Theoretical-plate Concept in Chromatography

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The theoretical-plate concept in chromatography has been treated on the basis of continuous flow of eluent through the plates of the column. A treatment more precise in principle than the previous treatments is presented. General elution and deposition equations have been derived and applied to special cases of practical interest. The derived formulas have the advantage of precision, generality, and simplicity.

The theory was found adaptable to the treatment of gradient elution and also to the calculation of the fraction of solute which has been eluted or still-adsorbed on the column during the elution process.

A method for the determination of the number of theoretical plates in a chromatographic column is also described.

The similarity between the chromatographic and the distillation and extraction fractioning columns has been realized for a long time, but it was only recently that theories of chromatography based on the concepts which had been developed for distillation were worked out in detail.

The first detailed theory of chromatography using the concepts developed for distillation was offered by Martin and Synge in 1941 (*5*). They were able to give a picture of the concentration of solute at any time and place in the column. Their treatment was based on a continuous-flow model of the mobile phase through the plates.

In 1947 Mayer and Tompkins (*6*) applied a plate theory to the determination of the composition of the eluate and to the prediction of the distribution of the various substances on the column. Their theory was based on a discontinuous model where a finite eluent volume is equilibrated step by step with one theoretical plate in the column after another. They were able to derive an expression for the concentration distribution which they approximated to an error distribution for a large number of theoretical plates.

Martin and Synge, as well as Mayer and Tompkins, treated only the case where all the solute was deposited on the top plate of the column at the beginningof the elution process.

In 1955, Glueckauf (*4*) pointed out that the Mayer and Tompkins discontinuous model does not represent the physical picture of the process and would lead to large errors even if the number of theoretical plates were as high as 1,000. He derived a partial-differential equation based on a continuous-flow model and solved the equation to obtain an error distribution of solute on the column, but he had to assume a large number of theoretical plates. He developed equations both for the deposition process and for the elution of a zone which was evenly distributed over a finite number of theoretical plates.

This present theory relies on the same two basic assumptions as did the previous authors, namely, that solutes adsorbed on the column have linear-adsorption isotherms and that the chromatographic column is equivalent to a certain number of theoretical plates. It is based on a continuous-flow model of eluent through the plates, just as are the theories of Martin and Synge and of Glueckauf. Throughout the development of this theory no assumptions were made as to the number of theoretical plates or as to the relative width of the zone compared with the length of the column. The results obtained which gave the concentration distribution of the solute on the column and in the eluate are in the forms of Poisson summation distributions, the values of which are tabulated in many references (*7*). Charts are also available for these distributions (*2*). This makes the computations very simple as well as exact and the accuracy does not depend upon the relative distance from the peak of the zone; the approximations involved in the previous treatments, on the other hand, have made the results less applicable at regions far from the peak of the zone.

When a solute is deposited from a solvent at the top of a column consisting of a finite number of theoretical plates, it is evident that according to the two basic assumptions of this theory, the solute will not be totally deposited on the top plate only. It is also clear that the concentration of the solute on the plates will decrease from the top plate downward according to a certain distribution; therefore the assumption that the zone is deposited only on the top plate as well as that it is deposited evenly on a finite number of plates cannot accurately represent the actual distribution at the start of the elution process although the second assumption is a better approximation than the first. These two assumptions were the only cases dealt with by the previous authors. The present treatment, besides being a means by which these two cases can be handled, can also be used effectively for the actual case.

One of the advantages of this theory is the simplicity with which the process of gradient elution can be treated quantitatively. Gradient elution is relatively a new technique which was developed by Alm, Williams, and Tiselius (*1*) in an effort to overcome the tailing of elution bands. An attempt to apply the Mayer and Tompkins equations to gradient elution was made by Freiling (*3*), who obtained relations which would determine the efficiency of the separation of bands. These relations, besides being not simple, were also approximate—owing, mainly, to the fact that the author found it necessary during the derivations to use the Mayer and Tompkins equations at the beginning and at the end of a run where they are least applicable. It is hoped that the present treatment will be capable of predicting, without elaborate calculations, whether it is advantageous to use gradient elution for a certain separation.

