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APPLICATION OF DISPLACEMENT CHROMATOGRAPHY TO ISOTOPE SEPARATION

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ABSTRACT

It is shown that a chromatographic column, operating according to the band-displacement principle, with internal reflux at each end, may be compared to a countercurrent separation column. Simple formulas relate the three parameters which determine the separative performances of the column to the physicochemical characteristics of the process. The parameters are the separation coefficient, the height equivalent to a theoretical plate (HETP), and the theoretical flow. The determination of the HETP can be accomplished by either the method of frontal analysis or the method of isotope remixing, by comparing the evolution of the isotope concentration predicted by an appropriate mathematical model and that observed experimentally. The first method concerns a semi-infinite band, limited by a front situated either at the leading or trailing edge of the band and the enrichment directed toward either the solid or liquid phase. Therefore, there are four possible cases. In the second method, the isotope concentration at the top of the column is changed suddenly and the response at the exit-end is observed. For each above-mentioned case, the theoretical formulation of the model, the necessary calculations in a form suitable for solution with a desk computer, the operating mode for treating the experimental results, and some examples are presented.

INTRODUCTION

Several authors have studied the theoretical and experimental aspects of isotope separation by chromatography. In particular Shimokawa (1) has shown that the concepts of cascade theory may be applied to this method of separation. He has also given a mathematical solution of the system of equations which gives the isotope evolution of the column in a frontal process (direct or reverse). Other authors (2,3) have numerically solved the same problem with a step-by-step simulation of the process. This paper presents a practical but sufficiently accurate analytical formulation which yields the successive profiles of the concentration in a frontal process. This formulation is well adapted to the evaluation of the HETP, and thus to the performance of a chromatographic column utilized in isotope separation. For the case where a frontal process is not realizable, an alternative method, the isotope remixing experiment, can give the same information.

Outline of the Process

Isotope separation in a chromatographic column is based on the following assumptions: (1) a flowing liquid phase in contact with a stationary solid phase (resin); (2) the two phases contain the element to be separated at chemical equilibrium and constant concentration. This equilibrium is achieved within a band; (3) each end of the band is refluxed, such that the element transfers from one phase to another. This is shown in Fig. 1.

Determination of the Displacement Velocity of the Band

Given the following parameters:

Θ - holdup of the element in solution (moles/cm of column),

h - holdup of the element in resin (moles/cm of column),

L - flow of the element in solution (moles/sec).

the displacement velocity can be obtained from a material balance at each end of the band:

$$L\,dt = (h + \Theta)dz.$$

Thus:

$$V = \frac{dz}{dt} = \frac{L}{h + \Theta}\ .$$

V is proportional to the real displacement velocity of the liquid $v = L/\Theta$, according to the relation

$$V = \frac{v\nu}{1 + \nu}$$

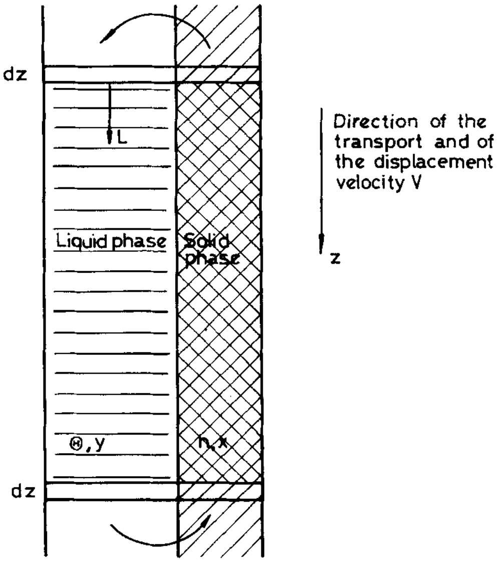

FIGURE 1. Schematic diagram showing the band-displacement principle.

where

$$\nu = \frac{\Theta}{h} .$$

For physicochemical reasons, occasionally it is not possible to achieve either or both refluxes within the column itself. For these systems chemical change and transfer of the element to be separated can be accomplished in appropriate systems exterior to the column. It can be shown that the equivalence with a counter-current separation cascade and the corresponding system of equations derived below remain valid.

THEORY OF ISOTOPE SEPARATION

We assume that the transfer of each isotope from one phase to the other is proportional to the deviation from isotope equilibrium with a constant K (moles/cm-sec) characterizing the intensity of the transfer. Following the hypothesis of chemical equilibrium, the quantity of isotope passing from one phase to the other cancels. We also include isotope exchange in the derivation. The balance equations are

$$\Theta \frac{\partial y}{\partial t} + L \frac{\partial y}{\partial z} = - h \frac{\partial x}{\partial t} = K(x - x^*) = - K(y - y^*), \qquad (2)$$

where x and y are the isotopic concentrations in the resin and solution, respectively, and x* and y* are the corresponding equilibrium concentrations. The separation coefficient, ε, is defined as

$$\frac{y(1 - x)}{x(1 - y)} = 1 + 2\varepsilon. \qquad (3)$$

In the following we assume that the separation coefficient 2ε is very small and consequently neglect terms of order ε^2. Equation (3) may then be written:

$$x^* = y[1 - 2\varepsilon(1 - y)] \text{ or } y^* = x[1 + 2\varepsilon(1 - x)]. \qquad (4)$$

We transform Eq. (2) using mobile axes bound to the band and moving at velocity V. The corresponding coordinate transformation goes from the variables t,z to the variables t and Z = z - Vt. Replacing $(\partial/\partial t)$ by $(\partial/\partial t - V/\partial z)$, and $(\partial/\partial z)$ by $(\partial/\partial Z)$, one can derive the equation

$$\Theta \frac{\partial y}{\partial t} + (L - V\Theta) \frac{\partial y}{\partial Z} = - h \frac{\partial x}{\partial t} + Vh \frac{\partial x}{\partial Z} = K(x - x^*). \qquad (5)$$

