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Two-Dimensional Development in Staged Systems

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Abstract

A new technique for two-dimensional development in staged systems utilizing the two-dimensional cross-flow cascade is presented. Ideal theories for two sequential and one simultaneous development technique are presented and the results are compared. All three development techniques will separate mixtures which cannot be separated by one-dimensional development. The simultaneous development technique appears to be preferable because it is less time consuming and requires fewer stages. It is also shown that a three-dimensional cross-flow system will give the same distributions as simultaneous development in two-dimensional cross-flow except the system can have a continual feed instead of a batch feed.

INTRODUCTION

There are several classical techniques to increase the separation achieved for multicomponent mixtures. Increasing the size of the system by adding more stages or increasing the length of travel of the components is often an effective means that can be used with most separation methods. However, there is a practical limit to size increases, and for components with equal distribution coefficients no increase in size will facilitate the separation. Because of this problem, many other ingenious techniques for increasing the separation of difficult components have been developed for specific separation methods. Examples of such techniques are temperature and flow programming in gas chroma-

tography (*1*), vapor programming in thin-layer chromatography (*2*), and various two-dimensional development techniques (*3*, *4*). The various programming techniques have been applied to discontinuous separation techniques such as countercurrent distribution (CCD), but two-dimensional development techniques for discontinuous systems have apparently not been tried.

The two-dimensional cross-flow (2DCF) system was shown to give essentially the same separation as CCD but in continual operation (*5*). In this case there is essentially one-dimensional development since each component is distributed between two phases and has only one distribution coefficient. This is analogous to continuous paper electrophoresis (*6*) where there is a distribution between migration due to the electric field and flow of the solvent. In continuous operation the paper acts only as a channel for the solvent. In discontinuous operation paper electrophoresis followed by paper chromatography is a well-known two-dimensional development technique (*4*, *6*). By analogy we might expect that a two-dimensional development technique could be developed for 2DCF.

In this paper a two-dimensional development technique for staged systems requiring three phases is presented. In this technique the two dimensions of the 2DCF apparatus can be developed simultaneously or sequentially. Several ideal theories show that the resulting distributions are similiar to the binomial distribution obtained for CCD (*7*) except that they are expanded in two spatial directions plus time. It is then shown that time can be replaced by a third spatial direction. This three-dimensional cross-flow (3DCF) system can theoretically give simultaneous two-dimensional development in either continuous or continual operation.

TWO-DIMENSIONAL CROSS-FLOW

Apparatus and Operation

The basic 2DCF configuration is shown in Fig. 1. 2DCF is a two-dimensional array of stages where each row and each column acts as a cross-flow cascade. The stages do not have to be arranged in a rectangular or square array. In discontinuous operation with continual feed 2DCF will give the same separation as CCD (*5*). In this paper the possible applications of 2DCF to two-dimensional development will be considered. In order to have two-dimensional development it is necessary to

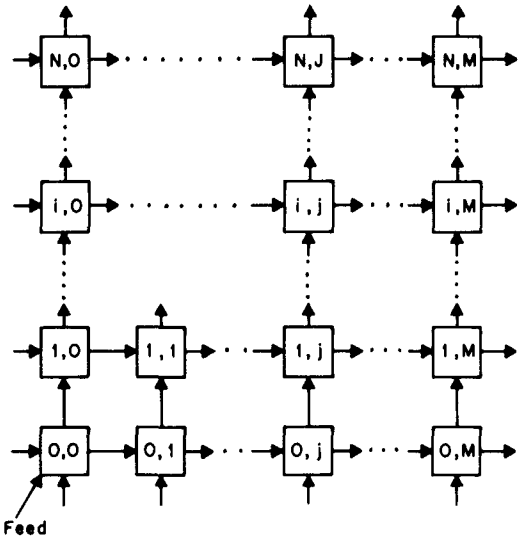

FIG. 1. Two-dimensional cross-flow cascade.

have three phases. These three phases can be present either simultaneously or sequentially, and could be any three phases which can be used in a staged apparatus. To be definite, this paper will be restricted to two liquid phases and a solid phase, but the results obtained are general and are applicable to other combinations of phases.

