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### Solute Retention in Column Liquid Chromatography. III. Computer Optimization of Mobile-Phase Compositions: Program Window

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**SOLUTE RETENTION IN COLUMN LIQUID CHROMATOGRAPHY. III.  
COMPUTER OPTIMIZATION OF MOBILE-PHASE  
COMPOSITIONS: PROGRAM WINDOW**

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**ABSTRACT**

A program is described that calculates solute retentions (thence optimized conditions for their separation) from data acquired solely from chromatographic measurements. A pre-sorting loop identifies the relevant (window-diagram boundary) pairs of solutes within a user-defined value of the most-difficult separation factor,  $S_f$ . The program run time is consequently shortened by several factors over previously-used "brute-force" techniques wherein all possible pairs are considered at each value of the independent parameter(s) to be optimized. The required CPU space reserved for arrays is thereby also diminished. The program was written for an APPLE II Plus system; statements not compatible with other versions of BASIC are pointed out and discussed.

**INTRODUCTION**

The major drawback to chromatographic separations in general is that it is impossible at the present time to predict on an a priori basis the precise set of conditions which will effect resolution of the mixture at hand. As a result, a number of optimization strategies have been proffered over the years, these including SIMPLEX (1) and the Laub-Purnell window-diagram strategy (2,3). The former makes use of what amounts to an intelligent yet near-random search for the **single** optimum of the parameter

of interest and is hence subject to local minima. In contrast, the latter defines pictorially the **global set** of optima; it is then left to the user to superpose additional local criteria (such as analysis time, cost, and so forth). The overall **practical** optimum is then determined simply by inspection of the global set.

A number of requests have been received for the global optimization algorithm presented in a recent technical report by Laub (4) and so, the computer program is presented here in detail.

### THEORY

The independent variable most frequently employed in optimizing column liquid-chromatographic separations is the composition of the mobile phase. As a result, there have been formulated over the years a number of relations which purport to describe solute retentions as a function of mobile-phase solvent/additive ratio in terms of mole-, weight-, or volume-fraction or molar or molal concentration. The most successful of these is that by McCann, Purnell, and Wellington (5), followed by Madden, McCann, Purnell, and Wellington (6), as described in the previous two papers. They modified the relation first proposed by Scott and Kucera (7) such that all isotherm shapes common to lc could be represented. The result, for which no exception is known at this time, can be expressed in terms of raw retentions with a given column and fixed flow rate as:

$$\frac{1}{t_{R(M)}} = \phi_A \left\{ \frac{1}{t_{R(A)}} + \frac{b\phi_S}{1 + b'\phi_S} \right\} + \frac{\phi_S}{t_{R(S)}} \quad (1)$$

where values of  $b$  and  $b'$  are derived from an analysis of the experimental data.

The fitted parameters have yet to be rationalized either from one solute to the next or from one solvent system to another. Nevertheless, the ability to represent generally (hence predict) the variation of solute retentions as a well-defined function of mobile-phase composition represents a very considerable advance since relative retentions (i.e.,

separations) can then be reduced also to a mathematical formulation. The two relevant equations are:

$$\alpha_{i/j} = \frac{t'_{R(M) i}}{t'_{R(M) j}} \quad (2)$$

$$S_f = \frac{2R_s}{N^{1/2}} = \frac{t_{R(M) i} - t_{R(M) j}}{t_{R(M) i} + t_{R(M) j}} \quad (3)$$

where  $\alpha_{i/j}$  and  $S_f$  are referred to here as the alpha value and the separation factor, and where  $R_s$  and  $N$  are the resolution and number of theoretical plates. The latter expression, derived initially by Jones and Wellington (8), has some advantage in practice (see preceding paper) since  $t_R$  represents a raw retention time, i.e., uncorrected for column void space. Thus, the dead time  $t_A$  (or peak baseline or half-height widths) need not be determined. In addition, for  $R_s$  set to unity ( $4\sigma$  separation), the number of plates required  $N_{req}$  to effect a separation is calculable directly as  $(2/S_f)^2$ . In contrast, capacity factors or adjusted retention times (hence  $t_A$ ) must be known in order to do so with values of alpha, where (9):

$$N_{eff} = 16 \left( \frac{\alpha}{\alpha - 1} \right)^2 \left( \frac{k' + 1}{k'} \right)^2 \quad (4)$$

and where  $N$  and  $N_{req}$  are related by:

$$N_{eff} = N \left( \frac{k'}{k' + 1} \right)^2 \quad (5)$$

Eqn. 3 is therefore used in what follows.

