Column Height Required for Continuous Chromatographic Separation: A Probabilistic Model

C. T. SCIANCE and O. K. CROSSER
University of Oklahoma, Norman, Oklahoma

A probabilistic model is used to develop the mathematical theory of a continuous chromatographic column. Equations are developed relating column height, feed location, degree of separation, and flow rates. Necessary sorption data can be obtained from a fixed-bed chromatographic column.

Chromatography is a widely used method for separating substances, in which a sample mixture is injected into a moving fluid which carries it through a fixed adsorbing bed. The adsorption characteristics differ among the components of the sample, causing each to move through the bed with its own average velocity. The bed is made long enough so that the sample can separate into bands containing a single substance, each emerging from the column at a different time.

In the last few years, it has been demonstrated (*1*) that azeotropic and close-boiling mixtures can be separated continuously in a moving-bed column. A diagram of one method is shown in Figure 1. (Reference *1* refers also to references *2* through *9*.)

For the moving-bed column, this paper develops the relationship among column height, feed location, and degree of separation of a binary mixture. Application of probability theory results in simple equations requiring only data from a standard (fixed-bed) chromatography column.

These equations should provide a quick estimate of the feasibility of a proposed separation process, as a guide to whether further experimental work is justified.

For convenience in notation, a binary mixture separated by gas chromatography is referred to in this paper. The subscript P may be understood to refer to the packing or to the liquid film on the packing. If two key components are selected; a multicomponent mixture can be treated in the same way, and the random-walk principle applies to any kind of chromatography.

DISPLACEMENT OF A MOLECULE DURING ONE PATH PAIR

The Concept of the Path Pair

A molecule moving through the column will move in discrete steps consisting of an "adsorbed path" and a "free path." It will be convenient to speak of these as always occurring together and to refer to this combination of movements as a "path pair." All equations which will be derived are based on the assumption that the movement of each molecule is a series of path pairs; this excludes from consideration any case where the length of the adsorbed path would be identically zero. The relationships to be developed will not, therefore, reduce to those for a fixed-bed column by setting the velocity of the packing to zero. In addition, the possibility of a molecule passing through the column unadsorbed is excluded; but in any nontrivial case this should introduce a negligible error. It is further assumed that the volume flow rate of the feed is negligible in comparison with that of the carrier gas, and that all velocities and other properties remain constant through the column.

The path of the molecule during a single path pair is illustrated in Figure 2*a*. In this development, it will be assumed that when a molecule of A or B is in the gas phase, it will move with the average velocity of the carrier gas (V_G); and when it is adsorbed it moves with the average velocity of the bed (V_P). If the total displacement of the molecule during one path pair is denoted by X

$$X = t_f V_G - t^* V_P \tag{1}$$

where t_f and t^* are the times that the particle spends in the carrier gas and the liquid phase, respectively. It should be emphasized that the positive direction is in the direction of flow of the carrier fluid, and the packing

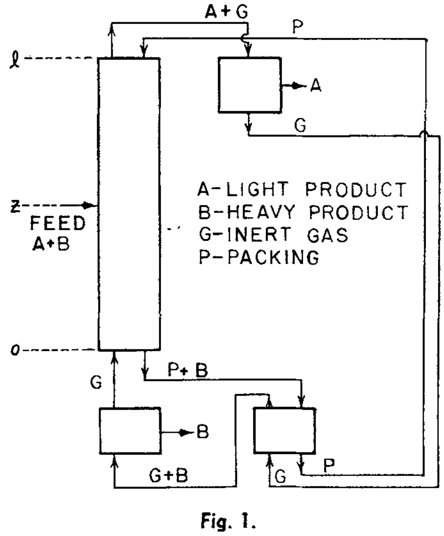

Fig. 1.

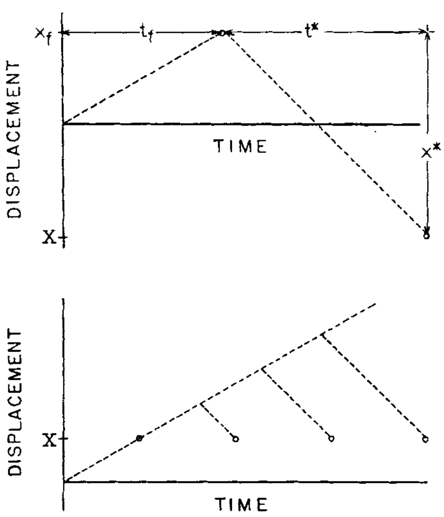

Fig. 2*a* (*top*) and Fig. 2*b* (*bottom*).

moves in the negative direction. V_G and V_P are both positive numbers.