For these mobile axes we introduce the following transport parameters:

Total transport: $\emptyset = L - V(\Theta + h)$, (6)

Isotope transport: $I = (L - V\Theta)y - Vhx$, and (7)

Net transport: $I - \emptyset y = Vh(y - x)$. (8)

The difference (y - x) can be eliminated with the aid of Eqs. (4) and (5) to obtain the unique equation

$$\begin{aligned} y - x &= (y - x^*) + (x^* - x) \\ &= 2\varepsilon y(1 - y) - \frac{1}{K} [\Theta \frac{\partial}{\partial t} + (L - V\Theta)\frac{\partial}{\partial Z}]y. \end{aligned} \qquad (9)$$

The quantity $(\emptyset/L)$ is generally of the order of ε (4). Consequently, since the ascending and descending flows are equal, we can write

$$L - V\Theta = Vh = \ell, \qquad (10)$$

Similarly, one may neglect the $(\partial/\partial t)$ term in Eq. (9), which is of the order ε^2, and utilizing Eqs. (8) and (10), obtain

$$I - \phi y = \ell[2\varepsilon y(1 - y) - \frac{\ell}{K}\frac{\partial y}{\partial Z}].$$

Here we recognize the normal form of the cascade equation

$$I - \phi N = \ell[2\varepsilon N(1 - N) - H\frac{\partial N}{\partial Z}), \tag{11}$$

where ℓ is the theoretical flow and N is the mean concentration. We may define the height equivalent to a theoretical stage or plate (HETP) as:

$$H = \frac{\ell}{K}. \tag{12}$$

The mean concentration is given by

$$N = \frac{\Theta y + hx}{\Theta + h} = (1 - \mu)y + \mu x, \tag{13}$$

where

$$\mu = \frac{h}{\Theta + h} = \frac{1}{1 + \nu} = \frac{\text{Resin holdup}}{\text{Total holdup}},$$

which can be obtained from the balance equation, which, by Eq. (5) is

$$\Omega\frac{\partial N}{\partial t} + \frac{\partial I}{\partial Z} = 0, \tag{14}$$

and $\Omega = \Theta + h$ is the total holdup per unit length of column. Knowing the mean concentration, we can calculate the concentrations x and y of each phase. From Eq. (9), the difference in concentration to order ε is

$$y - x = 2\varepsilon N(1 - N) - H\frac{\partial N}{\partial Z}; \tag{15}$$

this equation will be applied in the next section.

One can introduce a diffusional effect such that the first term of Eq. (2) becomes

$$\Theta\frac{\partial y}{\partial t} + L\frac{\partial y}{\partial z} - \Delta\frac{\partial 2y}{\partial z^2}.$$

With the assumptions we have made previously, it can be shown that the diffusional term gives the additional term $(-\Delta\frac{\partial y}{\partial Z})$, and in the HETP an additional term $H_{diff} = \frac{\Delta}{\ell}$, such that the total HETP becomes $H = \frac{\ell}{K} + \frac{\Delta}{\ell}$. The diffusional effect is thus analogous to axial mixing in countercurrent separation columns.

FRONTAL ANALYSIS

Definition

The band has only one reflux, either behind the band (inverse frontal analysis or IFA) or in front of the band (direct frontal analysis or DFA). Furthermore, the separation coefficient ε, defined by Eq. (3), may be either positive or negative. Thus we have four cases to consider, as represented in Fig. 2.

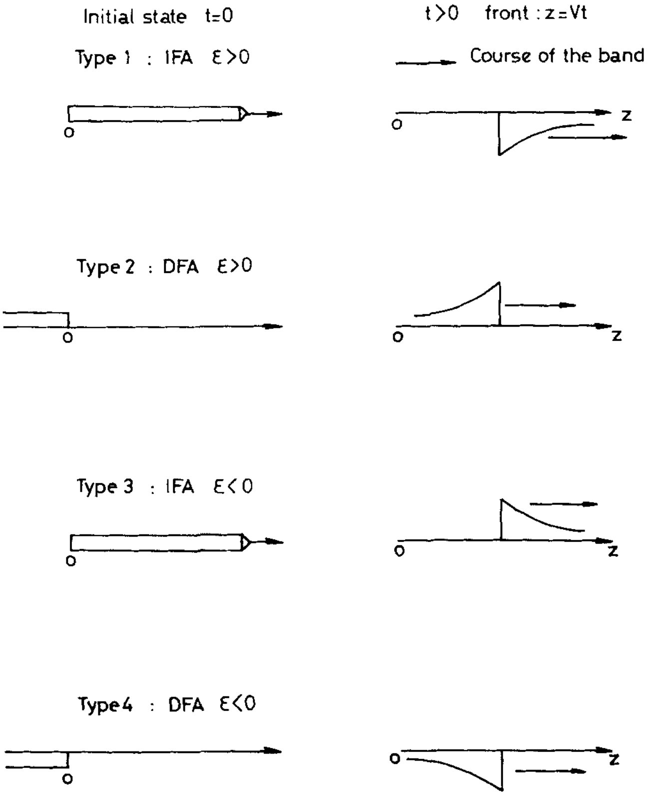

FIGURE 2. Schematic representation showing the evolution of concentration profiles in the different modes.