Two-dimensional development for thin-layer and paper chromatography is run sequentially with the first solvent being removed before the second solvent is run. This mode of operation can be utilized for the 2DCF apparatus shown in Fig. 1. In this case, Phase 1, the first solvent, would run up the columns and the second solvent, Phase 2, would run across the rows after the first solvent was removed. The solid material, Phase 3, would remain in each stage. The development would be started with a single pulse of feed in stage (0,0). Although it would work, this mode of operation would be awkward and time consuming because of the large volumes of solvent to be removed. An alternate sequential technique which would not require removal of the first solvent could also be used if the two solvents were immiscible. The first solvent would be run up the first column as in CCD. Next the second solvent would be run across the rows without removing the first solvent. In this case the first stage in each row would have solute distributed between three

phases while all other stages would have two phases. Phases 1 and 3 would be stationary during the second development. Both sequential operations have the disadvantage of being time consuming even if a mechanical robot is used to do the individual transfers.

A simultaneous two-dimensional development would require less time then the fastest sequential technique. Phase 1 would be transferred up the columns while Phase 2 was transferred across the rows. The solid, Phase 3, would not move. The discontinuous 2DCF apparatus has the advantage that it can easily be operated with simultaneous development while the chromatographic techniques would be very difficult to operate this way. To visualize the expected separation, consider a multicomponent mixture fed into stage (0,0) at time zero. A component which greatly prefers Phase 1 will follow that phase up the first column and will be distributed at the top of that column. A component greatly preferring Phase 2 will follow that phase across the first row and will be distributed at the right of that row. A component greatly preferring Phase 3 will move very little and will be distributed near stage (0,0). A component with equal preference for Phases 1 and 2 and a dislike for Phase 3 will follow both Phases 1 and 2 and will move towards stage (N,M) in Fig. 1. After s transfers, this component would distribute in an oval-shaped pattern with the long axis of the oval parallel to a line from stage $(0,s)$ to stage $(s,0)$. The exact pattern that can be expected is shown later.

Theory

The theoretical calculations needed for two-dimensional sequential development are simple variations of the binomial results obtained for CCD. In both sequential development schemes the first development is essentially a CCD along the first column (column zero) of Fig. 1. The resulting distribution can be calculated by the usual equations used for CCD (*7*). If the first solvent is removed before the second development, then each row is essentially a CCD. The resulting distributions can be calculated from the CCD distribution using the distribution obtained from the first development as the initial conditions. This scheme is very flexible since the number of transfers and number of stages do not have to be the same in the two directions. For this case Phases 1 and 2 could be miscible, and Phase 3 could be a liquid immiscible with Phases 1 and 2. Since the resulting distributions are easily obtained by multiplying two CCD distributions, the equations will not be presented here.

If the first solvent remains in the first column during the second development, the resulting equations become somewhat more complicated. Assume that the system is ideal so that the distribution coefficients are constant and are not affected by the presence of the third phase. Let V_1, V_2, and V_3 be the volumes of Phases 1, 2, and 3, respectively. For the second development assume that V_2 and V_3 are constant for all the stages, and that V_1 is constant for all the stages in column zero, but zero in all other stages. We also assume that the phase separation is complete for each transfer step. If we let q_A = fraction of Component A in Phase 2 in stages of the first column, f_A = fraction of Component A in Phase 2 for all other columns, $K_{A_1} = C_{A_1}/C_{A_3}$, and $K_{A_2} = C_{A_2}/C_{A_3}$ it can be shown that

$$f_A = \frac{K_{A_2}V_2/V_3}{K_{A_2}V_2/V_3 + 1} \tag{1}$$

$$q_A = \frac{K_{A_2}V_2/V_3}{K_{A_1}V_1/V_3 + K_{A_2}V_2/V_3 + 1} \tag{2}$$

If $M_{A_{i,j,s_2}}$ is the mass of Component A in stage (i,j) after transfer step s_2 of the second development, there are three recursion relations which define the system.

For $j = 0$,

$$M_{A_{i,0,s_2}} = (1 - q_A)M_{A_{i,0,s_2-1}} \tag{3}$$

For $j = 1$,

$$M_{A_{i,1,s_2}} = (1 - f_A)M_{A_{i,1,s_2-1}} + q_A M_{A_{i,0,s_2-1}} \tag{4}$$

For $j \geq 2$,

$$M_{A_{i,j,s_2}} = (1 - f_A)M_{A_{i,j,s_2-1}} + f_A M_{A_{i,j-1,s_2-1}} \tag{5}$$

These three equations are subject to the initial conditions

$$M_{A_{i,0,0}} = M_{A_{iF}} \tag{6}$$

$$M_{A_{i,j,0}} = 0, \qquad j > 0 \tag{7}$$

where $M_{A_{iF}}$ is the mass of Component A in stage $(i,0)$ after the first development. This quantity can be found from the usual CCD equations.

