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Model-Based Analysis of Data from Countercurrent Liquid-Liquid Extraction Processes

An efficient iterative method for solving the equations which describe the steady state of a staged countercurrent extraction process is described. The equations include the effects of backmixing, and apply to an arbitrary number of solutes, to nonlinear equilibrium relations, and to variable net phase flow rates (and thus to partially miscible solvents). The solution procedure, based on partial linearization of the equations, is related to and extends the method of Ricker et al. (1980).

This solution procedure has been used, in conjunction with nonlinear regression methods, to investigate problems related to the determination of parameters by analyzing steady state data. The simultaneous determination of several parameters, including mass transfer coefficients, backmixing coefficients, and equilibrium constants, is shown to be possible. The accuracy with which the parameters can be estimated depends, however, on many factors, including the number and location of the sampling points, the intensity of the backmixing, and the extent to which equilibrium is approached in the column.

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SCOPE

In the usual method of scaling-up extraction columns based on transfer unit height estimated from pilot plant data, the separate variation of axial dispersion and mass transfer coefficients with column diameter is not taken into account. In order to develop an improved design procedure, it will be necessary to analyze data from pilot plant or bench scale col-

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umns to determine mass transfer coefficients, and the effects of axial mixing have to be allowed for in the analysis.

The goals of the work reported here were:

1. To develop an efficient iterative method for the solution of the equations which describe the steady state of a general cell-backmixing model for a countercurrent extraction column.

2. To use this method, in conjunction with parameter estimation techniques, to investigate questions related to the analysis of data from extraction experiments in which samples are obtained at points within the column. The questions involve the nature and importance of mixing effects, the possibility of determining several parameters simultaneously, the accuracy attainable in the parameter estimates, and the optimal location of sampling points.

The techniques developed and the results obtained should be of use not only in the design of experiments and the analysis of data, but also in the design of full-scale extraction columns.

CONCLUSIONS AND SIGNIFICANCE

An efficient iterative method was developed for the solution of the equations which describe the steady state of a cell-backmixing model of a countercurrent extraction column. The model is general in the sense that it applies to an arbitrary number of species and stages, with arbitrary equilibrium relations. In particular the case of partially miscible solvents can be handled, that is the solution of the equations may correspond to net phase flow rates which vary from stage to stage. In the model backmixing coefficients, equilibrium constants, and mass transfer coefficients may vary with stage number or with composition, and additional feed streams may enter the column at any stage. In all cases studied, rapid convergence to an accurate solution of the equations was observed.

In computational studies related to parameter estimation, it was shown that nonlinear regression techniques can be used to estimate mass transfer coefficients for both solute and solvent species, basing the estimates on samples obtained from points within the column as well as exit stream samples. The errors which result if the effects of backmixing are neglected were calculated, and in certain cases were found to be significant. In addition it was shown that, given sufficient data, several parameters can be estimated simultaneously. The parameters estimated can include backmixing coefficients and equilibrium constants, as well as mass transfer coefficients. Finally the problem of optimal location of sampling points was considered, and a method was developed for showing how the value of an additional sample in reducing the standard error of a parameter estimate varies with the location of the sample point. The results show clearly that certain sample locations are particularly effective in providing information related to the value of a given parameter.

INTRODUCTION

The scale-up of extraction columns is a pressing industrial problem (Misek et al., 1977). Scale-up is still commonly based on the evaluation of transfer unit height from pilot plant data, as described for example by Karr and Lo (1976). The data usually correspond to feed and exit stream concentrations for a column with a diameter of at least 15 cm. Corrections based on experience are often applied in designing the full scale column, which may be over 1 meter in diameter.

This method has the disadvantage that the results depend on the mass transfer coefficient and on the backmixing in both phases, and these cannot both be determined from exit stream concentrations alone. Ideally the mass transfer coefficients and the intraphase mixing (as described for example by eddy diffusion coefficients) should be scaled-up separately. Little information is available, however, on the variation of either of these parameters with column diameter and other variables, although it is clear that the circulation of the two phases increases with column diameter.

A more sophisticated approach consists in extracting both mass transfer coefficients and eddy diffusivities (or equivalent measures of mixing) from the experimental data, data derived from pilot plant or bench scale columns which are not necessarily similar to, or even of the same type as, the full-scale column. The mass transfer coefficients so obtained, corrected if necessary for the effects of drop size, intensity of turbulence, holdup, and other parameters, are then incorporated into a model which accounts for mixing in both phases. This model is used to design the full-scale column.

In this paper we examine in some detail the problem of analyzing data from an extraction column, obtained at internal as well as external sampling points, in order to determine mass transfer coefficients and in some cases other parameters. The analysis is based on a model for the column which accounts for backmixing in both phases. Nonlinear regression methods are used to determine the best (least-squares) parameter values. Specific goals were:

1. To develop an efficient method for the iterative solution of the equations which describe the steady state of a general (arbitrary number of stages and species, arbitrary equilibrium relations) cell backmixing extraction column model.
2. To couple this model and solution method to a general nonlinear regression program.

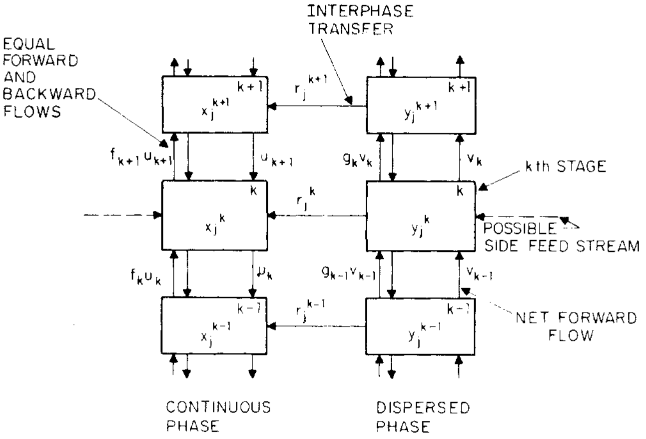

Figure 1. Schematic diagram showing stages $k - 1$, k, and $k + 1$ in the model of an N-stage countercurrent extraction column.

3. To use the resulting program to study a number of questions related to the acquisition and analysis of data, including the nature and importance of mixing effects, the possibility of determining several parameters simultaneously, the accuracy attainable in the parameter estimates, and the optimal location of sampling points.

