Chromatographic Columns Containing a Large Number of Theoretical Plates

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To obtain numerical answers for the concentration distribution of solute on a chromatographic column or in the effluent, tables and charts of the Poisson distribution are used. Their use however is limited to a small number of theoretical plates. The transformation of the Poisson to the normal distribution enables the calculations to be performed for any number of theoretical plates through the use of the normal distribution tables.

Equations derived previously for columns containing a large number of plates and employing elaborate mathematical procedures and approximations have been simply deduced by applying a limit property of the Poisson distribution to the exact equations.

A relationship between the Poisson and normal distribution is derived, and charts are drawn which allow the rapid evaluation of the Poisson in terms of the normal values.

In accordance with the plate theory of chromatography a chromatographic column is assumed to be equivalent to a certain number of theoretical plates with the eluent passing continuously, without mixing, through these plates, while equilibrium is established between the solute on any plate in the column and the solute in the eluent passing through the plate. The results expressing the concentrations of solute at different parts of the column and in the effluent are in the forms of Poisson or Poisson-summation distributions (*4*). For the purpose of numerical calculations tables (*3*) and charts (*1*) are available which list the values of ϕ_n^u and P_n^u for different values of the solution parameter and the column parameter, but the use of these tables and charts is limited to columns containing not more than 200 theoretical plates. In practice however chromatographic columns may contain many thousands of theoretical plates.

Fortunately, for large values of u and n the Poisson distribution can be approximated by the normal distribution, and the larger the values of u and n, the better is the approximation. It is true for the Poisson-summation distribution P_n^u that if one transforms to the variable t and then allows u to tend to infinity, P_n^u approaches the normal distribution $A(t)$, where

$$A(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{t} e^{-x^2/2}\, dt$$

In other words

$$\lim_{u\to\infty} P_n^u = A(t) \qquad (1)$$

Since the maximum of the zone occurs at $u \cong n$, values of u of practical interest when n is large, also should be large and in the neighborhood of n.

Applying this limit property of the Poisson distribution to the case of eluting an originally uniform zone, one finds that the concentration distribution or elution equation

$$R_n = P_{n-M}^u - P_n^u$$

reduces to

$$R_n = A(t') - A(t) \qquad (2)$$

where

$$t = (u - n)/\sqrt{u}$$

and

$$t' = \{u - (n - M)\}/\sqrt{u}$$

and for the deposition of a zone at the top of a column the equation

$$R_n = P_n^u$$

reduces to

$$R_n = A(t) \qquad (3)$$

Equations (2) and (3) were derived by Glueckauf (*2*), who set up the elution process as a partial-differential equation and then, by assuming a large number of theoretical plates, was able to reduce that equation to one of a standard form leading to a solution in the form of a normal distribution through a series of approximations and elaborate mathematical manipulations.

The advantage of deducing these

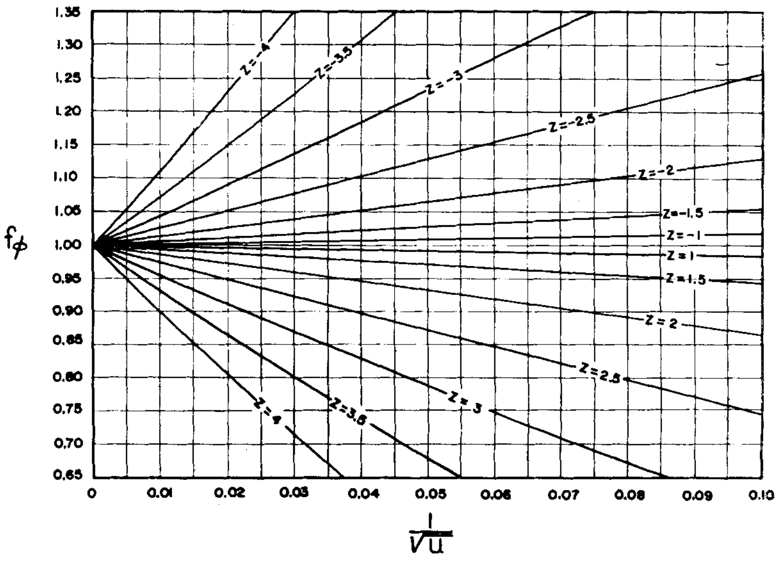

Fig. 1. Plot of Equation (4).

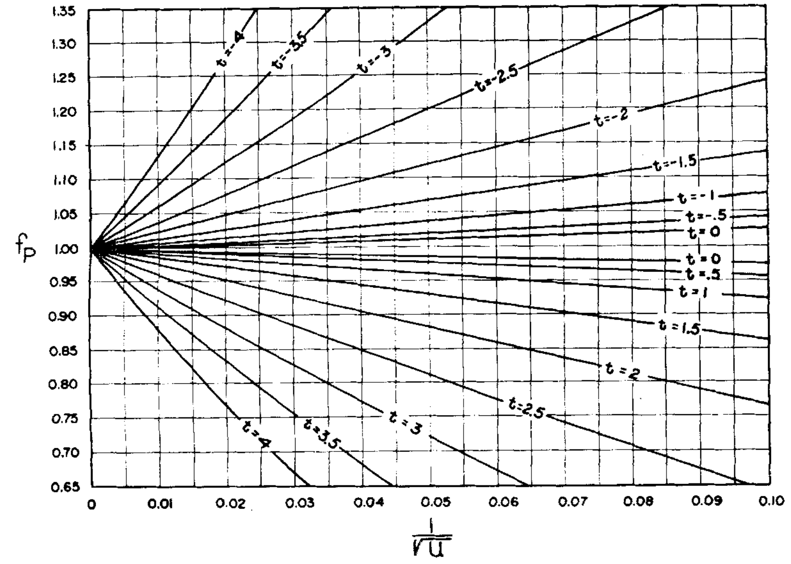

Fig. 2. Plot of Equation (5).

relationships from the exact Poisson solution is clear, since aside from the simplicity of the derivation one can also test the validity of the approximation and determine the limits of the applicability of Equations (2) and (3).