DEVELOPMENT OF THE THEORY

In the development of this theory the following assumptions were made.

1. The chromatographic column is equivalent to a plate column consisting of N theoretical plates. Each plate contains S/N g. adsorbent where S is the total weight of adsorbent and N is the total number of theoretical plates. The distance between every two successive plates $= v_f/NA$ where v_f is the free volume and A is the cross-sectional area of the column.
2. The eluent passes continuously and without mixing through these plates.
3. The adsorption isotherms are linear.

Derivation of the General Equation for the Elution Process

At the beginning of the process the concentration of solute on Plates 1, 2, 3, 4, $\cdots$, n, $\cdots$, N is assumed to be $y_1^0, y_2^0, y_3^0, y_4^0, \cdots, y_n^0, \cdots, y_N^0$ respectively, and at any time during the elution the concentrations are $y_1, y_2, y_3, \cdots, y_n, \cdots, y_N$ as shown in the following figure.

As the eluent crosses plate 1, the solute will pass gradually from the plate to the eluent so that at all times the ratio of weight of solute per gram of eluent to weight per gram of adsorbent is a con-

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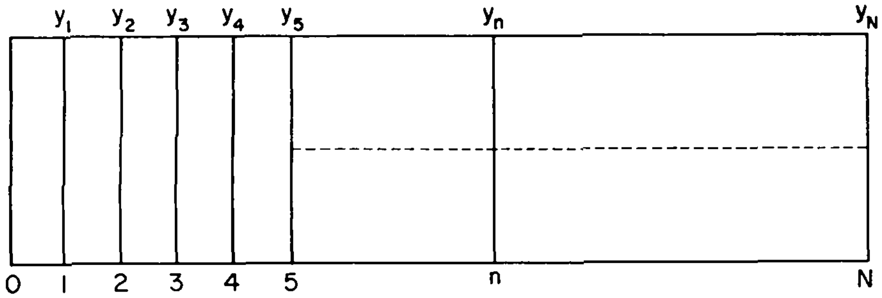

stant k. If the weight of eluent that has crossed any plate at any time is denoted by w, then a differential material balance around plate 1 gives

$$k y_1\, dw = -\frac{S}{N}\, dy_1$$

$$\therefore \frac{dy_1}{y_1} = -\frac{kN}{S}\, dw$$

$$(N/S)w = x = \frac{\text{weight of eluent which has crossed the plate}}{\text{weight of adsorbent on one plate}}$$

$$\therefore \frac{dy_1}{y_1} = -k\, dx$$

$$\therefore \ln y_1 = -kx + c$$

where c is a constant

When $x = 0$, $y_1 = y_1^0$

$$\therefore \ln y_1^0 = 0 + c$$

$$\therefore \ln \frac{y_1}{y_1^0} = -kx$$

$$y_1 = y_1^0 e^{-kx}$$

Before entering plate 2, the eluent will have acquired a solute concentration which is a function of x resulting in

$$\bar{y}_1 = k y_1 = k y_1^0 e^{-kx}$$

A differential material balance around plate 2 gives

$$(k y_2 - k y_1^0 e^{-kx})\, dw = -\frac{S}{N}\, dy_2$$

Rearranging and substituting dx for $(N/S)\, dw$ gives

$$\therefore \frac{dy_2}{dx} + k y_2 = k y_1^0 e^{-kx}$$

This is a linear first-order differential equation in the form

$$\frac{dy}{dx} + Py = Q$$

where P and Q are functions of x only.