When the separation factors of the relevant pairs of solutes (see later) are plotted graphically against the independent parameter (here, mobile-phase composition), the result (window diagram) resembles a set of inverted and partially-overlapped triangles. A perpendicular dropped to the abscissa from the point of the tallest open region (window) formed by the intersection of the sides of two of these triangles (or one triangle with an ordinate) then specifies the optimum mobile-phase composition. A

horizontal line from the top of the window to the left-hand ordinate subsequently yields the most-difficult separation factor (all others are easier). The number of plates (hence the column efficiency) required to effect the separation can then be calculated. Reference back to eqn. 1 also provides the order of elution of the solutes at the chosen optimum (10).

### PROGRAM DESCRIPTION

In the program that follows, it is assumed that the liquid-chromatographic separation of solutes is to be optimized in terms of mobile-phase composition in accordance with eqns. 1 and 3. Substitution of appropriate functions for other variables, such as  $\log(t_{R(M)})$  against  $T^{-1}$ , could of course also be appended (11,12). For the sake of clarity, the program statements have not in many instances been concatenated where it would otherwise be possible (and even beneficial) to do so and, for the same reason, potential savings in execution time are sacrificed in favor of presentation of the logic in expanded form.

#### Data Input (Statements 1000-1200)

```

1000 REM DATA INPUT— INPUT THE SOLVENT AND SOLUTE
      NAMES, AND THE RESPECTIVE RETENTIONS. THEN DISPLAY
      THESE VALUES.
1010 HOME : PR#0 : DIM N$(51), A(51), S(51), B1(51), B2(51), X(500),
      Y(500), M$(500)
1020 PRINT : PRINT : PRINT : PRINT : PRINT : PRINT
1030 PRINT "SOLVENT 'A' IS: ";
1040 INPUT A$
1050 PRINT : PRINT
1060 PRINT "SOLVENT 'S' IS: ";
1070 INPUT S$
1080 PRINT : PRINT
1090 PRINT "THE NUMBER OF SOLUTES (MAXIMUM OF 50) IS: ";
1100 INPUT N
1110 HOME
1120 PRINT : PRINT
1130 PRINT "ENTER THE RESPECTIVE SOLUTE NAMES AND
      RETENTIONS WITH SOLVENTS 'A' AND 'S' "
1140 PRINT : PRINT
1150 PRINT "SOLUTE NAME, TR(A), TR(S), B1, AND B2" : PRINT

```

```

1160 FOR I = 0 TO N - 1: INPUT N$(I), A(I), S(I), B1(I), B2(I): NEXT I
1165 HOME : PRINT : PRINT : PRINT : PRINT
1170 PRINT "THE LOWER MOBILE-PHASE COMPOSITION PERCENT
      TO BE CONSIDERED IS (WHOLE NUMBER) ";
1175 INPUT DL
1180 PRINT : PRINT "THE UPPER MOBILE-PHASE COMPOSITION
      PERCENT TO BE CONSIDERED IS (WHOLE NUMBER) ";
1185 INPUT DU
1190 PRINT : PRINT "THE MOBILE-PHASE COMPOSITION PERCENT
      INTERVAL TO BE CONSIDERED IS (WHOLE NUMBER; SMALLEST
      PERMISSIBLE IS 1%) ";
1200 INPUT D

```

These statements first clear the screen (1010), dimension the variables, and then query the user for the names of the solvents and the number of solutes. The program then clears the screen again (1110) and asks for the names of the solutes, the respective retentions with solvents A and S, and the fitted values of b (B1) and b' (B2) (1130 ff.). The data entry format is as shown, namely, SOLUTE NAME (comma), TR(A) (comma), TR(S) (comma), B1 (comma), B2, then <RETURN>. The program then asks for the mobile-phase composition range and interval (e.g., every 1%, every 5%, etc.) to be considered (1170-1200); note that the lowest permitted interval, for reasons of memory conservation, is 1%.