Probability Density Function for Displacement

There are infinitely many combinations (t_f, t^*) which will result in any given X. This fact is illustrated in Figure 2*b*. It now becomes necessary to develop an expression for the probability that a path pair will result in a given total displacement X.

The times t_f and t^* are assumed to be independent of each other, and so the probability of any *particular* combination of free path length x_f and adsorbed path length x^* can be written

$$P(x_f, x^*) = P(x_f) \cdot P(x^*) \tag{2}$$

In general, the probabilities for x_f and x^* will be different functions, and the corresponding probability density functions will be denoted by $p_1(x)$ and $p_2(x)$, respectively. A probability density function is defined as the function $p(x)$ from which the probability $P(E)$ of an event E can be obtained by integrating $p(x)$ over E; for example, $P(E) = \int_E p(x)dx$; $p(x) \geqq 0$ for all x in E. In this case an event E is defined as a net displacement X resulting from some combination (x_f, x^*). Equation (2) then leads to

$$p(x_f, x^*) = p_1(x_f) \cdot p_2(x^*) \tag{3}$$

Figure 1*a* illustrated that $X = x_f - x^*$, so the probability density function $p(X)$ is obtained from the equation

$$p(X) = \int_{x_f} p_1(x) \cdot p_2(x - X)dx \tag{4}$$

The integration is over all possible values of x_f, as can be seen by comparing Equations (3) and (4). There are *two cases* which must be considered:

1. If $X \geqq 0$, then x_f must have been at least as large as X, because during time t^* the molecule moves so as to decrease X, and t^* must be greater than or equal to zero.
2. If $X \leqq 0$, then x_f could be any value greater than or equal to zero.

The probability density function of the random variable X is therefore described by Equations (5) and (6). X can be any real number.

$$p(X) = \int_X^\infty p_1(x) \cdot p_2(x - X)dx; \quad X \geqq 0 \tag{5}$$

$$p(X) = \int_0^\infty p_1(x) \cdot p_2(x - X)dx; \quad X \leqq 0 \tag{6}$$

In the development leading to Equations (5) and (6), it was assumed that probability density functions p_1 and p_2 could be found to describe the likely length of either a free path or an adsorbed path. The source for this kind of information should be the fixed-bed chromatographic column. In particular, what is wanted is a rate expression which will give the probable time remaining before the molecule changes phase.

Giddings and Eyring (*11*) have developed a dynamic theory of chromatography by using the Poisson probability law. By using their method and a standard fixed-bed column as much like the proposed moving-bed column as possible, we can obtain the rate constants k and k'. The significance of these constants is explained (*11*):

> "When a molecule is in the liquid [gas] phase there is a definite, non-varying constant k_1 representing the probability per unit time that the molecule will adsorb on the surface. Also, when the molecule is on the surface, there is a definite probability per unit time of desorption which we call k_1'. k_1' is simply the unimolecular rate constant for dissociation of the surface and the solute molecule. k_1 is a rate constant for adsorption multiplied by the concentration of sites."

The reader is referred to this article for a detailed discussion of assumptions, which, of course, are also implied in this development.

The Poisson probability law in the form

$$P(k; \lambda t) = e^{-\lambda t} \frac{(\lambda t)^k}{k!} \tag{7}$$

expresses the probability of the occurrence of exactly k events in a fixed time interval of length t. If t° is the residence time of the carrier fluid in a chromaotgraphic column, then t° is also the time that each molecule spends in the carrier phase. The probability that a molecule experiences exactly r adsorptions while passing through the column is given by $P(r; kt^\circ)$. The probability of at least one adsorption in an arbitrary interval of length t is then

$$1 - P(0; kt) = 1 - e^{-kt} \tag{8}$$

If Equation (8) is used to express the probability that the free path will terminate before time t_f, and we recall that $t_f = x_f/V_G$

$$1 - P(0; kt_f) = 1 - e^{-kx_f/V_G} \tag{9}$$

The probability density function for the free path length $p_1(x)$ can be formally obtained by differentiating the probability distribution function in Equation (9). The result is the well-known exponential probability density function.