COMPUTATIONAL METHODS

The formulation and iterative solution of the steady state equations for a cell-backmixing model of a countercurrent extractor have been discussed by Mecklenburgh and Hartland (1975), by McSwain and Durbin (1966), and recently by Ricker et al. (1980). If the equilibria are linear and the net phase flow rates do not vary from stage to stage, the equations are linear and the Newton-Raphson method converges in one iteration. Since in many practical cases the above conditions are approximately satisfied, methods based on linearization would be expected to converge rapidly, and this has in fact been observed by McSwain and Durbin (1966), and also by Ricker et al. (1980). Thus the method described below, which applies to the general case involving (a) multiple species, (b) nonlinear equilibria, (c) partially miscible solvents, and (d) net phase flow rates which vary from stage to stage, is based on a combination of the Newton-Raphson method and the method of successive approximations. The method represents an extension to the case of partially miscible solvents (i.e., variable net phase flow rates) of the procedure reported by Ricker et al. (1980), with the difference that the linearization of the equilibrium relations is not required, and a smaller number of equations has to be solved. The method is designed for use in parameter estimation problems, where iterative determination of the parameters depends on the efficient and accurate solution of the equations of the model.

The cell-backmixing model of a countercurrent extractor used in this work is shown schematically in Figure 1. The continuous phase and dispersed phase feeds are assumed to enter stages N and 1 respectively. Feed entry at stages N-1 and 2, as assumed by Ricker et al. (1980), produces only minor changes in the equations. Backmixing is represented by an interchange of fluid between cells k and $k + 1$ at rate $f_{k+1}u_{k+1}$ for the continuous phase and rate $g_k v_k$ for the dispersed phase. The backmixing coefficients f_k and g_k are assumed known, and are usually constant from stage to stage. As indicated by the broken lines, provision can also be made for feed streams which enter intermediate stages.

Without loss of generality the interphase mass transfer rates r_j^k can be expressed as

$$r_j^k = L_j(K_j y_j^k - x_j^k),\ j = 1, 2, \ldots, S,\ k = 1, 2, \ldots, N \qquad (1)$$

Here L_j, the overall mass transfer coefficient for the jth species in continuous phase, is the product of the conventional mass transfer coefficient and the interfacial area for the stage. The equilibrium constant K_j and the overall mass transfer coefficient L_j can in general be functions of the stage number and of the continuous phase and dispersed phase mass fractions x_j^k and y_j^k. (Note that x and y can equally well denote continuous and dispersed phases respectively.)

An alternate formulation of the problem (Ricker et al., 1980) involves the introduction of interfacial concentrations as additional unknown variables. The rate of mass transfer is assumed proportional to the difference between the bulk and interfacial concentrations, and the interfacial concentrations are assumed to be at equilibrium; these assumptions correspond to the requisite additional equations. It is easily shown, however, that Eq. 1 is equivalent to the formulation described above if the mass transfer coefficient L_j is allowed to vary with concentration. Since this causes no problems in the iterative solution method described below, we have elected to work with a smaller number of equations and variables.

It should be noted that, while the cell-backmixing model discussed here applies most directly to staged countercurrent contactors, it can also be applied in many practical cases to differential contactors. In such an application the number of stages can be chosen almost arbitrarily, subject to the requirement that the backmixing coefficients must have positive values.

The state of the kth stage is described by $2S$ independent variables, namely the net phase flow rates u_k and v_k and $S - 1$ mass fractions for each phase. It is convenient to define a mass fraction vector, w^k, for the kth stage as follows:

$$\begin{aligned}
w_1^k &= x_1^k \ - \text{dispersed phase solvent}\\
w_2^k &= x_2^k \ - \text{first solute}\\
w_3^k &= x_3^k \ - \text{second solute}\\[4em]
w_{S-1}^k &= x_{S-1}^k \ - \text{last solute}\\
w_S^k &= y_2^k \ - \text{first solute}\\[4em]
w_{2S-3}^k &= y_{S-1}^k \ - \text{last solute}\\
w_{2S-2}^k &= y_S^k \ - \text{continuous phase solvent}
\end{aligned} \qquad (2)$$

Note that the mass fractions of the mutually dissolved solvents, x_S^k and y_1^k, are omitted in forming the vector w^k. The $2(S - 1)$ individual species mass balance equations for the kth stage are now in the form

$$A^k w^{k-1} + (B^k + R^k)w^k + C^k w^{k+1} = a^k,\ k = 1, 2, \ldots, N \qquad (3)$$

where A^k, B^k, R^k, and C^k are $2(S - 1) \times 2(S - 1)$ matrices and a^k is a $2(S - 1)$-dimensional vector. A^k, B^k, R^k, C^k and a^k are shown in the Appendix for $S = 4$, i.e., for the case of two solutes transferring between a raffinate and an extract solvent. Note that the A, B, R, and C matrices are functions of the net phase flow rates u_k and v_k, as well as the equilibrium constants K_j. The equilibrium constants and the mass transfer coefficients and rates are in turn functions of the mass fraction vectors w^k.

The steady-state equations for the kth stage are completed by writing overall balances for the continuous and dispersed phases, namely:

$$u_{k+1} = u_k + \sum_{j=1}^{S} r_j^k, \quad k = 1, 2, \ldots, N$$
$$v_k = v_{k-1} - \sum_{j=1}^{S} r_j^k, \quad k = 1, 2, \ldots, N \tag{4}$$

with u_{N+1} and v_0 the feed stream flow rates. There are, in total, $2NS$ independent nonlinear algebraic equations which determine the $2NS$ variables represented by w^k, u_k, and v_k.