Equation (3) is easily solved to give

$$M_{A_{i,0,s_2}} = (1 - q_A)^{s_2}M_{A_{iF}} \tag{8}$$

Substitution of Eq. (8) into Eq. (4) gives

$$M_{A_{i,1,s_2}} = (1 - f_A)M_{A_{i,1,s_2-1}} + q_A(1 - q_A)^{s_2-1}M_{A_{iF}} \tag{9}$$

Equations (7) and (9) can now be used as the initial conditions for Eq. (5). Since K values are constant, this set of equations can be solved by considering a linear superposition of binomial distributions. The material transferred to stage $(i,1)$ in the first transfer step will form a binomial distribution in stages $(i,1)$ to (i,s_2) in the remaining $s_2 - 1$ transfer steps. Material transferred to stage $(i,1)$ in the second transfer step will form a binomial distribution in stages $(i,1)$ to $(i,s_2 - 1)$ in the remaining $s_2 - 2$ transfer steps. The same thing will happen to all additional material transferred to stage $(i,1)$. Adding up all the binomial distributions and being careful to keep the correct subscripts, we obtain the following distribution:

$$\frac{M_{A_{i,j,s2}}}{M_{A_{iF}}} = \frac{(s_2 - 1)!}{(j-1)!(s_2 - j)!} f_A^{j-1}(1 - f_A)^{s_2-j} q_A(1 - q_A)^0$$

$$+ \frac{(s_2 - 2)!}{(j-1)!(s_2 - j - 1)!} f_A^{j-1}(1 - f_A)^{s_2-j-1} q_A(1 - q_A)^1 + \cdots$$

$$+ \frac{(s_2 - 1 - (s_2 - j))!}{(j-1)!0!} f_A^{j-1}(1 - f_A)^0 q_A(1 - q_A)^{s_2-j} \tag{10}$$

where $j \geq 1$, $s_2 \geq 1$ and $j \leq s_2$. Since Eq. (10) will be fairly complicated to use, it may be simpler to solve recurrsion relations (3), (4), and (5) directly.

In simultaneous two-dimensional development, Phases 1 and 2 are transferred at the same time. The solutes are then distributed between all three phases in each stage. Again we will develop equations for the ideal case of constant K and V. If we let p_A = fraction of Component A in Phase 1 and q_A = fraction of Component A in Phase 2, then q_A is given by Eq. (2) and

$$p_A = \frac{K_{A_1}V_1/V_3}{K_{A_1}V_1/V_3 + K_{A_2}V_2/V_3 + 1} \tag{11}$$

A mass balance around stage (i,j) after transfer step s can be written as

$$M_{A_{i,j,s}} = p_A M_{A_{i-1,j,s-1}} + q_A M_{A_{i,j-1,s-1}} + (1 - p_A - q_A)M_{A_{i,j,s-1}} \tag{12}$$

This recurrsion relation is subject to the following initial conditions:

$$M_{A_{-1,j,s}} = M_{A_{i,-1,s}} = 0 \tag{13}$$

$$M_{A_{0,0,0}} = M_{A_F} \tag{14}$$

$$M_{A_{i,j,0}} = 0 \quad \text{for} \quad i > 0 \quad \text{or} \quad j > 0 \tag{15}$$

Equation (12) is similiar to the recurrsion equations obtained for 2DCF (*5*) and for CCD (*7*) except that there are additional terms due to the additional phase. By patterning a solution after the solutions obtained for 2DCF and CCD, the following expression for $M_{A_{i,j,s}}$ satisfying Eqs. (12) to (15) is quickly found:

$$\frac{M_{A_{i,j,s}}}{M_{A_F}} = \frac{s!}{i!j!(s-i-j)!} p_A{}^i q_A{}^j (1 - p_A - q_A)^{s-i-j} \tag{16}$$

where $s \geq 0, i \geq 0, j \geq 0$, and $i + j \leq s$.

Before proceeding to the results, we will show how simultaneous two-dimensional development can be obtained with continual injection of feed at each transfer step.

THREE-DIMENSIONAL CROSS-FLOW

It was shown previously (*5*) that the discontinyous one-dimensional CCD could be reproduced in a continual fashion by replacing the time coordinate with a second spatial direction and moving both phases. The result was 2DCF. It appears to be reasonable that a continual two-dimensional development could be obtained by replacing the time coordinate in 2DCF and by moving all three phases. The result will be called three-dimensional cross-flow (3DCF).