Analysis

In the IFA case, the column is initially filled with the element to be separated, usually at natural assay. The rear of the band runs through the column and we observe the isotope concentration at the bottom from the initial time $t = 0$ to the exit of the front. In the DFA, the column is initially empty and the solution is introduced at the top. The concentration is observed at the bottom of the column until the band front arrives.

If the separation coefficient has been previously measured at isotopic equilibrium, as well as the holdups Θ and h, frontal analysis permits the evaluation of the HETP. This may be accomplished by comparing the evolution of the isotopic concentration observed at the column exit and that which can be calculated from the following mathematical model.

Mathematical Model

According to Eqs. (11) and (14) with total reflux and $\phi = 0$, the evolution of the mean concentration N, assumed to be much less than unity, will be given by

$$\frac{\Omega}{\ell}\frac{\partial N}{\partial t} + \frac{\partial}{\partial Z}\left(2\varepsilon N - H\frac{\partial N}{\partial Z}\right) = 0. \tag{16}$$

Introducing the dimensionless variables

$$\xi = 2\varepsilon\frac{Z}{H} = 2\varepsilon\,\frac{z - Vt}{H}\ , \tag{17}$$

$$\tau = (2\varepsilon)^2\,\frac{\ell}{H\Omega}\,t = (2\varepsilon)^2\mu\,\frac{Vt}{H}\ , \tag{18}$$

this equation becomes

$$\frac{\partial N}{\partial \tau} = \frac{\partial^2 N}{\partial \xi^2} - \frac{\partial N}{\partial \xi}\ . \tag{19}$$

The boundary condition is $N = N_F$ at $\tau = 0$, where N_F is typically the natural assay. The problem is linear with respect to the concentrations, and we can assume $N_F = 1$. At the two ends of the band, $\xi = 0$ and $\xi = \xi_1$, and thus $I = 0$; there is no isotope transport. According to Eq. (11), this condition results in

$$\frac{\partial N}{\partial \xi} - N = 0.$$

The solution of the problem may be achieved with the aid of the Laplace transform (variable s); the result is

$$\overline{N - 1} = \frac{(1/r_2)\ e^{r_1\xi}(e^{r_2\xi_1} - 1) - (1/r_1)e^{r_2\xi}(e^{r_1\xi_1} - 1)}{s(e^{r_1\xi_1} - e^{r_2\xi_1})},$$

with the characteristic roots

$$r_i = \frac{1}{2} \pm (\frac{1}{4} + s)^{1/2}.$$

The Laplace inversion may be accomplished under the following two assumptions. First, if the band is considered as semi-infinite, that is, $\xi_1 \to \infty$, then Eq. (20) takes the simpler forms, for Types 1 and 4 (see Fig. 2),

$$\overline{N - 1} = -\frac{e^{r_2\xi}}{r_1 s},$$

and, for Types 2 and 3,

$$\overline{N - 1} = -\frac{e^{r_1\xi}}{r_2 s}.$$

Secondly, if the observation time is small, such that $\tau << 1/4$ (in application τ is of the order of 10^{-4}), we can replace $(s + 1/4)^{1/2}$ by $(s)^{1/2}$ and obtain (5)

$$N - 1 = 2[e^{\xi + \tau/4}\ \mathrm{erfc}\ (Y \pm \frac{(\tau)^{1/2}}{2}) - e^{\xi/2}\ \mathrm{erfc}\ Y], \qquad (21)$$

where

$$Y = \frac{|\xi|}{2(\tau)^{1/2}},$$

and

$$\mathrm{erfc}\ Y = 1 - 2\pi^{-1/2} \int_0^Y e^{-x^2}\ dx.$$

For Types 1 and 4 we take the positive root and ξ is positive; for Types 2 and 3 we take the negative root and ξ is negative.

The isotopic concentration of the solution, which is the only observable, may be obtained from Eqs. (13), (15), (17), and (21), yielding

$$y = (1 + 2\varepsilon\mu - \mu H \frac{\partial}{\partial Z})N = [1 + 2\varepsilon\mu(1 - \frac{\partial}{\partial \xi})]N$$

$$= N + 2\varepsilon\mu(1 - e^{\xi/2} \operatorname{erfc} Y). \qquad (22)$$

We have verified that this formula gives practically the same results as the step-by-step simulation method (2,3).

Comparison with Observation

Observations give the isotopic concentration y of the solution at the column exit as a function of time. In point of fact, one collects volumes of solution $\delta\Lambda$ discontinuously (in isoplanes) during the intervals δt, which corresponds to a band-length $\delta\Phi = V\delta t = \delta\Lambda/\Sigma$, where Σ is the cross-section of the column; one measures the mean concentration in that length.

From the preceding formalism, the measured concentration depends on six variables: z, t, ε, μ, V, and H. But, both theoretically and experimentally, t is related to V and Φ through the relation $Vt = \Phi$. Since ε and μ may be measured independently, y is thus a function of five variables, three of which (ε, μ, Φ = **Vt**) are known and the remaining two (H, z) are parameters to be evaluated. The evaluation can be done by choosing two conditions on the a theoretical curve, thus permitting its normalization to an experimental one. One of the conditions is the concentration at the head of the band and the other is a general bearing on the surface of the isoplane.

Differences Between Theoretical and Experimental Conditions

Each isoplane includes a level corresponding to the end of the breakthrough curve in the case of DFA, and to the beginning of this curve in the case of IFA. The theoretical values of this level obtained from Eqs. (21) and (22) for DFA with $t = \infty$ and for IFA with $t = 0$ are $N_\infty = 1$ for the mean concentration and $y_\infty = 1 + 2\varepsilon\mu$ for the solution. These values are somewhat different from the experimental ones, the difference being of order of ε. The difference stems from the fact that the column has a finite length and the formulas we have established are valid for a semi-infinite band.