The $2N(S - 1)$ individual species material balance Eq. 3 can be written compactly in the form

$$\phi(z) = Dz + Ez - \alpha = 0 \tag{5}$$

Here z is a $2N(S - 1)$-dimensional vector

$$z = \begin{bmatrix} w^1 \\ w^2 \\ \vdots \\ w^N \end{bmatrix}, \tag{6}$$

D is a $2N(S - 1) \times 2N(S - 1)$ matrix that depends only on the net phase flow rates u_k and v_k, and E is a $2N(S - 1) \times 2N(S - 1)$ matrix that depends only on the equilibrium constants K_j. For example when $N = 4$ we have

$$D = \begin{bmatrix} B^1 & C^1 & 0 & 0 \\ A^2 & B^2 & C^2 & 0 \\ 0 & A^3 & B^3 & C^3 \\ 0 & 0 & A^4 & B^4 \end{bmatrix} \qquad E = \begin{bmatrix} R^1 & 0 & 0 & 0 \\ 0 & R^2 & 0 & 0 \\ 0 & 0 & R^3 & 0 \\ 0 & 0 & 0 & R^4 \end{bmatrix} \tag{7}$$

and

$$\alpha = \begin{bmatrix} a^1 + a^* \\ a^2 \\ a^3 \\ a^4 + b^* \end{bmatrix}$$

Note that D is block tridiagonal and E is block diagonal. The vectors a^* and b^* are defined in the Appendix.

The iterative procedure used to solve these equations can be summarized as follows:

1. Guess values for the mass fraction vectors w^k, and from these form the combined mass fraction vector z. Guess also the net phase flow rate vectors u and v. A reasonable initial guess corresponds to assuming no interphase transfer, in which case the feed compositions and flow rates can be extended to all stages. Call the initial guesses u^n, v^n, and z^n, where n indexes the iterations, and initially $n = 0$.

2. Based on the mass fractions z^n, evaluate the equilibrium constants K_j and then the interphase transfer rates r_j^k. From the transfer rates calculate new net phase flow rates $\bar{u}$ and $\bar{v}$ using Eq. 4.

3. Evaluate

$$\phi(z^n, u^n, v^n) = [D(u^n, v^n) + E(z^n)]z^{n+1} - \alpha$$

4. Solve the $2N(S - 1)$ linear equations

$$[D(u^n, v^n) + E(z^n)]\Delta z^n = -\phi(z^n, u^n, v^n) \tag{8}$$

for the mass fraction increment vector Δz^n. In solving these equations by Gaussian reduction, significant reductions in computing time can be obtained by taking advantage of the fact that $D + E$ is a block tridiagonal matrix, while A^k and B^k are diagonal matrices.

5. Let

$$\|\Delta z\| = [1/2N(S - 1)]\left[\sum_{k=1}^{N}\sum_{j=1}^{S}(\Delta w_j^k)^2\right]^{1/2}$$

or

$$\|\Delta z\| = [1/2N(S - 1)]\sum_{k=1}^{N}\sum_{j=1}^{S}|\Delta w_j^k|$$

Stop if $\|\Delta z\| < \epsilon$. Otherwise continue to Step 6.

6. Calculate new mass fraction and flow rate vectors z^{n+1}, u^{n+1}, and v^{n+1} using

$$\begin{aligned} z^{n+1} &= z^n + \beta\Delta z^n \\ u^{n+1} &= u^n + \beta'(\bar{u} - u^n) \\ v^{n+1} &= v^n + \beta'(\bar{v} - v^n) \end{aligned} \tag{9}$$

Here β and β' are step size parameters which can be chosen positive and small with respect to 1 in cases where relatively certain, but perhaps slow, convergence is desired. Return to Step 2.

Several comments are in order:

(a) Equation 8 is equivalent to the application of the Newton-Raphson method to the solution of Eq. 5, assuming that D and E are independent of w, and also that u and v are constant. In the case of linear equilibria and constant net phase flow rates these assumptions hold, and the iterative procedure will converge in one iteration from any initial guess. The differentiation of the equilibrium constants K_j with respect to the mass fractions is not required, thus avoiding a time consuming step (Ricker et al., 1980).

(b) At the risk of possible instability, Eq. 8 may be replaced by

$$[D(u^{n+1}, v^{n+1}) + E(z^n)]\Delta z^n = -\phi(z^n, u^{n+1}, v^{n+1})$$

in order to obtain more rapid convergence. In this case u^{n+1} and v^{n+1} are calculated from the transfer rates $r^k(z^n)$ using Eqs. 4 and 9.

(c) It seems preferable to decide convergence on the basis of $\|\Delta z\|$, rather than on the basis of $\|\phi\|$, since small ϕ does not necessarily correspond to small Δz. Also $\|\Delta z\|$ is in a sense an "average" mass fraction increment, and thus $\epsilon = 0.001$ or 0.0001 is a reasonable choice in most problems. It is difficult to judge in advance what value of $\|\phi\|$ can be considered small.

(d) It is often convenient to assume for the continuous phase solvent (species S) a transfer rate expression of the form

$$r_S^k = L_S(y_S^k - K_S x_S^k)$$

In this case the last row of the matrix R^k will appear as shown in the Appendix.

Parameter Estimation

Iterative methods for the estimation of parameters of mathematical models by fitting experimental data are well developed and widely used (Box, 1960; Marquardt, 1963). In this work a general program based on the procedure described by Marquardt (1963) was used to find values for certain parameters corresponding to a weighted least squares fit to the data. Data points consisted of values of solute or solvent mass fraction in one or both phases, and at several points in the extraction column. Except as noted, equal weights were used for all data points, since all mass fractions are likely to be measured with the same accuracy.

Let $\bar{z}$ be the vector of mass fractions at the points in the column where data are available. Then the matrix $\partial\bar{z}/\partial p$ is needed in the iterative process for determining the parameters. This matrix was calculated by varying in turn each parameter, say p_m, by an amount Δp_m (typically 1% of p_m) from its base value, solving the equations of the model to determine a new mass fraction vector $\bar{z} + \Delta\bar{z}$, and approximating $\partial\bar{z}/\partial p_m$ by $\Delta\bar{z}/\Delta p_m$.

Estimates for the standard error of the mth parameter estimate, σ_m, were calculated using

$$\sigma_m^2 = \{(O^TO)^{-1}\}_{mm}, \quad m = 1, 2, \ldots, P \tag{10}$$

Here $O = \partial\bar{z}/\partial p$, and d is the standard deviation of the measured variables. The RMS value of the residual $(\bar{z}^* - \bar{z})$ can be used as an estimate of d. The 95% confidence limits are proportional to σ_m, with the factor of proportionality being $[PF(P, M\text{-}P)]^{1/2}$, where P is the number of parameters estimated, M is the number of data points, and $F(P, M\text{-}P)$ is the 0.05 point of the F distribution with parameters P and $M\text{-}P$ (Box, 1960).