A schematic diagram of 3DCF is shown in Fig. 2. In 3DCF Phase 1 moves up each column, Phase 2 moves to the right across each row, and Phase 3 moves back into the paper. In discontinuous operation all three phases are transferred at the same time and material can be fed into stage (0,0,0) at each transfer step. Making the same assumptions and using the same nomenclature as before, we can write the following balance for Component A:

$$M_{A_{i,j,k,s}} = p_A M_{A_{i-1,j,k,s-1}} + q_A M_{A_{i,j-1,k,s-1}} + (1 - p_A - q_A) M_{A_{i,j,k-1,s-1}} \tag{17}$$

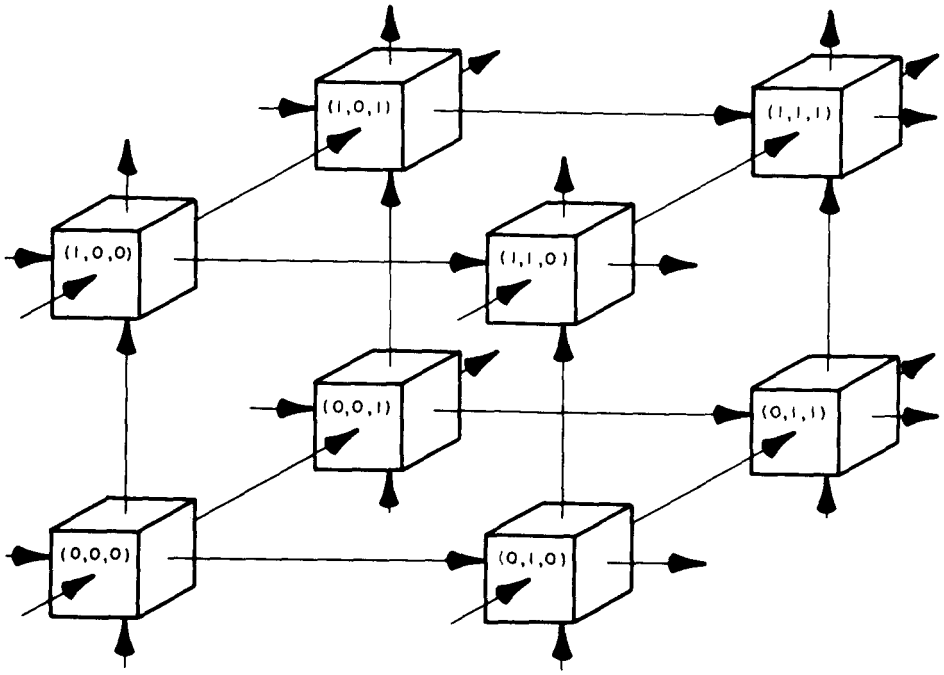

FIG. 2. Three-dimensional cross-flow cascade.

If the material to be separated is fed into stage (0,0,0) only at time zero, solute will appear only in stages where $s = i + j + k$. This is a plane of stages connecting the three stages $(s,0,0)$, $(0,s,0)$, and $(0,0,s)$. If material is fed into stage (0,0,0) at each transfer step, s can take on any value. However, material fed at different times never mixes, so that s now represents the time since a particular pulse was injected. When $s > \max(i + j + k)$ a steady state will have been reached, and the s can be dropped. For continual feed the boundary conditions are

$$M_{A_{0,0,0}} = M_{AF} \tag{18}$$

$$M_{A_{-1,j,k}} = M_{A_{i,-1,k}} = M_{A_{i,j,-1}} = 0 \tag{19}$$

where M_{AF} is now the mass of Component A fed at each transfer step. Equations (17) to (19) can be solved by the same method used pre-

viously for 2DCF. The solution is

$$\frac{M_{A_{i,j,k}}}{M_{A_F}} = \frac{(i+j+k)!}{i!j!k!} p_A{}^i q_A{}^j (1 - p_A - q_A)^k \tag{20}$$

If we let $s = i + j + k$ we note that Eqs. (16) and (20) are the same. Thus Eq. (20) predicts that 3DCF will give the same simultaneous two-dimensional development as 2DCF, but the operation will be continual.