The abscissa z of the sampling point could be considered as given by the column height. However, this is not necessarily the same as the initial length of the band in IFA or the final length in DFA since isotopic and chemical equilibrium at time zero and at the entrance of the column are only approximately realized. Nevertheless, the error resulting from the differences between the theoretical and experimental conditions will not affect the evaluation of the parameter H, since, as we shall see, it is relatively independent of the column height and depends on the shape of the curve in the zone of variable concentration.

The head of the band is the most enriched (in Types 2 and 3) or the most depleted (in Types 1 and 4) region. Its value is given by Eqs. (21) and (22) with $\xi = 0$,

$$N_o = y_o = 2e^{\tau_1/4}\,\mathrm{erfc}\left(\pm \frac{(\tau_1)^{1/2}}{2}\right) - 1, \tag{25}$$

where τ_1 is the reduced time of arrival at the sampling point. If this time is small, as noted previously, we can use the approximation

$$N_o = y_o \approx 1 \pm 2\,(\tau_1/\pi)^{1/2}, \tag{26}$$

with the appropriate sign (minus for Types 1 and 4 and plus for Types 2 and 3).

From the isotope balance relations we obtain the general conditions relative to the surface of the isoplane. This enables us to define and calculate a characteristic value $\Delta\tau$ of the reduced time. Comparing this value with the corresponding $\Delta\Phi$ obtained from the experimental curve, we can deduce the HETP by the relation which results from Eq. (18),

$$H = 4\varepsilon^2\mu\,\frac{\Delta\Phi}{\Delta\tau}\,. \tag{27}$$

The balance equations are obtained by noting that the amount of isotope to be separated entering the column minus that which is leaving is equal to the quantity accumulated in the column (that is, the final minus the initial). We shall treat the DFA and IFA cases independently.

DFA Case

Amount entering: $\int_0^t Ly_\infty \, dt$,

Amount leaving: $\int_{t_1}^t Ly \, dt$,

Initial amount: 0

Final amount: $\int_0^{z_1} \Omega dz$.

Thus

$$\int_0^t Ly_\infty \, dt - \int_{t_1}^t Ly \, dt = \Omega z_1.$$

Since $\Omega z_1 = Lt_1$ from the total material balance,

$$\int_{t_1}^t L(y_\infty - y)dt = \Omega z_1 - Lt_1 y_\infty = Lt_1(1 - y_\infty).$$

With the reduced variable τ proportional to t, this relation becomes

$$\int_{\tau_1}^{\tau} (y_\infty - y)d\tau = \tau_1(1 - y_\infty) = (y_\infty - y_0)\,\overline{\Delta\tau}. \tag{28}$$

The first term represents the surface covered by the theoretical isoplane (Fig. 3) between its limiting values y_∞ and y , while $\overline{\Delta\tau}$ represents the mean value of τ.

IFA Case

Amount entering: 0

Amount leaving: $\int_0^{t_1} Lydt$

Initial amount: $\int_0^{z_1} \Omega dz$

Final amount: 0

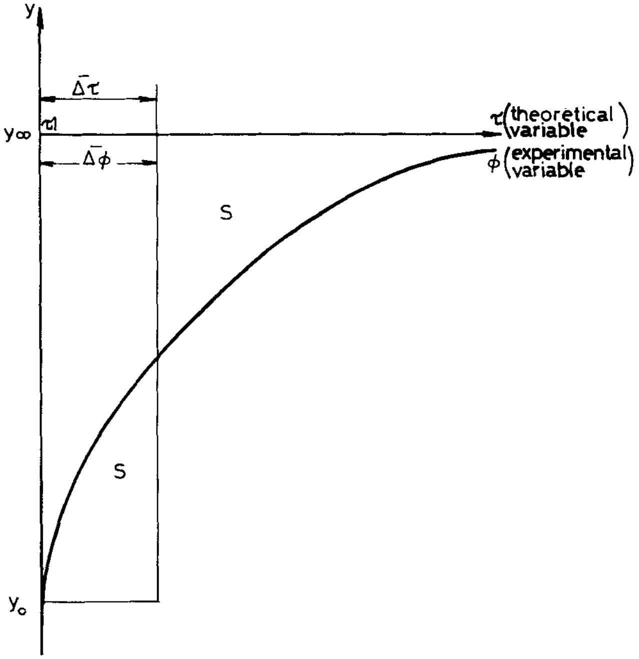

FIGURE 3. Shape of an isoplane for DFA ($\varepsilon < 0$).

The total material balance, which is the same as for DFA, yields

$$\int_0^{\tau_1} (y - 1)d\tau = 0. \tag{29}$$

That is, the point of natural concentration $y = 1$, or the neutral point B (Fig. 4), bisects the curve into two equal surfaces. Its abscissa τ_i has a value given by the equation