In fitting real data the standard deviation of the data, d, can be estimated from replicate measurements if these are available. In the absence of replicate measurements d can be estimated from the residuals corresponding to the best fit to the data, on the assumption that the model represents the physical system perfectly, i.e., that the residuals reflect only measurement errors, and not lack of fit.

If, in order to test the rapidity of convergence of the iterative parameter determination program, simulated data generated from the model itself are fitted, the residuals will necessarily be zero. In this case an estimate of the standard errors of the parameters can be calculated from Eq. 10, based on an arbitrary but presumably reasonable estimate of the measurement error d. This is the procedure adopted in the computational studies reported below.

In general it is possible to sample the continuous and dispersed phases only at a limited number of points in the column, and it is therefore interesting to consider the optimal location of the sampling points. We can approach this problem by assuming that samples are available at each stage, and calculating the effect of making an additional measurement at an arbitrary stage. (This corresponds to doubling the weight factor used at the point.) The availability of an additional data point will cause the standard error of the mth parameter to be reduced, and the amount of this reduction is a measure of the "value" of the additional sample, and also, we assume, a measure of the value of the first sample at the stage under consideration.

A straightforward calculation shows that, for a small increase in the weight factor, $\Delta\sigma_m^i$ is a negative quantity proportional to

$$[Q(Q^TQ)^{-1}]_{im}^{1/2} \tag{11}$$

Here $\Delta\sigma_m^i$ is the increment in the standard error of the mth parameter due to an additional measurement at point i, and i indexes the data points. Note that if the parameters are uncorrelated the variance-covariance matrix $(Q^TQ)^{-1}$ is diagonal and the value of each point can be judged from $Q = \partial z/\partial p$ directly. Thus, in the absence of parameter correlation, additional samples should be taken at points where the mass fraction profile is most sensitive to the parameter in question.

COMPUTATIONAL STUDIES

As a representative base case for computational studies related to solution of the equations of the model and to parameter estimation, the system

H_2O = Continuous Phase—Species 3
Acetic Acid (*AA*) = Solute—Species 2
MIBK = Dispersed Phase Solvent—Species 1

was selected. At 25°C, the following equilibrium relations hold:

$$\begin{aligned} y_{H_2O} &= (0.0173 + 0.366y_{AA})x_{H_2O} \\ x_{MIBK} &= (0.0177 + 0.0523x_{AA})y_{MIBK} \\ y_{AA} &= (0.5767 + 1.787x_{AA} - 2.0876x_{AA}^2)x_{AA} \end{aligned} \tag{12}$$

where x and y denote the continuous phase and dispersed phase mass fractions and *MIBK* denotes methyl isobutyl ketone. Feed compositions and flow rates were:

Continuous Phase (H_2O)	Dispersed Phase (*MIBK*)
$x_1^F = 0.0$	$y_1^F = 1.0$
$x_2^F = 0.08$	$y_2^F = 0.0$
$x_3^F = 1.0$	$y_3^F = 0.0$
$u_F = 0.05$ kg/s	$v_F = 0.03$ kg/s

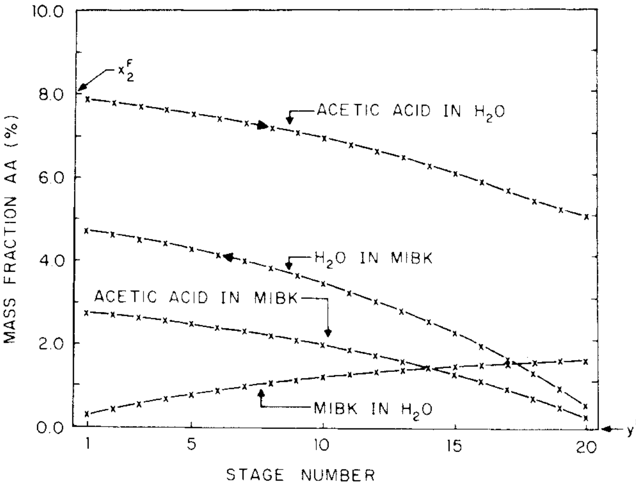

Figure 2. Mass fraction profiles for Case 1.

This corresponds to an 8% acetic acid in water feed, unsaturated solvents, and transfer of *AA* from the water to the *MIBK* phase.

Case 1

The column was assumed to contain 20 stages, with backmixing coefficient values of $f = 0.80$ and $g = 0.20$. For a column 1 meter long and 10 cm in diameter, and a dispersed phase holdup ratio of 30%, these backmixing coefficients correspond to axial diffusion coefficients of 59 cm²/s and 55 cm²/s for the continuous and dispersed phases respectively.

The overall mass transfer coefficients were chosen as

$$L_1 = 0.005 \text{ kg/s}$$
$$L_2 = 0.005 \text{ kg/s}$$
$$L_3' = 0.005 \text{ kg/s}$$

These conditions correspond to unsaturated solvent feeds and solvent-to-solvent mass transfer coefficients such that the partially miscible extract and raffinate solvents leave in an almost saturated condition.

Using the feed compositions and flow rates as initial guesses, the iterative procedure described above converged to a solution of the steady-state equations in five iterations, with $\|\Delta z\| < 10^{-6}$. $\|\Delta z\|$ decreased by a factor of approximately 10 at each iteration, which shows that the partial linearization produces, as expected, very rapid convergence. (Computing time for the five iterations on a CDC 6400 computer was about 1 second.) Mass fraction profiles for Case 1 are shown in Figure 2.

Case 2

The composition profiles generated in Case 1 were used as input data for the parameter estimation program. The overall mass transfer coefficient for *AA*, L_2, was determined by fitting: (a) the values of x_2^k; (b) the values of y_2^k; and (c) the values of x_2^k and y_2^k, in all cases for $k = 1, 2, \ldots, 20$. Using 0.004 as an initial guess for L_2, convergence to the correct value of 0.005 + 1% was always obtained in less than 6 iterations of the parameter determination procedure. In the three subcases the standard error of the mass transfer coefficient L_2 was (a) 4.8%, (b) 2.6% and (c) 1.0% based on an assumed value of 0.0005 for d, the standard deviation of the mass fraction measurement. This value for d corresponds to measuring a mass fraction of 1.0% with an error of ±5%, which is reasonable for most practical cases.