The 3DCF apparatus could also be operated in a continuous instead of a discontinuous fashion. Let V, L, and S be the flow rates of Phases 1, 2 and 3, respectively. Define $\bar{p}_A$ = fraction of Component A transferred in Phase 1 compared to total A transferred, $\bar{q}_A$ = fraction of Component A transferred in Phase 2 compared to total A transferred, and $Q_{A_{i,j,k}}$ = total Solute A transferred from stage (i, j, k) per unit time. If we assume that V, L, S, and the K values are all constant, it can be shown that

$$\bar{p}_A = \frac{K_{A_1} V/S}{K_{A_1} V/S + K_{A_2} L/S + 1} \tag{21}$$

$$\bar{q}_A = \frac{K_{A_2} L/S}{K_{A_1} V/S + K_{A_2} L/S + 1} \tag{22}$$

At steady state a mass balance around stage (i, j, k) can be written as

$$Q_{A_{i,j,k}} = \bar{p}_A Q_{A_{i-1,j,k}} + \bar{q}_A Q_{A_{i,j-1,k}} + (1 - \bar{p}_A - \bar{q}_A) Q_{A_{i,j,k-1}} \tag{23}$$

with the boundary conditions

$$Q_{A_{0,0,0}} = Q_{A_F} \tag{24}$$

$$Q_{A_{-1,j,k}} = Q_{A_{i,-1,k}} = Q_{A_{i,j,-1}} = 0 \tag{25}$$

Since Eqs. (23) to (25) are of the same form as Eqs. (17) to (19), the same form of solution can be used. Thus

$$\frac{Q_{A_{i,j,k}}}{Q_{A_F}} = \frac{(i+j+k)!}{i!j!k!} \bar{p}_A{}^i \bar{q}_A{}^j (1 - \bar{p}_A - \bar{q}_A)^k \tag{26}$$

The amount of A in any one phase leaving stage (i, j, k) can be obtained by multiplying $Q_{A_{i,j,k}}$ by $\bar{p}_A$, $\bar{q}_A$ or $(1 - \bar{p}_A - \bar{q}_A)$ for Phases 1, 2, or 3, respectively.

The analogy developed here can be extended further if desired. Thus with four phases we can conceive of a 3DCF apparatus with three-dimensional development. In this case one phase would be stationary, the other three phases would be transferred, and the operation would be

discontinuous. The solution for the resulting distribution with simultaneous development is a straightforward extension of the results presented for 2DCF and will not be given here. The analogy can be carried to even higher dimensional systems if we concern ourselves with the mathematics only and disregard physical reality.

RESULTS

The distributions resulting from two-dimensional development will be illustrated for 2DCF. The distribution for 3DCF with continual feed will not be shown, but it can be obtained from the simultaneous 2DCF results by replacing s with $i + j + k$.

A direct comparison between the distributions obtained for sequential

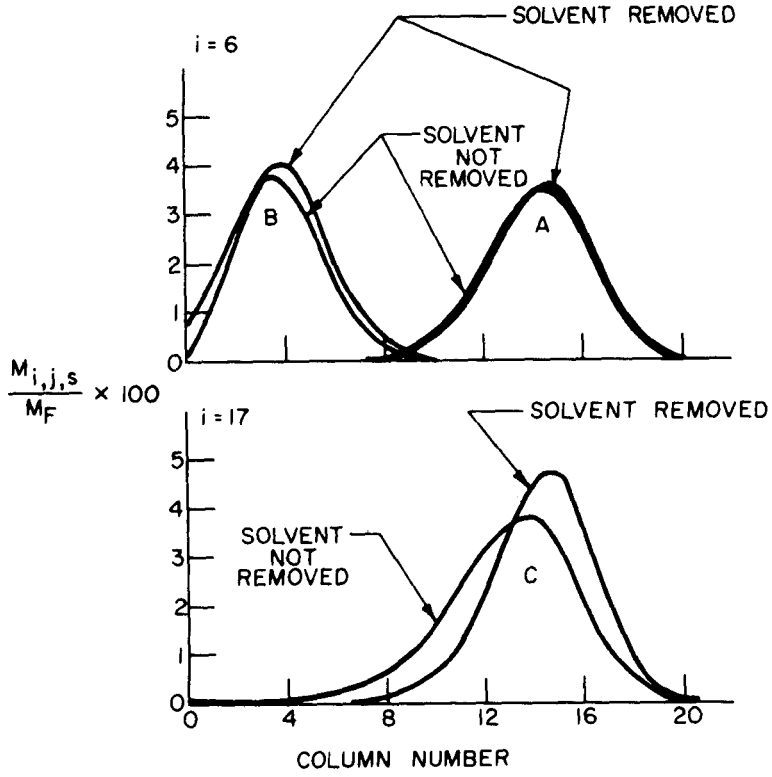

FIG. 3. Sequential development. Distribution along rows.