#### Data Verification (Statements 1210-1370)

```

1210 PR#1
1220 PRINT : PRINT
1230 PRINT TAB(26); "*****RETENTION DATA*****"
1240 PRINT : PRINT
1250 PRINT TAB(5); "SOLVENT 'A' IS "; A$
1260 PRINT TAB(5); "SOLVENT 'S' IS "; S$
1270 PRINT : PRINT
1280 PRINT TAB(5); "SOLUTE"; TAB(20); "TR(A)"; TAB(35); "TR(S)";
      TAB(52); "B1"; TAB(27); "B2"
1290 PRINT
1300 FOR I = 0 TO N - 1
1310 PRINT TAB(5); LEFT$ (N$(I),10); TAB(20); A(I); TAB(35); S(I);
      TAB(50); B1(I); TAB(55); B2(I): NEXT I
1330 PRINT : PRINT : HOME
1340 PRINT "MIXTURES OF 'A' WITH 'S' WILL BE CONSIDERED AT
      EVERY "; D; "% FROM 'A' = "; DL; " TO "; DU; "%."
1350 PRINT : PR#0: PRINT : PRINT : PRINT : PRINT : PRINT
1360 PRINT "FIRST, HOWEVER, THE RELEVANT PAIRS OF SOLUTES
      FOR CALCULATION OF THE WINDOW DIAGRAM WILL BE
      DETERMINED."

```

The solute and solvent data are printed out on the hard-copy device PR#1. The program uses a simple loop (1300,1310) to do so after the title (1230) and column headings (1280) are printed. Note that the solute names are contained as strings in the array N\$(I), and that the retentions with solvents A and S (named A\$ and S\$) are in the arrays A(I) and S(I), respectively.

### Determination of Relevant Pairs of Solutes (Statements 1500-1980)

```

1500  REM THIS SECTION OF THE PROGRAM WILL DETERMINE THE
      RELEVANT PAIRS OF SOLUTES FOR CALCULATION OF THE
      WINDOW-DIAGRAM ARRAY.
1510  PRINT : PRINT : PRINT
1520  PRINT "ENTER THE UPPER LIMIT OF SEPARATION FACTOR
      (>0) TO BE CONSIDERED: ";
1530  INPUT MAX
1540  Z = 0
1550  Z1 = 0
1560  FOR J = 0 TO N - 2
1580  HOME : PRINT : PRINT : PRINT : PRINT : PRINT "THE NUMBER
      OF RELEVANT PAIRS": PRINT : PRINT : PRINT "FOUND SO FAR
      IS ";Z1
1620  FOR I = J + 1 TO N - 1
1670  LP = (A(I) - A(J))/(A(I) + A(J))
1680  IF (ABS(LP)) < MAX THEN GOTO 1730
1690  LQ = (S(I) - S(J))/(S(I) + S(J))
1710  IF (ABS(LQ)) > MAX THEN IF (LP/LQ) > 0 THEN GOTO 4000

      4000  FOR P = DL TO DU STEP D
      4020  COMP = P * 0.01
      4030  L1 = COMP * ((1/A(I)) + (B1(I) * (1 - COMP)/(1 + B2(I) * (1 -
        COMP)))) + (1 - COMP)/S(I)
      4040  L2 = COMP * ((1/A(J)) + (B1(J) * (1 - COMP)/(1 + B2(J) * (1 -
        COMP)))) + (1 - COMP)/S(J)
      4050  SF = (L1 - L2)/(L1 + L2)
      4060  IF (ABS(SF)) > MAX THEN GOTO 4080
      4070  GOTO 1730
      4080  NEXT P
      4090  GOTO 1850

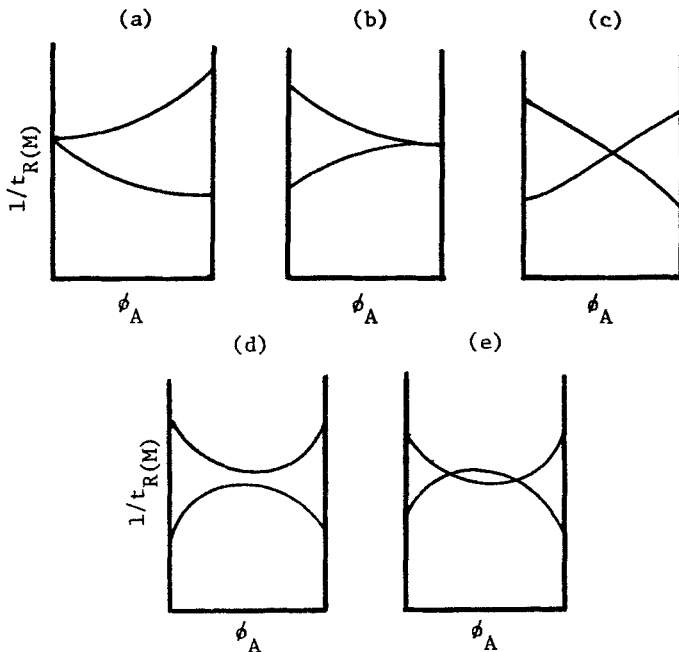
1730  Z1 = Z1 + 1
1740  HOME : PRINT : PRINT : PRINT : PRINT : PRINT "THE NUMBER
      OF RELEVANT PAIRS": PRINT : PRINT : PRINT "FOUND SO FAR
      IS "; Z1: FOR PAUSE = 1 TO 100: NEXT PAUSE
1750  K = J
1760  FOR Z = Z TO (Z + 1)
1770  X(Z) = A(K)

