kd_{f2})^2} \int_{L_1}^L dL \qquad (22)$$

where d_{f_1} is the film thickness in the region o to L_1 and d_{f_2} is the thickness in the region L_1 to L. Consider the hypothetical column in which half of the liquid is removed from the first half of the column and deposited in the outlet half so that in eqn. (22) the film thickness may be expressed as $d_f/2$ for the first half of the column length and as $3d_f/2$ in the outlet half.
Integration yields

$$H_{\mathrm{obs}} = S + \frac{Tkd_f^3}{4} \left[\frac{1}{(2 + kd_f)^2} + \frac{27}{(2 + 3kd_f)^2} \right] \qquad (23)$$

In the limiting case of $kd_f \ll 1$

$$H_{\mathrm{obs}} = S + {}^7/_4 Tkd_f^3 \qquad (24)$$

and for $kd_f \gg 1$

$$H_{\mathrm{obs}} = S + \frac{Td_f}{k} \qquad (25)$$

Comparison of these results with those for a uniform column, eqns. (20) and (21), reveals that band broadening due to chromatodiffusion is very nearly double for fast peaks but is unaltered for very slow peaks when there is uneven distribution.

The integrals of eqn. (22) are evaluated over the lengths of the respective regions and their values are independent of the location relative to the column outlet.

It is interesting to inquire if there is a particular stepwise distribution, i.e., values of the lengths of sections of column and their partitioner loads for which H_{obs} is less than that of the uniform column, or lacking this, if a maximum or minimum exists as these lengths and loads are varied. This question concerns the conditions for which the total derivative of H_{obs} vanished, i.e.,

$$\mathrm{d}H_{\mathrm{obs}} = \frac{\partial H_{\mathrm{obs}}}{\partial d_{f1}} \, \mathrm{d}(d_{f1}) + \frac{\partial H_{\mathrm{obs}}}{\partial d_{f2}} \, \mathrm{d}(d_{f2}) + \frac{\partial H_{\mathrm{obs}}}{\partial L_1} \, \mathrm{d}L_1 + \frac{\partial H_{\mathrm{obs}}}{\partial L_2} \, \mathrm{d}L_2 = 0 \qquad (26)$$

However, these thicknesses and lengths cannot be varied arbitrarily but must have values which satisfy the restraining conditions that there shall be no loss of partitioner from the column;

$$d_{f1}L_1 + d_{f2}L_2 = C = \text{constant} \qquad (27)$$

and that the length of column is constant;

$$L_1 + L_2 = L \qquad (28)$$

This problem is most easily approached by Lagrange's method of undetermined

multipliers which yields the set of six simultaneous equations in six unknowns, df_1, df_2, L_1, L_2 and the two undetermined multipliers μ and η.

$$\left[\frac{Tkdf_1^2}{L} \frac{(3 + kdf_1)}{(1 + kdf_1)^3} + \mu \right] L_1 = 0 \tag{29}$$

$$\left[\frac{Tkdf_2^2}{L} \frac{(3 + kdf_2)}{(1 + kdf_2)^3} + \mu \right] L_2 = 0 \tag{29}$$

$$\frac{Tkdf_1^3}{L(1 + kdf_1)^2} + \mu df_1 + \eta = 0$$

$$\frac{Tkdf_2^3}{L(1 + kdf_2)^2} + \mu df_2 + \eta = 0 \tag{29}$$

and equations (27) and (28).

It is sufficient to eliminate μ from the first two equations which, on noting that $Tk/L \neq 0$, gives

$$L_1 L_2 \left[\frac{df_1^2 (3 + kdf_1)}{(1 + kdf_1)^3} - \frac{df_2^2 (3 + kdf_2)}{(1 + kdf_2)^3} \right] = 0 \tag{30}$$

Since kdf_1 and kdf_2 cannot be negative so that $(3 + kdf_1)$ and $(3 + kdf_2)$ cannot vanish, it must be that for a maximum or a minimum either $L_1 = 0$, or $L_2 = 0$, or $df_1 = df_2$. All of these imply a uniform liquid load. Since it has been shown that an arbitrary stepwise distribution leads to an increased H_{obs} for fast peaks, the uniform column must represent a minimum in H_{obs} and any redistribution which leads to a stepwise or discontinuous distribution must show a loss of efficiency with use. This result holds for any particular partitioner load.