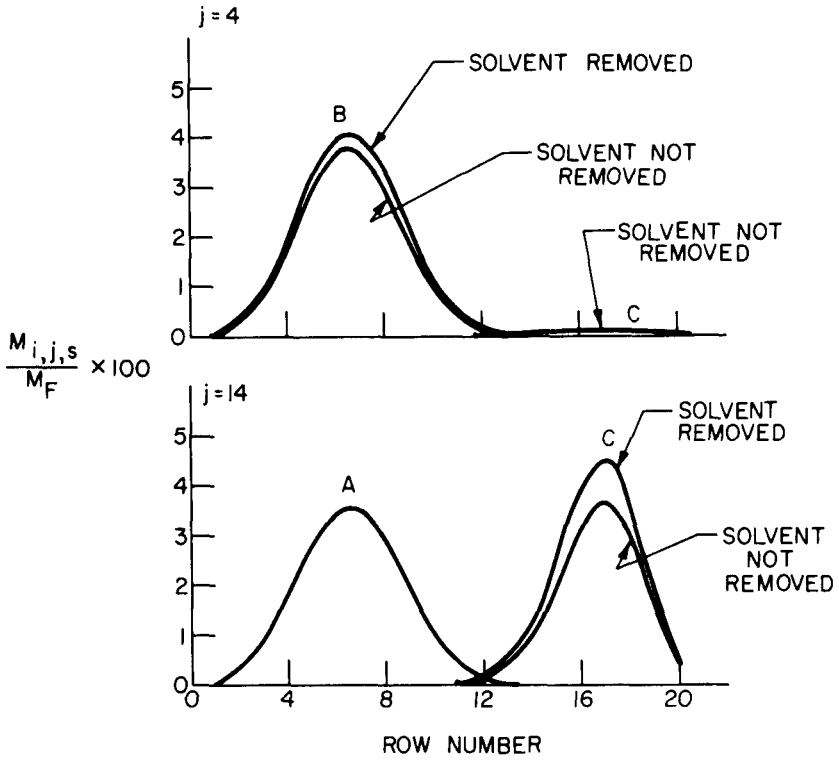

FIG. 4. Sequential development. Distribution along columns.

and simultaneous development cannot be made since it is impossible to have identical conditions for the two types of development. If $s_1 = s_2 = s$, the number of transfer steps for each phase will be the same, but the total number of transfers and therefore the number of stages containing material will be greater in sequential development.

A direct comparison between the two types of sequential development can be made for a specific system. Consider a hypothetical three component system where $K_{A_1} = 0.5$, $K_{A_2} = 2.5$, $K_{B_1} = 0.5$, $K_{B_2} = 0.25$, $K_{C_1} = 5.0$, and $K_{C_2} = 2.5$. This system was chosen so that Components A and B would not separate if only Phases 1 and 3 were present, Components A and C would not separate if only Phases 2 and 3 were present, and Components B and C would not separate if only Phases 1 and 2 were present. Thus all three phases are essential for a complete separa-

tion. The theoretical results are shown in Figs. 3 and 4 for a 21 × 21 element system ($N = 20$) with 20 transfer steps for both the first and the second solvents ($s_1 = s_2 = 20$).

In Fig. 3 the results are illustrated for Rows 6 and 17 of the 2DCF cascade shown in Fig. 1. These rows were chosen for illustration since the maximum value of material for Components A and B occurs in Row 6 and the maximum value for Component C occurs in Row 17. The concentrations of Component C in Row 6 and of Components A and B in Row 17 are negligible. For sequential development with removal of the first solvent the resulting curves have the expected Gaussian shape. When the first solvent is not removed the distributions are skewed since the cells in column zero act as a reservoir. The distributions become more skewed as the ratio q_A/f_A decreases. For $q_A/f_A = 1$ a Gaussian distribution would result, and for $q_A/f_A = 0$ all of the Component A would remain in column zero. From Eqs. (1) and (2) we see that increasing K_1V_1/V_3 will decrease q_A/f_A and thus cause the distribution to be skewed. Although it can not be seen in Fig. 3, the distribution for Component C is actually bimodal for sequential development without removal of the first solvent. There is more material in Column 0 than in Column 1.

