Uses of Digital Computers in Theoretical Analytical Chemistry II. Simulation of the Passage of a Compound Through a Countercurrent Distribution Apparatus

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Abstract

The progress of a compound through a countercurrent distribution apparatus has been followed theoretically by use of a digital computer. The computer avoids the usual assumption that all the tubes in the apparatus are alike. Instead, it deals with individual volumes and cutoff levels and allows time variation of solvent input rate. This gives a more realistic theoretical model and also makes it possible to test the properties of new designs of equipment before construction.

Introduction

COUNTERCURRENT DISTRIBUTION has been treated theoretically in the literature (2,4–6). Treatments using standard mathematical techniques have required the use of algebraic functions to represent the behavior of a compound. The application of algebra to repeated equilibrations and transfers leads to very involved algebraic expressions in the general case, since the condition of the system at any instant is a function of its entire past history. Hence it has been necessary to limit theoretical treatment to a few very special cases with simplifying assumptions.

A digital computer, using numerical methods instead of algebraic, need not deal with functions describing the entire past history of a system but only requires expressions describing the present state and one preceding state. The resulting mathematical simplification permits very general cases to be treated. For example, instead of representing the quantity of solute in each tube by a theoretical distribution function, it is possible to store within the computer a table of the amount in each tube independent of any distribution function. It is possible to deal with the basic equilibrium relations in each tube singly. It is also possible to dispense with the assumption that all tubes are alike and to use tubes of unequal dimensions.

Apparatus

Our computer program is based on the apparatus shown schematically in Figure 1. The variables are of the multiple-letter type used in the Fortran programming system (1,3). Quantities in parentheses following a multiletter symbol represent subscripts, as in VCUT(R) for example. R is the serial number of a tube; R-1 designates the tube whose upper layer is transferred into tube R. VLOW and VUPR are the volumes of the lower and upper solutions, respectively. VCUT is the volume of solution remaining in the tube after the upper layer is drained off into tube R+1. It is not assumed that the cutoff occurs at exactly the phase boundary between the two solutions. It is assumed that a certain volume VRET of the upper solution is retained by tube R, either by drainage or by the transfer tube not being identically at the phase boundary. The actual volume of upper solution transferred to the next tube is VTRAN. These variables for any one tube are interrelated by

$$\text{VTRAN} = \text{VUPR} - \text{VRET}$$
$$\text{VRET} = \text{VCUT} - \text{VLOW}$$

The concentration of solute in the two solution layers are CLOW and CUPR, and the total mass of solute in the tube is T. An apparatus containing 200 tubes is treated by our program. A table of 200 values of each of the following variables is stored within the computer: VLOW, VUPR, VCUT, CLOW, CUPR, T.

None of these need be assumed constant. The volumes can be varied as a function of R or as a function of time. For illustrating the programming method, however, the following assumptions will be made:

(a) It will be assumed that equilibrium is reached before solution is transferred from one tube to the next.

(b) Concentrations will be assumed to be low enough that the solutions are ideal and that the volumes of solutions do not change during equilibration.

(c) Dissociation, association, or other chemical changes will be ignored.

These assumptions are not absolutely necessary. If desired, activities could be used instead of concentrations, complex equilibria could be included, or nonequilibrium conditions could be taken into account. The computer is capable of handling these additional complexities, but they are beyond the scope of a paper illustrating the basic method.

Basic Computational Unit

The unit procedure consists of the following steps:

(a) Drain off volume VTRAN(R) from tube R into tube R + 1. This leaves an amount [2]

CLOW(R)* VLOW(R) + CUPR(R)* VRET(R)

of solute remaining in tube R.

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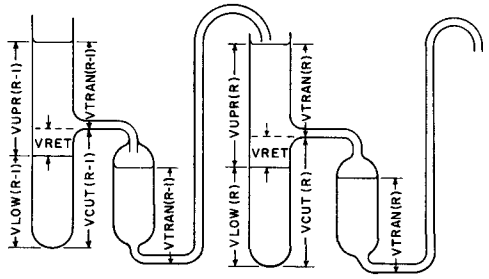

FIG. 1. Schematic of two tubes of countercurrent distribution apparatus.

[2] The asterisk is a multiplication symbol in this and other Fortran expressions to follow.

(b) Transfer volume VTRAN(R−1) into tube R from tube R−1. This introduces an amount

$$\text{CUPR(R−1)} * \text{VTRAN(R−1)}$$

of solute into tube R, so that the new total mass of solute in tube R is now

$$\text{T(R)} = \text{CLOW(R)} * \text{VLOW(R)} + \text{CUPR(R)} * \text{VRET(R)} + \text{CUPR(R−1)} * \text{VTRAN(R−1)}$$

The new volume of the upper layer in tube R thus becomes

$$\text{VUPR(R)} = \text{VRET(R)} + \text{VTRAN(R−1)}$$

(c) Rock the tube back and forth until the solute has distributed itself between the two layers according to the equilibrium condition

$$\frac{\text{CUPR(R)}}{\text{CLOW(R)}} = \text{K}$$

where K is the distribution constant.

These steps are accomplished by seven Fortran statements:

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VRET1 = VCUT(R−1) − VLOW(R−1)
VRET2 = VCUT(R) − VLOW(R)
VTRAN = VUPR(R−1) − VRET1
T(R) = CLOW(R) * VLOW(R) + CUPR(R) *
  VRET2 + CUPR(R−1) * VTRAN
VUPR(R) = VRET2 + VTRAN
CLOW(R) = T(R)/(VLOW(R) + K * VUPR(R))
CUPR(R) = K * CLOW(R)
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At the end of this sequence, the variables of tube R have been replaced by their new values.

Iteration

The basic computation unit is included within two loops, an outer loop controlled by N, the number of transfers, and an inner loop controlled by R. Physically, all the solutions are transferred simultaneously. In the computer, for any given value of N, each tube is calculated separately beginning with R = N and working downwards to R = 1. It is necessary to cycle R in reverse order because the new values of the variables for tube R depend on the old values for tube R − 1, which could have been destroyed if R moved upward instead of downward.

The transfer into the first tube (R = 1) is the input of solvent into the system.

Variations

This simple program is outfitted with subroutines which can expand it to any degree of complexity by varying the parameters as a function of N or as a function of R, under control of input data cards. Some examples follow.

In any real apparatus, the cutoff volumes VCUT are not the same for every tube, because of glassblowing difficulties. Actual measured volumes can be entered into the computer and the progress of a solute compared with a computation for equal VCUT values. The effect of extreme variations in VCUT can be investigated by generating a spread of VCUT values with a pseudorandom number generator. Other hypothetical functions can be tried, such as a continuous variation in VCUT from one end of the apparatus to the other. Numerous possibilities can be tested with much less expense than experimental glassblowing.

The input volume of solvent to the first tube can be varied as a function of N, either in random fashion or according to any desired mathematical function. Different values of distribution constant K can be investigated, as well as different values of ratio of input volume to VCUT, which has an effect similar to variation in K but is under experimental control. The effect of solvent input to tubes other than the first can be tried. The initial distribution of solute can be varied. It need not be all confined to the first tube but can be initially distributed among several tubes according to a predetermined function of R.

The "constants" of the apparatus can be changed during the course of a run. For example, VCUT can be made a function of N, causing this volume to change as the transfers proceed. The volume transferred out of the last tube can be led back and entered into the first tube, making a cyclic apparatus in which more than 200 transfers become possible.

The goal of all these experimental computations is to find some design of apparatus or running conditions which yield a better separation between two solutes having nearly equal values of K. We have several computational experiments in progress and several planned.

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