$$\therefore y_2 = e^{-kx}\left(\int k y_1^0 e^{-kx} e^{kx}\, dx + c\right)$$

$$= e^{-kx}(k y_1^0 x + c)$$

when

$$x = 0, \quad y_2^0 = 0 + c \quad \therefore c = y_2^0$$

$$\therefore y_2 = e^{-kx}(y_1^0 kx + y_2^0)$$

$$\bar{y}_2 = k e^{-kx}(y_1^0 kx + y_2^0)$$

Similarly, a differential material balance around plate 3 gives

$$\frac{dy_3}{dx} + k y_3 = k e^{-kx}(k y_1^0 x + y_2^0)$$

which is a first-order linear differential equation, the solution of which is

$$y_3 = e^{-kx}\left(\frac{y_1^0 x^2 k^2}{2} + y_2^0 kx + y_3^0\right)$$

In plate 4 it is found that

$$y_4 = e^{-kx}\left[y_1^0 \frac{(kx)^3}{2 \times 3} + y_2^0 \frac{(kx)^2}{2} + y_3^0 kx + y_4^0\right]$$

$$\vdots$$

$$y_n = e^{-kx}\left[y_1^0 \frac{(kx)^{n-1}}{(n-1)!} + y_2^0 \frac{(kx)^{n-2}}{(n-2)!} + \cdots + y_n^0\right]$$

By using the symbol u to denote kx, one gets

$$y_n = e^{-u}\left[y_1^0 \frac{u^{n-1}}{(n-1)!} + y_2^0 \frac{u^{n-2}}{(n-2)!} + \cdots + y_n^0\right]$$

$$= e^{-u} \sum_{r=1}^{n} y_r^0 \frac{u^{n-r}}{(n-r)!} \qquad (1)$$

Equation (1) expresses the solute concentration at any plate in the column after an amount of eluent = x units (both x and u are dimensionless weight ratios) has passed through the plate. It is a general equation which can be applied to any initial distribution of solute in the column.

SPECIAL CASES

1. *Only One Plate Loaded with Solute at the Beginning of Elution.* This is the case which was treated by Martin and Synge and also by Mayer and Tompkins. When Equation (1) is applied,

$$y_n = e^{-u} \sum_{r=1}^{n} y_r^0 \frac{u^{n-r}}{(n-r)!} \qquad (1)$$

one finds that it reduces to the first term only, as $y_2^0, y_3^0, \cdots, y_n^0$ all are equal to zero. Therefore,

$$y_n = e^{-u} y_1^0 \frac{u^{n-1}}{(n-1)!}$$

$$\frac{y_n}{y_1^0} = e^{-u} \frac{u^{n-1}}{(n-1)!} = \phi^u{}_{n-1} \qquad (2)$$

which is a Poisson distribution function. Equation (2) is comparable to the equation derived by Martin and Synge. Mayer and Tompkins arrived at a solution in the form of a binomial distribution, owing to the fact that they did not use the concept of continuity of the volume elements in their approach. Nevertheless, both solutions approach the normal distribution as n and u become larger and larger.

After approximating their binomial distribution with a normal distribution for large values of n, Mayer and Tompkins proved that, for a large n the peak of the concentration arrives after the passage of u units of eluent such that $u = n$.

Equation (2) can be differentiated with respect to u (at constant n) to find the values of u at which y_n/y_1^0 is maximum.

$$\frac{d}{du}\left(e^{-u} \frac{u^{n-1}}{(n-1)!}\right)$$

$$= e^{-u} \frac{u^{n-2}}{(n-2)!}\left(1 - \frac{u}{n-1}\right)$$

The first derivative is equal to zero at the following points:

$$u = n - 1; \qquad u = 0; \qquad u = \infty$$

The curve has a maximum at $u = n - 1$ and therefore it must have two minima at $u = 0$ and $u = \infty$.