$$p_1(x) = (k/V_G)\, e^{-kx/V_G} \tag{10}$$

A similar treatment for the adsorbed path leads to the probability density function

$$p_2(x) = (k'/V_P)\, e^{-k'x/V_P} \tag{11}$$

Define the new constants

$$\alpha \equiv k/V_G \tag{12}$$

$$\beta = k'/V_P \tag{13}$$

Substitution of Equations (10), (11), (12), and (13) into (5) and (6) gives

$$p(X) = \alpha\beta\, e^{\beta X} \int_X^\infty e^{-(\alpha+\beta)x}\, dx \quad X \geqq 0 \tag{14}$$

$$p(X) = \alpha\beta\, e^{\beta X} \int_0^\infty e^{-(\alpha+\beta)x}\, dx \quad X \leqq 0 \tag{15}$$

Integration of Equations (14) and (15) yields expressions for the probability that a molecule will be displaced a distance X after one path pair.

$$p(X) = \left(\frac{\alpha\beta}{\alpha + \beta}\right) e^{-\alpha X} \quad X \geqq 0 \qquad (16)$$

$$p(X) = \left(\frac{\alpha\beta}{\alpha + \beta}\right) e^{\beta X} \quad X \leqq 0 \qquad (17)$$

Probability Mass Function for Displacement

Up to this point the displacement X has been permitted to take on any real value. Suppose X is allowed to take on only certain values, spaced uniformly in integral multiples of a basic length δ. The probability that $(c - \frac{1}{2})\delta \leqq X \leqq (c + \frac{1}{2})\delta$ is

$$P_c \equiv \int_{(c-1/2)\delta}^{(c+1/2)\delta} p(X)\, dX \qquad (18)$$

From the definition of probability comes the relationship

$$\sum_{c=-\infty}^{+\infty} P_c = 1 \;\; (c \text{ an integer}) \qquad (19)$$

It is easy to verify that one could choose a large positive integer μ so that the sum $\sum_{c=\mu}^{\infty} P_c < \epsilon$, where ϵ is arbitrarily small. Similarly, a large negative integer ν can be found so that $\sum_{c=-\infty}^{\nu} P_c < \epsilon$. By adding these sums to P_μ and P_ν, respectively, we obtain a discrete representation of X, which is designated the probability mass function. Equation (19) still holds with limits ν and μ on the sum.

The reason for doing this is that the treatment of a generalized one-dimensional random walk, applicable to a discrete probability distribution, has been presented in a straightforward manner by Feller (*10*). A summary of these results follows.

Define P_c as the probability that at each step the particle will move from point x to the point $x + c$, where c may be any integer in the range $\nu \leqq c \leqq \mu$, including zero.

Define u_z as the probability that a particle, starting at some position z such that $0 < z < l$, will arrive at some position $\leqq 0$ before reaching any position $\geqq l$. (l is the column height.)

Define ξ to be the unique positive root different from unity of the characteristic equation*

$$\sum_{c=\nu}^{\mu} P_c s^c = 1 \qquad (20)$$

Finally, Feller develops the inequality

$$\frac{\xi^l - \xi^z}{\xi^l - \xi^{\nu+1}} \leqq u_z \leqq \frac{\xi^{l+\mu-1} - \xi^z}{\xi^{l+\mu-1} - 1} \qquad (21)$$

Generalization to the Continuous Model

Let us examine this equation as $\nu \to -\infty$ and $\mu \to \infty$. We get two possible results, according to $\xi < 1$ or $\xi > 1$. Recall that we neglect the event $\xi = 1$ as being of trivial interest.

