Uses of Digital Computers in Theoretical Analytical Chemistry: III. Some Computational Experiments on Irregularities in Countercurrent Distribution[1]

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Abstract

These computations were formulated to answer some questions concerning variations in construction and operation of countercurrent distribution apparatus. An optimum, ideal separation was simulated for passage of two compounds through a countercurrent distribution, followed by simulation of several departures from the optimum. A significant decrease in separating efficiency was found to be produced by deviation of upper-lower volume ratio from the optimum value, retainment of a portion of the upper (traveling) phase after transfer, and originally introducing solute into more than one tube before beginning the transfers. Little effect on separating efficiency was produced by randomness in tube volumes or randomness in upper (traveling) phase volumes due to time variation of solvent input. Variations in the distribution ratios can also cause significant enhancement or deterioration in separating efficiency.

Introduction

A previous publication (2) outlined a computer program for simulating the passage of a compound through a countercurrent distribution apparatus. In this paper, we present some uses of this program in investigating the effect of variations in apparatus and running conditions.

Standard Separation

A standard separation was chosen for this set of calculations, with the following characteristics: 200 transfers in an apparatus consisting of 200 tubes, each tube having a volume of 40 ml below the cutoff level; no retained solution, i.e., the interface between the two solutions assumed to be at the same level as the cutoff level of the apparatus; two compounds having distribution ratios of 1.5 and 1.0. The computer program performs a complete calculation on each solute and compares the two results. Variations from this standard were then computed and compared with the standard. A continuous feed method was also simulated to study the effects of a concentration-dependent distribution ratio. This method leads to high solute concentrations in the tubes and increases the deviation from theoretical predictions based on constant distribution ratios.

Criterion of Separating Efficiency

As a measure of separating efficiency for comparison among different procedures, the criterion illustrated in Figure 1 was chosen. The tubes are separated into two groups at the point where the two curves cross. The contents of all tubes to the right of the crossing point are collected together and recovered as one fraction. The contents of all tubes to the left are collected as the second fraction. The grey area under the lower curve at the right represents the amount of impurity in the first fraction. The grey area at the left represents impurity in the second fraction. The sum of the two grey areas represents the total impurity and is chosen as the measure of separating efficiency. The less this grey area is, the better the separation. Any other choice of dividing point between the two fractions would favor one fraction to the detriment of the other and would lead to a higher total impurity.

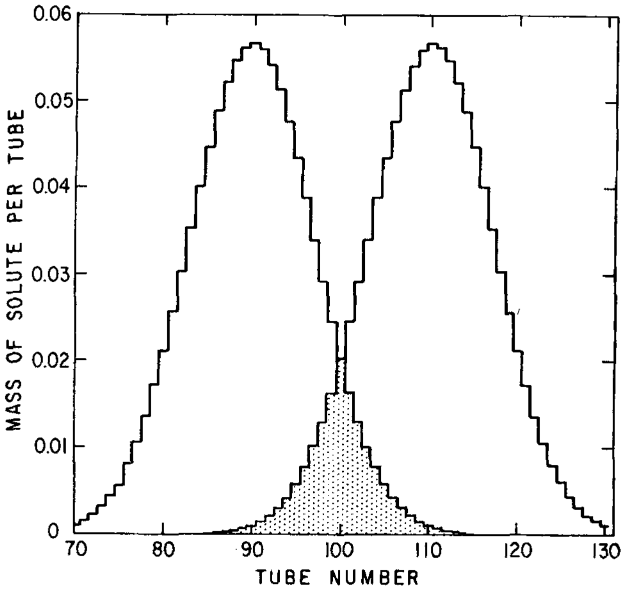

FIG. 1. Standard separation, after 200 transfers. Mass of solute in each tube, expressed as fraction of the initial mass loaded into the first tube. Left-hand curve is for solute having distribution ratio 1.0; right-hand curve is for distribution ratio 1.5.

Experimental Computations

Effect of Choice of Upper Phase Volume

The volume of the upper (traveling) phase in each tube is determined by the volume of pure upper solvent that is fed into the input end of the apparatus. Several values of this input volume were tried by computation, giving the following values of total impurity (the first figure of each pair is input volume; the second figure is total impurity): 15.00, 0.1836; 26.00, 0.1543; 27.66, 0.1532; 32.66, 0.1526; 37.66, 0.1533; 40.00, 0.1544; 48.99, 0.1607; 55.11, 0.1655. When the lower phase volume is 40 ml, a minimum in total impurity occurs for an input volume (upper phase volume) of 32.66 ml for these two solutes. The curves shown in Figure 1 are for this optimum input volume. This is a broad minimum,