The maximum concentration of the zone reaches the bottom of the column after u units of eluent equal to $N - 1$ have crosses the bottom plate.

$$\therefore R_N^{u_m} = \left(\frac{y_N}{y_1^0}\right)_{max}$$

$$= \frac{e^{-(N-1)}(N-1)^{N-1}}{(N-1)!} \qquad (3)$$

If N is very large, Stirling's approximation can be applied, i.e.,

$$(N-1)! = e^{-(N-1)}(N-1)^{N-1} \sqrt{2\pi(N-1)}$$

$$\therefore R_N^{u_m} = \frac{1}{\sqrt{2\pi(N-1)}}$$

$$\cong \frac{1}{\sqrt{2\pi N}} \qquad (4)$$

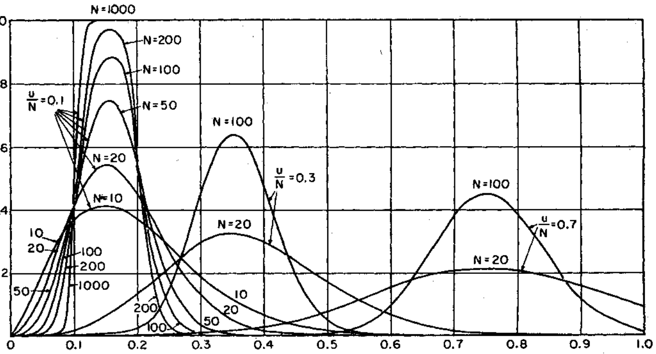

Fig. 1. Plot of Equation (6), $R_n = P^u{}_{n-M} - P_n{}^u$ for $M = 0.1N$ (concentration distribution curves).

2. *Solute Uniformly Distributed over the Entire Length of the Column at the Beginning of Elution.* In this case $y_n{}^0$ is constant and equal to y^0 and Equation (1) becomes

$$y_n = y^0e^{-u}\sum_{r=1}^{n}\frac{u^{n-r}}{(n-r)!}$$

$$= y^0e^{-u}\sum_{r=0}^{n-1}\frac{u^r}{r!}$$

$$= y^0e^{-u}\sum_{r=0}^{\infty}\frac{u^r}{r!} - y^0e^{-u}\sum_{r=n}^{\infty}\frac{u^r}{r!}$$

$$= y^0P_0{}^u - y^0P_n{}^u$$

$$\therefore \frac{y_n}{y^0} = R_n = P_0{}^u - P_n{}^u$$

$$= 1 - P_n{}^u \qquad (5)$$

P denotes a Poisson exponential summation distribution, $P_0{}^u = 1$ for any value of u.

3. *Solute Uniformly Distributed in a Zone at the Top of the Column Equivalent to* M *Theoretical Plates.* The only difference between this case and case 2 is in the limits of r, which will be from 1 to M instead of n,

$$R_n = \frac{y_n}{y^0} = \sum_{r=1}^{M} e^{-u}\frac{u^{n-r}}{(n-r)!}$$

$$= P^u{}_{n-M} - P_n{}^u \qquad (6)$$

Equation (6) expresses R_n as a function of both n and u. For a constant value of u the equation represents the solute-concentration distribution along the column after the passage of an amount of eluent equivalent to u units through the plates. If n is the constant, then the equation represents the change in the solute concentration on plate n as u changes and when n is equal to N the elution equation results,

$$R_N = P^u{}_{N-M} - P_N{}^u \qquad (6a)$$

where

$$R_N = \frac{y_N}{y^0} = \frac{ky_N}{ky^0} = \frac{\bar{y}_N}{\bar{y}^0}$$

Equation (6) is plotted in Figure 1 as a function of n/N. Both N and u/N are parameters (concentration-distribution curves). The following values were chosen:

N	u/N		
10	0.1		
20	0.1,	0.3,	0.7
50	0.1		
100	0.1,	0.3,	0.7
200	0.1		
1,000	0.1		

Derivation of the Deposition Equation When the Solute Concentration at the Beginning is Zero at Any Point in the Column

In order to derive the equation which represents the concentration distribution of a solute deposited at the top of a column when the solute concentration in the solvent before it enters the column is $\bar{y}_0$, one follows the same procedure as was followed in deriving the general elution equation.