In Fig. 4 the results are shown for Columns 4 and 14. These columns were chosen to give the maximum concentrations for the three components. In this figure both types of sequential development give Gaussian curves. These distributions reflect the Gaussian distribution obtained for the first development which is the same for both types of sequential development. For Component A the results for both types of development were essentially identical. For Component C the skewed distribution shown in Fig. 3 causes the occurrence of Component C in Column 4 when the first solvent is not removed.

To illustrate the distribution curves resulting from simultaneous development, the same three components were studied for the case $s = 20$. For this system there are 20 total transfers, 20 transfers for Solvent 1 and 20 transfers for Solvent 2. For simultaneous development only those stages with $i + j \leq s$ have material in them. Thus 231 stages will contain material. The results for simultaneous development are given in Fig. 5 for Rows 2, 5, and 12, and in Fig. 6 for Columns 3, 6, and 13. The rows and columns were chosen to show the maximum values of concentration for the three components. The resulting distributions are Gaussian.

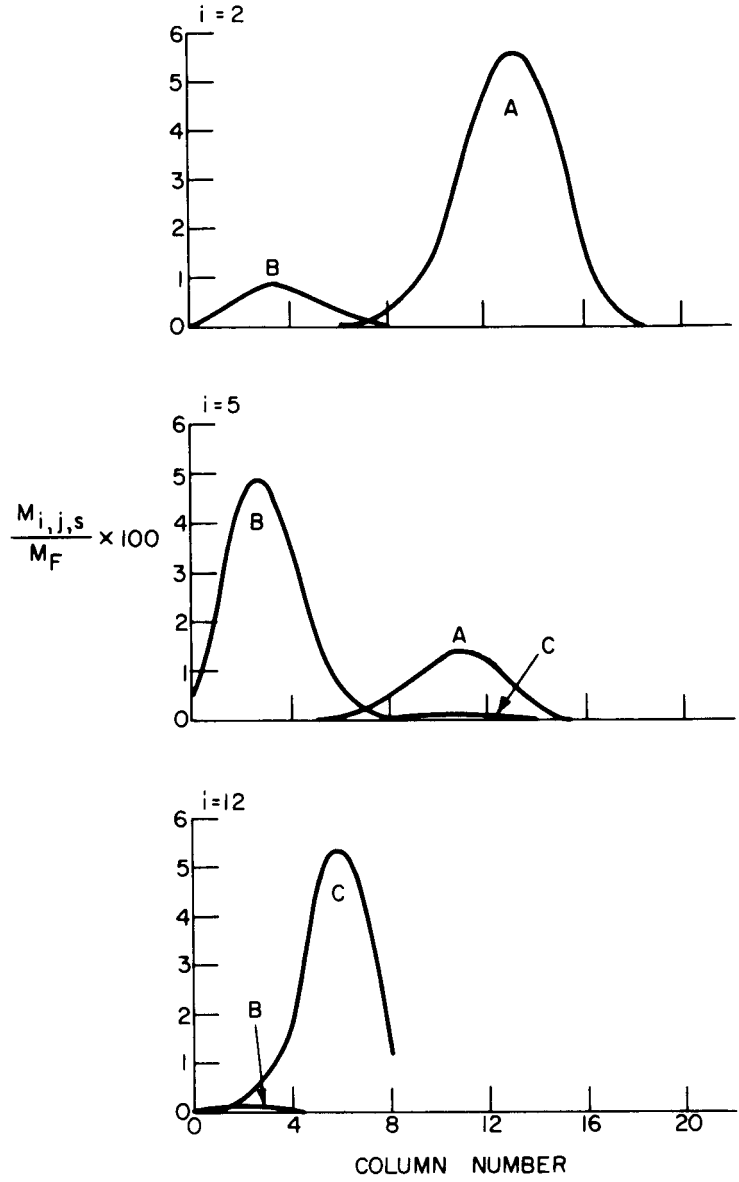

FIG. 5. Simultaneous development. Distribution along rows.