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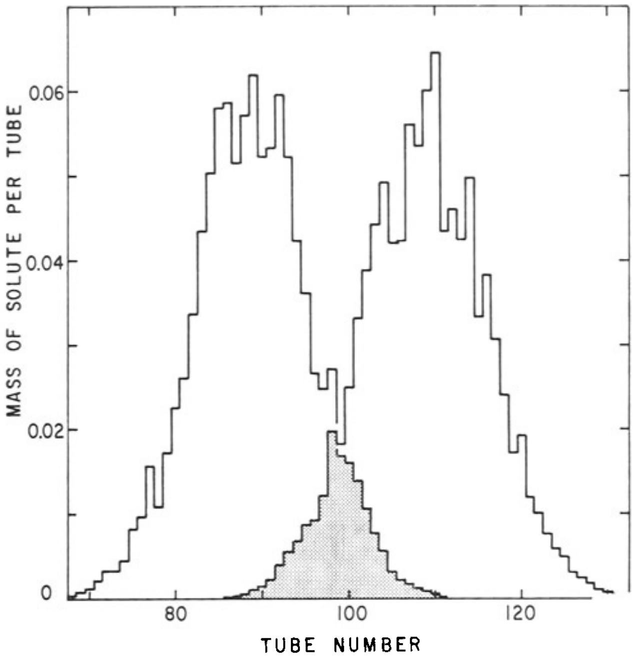

FIG. 2. Effect of randomness in volume of lower phase, after 200 transfers. Mass of solute in each tube, expressed as fraction of the initial mass loaded into the first tube.

with only minor loss of separating efficiency for input volumes between 26 and 40 ml for these two compounds. A substantial displacement from the optimum, however, leads to significantly poorer separation. This is in agreement with the finding of Bush and Densen (1) that greatest fractional separation is obtained when the volume ratio equals the reciprocal of the geometric mean of the two distribution ratios, for the ideal situation which they examined.

Effect of Tubes Having Unequal Cutoff Volumes

The tubes in our apparatus are actually not all of the same length, presumably because of glassblowing difficulties. Their cutoff volumes have a mean of 39.51 ml with a standard deviation of 0.55 ml. Use of the actual measured volumes in the computation, in place of the fixed 40 ml value, gave a total impurity of 0.1523 when using 32.66 ml as the upper (traveling phase) volume. In this computation, it was assumed that the volume of lower phase in each tube was equal to the cutoff volume of each tube, so that no upper phase was retained. For comparison, a set of normally distributed random numbers was generated by the computer, having mean 40 ml and standard deviation 0.5 ml. This produced 0.1524 total impurity. The small apparent superiority of the random volumes over the optimum fixed volumes (0.1524 vs. 0.1526) is due to the symmetry of the optimum results. In the latter, each value of total impurity appears twice, on two successive transfers, whereas the values show a steady progression when volumes are random. Thus, at 200 transfers the random is superior; at 199 transfers the random is inferior. The difference between random and optimum is too small to be significant.

Since computer simulation permits the exaggeration of a physical situation and since randomizing the cutoff volumes had so little effect, we generated random numbers with mean 40 ml and standard deviation 10 ml. To take care of the possibility that optimum upper phase volume may not be the same as that found when volumes are equal, we performed the computation for several upper volumes. Total impurity varied with upper volume in the following manner (the first figure of each pair is input volume; the second figure is total impurity): 22.66, 0.1660; 27.66, 0.1597; 30.00, 0.1583; 32.66, 0.1575; 35.00, 0.1577; 37.66, 0.1577; 42.66, 0.1605. These showed a small shift in the effect of upper volume and less sensitivity to choice of upper volume. The overall effect is a deterioration of separating efficiency to 0.1575 total impurity. Compared to 0.1526 for the fixed volume case, this is not a large change. It can be concluded that randomness due to glassblowing does not have a significant effect.