A differential material balance around plate 1 gives

$$(\bar{y}_0 - ky_1)\,dw = \frac{S}{N}\,dy_1$$

$$(\bar{y}_0 - ky_1)\,dx = dy_1$$

$$\bar{y}_0 = ky_0$$

y_0 is equal to the concentration on the adsorbent when it is in equilibrium with the eluent at a concentration $\bar{y}_0$

$$(ky_0 - ky_1)\,dx = dy_1$$

$$\frac{dy_1}{y_0 - y_1} = k\,dx$$

$$\ln(y_0 - y_1) = -kx + c$$

Substituting the boundary condition $y_1 = 0$ when $x = 0$ and solving for y_1, one finds

$$y_1 = y_0(1 - e^{-kx})$$

$$\bar{y}_1 = ky_0(1 - e^{-kx})$$

A material balance around plate 2 gives

$$(\bar{y}_1 - \bar{y}_2)\,dw = \frac{S}{N}\,dy_2$$

$$ky_0(1 - e^{-kx}) - ky_2 = \frac{dy_2}{dx}$$

which is a first-order linear differential equation. By solving and substituting the boundary condition $y_2 = 0$ when $x = 0$ it can be shown that

$$y_2 = y_0[1 - e^{-kx}(1 + kx)]$$

continuing up to plate n

$$\therefore y_n = y_0\left[1 - e^{-kx}\left(1 + kx + \frac{(kx)^2}{2!} + \cdots + \frac{(kx)^{n-1}}{(n-1)!}\right)\right]$$

$$\frac{y_n}{y_0} = R_n = 1 - \left(e^{-u} + e^{-u}u + e^{-u}\frac{u^2}{2!} + \cdots + e^{-u}\frac{u^{n-1}}{(n-1)!}\right)$$

$$= 1 - (P_0{}^u - P_n{}^u)$$

$$= P_n{}^u \qquad (7)$$

Equation (7) determines the actual distribution of a zone deposited at the top of the column and should have applications in the frontal analysis technique.

Physical Significance of u

u is a dimensionless parameter which will be called solution parameter, and n is the column parameter.

An amount of solvent equivalent to u units and containing the solute at a concentration $\bar{y}_0$ contains an amount of solute which will fill u plates at a concentration y_0.

If u_0 units of solvent are passed through a column which contains an infinite number of plates, all the solute will be deposited on the column and

$$\sum_{n=1}^{\infty} y_n = u_0y_0$$

$$\therefore u_0 = \sum_{n=1}^{\infty} R_n = \sum_{n=1}^{\infty} P_n{}^{u_0} \qquad (8)$$

This result can be confirmed by expanding and rearranging the sum

$$\sum_{n=1}^{\infty} P_n{}^{u_0}\ *$$

During the elution of a zone, the ratio u/N is a measure of the distance traveled by the zone down the column. It is almost exactly equal to the fraction of column traveled by the peak of the zone regardless of the value of N.

A zone deposited at the top of the column from an amount of solvent equiv-

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*Derivations of most important ensuing equations are given in tabular material deposited as document 5048 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

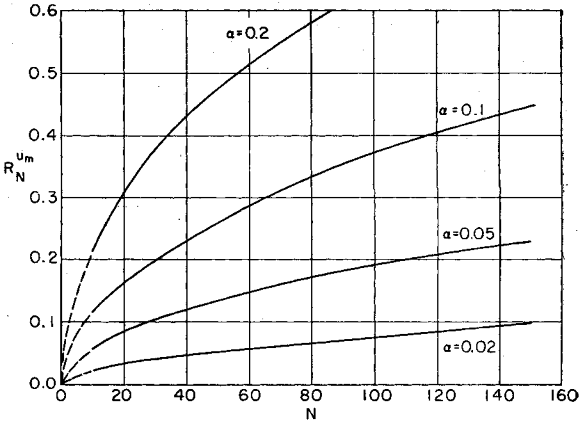

Fig. 2. Plot of Equation (22), $R_N{}^{u_m} = P^{u_m(1+\alpha)}{}_N - P_N{}^{u_m}$ (This plot is used for the determination of the number of theoretical plates.)

alent to u_0 units is actually distributed over the entire length of the column according to Equation (7); yet if the thickness of such a zone is defined as the distance from the top of the column to a point where $R_n{}^0$ is equal to a certain small fraction ϵ, then the relative thickness of the zone, i.e., the ratio between its thickness and the length of the column, will always be greater than the ratio u_0/N and will approach this value asymptotically as the number of theoretical plates becomes larger and larger.