In all of the discussion it has been tacitly assumed that the partitioning liquid undergoes no chemical change so that the distribution coefficient, α, as it appears in R, and the liquid diffusion coefficient, D_2, as it appears in the chromatodiffusion term of eqn. (11), undergo no change with use. This may not be true as has been pointed out previously[1,2]. Such changes have not been the subject of extensive study. One may expect that materials which polymerize further on ageing will lead to a decrease in D_2 with concomitant increase in the observed plate height. At this point it is difficult to generalize further.

EXPERIMENTAL

Two $1/4$ in. O.D. copper tubing columns, 1 m in length, were packed with 60–80 mesh Chromosorb P loaded with 7.5 and 15 % Apiezon L, respectively. The columns were joined in series and placed in a PE 154 unit with a thermal conductivity detector. The columns were conditioned for 4 h at 150° using He as carrier with the 15 % column at the outlet side. Four microliter samples of n-heptane were injected using the flow rates indicated by the experimental points in Fig. 1. The operating temperature was 100°. The column was reversed and the procedure repeated at otherwise identical conditions. Return of the column to the initial orientation and a repetition of the procedure gave results consistent with the initial run. Flow rates were deter-
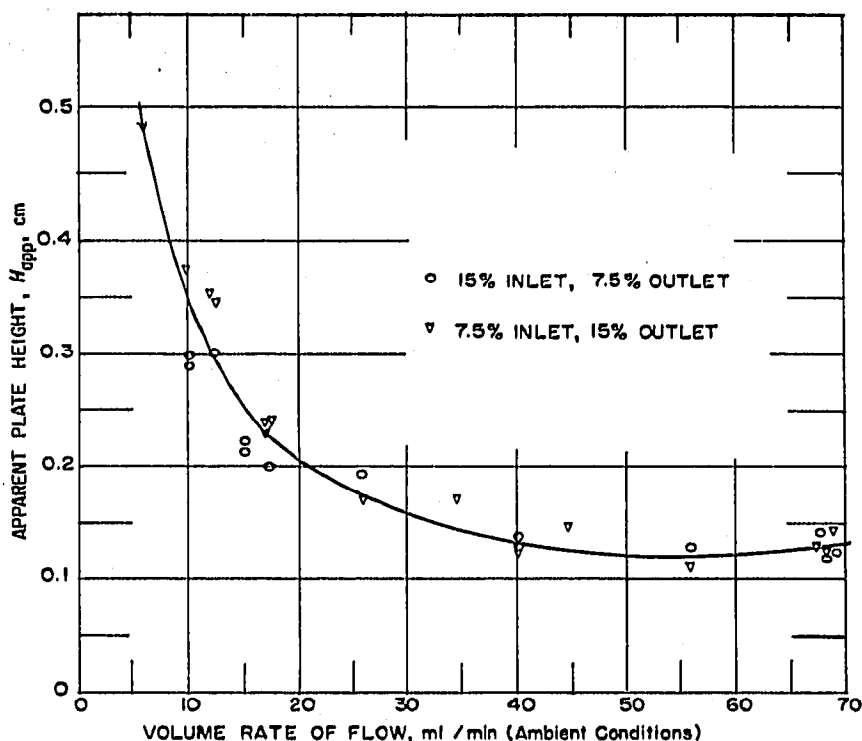
Fig. 1. The reversal of flow through a discontinuous column does not appreciably affect the apparent plate height. This illustrates the compensation of the elution effect by the R-gradient effect.

mined with a soap film flow meter. The results are shown in Fig. 1 where H_{app} is graphed *versus* the flowrate.

It is concluded that H_{app} is independent of column orientation within the precision of the experiment.