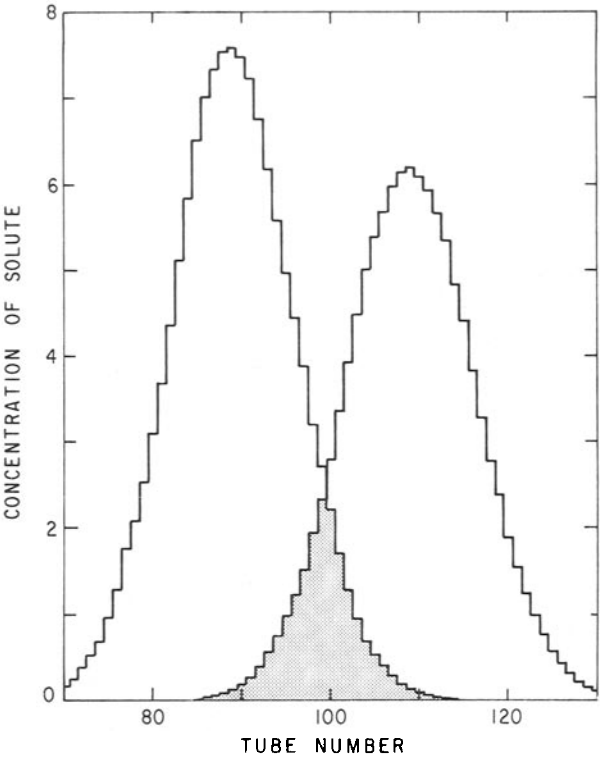

FIG. 3. Effect of randomness in volume of lower phase. Concentration of solute in lower phase of each tube, expressed as 10^4 times the fraction of initial solute mass per milliliter of solution.

One unexpected feature of the tests with random volumes was the difference between the effects on mass and on concentration of solute in each tube. Figure 2 shows the mass of solute in each tube for the 40 ± 10 ml volumes, while Figure 3 shows the concentration of solute in the lower phase at the same time. The rondomness is reflected in the mass of solute but not in the concentration.

The possibility that differences in lower volume were responsible for the changes in separating efficiency, rather than randomness by itself, was tested by arranging the same set of random numbers in regular order and using them as lower volumes. The resulting total impurity after 200 transfers was 0.1573 with volumes in increasing order, 0.1558 with volumes in decreasing order. Decreasing order led to better separation than either random order or increasing order, but neither was as good as the optimum with constant lower volume.

Effect of Variations in Solvent Input Volume

Variation in volume of upper phase was produced by varying the volume of solvent introduced into the first tube at each transfer. A set of normally-distributed random numbers with mean 32.66 and standard deviation 10 was used to represent the change of solvent input with time. This sends a sequence of random upper phase volumes through the apparatus, so that the volume ratio in each tube changes with time as well as with position. The result after 200 transfers was 0.1601 total impurity when lower volume was constant at 40 ml.

Both lower and upper volumes were also randomized simultaneously by using 40 ml (standard deviation 10 ml) for lower volumes and 32.66 ml (standard deviation 10 ml) for input volumes to the first tube. The lower set of random volumes thus remains fixed in place and time while the upper set of random volumes migrates across the lower set. The resultant total impurity was 0.1656, showing an increase from the optimum (0.1526) roughly equal to the sum of the increase due to each source of randomness alone.

Effect of Retainment of Traveling Phase

Theoretical treatments of countercurrent distribution usually assume that none of the traveling (upper) phase is left behind when the transfer takes place. In practice this is usually not true, either because of incomplete drainage or because of gradual decrease in volume of the stationary (lower) phase. Our program computes the values obtained when lower volume is chosen less than cutoff volume, so that the difference represents retained upper phase. Using 45 ml for cutoff volume, 40 ml for volume of lower (stationary) solution, and 32.66 ml for solvent input volume to the first tube, we obtained 0.2153 total impurity after 200 transfers. This is substantially worse than the optimum (0.1526 total impurity) and demonstrates the advantage to be gained by introducing lower solvent, along with the upper solvent input, to maintain the lower volume as close as possible to the cutoff volume.

Solute Initially Placed in More Than One Tube

The preceding calculations assumed that the entire batch of solute was initially confined to the first tube of the apparatus. A test was made of the effect of dividing the solute evenly among the first 10 tubes of the apparatus, using otherwise the standard 40 ml lower volume, equal cutoff volume and 32.66 ml upper volume. The resulting 0.1846 total impurity showed a significant deterioration of separating efficiency. There is an advantage in placing all of the solute in one tube initially, if concentration limitations permit.

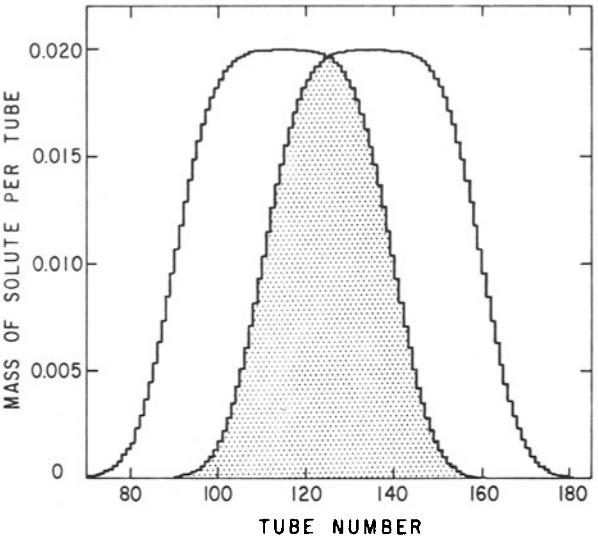

FIG. 4. Effect of loading solute initially into the first 50 tubes. Mass of solute in each tube, expressed as fraction of the total mass of solute initially loaded into 50 tubes.