Similarly, complete elution of a zone which has been deposited at the top of a column requires an infinite amount of eluent, theoretically. For practical purposes, it would be desirable to define complete elution as being elution of the zone until a certain small fraction $\bar{\epsilon}$ is still adsorbed on the column. Once complete elution has been defined in this fashion, then the ratio u/N for the complete elution of a zone deposited at the top of the column will be always greater than 1 and will approach the value 1 asymptotically as the number of theoretical plates gets larger and larger, and for an infinite number of plates, u/N is equal to 1 for complete elution.

Elution of a Zone Having an Initial Concentration-distribution Ratio $R_n{}^0 = P_n{}^{u_0}$

The intensity distribution of the zone after the passage of u units of eluent can be found by applying Equation (1).

$$y_n = e^{-u} \sum_{r=1}^{n} y_r{}^0 \frac{u^{n-r}}{(n-r)!}$$

Dividing both sides by y_0 gives

$$R_n = e^{-u} \sum_{r=1}^{n} R_r{}^0 \frac{u^{n-r}}{(n-r)!}$$

Since

$$R_r{}^0 = P_r{}^{u_0}$$

$$R_n = e^{-u} \sum_{r=1}^{n} P_r{}^{u_0} \frac{u^{n-r}}{(n-r)!}$$

After expanding and rearranging, one can show that

$$R_n = P_n{}^{u+u_0} - P_n{}^u \qquad (9)$$

Gradient Elution $k = f(x)$

In order to derive the general elution equation corresponding to Equation (1), the same procedure is followed as in deriving that equation except that k will be replaced by $f(x)$.

It can be proved that

$$y_n = e^{-\psi(x)} \sum_{r=1}^{n} y_r{}^0 \frac{(\psi_x)^{n-r}}{(n-r)!} \qquad (10)$$

where

$$\psi_{(x)} = \int_0^x f(x)\, dx$$

It can also be shown that k does not have to be a continuous function of x. If it is assumed that

$$\begin{aligned} k &= f_1(x) \quad \text{for} \quad 0 < x < x_1 \\ &= f_2(x) \quad \text{for} \quad x_1 < x < x_2 \\ &= f_3(x) \quad \text{for} \quad x_2 < x < x_3 \\ &\vdots \\ &= f_I(x) \quad \text{for} \quad x_{I-1} < x < x_I \end{aligned}$$

then

$$y_n{}^{x_2} = e^{-(u_1+u_2)}\left[y_1{}^0 \frac{(u_1+u_2)^{n-1}}{(n-1)!} + y_2{}^0 \frac{(u_1+u_2)^{n-2}}{(n-2)!} + \cdots + y_n{}^0 \right] \qquad (11)$$

and generally

$$y_n{}^{x_I} = e^{-u} \sum_{r=1}^{n} y_r{}^0 \frac{u^{n-r}}{(n-r)!} \qquad (11a)$$

where $y_n{}^{x_I}$ represents y_n after the passage of eluent equivalent to

$$x_1 + x_2 + \cdots + x_I$$

and

$$\begin{aligned} u &= u_1 + u_2 + \cdots + u_I \\ &= \int_0^{x_1} f_1(x)\, dx + \int_{x_1}^{x_2} f_2(x)\, dx \\ &\quad + \cdots + \int_{x_{I-1}}^{x_I} f_I(x)\, dx \end{aligned}$$

Calculation of the Fraction of Solute Eluted after the Passage of u Units of Eluent

If it is assumed that the solute was deposited at the top of the column by u_0 units of solvent, the distribution before the eluent is introduced would be

$$R_n{}^0 = \frac{y_n}{y_0} = P_n{}^{u_0}$$

and

$$\sum_{n=1}^{N} R_n{}^0 = \sum_{n=1}^{N} P_n{}^{u_0} = u_0 - u_0 f_e \qquad (12)$$

N is the total number of plates in the column and f_e = fraction of solute that left the column with the solvent.