Since the Poisson and normal distributions approach each other rather slowly and at different rates for different regions, these approximations are only valid for very large values of n and values of $|(u-n)/\sqrt{u}| < 2$. On the other hand when the column contains a small or moderately large number of plates, or when one is dealing with regions far from the peak of the zone, as in the case of calculating the impurities owing to one band in another, the Poisson distribution can be replaced by the normal distribution only after the inclusion of a correction factor.

It is shown in the Appendix* that ϕ_n^u can be rearranged and rewritten in the form

$$\phi_n^u = \frac{1}{\sqrt{2\pi u}} e^{-z^2/2}\left[1 + \frac{1}{\sqrt{u}} f_1(z) + \frac{1}{u} f_2(z) + \cdots + \frac{1}{u^{r/2}} f_r(z) + \cdots\right]$$

For values of $u > 100$ this series converges rapidly, and one can neglect terms containing $f_3(z)$ upward and

$$\phi_n^u = f_\phi \frac{1}{\sqrt{2\pi u}} e^{-z^2/2}$$

where

$$z = \frac{u - n - \frac{1}{2}}{\sqrt{u}}$$

$$f_\phi = 1 + \frac{1}{\sqrt{u}} f_1(z) + \frac{1}{u} f_2(z) \qquad (4)$$

$$f_1(z) = -\frac{z^3}{6}$$

and

$$f_2(z) = \frac{z^6}{72} - \frac{z^4}{12} + \frac{1}{24}$$

Equating $f_2(z)$ to zero, one finds that f_ϕ is equal to $1 + 1/\sqrt{u}\, f_1(z)$ at values of $z = \pm 0.87, \pm 2.43$. Actually for values of $|z|$ lying between 0 and 2.5 f_ϕ can be represented almost accurately by the straight line having the equation

$$y = 1 + \frac{1}{\sqrt{u}} f_1(z)$$

when f_ϕ is plotted vs. $1/\sqrt{u}$ with z as the parameter.

For values of z greater than 2.5 the deviation from the straight line equation becomes appreciable and increases rapidly with z.

It is also shown in the Appendix that P_n^u can be accurately represented by the relation

$$P_n^u = A(t)\left[1 + \frac{t^2+2}{6\sqrt{u}} \frac{E(t)}{A(t)} \cdot \left\{1 - \frac{t(t^2-3)}{12\sqrt{u}}\right\}\right]$$

Instead of a correction factor, defined in this case as simply the ratio between $A(t)$ and P_n^u, a more useful definition will be used, namely

$$f_P = \frac{P_n^u}{A(t)} \qquad \text{for} \quad t < 0$$

$$= \frac{1 - P_n^u}{1 - A(t)} \qquad \text{for} \quad t > 0$$

$$\left.\begin{aligned} \therefore f_P &= 1 + \frac{t^2+2}{6\sqrt{u}} \frac{E(t)}{A(t)} \cdot \left\{1 - \frac{t(t^2-3)}{12\sqrt{u}}\right\} \quad \text{for} \quad t < 0 \\ &= 1 - \frac{t^2+2}{6\sqrt{u}} \frac{E(t)}{[1 - A(t)]} \cdot \left\{1 - \frac{t(t^2-3)}{12\sqrt{u}}\right\} \quad \text{for} \quad t > 0 \end{aligned}\right\} \qquad (5)$$

Equating the last term to zero and solving for t one finds that f_P is equal to the first two terms for $t = 0, \pm\sqrt{3}$. Actually f_P can be represented almost accurately for values of t lying between 0 and 2 by the first two terms only, and a plot of f_P vs. $1/\sqrt{u}$ with t held constant is a straight line. For values of t greater than 2 deviations from the straight line equation become appreciable and increase rapidly with t. Figures 1 and 2, respectively, plot f_ϕ vs. $1/\sqrt{u}$ with z as the parameter and f_P vs. $1/\sqrt{u}$ with t as the parameter.

NOTATION

$A(t)$ = area under the normal distribution curve of error between $-\infty$ and t

$= 1/\sqrt{2\pi} \int_{-\infty}^{t} e^{-x^2/2}$

$E(t)$ = $1/\sqrt{2\pi}\, e^{-t^2/2}$

f_P = Poisson-summation correction factor

$f_r(z)$ = function of z

f_ϕ = Poisson correction factor

n = theoretical plate number or column parameter

r = positive integer

R_n = concentration ratio of solute in eluent at plate n

t = $(u - n)/\sqrt{u}$

u = solution parameter

x = variable

$$z = (u - n - \tfrac{1}{2})/\sqrt{u} = t - \frac{1}{2\sqrt{u}}$$

$$\phi_n^u = e^{-u} \frac{u^n}{n!}$$

$$P_n^u = \sum_{r=n}^{\infty} \phi_r^u$$

LITERATURE CITED

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2. Glueckauf, E., *Trans. Faraday Soc.*, 51, 34 (1955).
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*Tabular material has been deposited as document 5876 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.