As expected, L_2 is determined best when measurements are

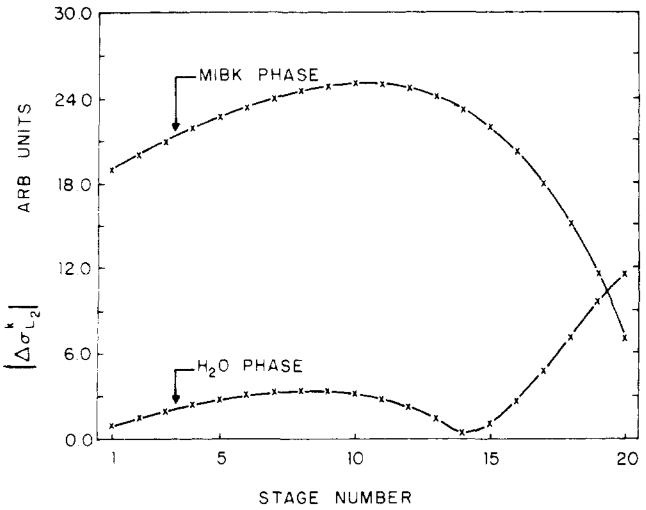

Figure 3. Increment to standard error of parameter L_2 as a function of stage number.

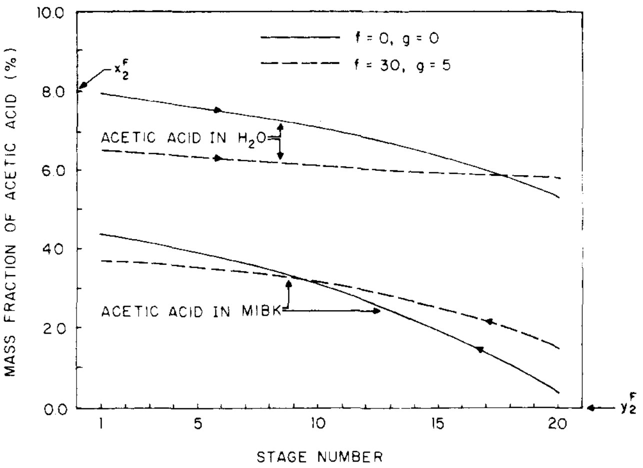

Figure 4. Calculated mass fraction profiles for $f = 5$ and $g = 30$, and least-squares profiles for $f = 0$ and $g = 0$, with L_2 as the free parameter.

made in both phases or in the phase in which the solute (*AA*) mass fraction undergoes the largest change, in this case the *MIBK* phase. When measurements are available in both phases but only at stages 1, 4, 7, 12, 17, and 20, the standard error of L_2 is 1.8%. When measurements are available only for the leaving streams, the standard error of L_2 increases to 4.3%. Thus, sampling at internal points is valuable in improving the accuracy with which L_2 can be estimated. The decrease in standard error resulting from internal sampling is more evident if the mass transfer coefficients are large, since in this case the product stream compositions do not depend strongly on the mass transfer coefficients.

Figure 3 shows $\Delta\sigma^k_{L_2}$, the incremental value of an additional sample in determining L_2, as a function of stage number, and for both phases. The largest values occur in the *MIBK* stream near the middle of the column. This is reasonable, since the mass fraction of *AA* near the entry point of the stream is little affected by the mass transfer coefficient, and the mass fraction near the exit for the low flow rate stream (in this case *MIBK*) is determined more by the equilibrium relation than by mass transfer. The incremental value curve for the H_2O phase is more interesting, in that it shows a minimum near stage 13. This is due to the fact that a small change in the mass transfer coefficient L_2 will lower the *AA* mass fraction at the exit (stage 20) and raise it near the entrance, leaving the *AA* mass fraction at stage 13 almost unchanged. Thus samples taken from the H_2O phase near stage 13 are of little value in improving the estimate of L_2.

The curves of $\Delta\sigma^k_{L_2}$ will of course depend on the particular case being studied. But in general we can see that internal samples are most valuable when taken from the stream in which the solute mass fraction changes most (i.e., the stream which has the lower flow rate). Further, it is useful to be aware of the fact that samples taken at certain points in the column may be much more valuable in determining the mass transfer coefficient (or any other parameter) than samples taken at other points. The optimal sampling points are evident from the values of $\Delta\sigma^k_m$, at least in the sense of additional samples. The problem of optimally locating a small fixed number of samples is more difficult.

Case 3

Neglecting the effects of backmixing, or using the wrong backmixing coefficients in analyzing the data, will lead to an error in the estimate for the mass transfer coefficient L_2. In order to assess the importance of accurately accounting for backmixing, mass fraction profiles corresponding to Case 1 ($f = 0.8$, $g = 0.2$, $L_2 = 0.005$) were fitted using $f = 0$ and $g = 0$. The least-squares value of L_2 was 0.0042, a 22% error relative to the correct value, i.e., the value used to generate the fitted profiles. The same profiles were then fitted using both L_2 and f as free parameters. While L_2 was determined with a standard error of 2.1% (based on $d = 0.0005$), the standard error for f was 27%. This reflects the rather weak dependence of the mass fraction profiles on the backmixing coefficient.

Ricker et al. (1980) have reported continuous phase Peclet numbers as low as 0.55 for a laboratory scale rotating disk contactor. If a 20 stage model is used, this corresponds to a backmixing coefficient, f, of 36, since the Peclet number and f are related by the equation (Hartland and Mecklenburgh, 1966)

$$f = \frac{N}{\text{Pe}} - \frac{1}{2}$$

Mass fraction profiles generated using $f = 30$ and $g = 5$ were fitted using $f = 0$ and $g = 0$. The least-squares value of L_2 in this case was 0.00355, quite different from the correct value of 0.0050. The mass fraction profiles for this case are shown in Figure 4.

Case 4

In theory samples can be obtained from both phases at multiple points in the extraction column, and these samples can be analyzed for all species. Thus enough information may be available to determine several parameters simultaneously. In order to demonstrate this, and to see whether correlation between parameters is strong enough to interfere with the effective estimation of the parameters, values of x_1^k, x_2^k, y_2^k, and y_3^k (*MIBK* in H_2O, *AA* in H_2O, *AA* in H_2O, *AA* in *MIBK*, and H_2O in *MIBK* respectively) were fitted using L_1, L_2, and L_3' as free parameters. In addition a multiplier on the equilibrium constant for the *AA* distribution, K_2^*, was used as the fourth free parameter. K_2^* is defined by the equation

$$y_{AA} = K_2^*(0.5767 + 1.787x_{AA} - 2.0876x_{AA}^2)x_{AA}.$$

Starting with initial guesses too small by 20%, rapid convergence of the parameter determination procedure to the correct values of all parameters was observed. The parameter values and the standard errors are shown below. The standard deviation of the measurement was assumed as before to be 0.0005.