$$y(\tau) - 1 = 0$$

where $y(\tau)$ is given by Eqs. (21) and (22) with

$$\xi = \frac{\tau_1 - \tau}{2\varepsilon\mu}$$

and τ_1 by Eqs. (25) or (26). If we add to each side of

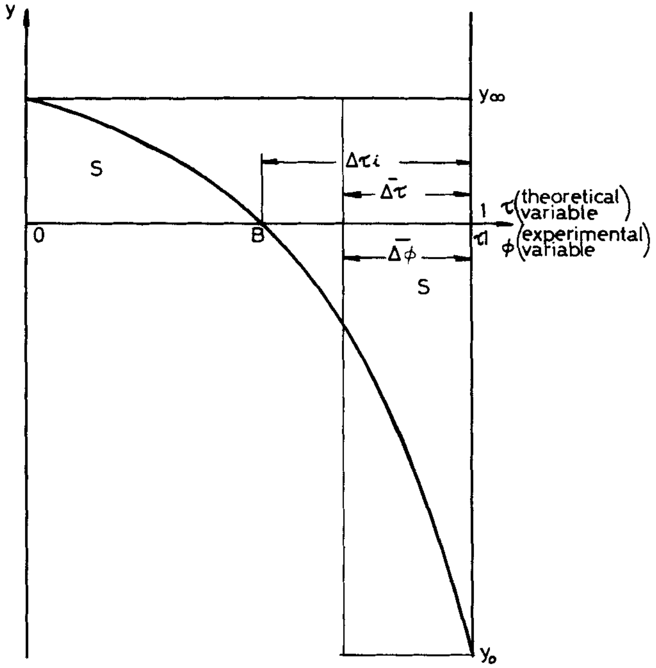

FIGURE 4. Shape of an isoplane for IFA ($\varepsilon > 0$).

Eq. (29) the quantity $(I - y_\infty)\tau_1$, we obtain the surface of the curve relative to its asymptote, that is:

$$\int_0^{\tau_1} (y - y_\infty)\, d\tau = (1 - y_\infty)\tau_1 = (y_0 - y_\infty)\, \overline{\Delta\tau}$$

which is analogous to Eq. (28) of DFA.

Application

From the considerations of the preceding section, we shall determine the HETP. H may be evaluated by Eq. (27),

$$H = 4\varepsilon^2\mu\, (\overline{\Delta\Phi}/\overline{\Delta\tau}),$$

where $\overline{\Delta\tau}$ is the mean value of the theoretical curve (DFA or IFA). Thus,

$$\overline{\Delta\tau} = \tau_1 \frac{(1 - y_\infty)}{(y_\infty - y_o)},$$

τ_1 is the time of arrival of the front from Eqs. (25) or (26),

$$\tau_1 \approx \frac{\pi}{4}(y_o - 1)^2,$$

and $\overline{\Delta\Phi}$ is the mean value of Φ corresponding to the theoretical value $\overline{\Delta\tau}$ and given by the experimental curve, such that:

$$\overline{\Delta\Phi} = \frac{\int (y - y_\infty)d\Phi}{y_o - y_\infty} \qquad (30)$$

For IFA, a variant is to take as characteristic values the distances between the head of the band and the neutral point B, whence, in terms of

$$\Delta\tau_i = \tau_1 - \tau_i \text{ and } \Delta\Phi_i,$$

$$H = 4\varepsilon^2\mu \frac{\Delta\Phi_i}{\Delta\tau_i}$$

In summary, the determination of the HETP requires the choice of a convenient scale from the theoretical curve, such that its mean value, defined by Eq. (30), coincides with the experimental one. A difficulty of the method is that it is sensitive to the determination of the extreme concentration y_o, which is somewhat imprecise. This difficulty may be overcome by adjusting y_o, such that the final verification of the parameter identification will be made by comparing the experimental and theoretical curves, the latter being calculated with Eqs. (21) and (22). This can be easily done with a desk calculator. For that purpose the complementary error function (erfc) can be either taken from appropriate tables or calculated from the expression (6):

$$\text{erfc}(y) = 2/\{1 + \exp[15y/(7 - |y|)]\} .$$

To illustrate the method, we have simulated experiments corresponding to different cases of frontal analysis and have taken the arbitrary values $2\varepsilon = \pm 10^{-3}$, $\mu = 0.9$, H = 1 cm, and a column length of 100 cm. Figures 5-8 give calculated isoplanes as a function of the theoretical variable τ or the

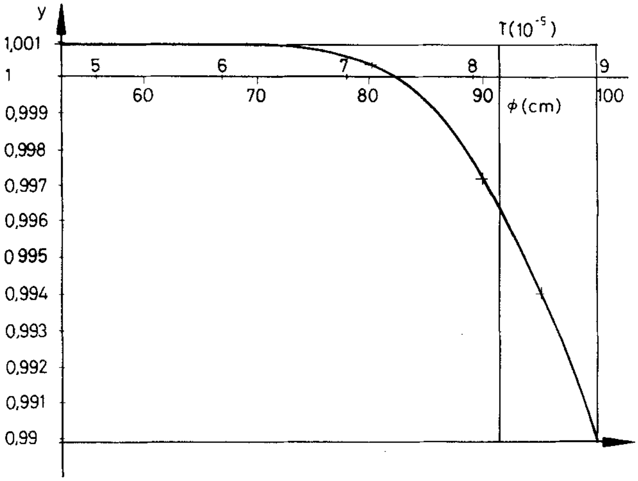

FIGURE 5. Simulated experiment in inverse frontal analysis. Case 1 (see Table 1).

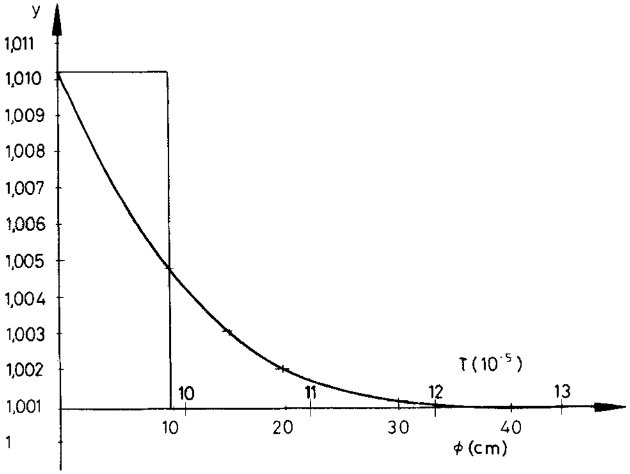

FIGURE 6. Simulated experiment in direct frontal analysis. Case 2 (see Table 1).