The curve of quantity of solute versus tube number showed none of the expected flattop shape after 200 transfers. Only a broadening of the curves was observed, along with increased overlap. A similar test with the solute initially divided among the first 50 tubes showed that the flattop was not completely washed out by 200 transfers, as shown in Figure 4. This also demonstrates that whenever a flattop shape persists the overlap is considerable, 0.5976 total impurity in this example. This is because two flat-topped functions have a greater overlap than two peaked functions when their centers are the same distance apart.

Effect of Variations in Distribution Ratios

The ideal equations describing countercurrent distribution assume constant values for the distribution ratios. This assumption is quite good at low solute concentrations but at relatively high concentrations large deviations from ideality may be observed.

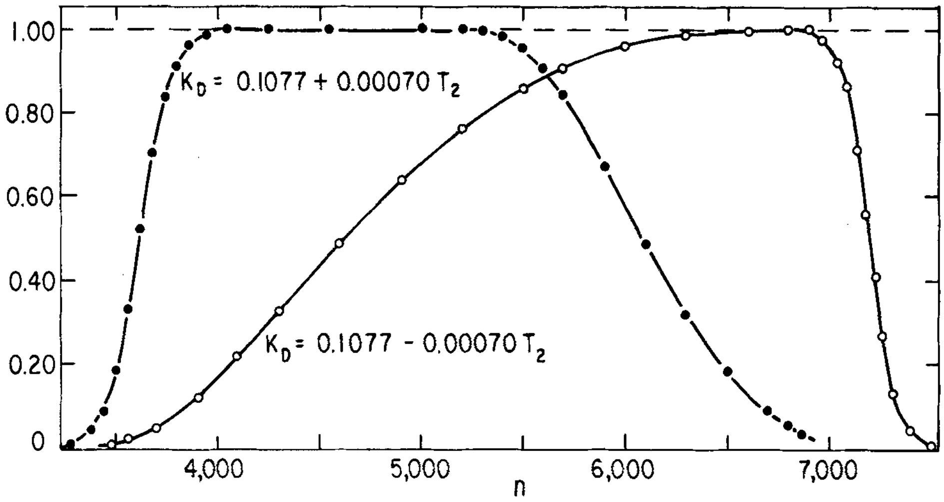

FIG. 5. Effect of variation of distribution ratio with concentration. Mass of solute in effluent from upper phase of 200th tube, as a function of number of transfers. Mass is expressed as grams per transfer when feed rate into first tube is one gram of solute per transfer. Equations give the variation of distribution ratio with total concentration of solute in upper and lower layers of one tube.

To study these deviations by computer simulation, the distribution ratio K_D was varied as a function of the total solute T_2 in a given tube. High solute concentrations were achieved by successively feeding increments of solute dissolved in upper phase into the first tube with one transfer taking place after each addition. After 2000 inputs of solute, pure upper phase was added until essentially all of the solute was washed out of the tubes.

Figure 5 shows transfer number vs. the concentration of solute in the upper phase which had been eluted from the 200th tube. If the K_D's had been constant, the output profiles would have been identical and symmetrical in shape. The output profiles in Figure 5 are clearly not symmetrical or coincident. It would appear that a partial separation had been achieved where the usual ideal calculations would have indicated that none was possible.

The distribution ratios can vary in such a way that the separation is either decreased or enhanced. The behavior of the distribution ratios in a given system must be known in order to make accurate predicitions.

Discussion

Some of the conditions simulated in this paper may seem to be extreme departures from normal operation of countercurrent distribution equipment. However, they indicate the direction of the effects to be expected from less extreme conditions. When even an extreme departure produces no significant effect, then normal variations need not be a cause for concern. For example, these simulations show that no special effort need be made to improve precision of glassblowing in an attempt to make all tubes equal. On the other hand, when an extreme effect is produced by variations normally encountered, it is worthwhile to make a serious attempt to reduce the departure from optimum. For example, a 10% retainment can occur in practice (Rothbart and Barford private communication). This paper finds that attempts to bring the interface closer to the physical cut off would then significantly improve the separation.

REFERENCES

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