Binomial Distribution in Multistage Extraction Processes

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A useful property of the binomial distribution is derived which should have applications in chemical engineering multistage intermittent processes. It is shown that the binomial distribution is a particular solution to the partial difference equation $\Delta_n y = -f\nabla_r y$, where y is a function of both the variables n and r. Both are non-negative integers. $n \geq 0$ and $r \geq 0$ and f is a positive fraction less than 1. The symbols Δ and ∇ refer to the forward and backward differences, respectively. A similar relation was derived by this author several years ago for the Poisson distribution. It was shown that the Poisson distribution is a particular solution to the differential-difference equation $dy/du = -\nabla y_n$, where y is a function of both the continuous variable u and the discontinuous variable n. $u > 0$ and n is a nonnegative integer $n \geq 0$. This function proved to be valuable in the development of the plate theory of chromatography where the mobile phase is assumed to pass continuously through the plates of the column. u is the solution parameter, and n is the plate number. It was shown that this equation is also a particular solution to the Poisson summation distribution. This extended its application to the general case where the solute is deposited on several plates at the start, and also to other initial conditions.

In this note, attention is focused on the simple case where the first stage only contains the solute at the start, leading to the above partial difference equation which has the binomial distribution as a solution.

Even though the binomial summation distribution should be also a particular solution to the same partial difference equation by comparison with the Poisson distribution case, no attempt is made here to extend it to the general case. This can be the subject of a future article.

Derivation of Partial Difference Equation

The binomial distribution is given by the formula

$$B(n,r) = [f + (1-f)]^n \tag{1}$$

where f is a positive fraction less than 1.

On expansion, we get $(n+1)$ terms such that

$$[f + (1-f)]^n = \Psi_0^n + \Psi_1^n + \Psi_2^n + \cdots + \Psi_n^n = \sum_{r=0}^{n} \Psi_r^n \tag{2}$$

where Ψ_r^n is the $(r+1)$th term in the expansion series (the first term corresponds to $r = 0$)

$$\Psi_r^n = \frac{n!}{r!(n-r)!} f^r (1-f)^{n-r} \tag{3}$$

Let

$$y = \Psi_r^n$$

$\Delta_n y$ is the forward difference of the function y with respect to n at constant r, therefore,

$$\Delta_n y = \Psi_r^{n+1} - \Psi_r^n = \Psi_r^n \left(\frac{\Psi_r^{n+1}}{\Psi_r^n} - 1 \right)$$

$$= \Psi_r^n \left(\frac{(n+1)(1-f)}{n-r+1} - 1 \right) = \Psi_r^n \left(\frac{-nf - f + r}{n-r+1} \right) \tag{4}$$

Furthermore, $\nabla_r y$ is the backward difference of the function y with respect to r at constant n, hence,

$$\nabla_r y = \Psi_r^n - \Psi_{r-1}^n = \Psi_r^n \left[1 - \frac{\Psi_{r-1}^n}{\Psi_r^n} \right]$$

$$= \Psi_r^n \left[1 - \frac{r(1-f)}{(n-r+1)f} \right] = \Psi_r^n \left[\frac{nf + f - r}{(n-r+1)f} \right] \tag{5}$$

comparing Eqs. 4 and 5 one gets

$$\Delta_n y = -f\nabla_r y \tag{6}$$

This means that the binomial distribution Ψ_r^n is a particular solution to the partial difference equation given by Eq. 6.

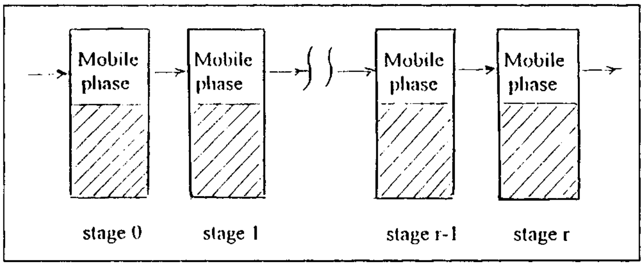

Figure 1. Multistage extraction process.

Application to Multistage Extraction Processes

Figure 1 represents a multistage intermittent extraction process where the solute is introduced in stage 0. During the extraction process, the upper mobile phase is equilibrated with the lower stationary phase before it is transferred to the following stage and is replaced by the mobile phase from the preceding stage.

If the total number of mols in stage r during the extraction process is denoted by Tr and if f is the fraction of solute in the upper mobile phase, then at the end of n transfers mols of solute in upper phase of stage $r-1$

$$= fT_{n,r-1}$$

and moles of solute in lower phase of stage r

$$= (1-f)T_{n,r}$$

In the next transfer number $(n+1)$, the total number of mols in stage r is given by the sum of the above two quantities, so that

$$T_{r\ n+1} = fT_{r-1,n} + (1-f)T_{r,n} \tag{7}$$

Rearranging, one gets

$$T_{r,n+1} - T_{r,n} = f(T_{r-1,n} - T_{r,n}) \tag{8}$$

or

$$\Delta_n T = -f\nabla_r T \tag{9}$$

Equation 9 is the partial difference equation for which the binomial distribution is a particular solution. Hence,

$$T_{r,n} = a\Psi_r^n + b \tag{10}$$

where a and b are constants.

Substituting the boundary condition for the simple case where we have one mol of solute in stage 0 and no solute in any of the other stages at the start, that is,

$$T_{0,0} = 1, \quad T_{r,0} = 0 \quad \text{for} \quad r > 0$$

we get $a = 1$ and $b = 0$ and, therefore,

$$T_{r,n} = \Psi_r^n = \frac{n!}{r!(n-r)!} f^r (1-f)^{n-r}. \tag{11}$$

In their Nobel Prize article, Martin and Synge (1941) introduced a theory of chromatography based on the theoretical plate model. They considered the chromatographic process as being mathematically equivalent to a continuous multistage extraction process in which the mobile phase moves continuously and without mixing between the stages. They started with the intermittent multistage process and derived the elution curve equation in the form of a binomial distribution which approached the Poisson distribution ($e^{-x}x^n/n!$) as the number of transfers tended to infinity. In this case the intermittent process became virtually a continuous process.

Said (1956) used simple calculus to derive the equation of the elution curve in the form of a Poisson distribution. This was accomplished directly and quite easily without going through the step of intermittent mobile phase flow. Said derived equations for the simple case where the solute is deposited on the first plate only, and for the general case where the solute is deposited on several plates at the start.

In his 1958 article, Said showed that the chromatographic elution process can be represented by the differential-difference equation $dy/du = -\nabla y_n$. He showed also that the Poisson distribution is a particular solution to this equation. u is the solution parameter, and n is the plate number. Based on this finding, he derived the elution curve equation for both the simple and general cases.

Literature Cited

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