DISCUSSION

The conclusion applies only to chromatographic columns in which there is a stepwise distribution of partitioning liquid. It is assumed that the change giving rise to this redistribution occurs with no net loss of partitioner from the column, *i.e.*, columns of constant total liquid content are compared. The first condition is realistic in the sense that carrier gas which is unsaturated with partitioner will lead to evaporation of this liquid at the column inlet. Upon the carrier gas becoming saturated, evaporation will suddenly cease to give a discontinuity. That such a situation arises experimentally was shown by earlier communications in this series. The second postulate is not encountered experimentally since it assumes a volatile partitioner without column bleeding. This restriction is made in order to isolate the effect of redistribution without compounding the difficulties of a theoretical treatment. Practically, it is of interest to inquire if such a distribution will enhance column performance. The treatment presented assumes that inlet and outlet pressures are nearly equal, that the carrier gas velocity at the outlet is the same as the average velocity through the column, that there is no change in the chemical and physical properties of the partitioner, that the support is perfectly inert and does not participate in retention, that the only term in the Van Deemter equation affected by the partitioner distribution is the one describing chromatodiffusion and that the entire equation is independ-

ent of solute identity, and that a microscopic equilibrium distribution of liquid on the support exists. The model chosen for calculations presumes a packing of perfect spheres, all of the same size, uniformly coated with liquid. Examples of the contributions of various geometries of partitioning liquid and flow patterns of the mobile phase to local plate heights have been presented by GIDDINGS[6]. Nonuniform columns introduce two new effects not encountered in uniform columns. The "elution" effect arises from a partitioner load at the outlet which is different than the average load in the body of the column and produces an eluted peak with a width different from the actual zone width on the column. If this were the only difference in behavior, the theoretically important plate height defined in terms of the actual peak variance and column length, eqn. (1), is not equivalent to its experimental counterpart, the measurement of the peak variance and position on the chromatographic record. The "R-gradient" effect produces a contraction or expansion of the peak as the zone encounters regions of different liquid load. This change points out that peak width is not a function of average liquid load. The "elution" and "R-gradient" effects operate in opposite senses and tend to compensate each other. Experiments with a column with a discontinuous distribution show that these two effects compensate each other in the respect that the directions of operation of the column are indistinguishable from the apparent plate height. Such a complete compensation may not exist for continuous non-constant liquid distributions. Such continuous distributions are artificial in the sense that they do not arise from normal column operation but must be introduced with deliberate intent.

An examination of the chromatodiffusion term of the Van Deemter equation, which includes mass transfer and diffusion effects, shows that a change from a uniform distribution to a stepwise distribution will lead to an increased plate height and a less efficient column and is independent of the direction of operation of the column. This conclusion includes all of the assumptions inherent in the Van Deemter equation, mainly that diffusion through the liquid phase is completely rate controlling. If this is not true, the mobile phase may also contribute to local zone spreading. It should be noted that spreading due to diffusional processes in the mobile phase are functions of the relative velocity R, and are also subject to change as a function of redistribution and column bleeding. This matter has been ignored here.

In the normal operation of a column there will not only be a redistribution of liquid but also a net loss of this liquid. If the liquid evaporated at the inlet is not deposited at the outlet end but bleeds off of the column, the film thickness will decrease at the inlet end and remain constant at the outlet end. The column will behave as one of lower loading and it has been amply demonstrated by other investigators that the efficiency of a column will improve with diminishing loads[7]. The tendency to increased plate height brought about by redistribution is counteracted by the trend to a lower load column. It might be that the combination of these two effects leads to H_{obs} passing through a maximum during the early history of the column. This interesting hypothesis has not yet been subjected to mathematical analysis.

It may happen that in the preparation of a column, a microscopic equilibrium distribution does not exist, i.e., the surface free energy is not constant over the liquid surface. During column conditioning, the liquid will redistribute until this condition exists. The liquid transport will take two forms. If liquid is thickly deposited in

some regions and too thinly in others, the liquid will spread. One might consider as a possible model for this situation a column containing excessively wet adsorbent in one part of the column and the sparsely covered support in the other part to give a discontinuous column. Conditioning would be a change toward the uniform column. The total amount of liquid in the column will remain constant and the average film thickness will remain constant. That this latter statement is true is shown by the hypothetical column where the film thickness is proportional to $(c/2)(L/2)$ in one half of the column and to $(3c/2)(L/2)$ in the remainder of the column (eqn. (16) relates film thickness directly to the volume of liquid). The average film thickness is the same as that of the companion uniform column. Conditioning would lead to a decrease in the plate height with this microscopic redistribution. This is a striking demonstration of the uselessness of considering the total amount of liquid and the average film thickness in relating plate heights to liquid distribution. Microscopic redistribution can also involve deposition of the liquid at the contact points between particles where the radius of curvature of the liquid surface is particularly small. This can only occur in the packed column during conditioning and will take place even if the partitioner is deposited on the support very slowly so that, before packing, the surface free energy of the liquid is constant over the support. According to the model proposed, the introduction of these "puddles" corresponds to the introduction of a discontinuity in the column, *i.e.*, the model would be a column where the packing carries a liquid load corresponding to the contact points in one part of the column and in the other, a liquid load corresponding to "non-contact point" load. Again, nothing need be known about the average film thickness to predict a decrease in column efficiency as liquid is transported to these contact points. The only supposition has been that a column containing regions differing dramatically in film thickness can be treated as a discontinuous column. With carefully prepared packing materials, it is probable that collection at the contact points is the principal change during microscopic redistribution. A column used before this equilibration is complete will likely show a maximum in the observed plate heights as this redistribution occurs and is followed by column bleeding.