If N is large enough compared with u_0, then f_e becomes negligibly small and

$$\begin{aligned} \sum_{n=1}^{N} R_n{}^0 &= \sum_{n=1}^{N} P_n{}^{u_0} \\ &= \sum_{n=1}^{\infty} P_n{}^{u_0} = u_0 \qquad (13) \end{aligned}$$

If N is not large enough, f_e will have an appreciable value and if the fraction that remains on the column is denoted by f_a, then

$$f_e + f_a = 1$$

$$f_a = \frac{\sum_{n=1}^{N} P_n{}^{u_0}}{\sum_{n=1}^{\infty} P_n{}^{u_0}} = \frac{\sum_{n=1}^{N} P_n{}^{u_0}}{u_0}$$

and

$$f_e = \frac{\sum_{n=N+1}^{\infty} P_n{}^{u_0}}{\sum_{n=1}^{\infty} P_n{}^{u_0}} = \frac{\sum_{n=N+1}^{\infty} P_n{}^{u_0}}{u_0}$$

It can be shown by expanding and rearranging that $\sum^N{}_{n=1} P_n{}^{u_0}$ is equal to

$$u_0(1 - P_N{}^{u_0}) + NP^{u_0}{}_{N+1} \qquad (14)$$

$$\begin{aligned} \therefore f_a &= \frac{\sum_{n=1}^{N} P_N{}^{u_0}}{u_0} \\ &= \frac{u_0(1 - P_N{}^{u_0}) + NP^{u_0}{}_{N+1}}{u_0} \\ &= 1 - P_N{}^{u_0} + \frac{N}{u_0} P^{u_0}{}_{N+1} \qquad (15) \end{aligned}$$

and

$$f_e = 1 - f_a = P_N{}^{u_0} - \frac{N}{u_0} P^{u_0}{}_{N+1} \qquad (16)$$

If the zone is eluted, then after the passage of u units of eluent the new distribution of the zone will be according to the equation

$$R_n = P_n^{u_0+u} - P_n^{u}$$

$$f_a = \frac{\sum_{n=1}^{N} (P_n^{u_0+u} - P_n^{u})}{u_0}$$

$$= \frac{(u_0 + u)(1 - P_N^{u_0+u}) + NP^{u_0+u}{}_{N+1} - u(1 - P_N^{u}) - NP^{u}{}_{N+1}}{u_0}$$

$$= 1 + \frac{u}{u_0}(P_N^{u} - P_N^{u+u_0}) + \frac{N}{u_0}(P^{u_0+u}{}_{N+1} - P^{u}{}_{N+1}) \qquad (17)$$

$$f_e = 1 - f_a$$

$$= \frac{u}{u_0}(P_N^{u+u_0} - P_N^{u})$$

$$+ \frac{N}{u_0}(P^{u}{}_{N+1} - P^{u_0+u}{}_{N+1}) \qquad (18)$$

Determination of the Number of Plates in a Chromatographic Column

If a zone is introduced at the top of the column, it will have the distribution $R_n^0 = P_n^{u_0}$. If it is eluted with u units of eluent, then the distribution during the elution will be according to the equation

$$R_n = P_n^{u_0+u} - P_n^{u}$$

and at the bottom of the column where $n = N$,

$$R_N = P_N^{u_0+u} - P_N^{u}$$

To find the value of u when the peak of the zone reaches the bottom of the column (plate N), one differentiates R_N with respect to u and equates to zero.