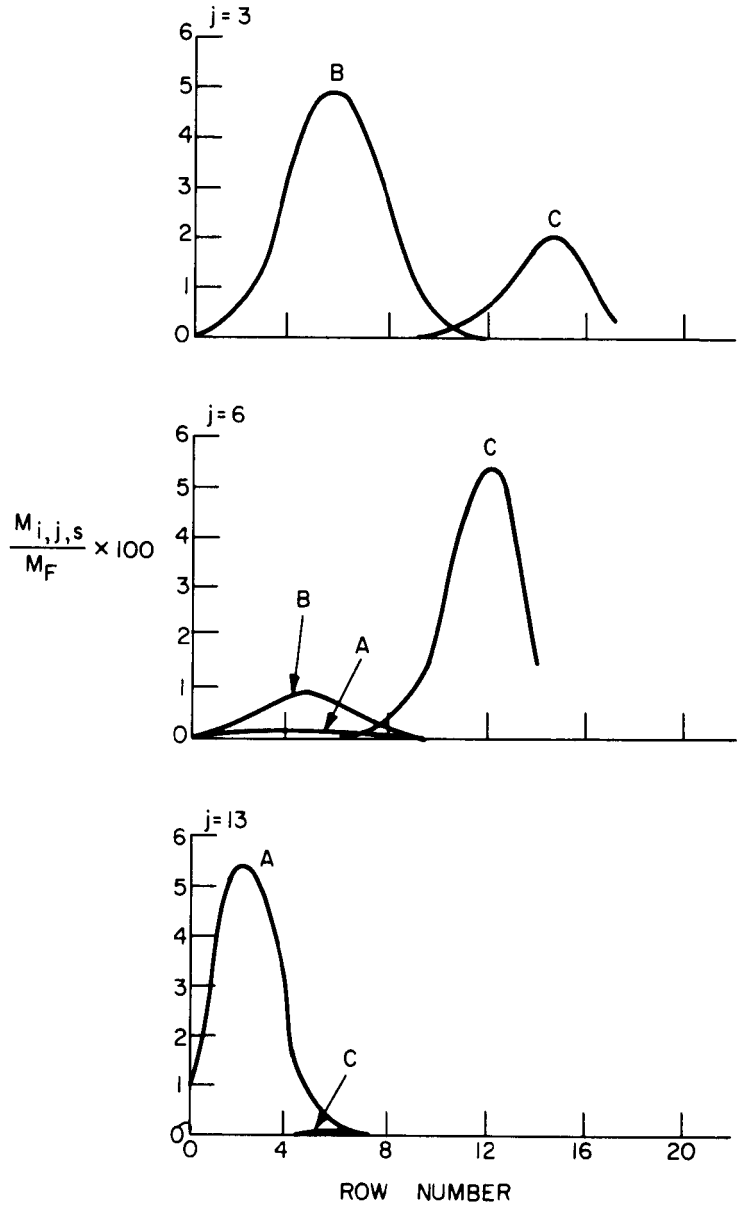

FIG. 6. Simultaneous development. Distribution along columns.

DISCUSSION

Of the three two-dimensional development methods for staged systems the most versatile method is sequential development with removal of the first solvent. This method allows use of miscible solvents, but would be very time consuming since the first solvent must be removed. The distribution curves resulting from this technique are Gaussian, which is convenient for analysis. The second sequential development technique appears to be less desirable even though it is less time consuming since it produces skewed and occasionally bimodal distributions. The separation achieved could be much worse than that found with the first technique due to the skewed distributions. Since the simultaneous development technique requires fewer transfers than the sequential techniques, it will save considerable time. Also, fewer stages are required, the curves are Gaussian with higher peaks, but the separation achieved is slightly less than that obtained with sequential development. Due to these advantages simultaneous development would be preferable when it can be used. The separation could be increased by increasing the number of stages and transfers.

Two-dimensional development in a 2DCF apparatus could be carried out with a separate transfer step for each stage. To avoid this time-consuming technique it would be desirable to construct a mechanical robot. As discussed by Wankat (*5*), a counter-double-current distribution apparatus could probably be converted to 2DCF. The solid phase could be held in a cage which allowed the two liquid phases to pass through for ease of equilibration and phase separation. The 3DCF system is probably feasible only in special cases which would require a special design. Both 2DCF and 3DCF require a large number of stages. This would place a practical limitation on the value of N.

Note Added in Proof: The simultaneous two-dimensional development technique was studied experimentally and theoretically by Meltzer and his co-workers [H. L. Meltzer, J. Buchler, and Z. Frank, *Anal. Chem.*, *37*, 721 (1965); H. L. Meltzer, *J. Biol. Chem.*, *233*, 1327 (1958)].

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