

The object of this column is to enhance our readers' collection of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested as well as those that are more traditional in nature, which elucidate difficult concepts. Please submit them to Professor James O. Wilkes and Professor T. C. Papanastasiou, ChE Department, University of Michigan, Ann Arbor, MI 48109.

NUMERICAL SIMULATION OF MULTICOMPONENT CHROMATOGRAPHY USING SPREADSHEETS

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Large-scale chromatography is widely used as a purification process in the biotechnology and pharmaceutical industries [1,2]. It is therefore important to include discussions of this process in separations courses taught in the chemical engineering curriculum.

This paper illustrates the use of spreadsheet programs for implementing finite difference numerical simulations of chromatography as an instructional tool in a separations course. This approach is motivated by the fact that numerical solutions are needed to investigate realistic chromatographic processes (e.g., those involving nonlinear equilibrium), but the use of traditional programming languages such as FORTRAN for this purpose involves excessive demands on students' time. In contrast, an equivalent spreadsheet program can be constructed with little effort. Although the computation time is larger for a spreadsheet program than for

a comparable FORTRAN program, the fact that spreadsheet programs require very little time to develop outweighs this disadvantage if only a few simulations are performed. It should be noted that several authors have previously recognized the convenience of spreadsheet programs for engineering calculations [3-5].

DIFFERENTIAL EQUATIONS

The equations describing chromatography can be written as follows [6]:

$$\alpha \frac{\partial C_i}{\partial t} + \alpha v_{\text{fluid}} \frac{\partial C_i}{\partial z} - D_{\text{axial}} \frac{\partial^2 C_i}{\partial z^2} + \rho_b \frac{\partial q_i}{\partial t} = 0 \quad (1)$$

$$R_i \equiv \rho_b \frac{\partial q_i}{\partial t} = -\rho_b k_i a_s (q_i - q_i^*) \quad (2)$$

Equation 1 describes a differential material balance in the column, while Equation 2 describes interphase mass transfer using a linear driving force approximation. If diffusion in the particle is the dominant mass transfer resistance, the transport coefficients in Equation 2 can be approximated by [6,7]

$$k_i a_s = \frac{60 D_i}{d_p^2} \quad (3)$$

In most cases, the following form of the Langmuir isotherm gives an adequate description of equilibrium behavior:

$$q_i^* = \frac{a_i C_i}{1 + \sum b_i C_i} \quad (4)$$



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Although Equation 1 includes a term for axial dispersion, for simplicity's sake this term will be excluded in the following discussion.

DISCRETIZATION AND INTEGRATION

Equations 1 and 2 are readily solved using finite difference methods. For this purpose, the following three-point backward difference formula for the spatial first derivative usually gives excellent results [8,9]:

$$\left(\frac{\partial C_i}{\partial z}\right)_t = \frac{3(C_i)_{z,t} - 4(C_i)_{z-\Delta z,t} + (C_i)_{z-2\Delta z,t}}{2\Delta z} \quad (5)$$

Provided that the number of theoretical equilibrium stages is not excessively large, Equations 1