$$\frac{d}{du}(R_N) = \frac{d}{du}[P_N^{u_0+u} - P_N^{u}]$$

By expanding P_N^{u} and differentiating term by term one can prove that

$$\frac{d}{du}(P_N^{u}) = e^{-u}\frac{u^{N-1}}{(N-1)!} \qquad (19)$$

Similarly,

$$\frac{d}{du}(P_N^{u_0+u}) = \frac{e^{-(u_0+u)}(u_0 + u)^{N-1}}{(N-1)!}$$

For maximum intensity at N,

$$\frac{d}{du}(R_N) = 0$$

$$\frac{e^{-(u_0+u_m)}(u_0 + u_m)^{N-1}}{(N-1)!} = \frac{e^{-u_m}u_m^{N-1}}{(N-1)!}$$

$$\therefore u_0 = (N-1)\ln\left(1 + \frac{u_0}{u_m}\right)$$

If the ratio u_0/u_m is denoted by α, then

$$u_m = (N-1)\frac{\ln(1+\alpha)}{\alpha} \qquad (20)$$

if α is sufficiently small; i.e., for a very thin zone $\ln(1+\alpha) = \alpha$

and

$$u_m = N - 1 \cong N \qquad (21)$$

for a large N

Equation (20) together with the equation

$$R_N^{u_m} = P_N^{u_0+u_m} - P_N^{u_m}$$

$$= P_N^{u_m(1+\alpha)} - P_N^{u_m} \qquad (22)$$

can be used for determining the total number of theoretical plates in a column.

Both α and $R_N^{u_m}$ can be measured experimentally, and thus there are two equations in two unknowns, which can be solved to find the values of u_m and N.

A graph can be prepared where $R_N^{u_m}$ is plotted vs. N with α as a parameter. Such a chart can be used in the determination of the number of plates. It is necessary to know only α and $R_N^{u_m}$; then the value N is read directly from the chart (Figure 2).

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NOTATION

A = cross-sectional area of column
f_a = fraction of solute still adsorbed on column
f_e = fraction of solute that has left the column with eluent
$f(x)$ = adsorption or exchange coefficient when it is a function of x only and not of y_n (gradient elution), $f(x) = \bar{y}_n/y_n$
I = number of different continuous relations $f(x)$ during a run
k = adsorption or exchange coefficient when it is neither a function of x nor a function of y_n. $k = \bar{y}_n/y_n$
M = number of plates occupied by a uniform zone at the beginning of elution
N = total number of plates in column
n = plate number from top of column. The top plate number $n = 1$ and the bottom plate number $n = N$.
P_n^{u} = $\sum_{r=n}^{\infty} \phi_r^{u}$ = Poisson exponential summation
R_n = y_n/y_0 or y_n/y^0
R_n^{θ} = y_n^0/y_0
$R_N^{u_m}$ = maximum value of R_N
S = total weight of adsorbent in the column
u = $\sum_{i=1}^{I} \psi_i(x)$ during the elution process
u_m = value of u when the peak of the zone has reached plate N
u_0 = $\sum_{i=1}^{I} \psi_i(x)$ during the deposition of the solute from the solvent at the top of the column
v_f = free volume of column = volume occupied by eluent or solvent
w = weight of eluent or solvent that has passed through any plate in the column
x = wN/S
y_n = concentration of solute on plate n, g. solute/g. adsorbent, for the elution process
$\bar{y}_n$ = concentration of solute in eluent in equilibrium with plate n during elution
y_n^0 = concentration of solute on plate n for the deposition process
y^0 = initial concentration of solute on adsorbent when it is constant on all the plates or on a finite number of plates in the column
y_0 = $\bar{y}_0/f(x)$ = concentration of solute on adsorbent if in equilibrium with solvent containing the solute at a concentration $\bar{y}_0$
$\bar{y}_0$ = concentration of solute in solvent before entering plate 1
α = u_0/u_m
γ = $\ln(1+\alpha)/\alpha$
ϵ = a very small fraction
ϕ_n^{u} = $e^{-u}(u^n/n!)$ = Poisson exponential function
$\psi_i(x)$ = $\int_0^x f_i(x)\,dx$. When $f(x) = k$, then $\psi(x) = kx$

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