Parameter	Value and Standard Error
L_1	0.0005 ± 1.7%
L_2	0.0005 ± 1.6%
L_3'	0.0005 ± 2.0%
K_2^*	1.00 ± 0.6%

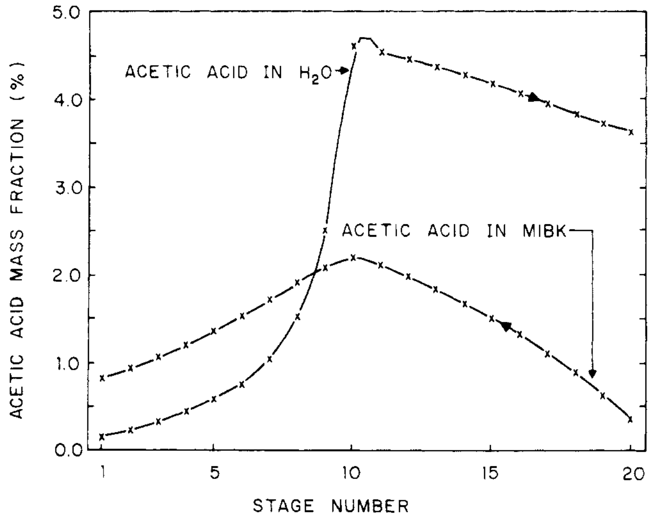

Figure 5. Mass fraction profiles for the case in which 20% acetic acid in H_2O is fed to stage 10.

The parameter correlation matrix for this case was:

	L_1	L_2	L_3'	K_2^*
L_1	1.00	−0.17	−0.29	−0.80
L_2	−0.17	1.00	0.03	0.05
L_3'	−0.29	0.03	1.00	0.03
K_2^*	−0.80	0.05	0.03	1.00

The specific results above are of course valid only for the conditions for which they were computed, and represent a best case in the sense that a large number of accurate data points is assumed. In general, however, they indicated the possibility of estimating several parameters simultaneously from the data obtained in a single run. We note that the three mass transfer coefficients are not strongly correlated. This is expected since the three species transfer from one phase to the other independently, except for weak interactions due to the concentration dependence of the equilibrium constants. A somewhat stronger correlation exists between L_2 and K_2^*, reflecting the fact that both parameters affect the *AA* mass fraction profiles. In the case studied, roughly half the column is dominated by mass transfer, while the streams are near equilibrium in the other half. This accounts for the fact that both the mass transfer coefficient and the equilibrium constant multiplier for *AA* can be estimated simultaneously with relatively small standard errors.

Case 5

It seems possible that, for the purpose of generating data that contain information on parameters such as mass transfer coefficients and backmixing coefficients, some advantage may be gained by feeding solvent containing a high concentration of solute at a stage near the center of the column. The mass fraction profiles calculated for a case in which 0.01 kg/s of 20% acetic acid in water was fed at stage 10 are shown in Figure 5. Pure solvents were fed at the ends of the column at rates of 0.05 and 0.03 kg/s for water and *MIBK* respectively. The profiles show large axial mass fraction gradients, and interphase mass transfer in opposite directions in the two halves of the column. When these profiles were used to determine L_2, there was no significant change in the standard error of the parameter estimate. Central stage feed of solute may be useful, however, in producing data which reveal variations in mixing intensity or in mass transfer coefficients with stage number.

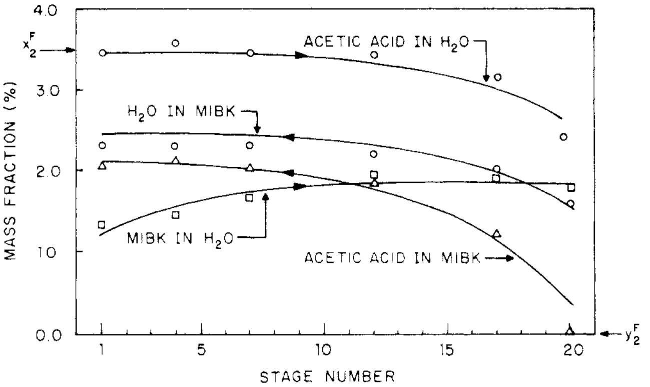

Figure 6. Least-squares mass fraction profiles and experimental values for Example 1.

ANALYSIS OF EXPERIMENTAL DATA

In this section we discuss the application of the computational and parameter determination methods presented above to the analysis of steady state data from a laboratory-scale countercurrent extraction column. The spray column, described in detail by Steiner et al. (1978), was 2 m high and 10 cm in diameter. The system used was water(continuous phase)-acetic acid-*MIBK*(dispersed phase). Continuous and dispersed phase samples were obtained at six stations within the column, corresponding to stages 1, 4, 7, 12, 17, and 20 in a 20-stage model of the column. Backmixing was estimated by analyzing inert tracer (KCl in the water phase and a dye in the *MIBK* phase) data obtained at the same sampling points. Within experimental error, the axial diffusion coefficients were consistent with backmixing coefficients $f = 0$ and $g = 0$, assuming a 20-stage model for the spray column. The equilibrium relations for the H_2O-*AA*-*MIBK* system at 25°C given in Eq. 17 were used in the calculations.

It should be noted that the choice of a 20-stage cell-backmixing model to represent the spray column is to a large extent arbitrary, and that a larger number of stages could have been used, possibly with an adjustment in the backmixing coefficients.

Example 1

The feed compositions and flow rates for this example were:

$x_1^F = 0.0102 \qquad y_1^F = 0.9871$

$x_2^F = 0.0348 \qquad y_2^F = 0.0$

$x_3^F = 0.9550 \qquad y_3^F = 0.0129$

$u_F = 0.0599 \qquad v_F = 0.0233$

This corresponds to a 3.48% acetic acid in water feed to the column, and to feed streams partially saturated with respect to the solvents.