```

```

1775 Y(Z) = S(K)
1780 M1(Z) = B1(K)
1785 M2(Z) = B2(K)
1790 M$(Z) = N$(K)
1795 K = I
1800 NEXT Z
1850 NEXT I
1900 NEXT J
1905 IF Z1 = 0 THEN GOTO 3300
1910 HOME : PR#1 : PRINT : PRINT
1915 PRINT TAB(26); "*****"
1920 PRINT : PRINT : PRINT TAB(5); "THE NUMBER OF RELEVANT
    PAIRS OF SOLUTES IS "; Z1; "."
1930 PRINT : PRINT
1940 PRINT TAB(5); "THE RELEVANT PAIRS ARE:" : PRINT
1960 FOR Z = 0 TO (Z1 * 2 - 1) STEP 2
1970 PRINT TAB(15); (LEFT$(M$(Z),10)); "/"; (LEFT$(M$(Z + 1),10))
1980 NEXT Z
    
```

Rather than calculating the separation factors for all pairs of solutes at all compositions, the program first determines the number and identity of pairs of solutes that have values of  $S_f$  less than the user-defined limit MAX at some point within the specified composition range of DL to DU% of A in (A + S). The task is straight-forward when the variation of solute retentions is known as a function of column composition. Five situations arise generally:





In situations (a) and (b), full overlap of the solutes occurs at one or the other of the ordinates.  $S_f$  is therefore  $\emptyset$  at each of these points. In the third case, (c), the order of elution of the solutes is reversed on passing from one extremum to the other. Hence, while  $S_f$  is greater (or less) than  $\emptyset$  at one ordinate, it will be less (or greater) than  $\emptyset$  at the other. Finally, situations (d) and (e) encompass those instances where the curves do not intersect at any or at more than one composition. These can be identified only by examination of the solute retentions at intermediate mobile-phase compositions.