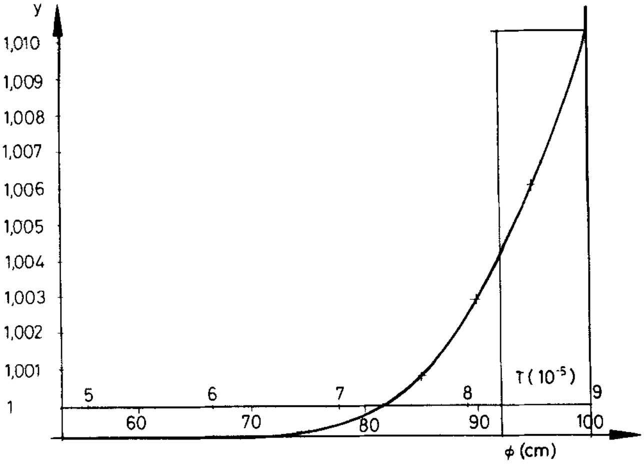

FIGURE 7. Simulated experiment in inverse frontal analysis. Case 3 (see Table 1).

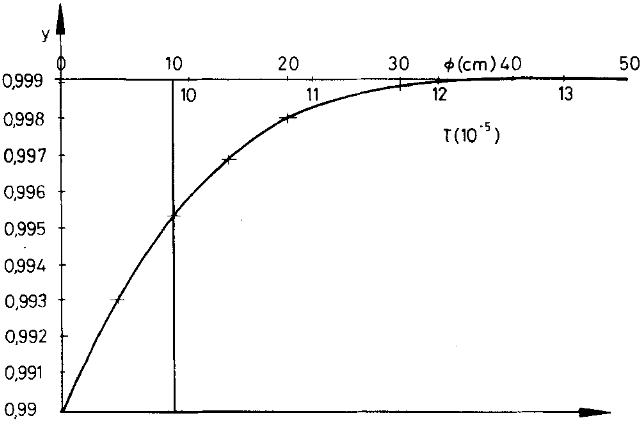

FIGURE 8. Simulated experiment in direct frontal analysis. Case 4 (see Table 1).

practical variable Φ. The intermediate variables and the equations utilized are presented in Table 1. Note that in an actual experiment, the measured variables will be ε, μ, and y_o.

ISOTOPE REMIXING

To include isotope remixing, we assume that the column is initially filled with a solution in chemical and isotopic equilibrium with the resin. The isotope concentration is suddenly changed at the top of the column and its evolution at the bottom is observed (Fig. 9). It is presumed that this change is in the form of a step, whose amplitude is large, so that separation effects (terms of order of ε) may be neglected. Thus we speak of the remixing method. The equilibrium relation is $x - y = 0$, and the system of equations which gives the evolution of concentration in both phases is, with the same notations as used previously (2),

$$\Theta \frac{\partial y}{\partial t} + L \frac{\partial y}{\partial z} = - h \frac{\partial x}{\partial t} = K(x - y),$$

with the boundary conditions $t = 0$, $x(z,0) = y(z,0) = x_o$, and $z = 0$, $t > 0$, $y(0,t) = y_o$. The solution may be obtained in terms of the dimensionless variables

$$\zeta = \frac{Kz}{L}, \tag{31}$$

$$\theta = \frac{Kt}{h}, \tag{32}$$

$$\Psi = \frac{y - x_o}{y_o - x_o} \tag{33}$$

where Ψ is the efficiency.

Using the Laplace transform we have

$$\overline{\Psi} = \frac{1}{s} e^{-[\nu + 1/(1 + x)]s} = \overline{E} e^{-\nu_s \zeta}.$$

The factor $e^{-\nu_s \zeta}$ expresses a delay $\theta_o = \nu\zeta = \frac{K}{h}\frac{z}{v}$ in reduced time and

$$t = z/v \tag{34}$$

in real time. This delay corresponds to the travel by the

TABLE 1

Parameters for the Calculation of Simulated Cases of Frontal Analysis (Figs. 5-8)

Case	1 IFA($\varepsilon > 0$)	2 DFA($\varepsilon > 0$)	3 IFA($\varepsilon < 0$)	4 DFA($\varepsilon < 0$)
2ε	10^{-3}	10^{-3}	$- 10^{-3}$	$- 10^{-3}$
μ	0.9	0.9	0.9	0.9
y_o	0.9898735	1.0102027	1.0102027	0.9898735
$\overline{\Delta\Phi}$	8.162	9.675	8.103	9.75
$\Delta\Phi_i$	17.9		17.9	
$y_\infty = 1 + 2\varepsilon\mu$	1.0009	1.0009	0.9991	0.9991
$\tau_1(y = y_o)$	9.10^{-5}	9.10^{-5}	9.10^{-5}	9.10^{-5}
$\overline{\Delta\tau} = \tau_1 \ (1-y_\infty)/(y_\infty - y_o)$	$0.7346 \ 10^{-5}$	$0.870713 \ 10^{-5}$	$0.729255 \ 10^{-5}$	$0.8779 \ 10^{-5}$
$\Delta\tau_i = \tau_1 - \tau_i, \ \tau_i(y=1)$	$1.617 \ 10^{-5}$		$1.612 \ 10^{-5}$	
$H = 4\varepsilon^2\mu \ (\overline{\Delta\Phi}/\overline{\Delta\tau})$	1	1	1	1
$H = 4\varepsilon^2\mu \ (\Delta\Phi_i/\Delta\tau_i)$	0.9963		0.9994	
Figure	5	6	7	8