Three parameters were determined by fitting the data, namely:

L_1 = overall mass transfer coefficient for the transfer of *MIBK* into the water phase, $r_1 = L_1(K_1y_1 - x_1)$
L_2 = overall mass transfer coefficient for the transfer of acetic acid from the *MIBK* phase to the water phase, $r_2 = L_2(K_2y_2 - x_2)$
L_3' = overall mass transfer coefficient for the transfer of water into the *MIBK* phase, $r_3 = L_3'(y_3 - K_3'x_3)$

As an indication of the rapidity with which the computational method converges to the solution of the steady state equations, we show below the RMS values of ϕ and Δz as a function of iteration number. The feed conditions were used as initial conditions in each stage, and the starting parameter values were $L_1 = 0.001$, $L_2 = 0.001$, and $L_3' = 0.0001$.

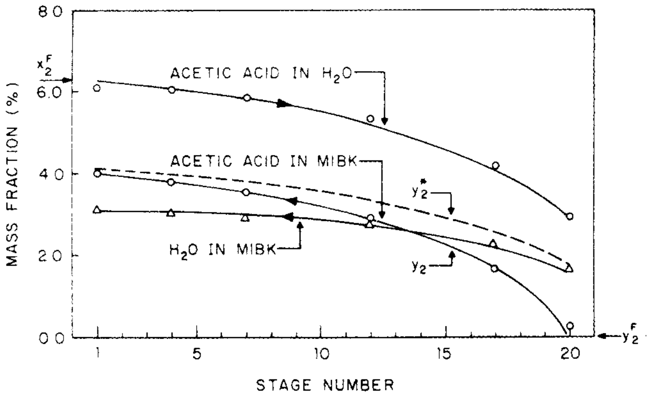

Figure 7. Least-squares mass fraction profiles and experimental values for Example 2.

Iteration	RMS(ϕ)	RMS(Δz)
1	0.154×10^{-3}	0.959×10^{-2}
2	0.339×10^{-4}	0.302×10^{-2}
3	0.572×10^{-6}	0.554×10^{-4}
4	0.124×10^{-6}	0.111×10^{-4}
5	0.909×10^{-8}	0.834×10^{-6}

The iterative parameter determination procedure converged from the parameter values given above to the final parameter values in nine iterations.

In Figure 6 are shown the experimental data and the least-squares fits to the steady state values of x_1 (*MIBK* in H_2O), x_2 (acetic acid in H_2O), y_2 (acetic acid in *MIBK*), and y_3 (H_2O in *MIBK*). The fit is reasonably good, with the standard deviation of the residuals, σ_M, equal to 0.00133. This corresponds roughly to 5% of the typical measured mass fraction value, and is consistent with the expected sampling and analysis errors. The largest residuals occur at the bottom of the column, where the dispersed phase feed enters. The existence of an entrance effect may be indicated.

The least-squares parameter values, and the corresponding standard errors, are shown below:

Parameter	Least-Squares Value	Standard Error (%)
L_1	0.01777	0.00590 (33%)
L_2	0.00702	0.00094 (13%)
L_3'	0.02211	0.01476 (67%)

As expected, L_2 is reasonably well determined. L_1 and L_3' are less well determined, reflecting the lower driving forces for mass transfer corresponding to these parameters. Considering the relatively large 95% confidence limits for L_1 and L_3', it is not possible to assert that they differ significantly from each other or from L_2. And it is not clear, in fact, that all three mass transfer coefficients should have the same value. The parameter correlation matrix, not shown, reflects the expected low correlation between the parameter estimates.

Example 2

The feed compositions and flow rates in this example were:

Continuous Phase(H_2O)	Dispersed Phase(*MIBK*)
$x_1^F = 0.9187$	$y_1^F = 0.9850$
$x_2^F = 0.0630$	$y_2^F = 0.0000$
$x_3^F = 0.0184$	$y_3^F = 0.0150$
$u_F = 0.0278$	$v_F = 0.0228$

Only two parameters, L_1 and L_2, were fitted. L_3 was assumed constant at zero. The data and the curves corresponding to the least-squares values of the parameters are shown in Figure 7. In this example, which was selected from a number of similar runs on the basis of having achieved steady operation for a relatively long time, the fit is excellent. The standard deviation of the residuals was 0.00101, roughly 2% of an average measured mass fraction. There are no unusually large residuals at the ends of the column, consistent with the absence of end effects. On the basis of this example, considered alone, the model can be considered acceptable.

The least-squares parameter values were:

Parameter	Least-Squares Value	Standard Error (%)
L_1	0.02354	0.01251(53%)
L_2	0.00911	0.00053(6%)

Again L_2, the overall mass transfer coefficient for the transfer of acetic acid from the water to the *MIBK* phase, is better determined than L_1, reflecting the larger driving force for the transfer of acetic acid. Also shown in Figure 7 is y_2^*, the mass fraction of acetic acid in the dispersed (*MIBK*) phase in equilibrium with the continuous (H_2O) phase. Note that most of the transfer takes place near the bottom of the column, while the extract and raffinate streams are close to equilibrium near the top. Thus the samples taken near the bottom of the column provide more information on L_2 than the other samples.

APPENDIX: DEFINITION OF MATRICES APPEARING IN EQ. 3

The $2(S - 1)$ individual species mass balances for the kth stage are given by Eq. 3

$$A^k w^{k-1} + (B^k + R^k)w^k + C^k w^{k+1} = a^k, \ k = 1, 2, \ldots, N \quad (3)$$

where w^k is a vector defined in Eq. 2. For the case in which two solutes transfer from a raffinate to an extract solvent, that is for $S = 4$, the matrices A^k, B^k, R^k, and C^k and the vector a^k appear as follows (for $k = 2, 3, \ldots, N - 1$):

$$A^k = \begin{bmatrix} fu_k & 0 & 0 & 0 & 0 & 0 \\ 0 & fu_k & 0 & 0 & 0 & 0 \\ 0 & 0 & fu_k & 0 & 0 & 0 \\ 0 & 0 & 0 & (1+g)v_{k-1} & 0 & 0 \\ 0 & 0 & 0 & 0 & (1+g)v_{k-1} & 0 \\ 0 & 0 & 0 & 0 & 0 & (1+g)v_{k-1} \end{bmatrix}$$