(1) $\xi < 1$. In this event, $\xi^{\nu+1} \to \infty$ and $\xi^{l+\mu+1} \to 0$, giving

$$0 \leqq u_z \leqq \xi^z \qquad (22)$$

(2) $\xi > 1$. In this event, $\xi^{\nu+1} \to 0$ and $\xi^{l+\mu+1} \to \infty$, giving

$$1 - \xi^{(z-l)} \leqq u_z \leqq 1 \qquad (23)$$

Returning to the characteristic Equation (20), we replace the sum by an integral ($\delta \to 0$), let $\nu \to -\infty$, and $\mu \to \infty$, and obtain

$$\int_{-\infty}^{\infty} p(X)\, s^X\, dX = 1 \qquad (24)$$

After substituting Equations (16) and (17) for $p(X)$, one can integrate Equation (24) to obtain

$$\xi = e^{\alpha-\beta} \qquad (25)$$

If $\alpha > \beta$, or $(k/V_G) > (k'/V_P)$, we have the slower moving component B; if $\alpha < \beta$ we have component A. Then (22) and (23) become

$$0 \leqq (u_z)_A \leqq e^{z(\alpha_A-\beta_A)} \qquad (26)$$

$$1 - e^{-(l-z)(\alpha_B-\beta_B)} \leqq (u_z)_B \leqq 1 \qquad (27)$$

Procedure for Sizing the Column

Degree of Separation Required. Suppose there are two requirements: at least 99.99% of component A must go out the top of the column, but not more than 0.01% of component B may do so. By recalling the definition of (u_z), we find that this means

$$(u_z)_A \leqq 0.0001$$

$$(u_z)_B \geqq 0.9999$$

By comparing these restrictions with Equations (26) and (27), we find apparent that a *conservative* estimate is obtained by solving simultaneously Equations (28) and (29) with $(u_z)_A = [1 - (u_z)_B] = 10^{-4}$.

$$z(\alpha_A - \beta_A) = \ln\, (u_z)_A \qquad (28)$$

$$-(l - z)(\alpha_B - \beta_B) = \ln\, [1 - (u_z)_B] \qquad (29)$$

Determination of V_G *and* V_P. These quantities may be selected anywhere in the range that A moves, on the average, up the column while B moves down. In other words, as long as $\alpha_B > \beta_B$ and $\alpha_A < \beta_A$, V_G and V_P are arbitrary. They would ordinarily be adjusted so that $z \sim \frac{1}{2}l$. In fact, if $z = \frac{1}{2}\, l$, solving the equations for (V_G/V_P) and l is straightforward.

COMPARISON WITH EXPERIMENTAL RESULTS

If a column is designed so that the feed is introduced in the middle, then $z = \frac{1}{2}l$. If the reactions of adsorption and desorption are in equilibrium, the ratios (k_i/k_i') can be approximated by K_i^∞, the partition coefficient. In this form (28) and (29) can be rearranged as follows:

$$\ln\, [(u_z)_A] = \frac{lk_A'}{2V_G}\left(K_A^\infty - \frac{V_G}{V_P}\right) \qquad (30)$$

$$\ln\, [1 - (u_z)_B] = \frac{-lk_B'}{2V_G}\left(K_B^\infty - \frac{V_G}{V_P}\right) \qquad (31)$$

$(u_z)_A$ is the ratio $\left(\frac{\dot{M}_{A,\ \text{bottom}}}{\dot{M}_{A,\ \text{feed}}}\right)$, and $[1 - (u_z)_B]$ is $\left(\frac{\dot{M}_{B,\ \text{top}}}{\dot{M}_{B,\ \text{feed}}}\right)$ where $\dot{M}$ is the mass flow rate. Unfortunately, k_A' and k_B' must still be measured or determined from a data point, even if values for K_i^∞ are available. Although published data are scarce and have enough scatter so as to deny direct comparisons, one useful fact can be emphasized. Because the left sides of (30) and (31) are negative and all quantities on the right are positive

$$K_A^\infty < \frac{V_G}{V_P} < K_B^\infty \qquad (32)$$

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* Because ν is negative, $s = 0$ makes the sum infinite. As $s \to \infty$, the function also becomes infinite. One root is 1, from Equation (19). The function is convex; therefore, exactly one other positive root exists. If the other root were also 1, it would mean that $p(X)$ is symmetric about $X = 0$. Consequently no driving force would exist to make the component go either up or down the column. We discard this trivial case; hence the root $\xi \neq 1$.

This result is known (*1*) to be the theoretical maximum range. This is the same restriction mentioned above under *Determination of* V_G *and* V_P.