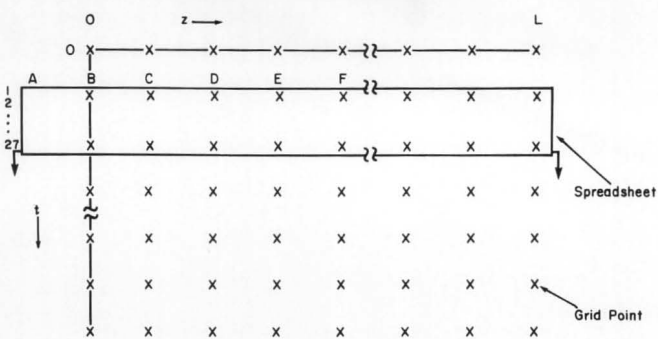


FIGURE 1. Location of spreadsheet on computation grid.

```
A1: (F5) +$COMP1
A2: (F5) +$COMP2
A3: (F5) +$COMP3
A19: (F5) +$COMP1
A20: (F5) +$COMP2
A21: (F5) +$COMP3

B1: (F5) +$COMP1
B2: (F5) +$COMP2
B3: (F5) +$COMP3
B19: (F5) +$COMP1
B20: (F5) +$COMP2
B21: (F5) +$COMP3

C1: (F5) (C19)
C2: (F5) (C20)
C3: (F5) (C21)
C4: (F5) (C22)
C5: (F5) (C23)
C6: (F5) (C24)
C7: (F5) (C25)
C8: (F5) (C26)
C9: (F5) (C27)
C10: (F5) ((-SVFLUID*$DELTA T/(2*$DELTA Z))*((3*C1-4*B1+A1))+C1-(C7*$DELTA T/SALPHA)
C11: (F5) ((-SVFLUID*$DELTA T/(2*$DELTA Z))*((3*C2-4*B2+A2))+C2-(C8*$DELTA T/SALPHA)
C12: (F5) ((-SVFLUID*$DELTA T/(2*$DELTA Z))*((3*C3-4*B3+A3))+C3-(C9*$DELTA T/SALPHA)
C13: (F5) (C4+C7*$DELTA T/$RHOB)
C14: (F5) (C5+C8*$DELTA T/$RHOB)
C15: (F5) (C6+C9*$DELTA T/$RHOB)
C16: (F5) (-$K(1)*$A*$RHOB*(C13-(SA(1)*C10/(1+$B(1)*C10+$B(2)*C11+$B(3)*C12))))
C17: (F5) (-$K(2)*$A*$RHOB*(C14-(SA(2)*C11/(1+$B(1)*C10+$B(2)*C11+$B(3)*C12))))
C18: (F5) (-$K(3)*$A*$RHOB*(C15-(SA(3)*C12/(1+$B(1)*C10+$B(2)*C11+$B(3)*C12))))
C19: (F5) (-SVFLUID*$DELTA T/(2*$DELTA Z))*((3*((C1+C10)/2)-4*((B1+B19)/2)+((A1+A19)/2))+C1-(((C16+C7)/2)*$DELTA T/SALPHA)
C20: (F5) (-SVFLUID*$DELTA T/(2*$DELTA Z))*((3*((C2+C11)/2)-4*((B2+B20)/2)+((A2+A20)/2))+C2-(((C17+C8)/2)*$DELTA T/SALPHA)
C21: (F5) (-SVFLUID*$DELTA T/(2*$DELTA Z))*((3*((C3+C12)/2)-4*((B3+B21)/2)+((A3+A21)/2))+C3-(((C18+C9)/2)*$DELTA T/SALPHA)
C22: (F5) (C4+((C16+C7)/2)*$DELTA T/$RHOB)
C23: (F5) (C5+((C17+C8)/2)*$DELTA T/$RHOB)
C24: (F5) (C6+((C18+C9)/2)*$DELTA T/$RHOB)
C25: (F5) (-$K(1)*$A*$RHOB*(C22-(SA(1)*C19/(1+$B(1)*C19+$B(2)*C20+$B(3)*C21))))
C26: (F5) (-$K(2)*$A*$RHOB*(C23-(SA(2)*C20/(1+$B(1)*C19+$B(2)*C20+$B(3)*C21))))
C27: (F5) (-$K(3)*$A*$RHOB*(C24-(SA(3)*C21/(1+$B(1)*C19+$B(2)*C20+$B(3)*C21))))
```

FIGURE 2. Cell contents for a 1-2-3 spreadsheet program

and 2 in finite difference form can be integrated in time using a modified Euler predictor-corrector method. Starting from time, t, this method involves making an explicit forward Euler step in time to obtain estimates of quantities at t+dt. This is followed by a second explicit forward Euler step from t to t+dt in which the rates of mass transfer and the spatial derivatives are evaluated at the average conditions of the time step.

SPREADSHEET DEVELOPMENT

Figure 1 shows the basic strategy of the spreadsheet program. At any time, two adjacent time points are stored in the cells of the spreadsheet. One recalculation of the spreadsheet corresponds to advancing one time step down the computational grid. If the concentration history at the column outlet is desired, rather than a spatial composition profile at a specific time, the cells at z = L can be written to a separate file as the computation proceeds.

Figure 2 shows cell contents from a spreadsheet program constructed using 1-2-3™ (Lotus Development Corporation). This spreadsheet implements the computation strategy shown in Figure 1 for isocratic conditions. The cell contents in Figure 2 were printed using the 1-2-3 PRINT command. The entry F5 in each cell is the format, which in the present case indicates that 5 decimal places are to be displayed. Each column in the spreadsheet corresponds to one spatial grid point and two adjacent time points, as shown in Figure 1. The composition of the feed, which is composed of three solutes in this example, is entered into cells A1 to A3, B1 to B3, A19 to A21, and B19 to B21 to provide two upwind points for the spatial difference formulas for both the predictor and corrector steps in column C.