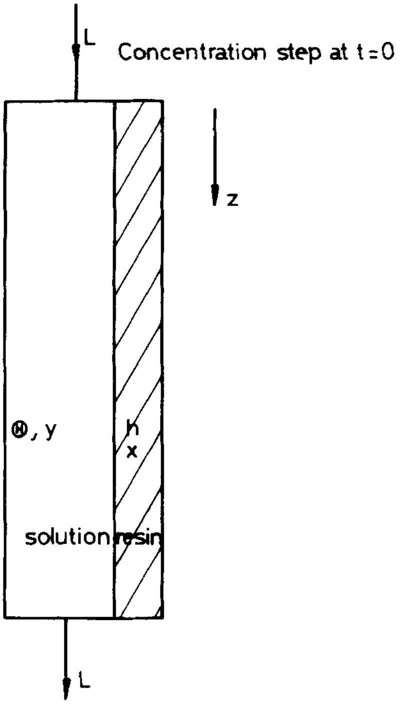

FIGURE 9. Schematic representation of isotope remixing.

liquid from the entry of the column to the sampling point at the exit. Thus we have

$$\Psi(\theta) = E(\theta_r)\ U(\theta_r),$$

where $\theta_r = \theta - \theta_o$ is the delayed time and $U(\theta_r)$ is a step function. The inversion of $\bar{E}$ gives

$$E = e^{-\zeta}\{1 + \int_0^{\theta} e^{-\theta'} (\frac{\zeta}{\theta})^{1/2}\ I_1[2(\zeta\theta')^{1/2}]d\theta'\}, \qquad (35)$$

where $I_1(x) = \frac{1}{i} J_1(ix)$ is the first order Bessel function of imaginary argument. The parameter E may be calculated using the expansion

$$E = e^{-\zeta}\ \{1 + \sum_{n=1}^{\infty} \frac{\zeta^n}{n!}\ [1 - e^{-\theta} \sum_{m=0}^{n-1} \frac{\theta^m}{m!}]\}.$$

If ζ is sufficiently large (>10) we may use the approximation

$$E \approx \frac{1}{2}\left[1 + \operatorname{erf}\left(\frac{\theta - \xi}{2\xi^{1/2}}\right)\right].$$

Properties of Ψ and Determination of the Parameters

If V is the displacement velocity and ζ, the number of theoretical stages, is $(1 + \nu)$, then, when $\theta \to \infty$, $\Psi \to 1$. That is, as $t \to \infty$, isotopic equilibrium is approached, $y \to y_o$.

From the mathematical expression for Ψ or E, it can be shown that

$$\int_{\theta_o}^{\infty} (1 - \Psi)d\theta = \int_0^{\infty} (1 - E)d\theta = \zeta \ . \tag{36}$$

This relation expresses the isotope balance between the entrance and the exit of the column. Physically, the balance is

$$\int_0^T Ly_o\, dt - \int_{t_0}^T Lydt = \int_0^z [(\Theta + h)y_o - hx_o]dz.$$

Recalling that for sufficiently large T, the final values of x and y are at equilibrium, whence

$$Ly_o t_o + \int_{t_o}^T L(y_o - y)dt = [\Theta y_o + h(y_o - x_o)]z.$$

The first term on each side is eliminated through Eq. (34) and, introducing the efficiency

$$\int_{t_o}^T (1 - \Psi)dt = \frac{hz}{L} \ .$$

Using the reduced variables defined by Eqs. (31) and (32), this corresponds to Eq. (36) for $T \to \infty$. The balance from $t = 0$ to $t = \infty$ gives

$$\int_0^{\infty} (1 - \Psi)\ dt = t_o + \frac{hz}{L} = \frac{z}{v} + \frac{hz}{L} = \frac{z}{V} = \bar{t}. \tag{37}$$

The corresponding mean values of θ_r and θ are $\bar{\theta}_r = \zeta$ and $\bar{\theta} = \zeta(1 + \nu)$. The mean time $\bar{t}$ can be easily determined from the experimental curve as shown in Fig. 10.

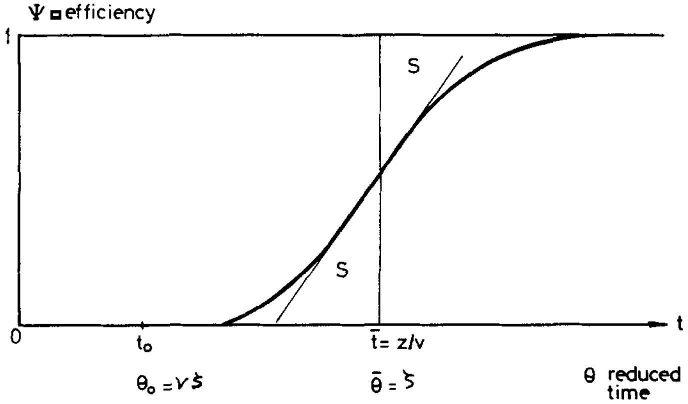

FIGURE 10. Efficiency curve in an isotope remixing experiment.