$$B^k = \begin{bmatrix} -d & 0 & 0 & 0 & 0 & 0 \\ 0 & -d & 0 & 0 & 0 & 0 \\ 0 & 0 & -d & 0 & 0 & 0 \\ 0 & 0 & 0 & -e & 0 & 0 \\ 0 & 0 & 0 & 0 & -e & 0 \\ 0 & 0 & 0 & 0 & 0 & -e \end{bmatrix}$$

$$d = (1+f)u_k + fu_{k+1}, \quad e = (1+g)v_k + gv_{k-1}$$

$$R^k = \begin{bmatrix} -L_1 & 0 & 0 & -L_1K_1 & -L_1K_1 & -L_1K_1 \\ 0 & -L_2 & 0 & L_2K_2 & 0 & 0 \\ 0 & 0 & -L_3 & 0 & L_3K_3 & 0 \\ 0 & L_2 & 0 & -L_2K_2 & 0 & 0 \\ 0 & 0 & L_3 & 0 & -L_3K_3 & 0 \\ -L_4 & -L_4 & -L_4 & 0 & 0 & -L_4K_4 \end{bmatrix}$$

$$C^k = \begin{bmatrix} (1+f)u_{k+1} & 0 & 0 & 0 & 0 & 0 \\ 0 & (1+f)u_{k+1} & 0 & 0 & 0 & 0 \\ 0 & 0 & (1+f)u_{k+1} & 0 & 0 & 0 \\ 0 & 0 & 0 & gv_k & 0 & 0 \\ 0 & 0 & 0 & 0 & gv_k & 0 \\ 0 & 0 & 0 & 0 & 0 & gv_k \end{bmatrix}$$

$$a^k = \begin{bmatrix} -L_1K_1 \\ 0 \\ 0 \\ 0 \\ 0 \\ -L_4 \end{bmatrix}$$

For the Sth species, the continuous phase solvent, it is often convenient to replace the rate expression

$$r_S = L_S(K_S y_S - x_S)$$

by

$$r_S = L_S'(y_S - y_S^*) = L_S'(y_S - K_S' x_S)$$

Here L_S' is the overall mass transfer coefficient for the dispersed phase, and K_S' is the equilibrium constant that relates y_S^* at the interface ($y_S^* = K_S' x_S$) to the continuous phase mass fraction x_S. In this case the last row of the matrix R becomes, for $S = 4$,

$$\begin{bmatrix} -L_4'K_4' & -K_4'K_4' & L_4'K_4' & 0 & 0 & -L_4' \end{bmatrix}$$

In addition, the last element of a^k is replaced by $-L_4'K_4'$.

For the end stages, $k = 1$ and $k = N$, the above equations also are valid, except that

$$B^1 = \begin{bmatrix} -(fu_2 + u_1) & 0 & 0 & 0 & 0 & 0 \\ 0 & -(fu_2 + u_1) & 0 & 0 & 0 & 0 \\ 0 & 0 & -(fu_2 + u_1) & 0 & 0 & 0 \\ 0 & 0 & 0 & -(1 + g)v_1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -(1 + g)v_1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -(1 + g)v_1 \end{bmatrix}$$

$$B^N = \begin{bmatrix} -(1 + f)u_N & 0 & 0 & 0 & 0 & 0 \\ 0 & -(1 + f)u_N & 0 & 0 & 0 & 0 \\ 0 & 0 & -(1 + f)u_N & 0 & 0 & 0 \\ 0 & 0 & 0 & -h & 0 & 0 \\ 0 & 0 & 0 & 0 & -h & 0 \\ 0 & 0 & 0 & 0 & 0 & -h \end{bmatrix}$$

$$h = (gv_{N-1} + v_N)$$

Note that in all the equations above, the backmixing coefficients f_k and g_k have been assumed not to vary with stage number, i.e., $f_k = f$, $g_k = g$.

The vectors a^* and b^* which appear in Eq. 7 are given by

$$a^* = \begin{bmatrix} 0 \\ 0 \\ 0 \\ -v_F y_1^F \\ -v_F y_2{}^F \\ -v_F y_3^F \end{bmatrix}, \quad b^* = \begin{bmatrix} -u_F x_1^F \\ -u_F x_2^F \\ -u_F x_3^F \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

NOTATION

a^k = vector, Eq. 3 and Appendix
a^* = vector, Eq. 7 and Appendix
A^k = matrix, Eq. 3 and Appendix
b^* = vector, Eq. 7 and Appendix
B^k = matrix, Eq. 3 and Appendix
C^k = matrix, Eq. 3 and Appendix
d = standard deviation of data
D = matrix, Eq. 7
E = matrix, Eq. 7
f = continuous phase backmixing coefficient
f_k = continuous phase backmixing coefficient
g = dispersed phase backmixing coefficient
g_k = dispersed phase backmixing coefficient
K_j = equilibrium constant for the jth species, Eq. 1
L_j = overall mass transfer coefficient for the jth species, mass time^{-1}, Eq. 1
M = number of data points
N = number of stages
p_m = mth undetermined parameter
P = number of undetermined parameters
Pe = Peclet number
Q = matrix = $\partial\bar{z}/\partial p$
r_j^k = interphase transfer rate for the jth species, mass time^{-1}
R^k = matrix, Eq. 3
S = number of species including solvents and solutes
u_k = flow rate of continuous phase leaving the kth stage, mass time^{-1}, Eq. 4
v_k = flow rate of dispersed phase leaving the kth stage, mass time^{-1}, Eq. 4
w^k = vector, Eq. 2
x_j^k = mass fraction of the jth species in the continuous phase
y_j^k = mass fraction of the jth species in the dispersed phase
z = vector of mass fractions, Eq. 6
$\bar{z}$ = vector of calculated mass fractions at sample points
$\bar{z}^*$ = vector of measured mass fractions at sample points

Superscripts

F = feed stream property

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i = stage index
k = stage index
n = iteration index

Subscripts

F = feed stream property
j = species index
k = stage index
m = undetermined parameter index

Greek Symbols

α = vector, Eq. 7
β = convergence parameter, Eq. 9
ϵ = convergence parameter
σ_m = standard deviation of mth parameter, Eq. 10
σ_M = standard deviation of the measurements
$\Delta\sigma_m^i$ = increment to σ_m at the ith stage
ϕ = vector, Eq. 8

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