The foregoing presentation demonstrates the difficulties involved in the evaluation of the parameters of a plate height expression in terms of observed plate height. Even in the absence of longitudinal nonuniformity of the column packing, there will always exist a pressure and velocity gradient. The low velocity extant at the inlet end of the column leads to a greater retention of zones in this region of the column and a greater contribution to the spreading by the local parameters in this end of the column. Another way of expressing this is to say that the solute does not experience in time the geometrical distribution of partitioner along the column. Calculation of the "time distribution" from the "geometrical distribution" is formidable since the relation between the two is non-linear. This is the motivation for assuming equal outlet and average carrier gas velocities in the theoretical calculations. In such a case, these two distributions are identical. A pressure gradient will magnify the effects of the loss of material at the column inlet.

Remarks pertinent to the participation of the support in retention as it depends on the liquid load have been made elsewhere[8].

SYMBOLS

A_1	cross-sectional area of the immobile liquid phase
c	concentration of partitioning liquid in the column
d_f	effective liquid film thickness; d_{s_1}, d_{s_2} effective film thicknesses in parts 1 and 2 of a column with a discontinuous liquid distribution
d_p	particle diameter
D	effective diffusion coefficient of the solute
$D_1' = D_1 p_i$	molecular diffusivity of the solute in the mobile phase times the pressure at column position i.
D_2	molecular diffusivity of the solute in the immobile liquid phase
H_{app}	apparent plate height
H_{local}	local plate height
H_{obs}	observed plate height
j	length of column occupied by the solute zone
k, k_1, k_2	constants
L	column length; L_1, L_2 lengths of sections of the column with different partitioner concentrations for a discontinuous liquid distribution
p	pressure
p_i	pressure at column position i
p_o	pressure at column outlet
r	radius of a support particle
R	fraction of solute molecules in the gas phase
R_i	R value at column position i
R_{in}	R value at column inlet
R_o	R value at column outlet; $R_o(1)$, $R_o(2)$: R value in parts 1 and 2 of a column with a discontinuous liquid distribution
S, T	constants independent of the column position and length
α	partition coefficient of the solute between the mobile and imobile phase
η	Lagrangian undetermined multiplier
λ	factor in eddy diffusivity
μ	Lagrangian undetermined multiplier
ρ	number of particles of packing in unit length of column
σ	standard deviation of a Gaussian distribution measured in units of length
σ_i	value of standard deviation at column position i
$\delta\sigma$	increment of standard deviation
τ	standard deviation of a Gaussian distribution measured in units of time.

SUMMARY

This third communication of a series dealing with the effects of a nonuniform distribution of partitioning liquid in a column on gas–liquid chromatographic behavior treats relationships between the observed plate height and the plate height contributions of each section of the column. The specific distribution considered is stepwise, *i.e.*, the liquid load is assumed to be constant up to a certain position whereupon it suddenly changes to some new value which is then constant throughout the remainder of the column. The apparent plate height depends upon an "elution" effect arising from a liquid load different at the outlet from the average liquid load. The "elution" effect is opposed by an "*R*-gradient" effect arising from a change in the fraction of the number of solute molecules in the mobile phase with a change in the liquid load. Experiment shows that these two effects essentially cancel each other. An examination of the chromatodiffusion term of the Van Deemter equation, which deals with mass transfer and diffusion effects, shows that for a constant total amount of liquid in the column with the assumed distribution, is less efficient than one with a uniform distribution. The results are independent of the direction of carrier gas flow. The implications of these results with regard to column conditioning and use are discussed.

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