ANALOGY WITH THE TRANSFER UNIT APPROACH

Although continuous chromatography is a novel process, the model developed above is applicable to any continuous countercurrent mass transfer process. The assumptions included: constant phase flows, straight equilibrium and operating lines, and key components entering only in the feed. King (*12*) has pointed out that by applying one Colburn type of equation, as described by Sherwood and Pigford (*13*), to the column section below the feed and another to the section above the feed, the following definition of $(u_z)_i$ is obtained:

$$(u_z)_i = \frac{1 - \exp\left[(N_{OGi})_1(1-\lambda_i)\right]}{\lambda_i \exp\left[(N_{OGi})_2(\lambda_i - 1)\right] - \exp\left[(N_{OGi})_1(1-\lambda_i)\right]} \tag{33}$$

where $(N_{OGi})_1$ is the number of transfer units in the section above the feed, $(N_{OGi})_2$ is the number in the lower section, and λ_i is the ratio $(m_i G_M/L_M)$ of Sherwood and Pigford.

King also suggests that the term λ_i is directly analogous to the ratio (β_i/α_i); and further that the height of a transfer unit is equivalent to the expected value (average) of the "free path" explained above, for example, that $H_{OGi} = 1/\alpha_i$. Consistent with these suggestions, Equation (33) becomes

$$(u_z)_i = \frac{1 - \exp\left[(l-z)(\alpha_i - \beta_i)\right]}{(\beta_i/\alpha_i)\exp\left[-z(\alpha_i - \beta_i)\right] - \exp\left[(l-z)(\alpha_i - \beta_i)\right]} \tag{34}$$

which holds for both components.

Equation (34) satisfies the inequalities (26) and (27), as can be verified by recalling that $\alpha_A < \beta_A$ and $\alpha_B > \beta_B$.

CONCLUSIONS

Data required for this procedure are readily obtained from standard apparatus. The simplicity of the calculation allows a quick estimate of the practicability of continuous chromatographic separation.

This probabilistic model establishes the connection between the fixed-bed parameters of a chromatographic process and its continuous analog.

ACKNOWLEDGMENT

The authors wish to acknowledge the helpful comments of Professor King in his review of this article. C. T. Sciance gratefully acknowledges the financial support of the National Aeronautics and Space Administration and of Conch Methane, Ltd., and the helpful discussions with Dr. John E. Powers.

NOTATION

c = integer in the range $\nu \leq c \leq \mu$
e = base of natural logarithms
k = probability per unit time that a molecule will adsorb
k' = probability per unit time that a molecule will dissociate from the surface of the bed
l = column length
$p(E)$ = probability density function of event E
$p_1(x)$ = probability density function for a free path of length x
$p_2(x)$ = probability density function for an adsorbed path of length x
s = variable in the characteristic Equation (20)
t = time
t_f = time elapsed during the free path
t^* = time elapsed during the adsorbed path
t° = residence time of the carrier fluid in a fixed-bed chromatographic column
u_z = probability that a particle starting from point z will cross the line at 0 before crossing the line at l
x = displacement
x_f = displacement during free path
x^* = displacement during adsorbed path
z = location of feed from the bottom of the column
$\dot{M}$ = mass flow rate
$P(E)$ = probability of event E
$P(k;\lambda t)$ = Poisson probability law, expressing the probability of exactly k events occurring in a fixed time interval of length t. λ is a parameter expressing the expected number of occurrences.
P_c = probability that $(c - \frac{1}{2})\delta \leq X \leq (c + \frac{1}{2})\delta$
V = average linear velocity of the phase or component
X = total displacement of a molecule during one path pair

Greek Letters

α = k/V_G, Equation (12)
β = k'/V_P, Equation (13)
δ = arbitrary length. All molecules are assumed to move up or down the column in integral multiples of length δ
ϵ = arbitrarily small constant
μ = maximum possible displacement in the positive direction during one path pair
ν = maximum possible displacement in the negative direction during one path pair. ν is a negative number
ξ = unique positive root other than unity of Equation (20)

Subscripts

A = component A, the faster moving key
B = component B, the slower moving key
G = carrier gas
P = packing, or bed

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Manuscript received March 9, 1965; revision received September 9, 1965; paper accepted September 10, 1965. Paper presented at A.I.Ch.E. San Francisco meeting.