In order to test for each of the above possibilities (hence identify the relevant pairs), the separation factors for each solute pair are calculated at each of the ordinates (154 $\emptyset$ -19 $\emptyset\emptyset$ ) and, where necessary, at intermediate compositions (subroutine 4 $\emptyset\emptyset\emptyset$ -4 $\emptyset\emptyset\emptyset$ ). First, however, and following a displayed message so indicating, the user is prompted to enter the upper limit of  $S_f$  which will be used to define what constitutes a relevant pair. Judicious choice of the limiting separation factor can lead to an enormous savings in the time of calculation of the window boundary, since whatever pairs are eliminated at this point will not be considered again. (An  $S_f$  of 0.02828 corresponds to a column of 5 $\emptyset\emptyset\emptyset$  plates and minimum resolution  $R_s$  of unity.) If no relevant pairs are found, the program branches at 19 $\emptyset\emptyset$  to statement 33 $\emptyset\emptyset$  and displays a message so informing the user:

```

33 $\emptyset\emptyset$  HOME : PRINT : PRINT : PRINT : PRINT : PRINT : PRINT "NO
      PAIRS FOUND— ALL COMPOSITIONS WILL PROVIDE GOOD
      RESOLUTION. WANT TO TRY A HIGHER VALUE OF SF (Y/N)?:
      INPUT ANS$
331 $\emptyset$  IF ANS$ = "N" THEN GOTO 327 $\emptyset$ 
332 $\emptyset$  PRINT : PRINT : PRINT : GOTO 152 $\emptyset$ 

```

The final task of this section of the program (191 $\emptyset$ -198 $\emptyset$ ) gives a hard-copy print-out of the number and identity of the relevant pairs of solutes.

#### Calculation of the Window Boundary Array (Statements 3 $\emptyset\emptyset\emptyset$ -32 $\emptyset\emptyset$ )

```

3 $\emptyset\emptyset\emptyset$  REM THIS SECTION OF THE PROGRAM CALCULATES THE
      WINDOW DIAGRAM ARRAY, HERE, SF AS A FUNCTION OF

```

```

MOBILE-PHASE COMPOSITION FOR LIQUID CHROMATOGRAPHY.
3010 HOME : PR#0
3020 DIM Q$(101), R$(101), SFP(101)
3040 BSFP = 0
3045 FOR P = DL TO DU STEP D
3050 HOME : PRINT : PRINT : PRINT : PRINT : PRINT : PRINT : PRINT
      : PRINT
3060 PRINT "THE COLUMN COMPOSITION CURRENTLY BEING":
      PRINT : PRINT "CONSIDERED IS "; P; "%"
3070 SFP(P) = MAX
3075 COMP = P * 0.01
3080 Q$(P) = "(NONE)"
3085 R$(P) = "(NONE)"
3100 FOR Z = 0 TO (Z1 * 2 - 1) STEP 2
3110 L1 = COMP * ((1/X(Z)) + (M1(Z) * (1 - COMP)/(1 + M2(Z) * (1 -
      COMP)))) + (1 - COMP)/Y(Z)
3115 L2 = COMP * ((1/X(Z + 1)) + (M1(Z + 1) * (1 - COMP)/(1 + M2(Z + 1)
      * (1 - COMP)))) + (1 - COMP)/Y(Z + 1)
3120 SF = (L1 - L2)/(L1 + L2)
3125 IF (ABS(SF)) > SFP(P) THEN GOTO 3170
3130 SFP(P) = ABS(SF)
3140 Q$(P) = M$(Z): R$(P) = M$(Z + 1)
3170 NEXT Z
3175 IF SFP(P) < BSFP THEN GOTO 3200
3180 BSFP = SFP(P)
3185 BA$ = Q$(P)
3190 BS$ = R$(P)
3195 OPT = P
3200 NEXT P

```

Once the relevant pairs of solutes have been identified, separation factors for each are calculated in turn at each column composition and the lowest (most-difficult) is saved in the array subscripted as P. Thus, SFP(P) (3130) is the most-difficult (window-boundary) value of  $S_f$  at the column composition corresponding to P, while solutes Q\$(P) and R\$(P) (3140) are the names of the solutes. The **overall best** value of SFP(P), BSFP (3180), is updated on each pass through the outer loop, as are the names of the corresponding most-difficult solutes, BA\$ (3185) and BS\$ (3190). The **overall best** (optimum) column composition is also stored (3195) as OPT.

This section of the program is by far the slowest, the rate-limiting statements being 3110 and 3115. To indicate that the computer is still working (and to time the program if desired), the composition currently being considered is displayed.

SFP(P), Q\$(P), and R\$(P) default (3070,3080,3085) to the value of MAX and the string "(NONE)" if, at a given column composition, the separation factors of all relevant pairs of solutes exceed that of MAX (see later).