The slope $\partial\Psi/\partial t$ will be calculated at the mean time $\bar{t}$. For $t = \bar{t}$,

$$\left(\frac{\partial\Psi}{\partial\theta}\right)_{\theta=\bar{\theta}} = \left(\frac{\partial E}{\partial\theta_r}\right)_{\theta_r=\xi} = e^{-2\zeta}\, I_1(2\xi)$$

or

$$\bar{t}\left(\frac{\partial\Psi}{\partial t}\right)_{t=\bar{t}} = -\left(\frac{\partial\Psi}{\partial\theta}\right)_{\theta=\bar{\theta}} = \zeta(1 + \nu)e^{-2\zeta}\, I_1\,(2\zeta). \tag{38}$$

This relation enables us to calculate ζ if ν is known, and thus the HETP from the slope of the experimental curve, $(\partial\Psi/\partial t)$at $t = \bar{t}$. Thus, the experimental and theoretical curves will have same mean value $\bar{t}$ and same slope at that mean time.

If $\zeta > 1$,which is generally the case, we can use the approximation

$$I_1(2\zeta) = \frac{e^{2\zeta}}{\zeta}\left(\frac{\zeta - 0.38}{4\pi}\right)^{1/2},$$

whence

$$\zeta = 0.38 + 4\pi\left[\bar{t}\cdot\frac{\partial\Psi/\partial t}{1 + \nu}\right]^2. \tag{39}$$

From Eqs. (10), (12), and (31) we can deduce the number of theoretical plates

$$n = \frac{z}{H} = (1 + \nu)\zeta.$$

Figure 11 shows a typical comparison between experiment and theory

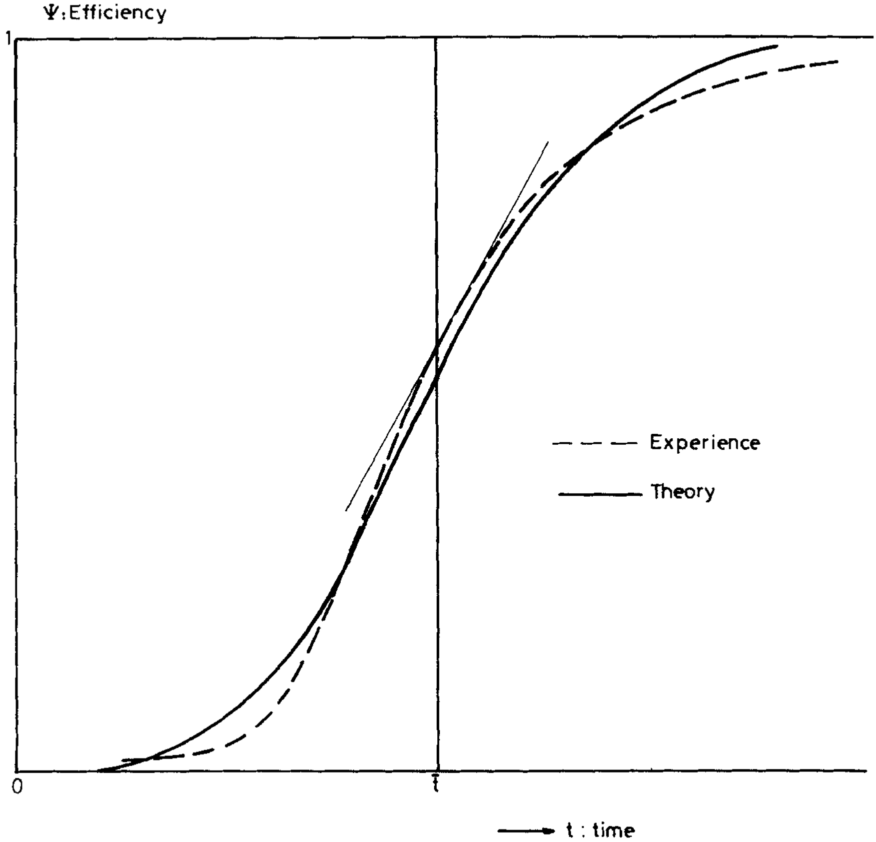

FIGURE 11. Comparison between experiment and theory in an isotope remixing experiment.

with the appropriate determination of $\bar{t}$ and $(\partial\Psi/\partial t)$ taken at $t = \bar{t}$.

We observe a small but systematic difference between the theoretical and experimental curves. This difference can be explained by the presence of two types of resins, the second of which is the so-called micropores (7). There is only a small amount of this second resin but the kinetics are slower than that for the first. We have treated this mixed resin case theoretically by the addition of appropriate terms. However, it is not presented here, but we note that the calculated results are in excellent agreement with observation, thus confirming this assumption.

NOMENCLATURE

h	holdup in resin (moles/cm)
H	height equivalent to a theoretical plate-HETP (cm)
I	isotope transport (moles/sec)
K	exchange transfer constant (moles/cm-sec)
ℓ	Vh (mole/sec)
L	flow rate (moles/sec)
N	mean mole fraction in resin and solution
r_i	characteristic roots in Laplace transform
s	Laplace variable
t	time (sec)
v	L/Θ displacement velocity of liquid (cm/sec)
V	$L/(h + \Theta)$, displacement velocity (cm/sec)
x	isotopic mole fraction in resin
y	isotopic mole fraction in solution
Y	$\|\xi\|/2\tau^{1/2}$
z	column height (cm)
Z	$z - Vt$ (cm)
ε	separation coefficient
ζ	Kz/L
θ	Kt/h
Θ	holdup in solution (moles/cm)
Λ	volume of solution (cm^3)
μ	$h/(\Theta + h)$
ν	Θ/h
ξ	$2\varepsilon Z/H$
Σ	cross-section of the column (cm^2)
τ	$(2\varepsilon)^2 \mu Vt/H$
ϕ	total transport (moles/sec)
Φ	Vt (cm)
Ψ	$(y - x_o)/(y_o - x_o)$
Ω	$\Theta + h$, total holdup per unit length of column (moles/cm)

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