The purpose of each cell in column C is described in Figure 3. The 1-2-3 COPY command can be used to copy

column C into as many cells to the right of this column as desired to produce a grid of the appropriate size. After construction of the grid, the numerical simulation is advanced one time step by recalculating the entire spreadsheet column by column. The feed composition can be changed at any time by stopping the recalculation iterations, changing the entries in the feed composition cells, and then restarting the recalculation iterations. Note that instead of having the feed compositions in column B, column C can also be copied into column B. However, the spatial derivatives in column B must then be changed to Euler formulas since there is only one upstream point relative to column B.

Variables in Figure 2 incorporating the symbol \$ refer to named absolute cell references containing the indicated variables, e.g., \$COMP1 indicates an absolute reference to a cell containing the composition of component 1 in the feed to the column. For simplicity, these cells are not shown in Figure 2, but can be located beneath those corresponding to the feed composition.

COMPUTER REQUIREMENTS

Simulations using the 1-2-3 spreadsheet program shown in Figure 2 can be performed conveniently on an IBM AT personal computer operating at 8MHz clock speed. With such a computer, a spreadsheet program involving three solutes and two hundred spatial grid points requires approximately 400 kB of RAM and 5 s for each recalculation, i.e., for each time step. Since 5,000 to 10,000 time steps are often required to ensure stability and accuracy, the time needed for a complete simulation is usually about ten hours for the case where three solutes are present and about three hours for the case where only one solute is present. Faster simulations can be performed by writing spreadsheet subroutines which add downstream grid points only as needed and which delete upstream grid points if that portion of the column has come to equilibrium with the feed.

TYPICAL SIMULATION RESULTS

Figure 4 illustrates an effluent concentration profile calculated using the spreadsheet program in Figure 2 for the isocratic elution of three solutes having Langmuir isotherms. The physical parameters used were as follows:

$$\begin{aligned} D_i &= 10^{-6} \text{ cm}^2/\text{s} \\ v_{\text{fluid}} &= 0.1 \text{ cm/s} \\ d_p &= 0.005 \text{ cm} \\ \rho_p &= 1 \text{ g/cm}^3 \\ \alpha &= 0.4 \end{aligned}$$

$$L = 5 \text{ cm}$$

$$a_1 = 1.6 \cdot a_2 = 0.6 \cdot a_3 = 2.08 \text{ cm}^3/\text{g}$$

$$b_1 = 2.3 \cdot b_2 = 0.6 \cdot b_3 = 0.025 \text{ cm}^3/\text{n-mole}$$

The feed was injected as a square-wave pulse of 87.5 s duration. The concentration of all three solutes in the feed slug was 10 n-mole/cm³ (i.e., 1 mg/cm³ of an average-sized protein). Under these conditions, the chromatographic column had an efficiency of approximately 200 theoretical plates based on linear isotherms. Note that Figure 4 employs a dimensionless concentration and time, the latter being defined as

$$T = \alpha v_{\text{fluid}} C_{1,\text{feed}} (t - L/v_{\text{fluid}}) / (L \rho_b q_{1,\text{feed}}) \quad (6)$$

SUMMARY

Over the last several years, spreadsheet programs which simulate multicomponent chromatography using finite difference methods have been used in the undergraduate separations course at Yale University. These programs permit students to study complex phenomena which would otherwise be difficult to investigate, such as the compression of the

| Cell | Description |
|------|--|
| C1 | Copy C(1) from cell C19 to advance one time step |
| C2 | " C(2) " " C20 " " " " " " " " " " |
| C3 | " C(3) " " C21 " " " " " " " " " " |
| C4 | " q(1) " " C22 " " " " " " " " " " |
| C5 | " q(2) " " C23 " " " " " " " " " " |
| C6 | " q(3) " " C24 " " " " " " " " " " |
| C7 | " R(1) " " C25 " " " " " " " " " " |
| C8 | " R(2) " " C26 " " " " " " " " " " |
| C9 | " R(3) " " C27 " " " " " " " " " " |
| C10 | Euler predictor step for C(1) at t+dt |
| C11 | " " " " C(2) " " " " " " " " " " |
| C12 | " " " " C(3) " " " " " " " " " " |
| C13 | " " " " q(1) " " " " " " " " " " |
| C14 | " " " " q(2) " " " " " " " " " " |
| C15 | " " " " q(3) " " " " " " " " " " |
| C16 | Calculate R(1) at t+dt using results from predictor step |
| C17 | " R(2) " " " " " " " " " " " " " " |
| C18 | " R(3) " " " " " " " " " " " " " " |
| C19 | Recalculate C(1) at t+dt using average values of R(1) and spatial derivative |
| C20 | " C(2) " " " " " " " " " " " " " " |
| C21 | " C(3) " " " " " " " " " " " " " " |
| C22 | " q(1) " " " " " " " " " " " " " " |
| C23 | " q(2) " " " " " " " " " " " " " " |
| C24 | " q(3) " " " " " " " " " " " " " " |
| C25 | Recalculate R(1) at t+dt using quantities recalculated in cell C19-C24 |
| C26 | " R(2) " " " " " " " " " " " " " " |
| C27 | " R(3) " " " " " " " " " " " " " " |

FIGURE 3 Description of cell contents from column C of Figure 2.

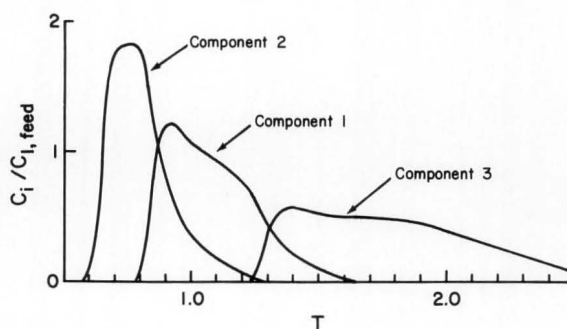


FIGURE 4. Numerical simulation of isocratic elution chromatography of solutes having Langmuir isotherms.

upstream band shown in Figure 4. Students can also gain insights into numerical calculations, such as the effects of numerical instability, since they are able to observe the calculation proceed in time. Many types of spreadsheet programs also incorporate graphics capabilities, which further enhances their educational value. In particular, when using version 2.x of 1-2-3, we recommend also using the program *SeeMORE*TM (Personics Corporation), which can be employed to produce multiple live graphs as the simulation proceeds.

NOMENCLATURE

- a_s = interfacial area per unit volume in bed (cm^{-1})
 a_i = Langmuir isotherm parameter (cm^3g^{-1})
 b_i = Langmuir isotherm parameter ($\text{cm}^3\text{mole}^{-1}$)
 C_i = concentration of component i (mole cm^{-3})
 $C_{i,\text{feed}}$ = feed concentration (mole cm^{-3})
 D_{axial} = axial dispersion coefficient (cm^2s^{-1})
 D_i = diffusivity of component i in particle (cm^2s^{-1})
 d_p = particle diameter (cm)
 L = length of bed (cm)
 k_i = coefficient in linear driving force approximation, (cm s^{-1})
 q_i = amount adsorbed per mass of sorbent averaged over particle ($\text{mole (g of sorbent)}^{-1}$)
 q_i^* = value of q_i in equilibrium with interparticle fluid ($\text{mole (g of sorbent)}^{-1}$)
 $q_{i,\text{feed}}^*$ = value of q_i in equilibrium with $C_{i,\text{feed}}$ ($\text{mole (g of sorbent)}^{-1}$)
 R_i = rate of solute uptake per bed volume ($\text{mole cm}^{-3}\text{s}^{-1}$)
 t = time (s)
 T = dimensionless time
 v_{fluid} = interstitial fluid velocity (cm s^{-1})
 z = distance in column (cm)

Greek Symbols

- α = bed void volume
 ρ_b = bulk density of bed (g cm^{-3})
 ρ_p = particle density (g cm^{-3})

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ChE book review

THERMODYNAMICS: AN ADVANCED TEXTBOOK FOR CHEMICAL ENGINEERS

Gianni Astarita

Plenum Press, 233 Spring St., New York 10013

444 pages, \$69.50 (1989)

Reviewed by

Athanasios Panagiotopoulos
Cornell University

Thermodynamics, as the subtitle implies, is primarily a textbook intended for an advanced thermodynamics course for chemical engineers. Such a course is typically part of the graduate core curriculum, and the graduate and advanced undergraduate students taking it would have completed beginner's courses in thermodynamics, physical chemistry, and transport phenomena. The book has two parts, the first emphasizing macroscopic theory and the second engineering applications. The subject coverage is unusually broad, including chapters on the thermodynamics of relaxation, surface thermodynamics, and dissipative phenomena in the first part, and electrochemistry, polymers (written by G. Marrucci) and the thermodynamics of electromagnetism (by R.E. Rosenweig) in the second part. The point of view of the authors is almost entirely macroscopic.

There are a number of strong points to this book. It is perhaps the most comprehensive in coverage of the current graduate thermodynamics textbooks for chemical engineers. With research activities shifting away from "traditional" chemical engineering areas into new intellectual territories, the need for a fresh look at what is included in a thermodynamics course is clear. By discussing topics such

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