#### Data Output (Statements 3205-3290)

```

3205  PR#1
3210  HOME : PRINT : PRINT : PRINT TAB(5); "THE WINDOW-
      BOUNDARY DATA ARE:"
3215  PRINT : PRINT
3220  PRINT TAB(11); "SOLUTE"; TAB(36); "COL."; TAB(57); "SEPN."
3225  PRINT TAB(12); " PAIR"; TAB(36); "COMP."; TAB(16); "FACTOR"
3230  PRINT : PRINT
3235  FOR P = DL TO DU STEP D
3240  PRINT TAB(5); LEFT$ (Q$(P),10); "/" ; LEFT$ (R$(P),10); TAB(37);
      P; TAB(54); (INT(10 ^ 5 * (SFP(P)) + 0.02))/10 ^ 5
3245  NEXT P
3250  HOME : PRINT : PRINT
3255  PRINT "THE BEST COLUMN COMPOSITION IS: "; OPT; "%."
3260  PRINT : PRINT "THE MOST-DIFFICULT SEPARATION FACTOR
      AT THIS COMPOSITION IS: "; BSFP; "."
3265  PRINT : PRINT "THE MOST DIFFICULT SOLUTES TO SEPARATE
      AT THIS COMPOSITION ARE: "; BA$; " FROM "; BS$; "."
3270  PR#0
3275  PRINT : PRINT : PRINT : PRINT : PRINT : PRINT : PRINT :
      PRINT : PRINT TAB(10); "*****THAT'S ALL, FOLKS*****"
3290  END

```

A hard-copy print-out of the window-boundary array is accomplished by the loop, 3235-3245. For easier reading, the separation-factor data are truncated (3240) to five places. If at a given column composition the separation factors of all relevant pairs exceed the value of MAX, the solute-pair print-out is (NONE)/(NONE) and the separation factor printed is MAX. (A plot of the data in this composition region thus would show a flat top.) Also printed out (3255-3265) are the overall best column composition, the most-difficult  $S_f$  at this composition, and the associated (most-difficult) solute pair.

**Generalization of the Algorithm**

The program as written considers that inverse retentions vary in a non-linear fashion with mobile-phase composition. If the regression is in fact linear, eqn. 1 reduces to the trivial form:

$$\frac{1}{t_{R(M)}} = \phi_A \left( \frac{1}{t_{R(A)}} \right) + \phi_S \left( \frac{1}{t_{R(S)}} \right) \quad (6)$$

That is, both  $b$  and  $b'$  are negligible. The program and data entry procedure need not be modified in this instance other than to enter  $\emptyset$  when asked for values of  $B1$  and  $B2$ .

The terms  $(1/t_{R(i)})$  ( $i = A, S,$  or  $M$ ) could of course also be used to represent ordinate data from some other function which may or may not be linear. For example, the (linear) diachoric solutions relation pertinent to retentions in gas chromatography is (13,14):

$$K_{R(M)}^0 = \phi_A K_{R(A)}^0 + \phi_S K_{R(S)}^0 \quad (7)$$

where  $K_{R(i)}^0$  are solute liquid-gas partition coefficients with the stationary phases  $A, S,$  and  $M (= A + S)$ . To utilize the program, in this instance for optimization of the stationary-phase composition,  $\emptyset$  would be entered for  $B1$  and  $B2$ , and  $1/K_{R(i)}^0$  entered for " $t_{R(i)}$ ". Eqns. 6 and 7 would thereby be made equivalent. However, the value of " $S_f$ " thence calculated would no longer be equal to  $2R_s/N^{1/2}$  unless it were true that the sum of the raw retentions were much larger than twice the average of the column dead times:

$$\frac{K_{R(M)2}^0 - K_{R(M)1}^0}{K_{R(M)2}^0 + K_{R(M)1}^0} = \frac{t_{R(M)2} - t_{R(M)1}}{t_{R(M)2} + t_{R(M)1} - 2t_A} \quad (8)$$

Fortunately, this can be expected to be the case more often than not in open-tubular column gc, and will certainly be true for conventional packed-column gas chromatography.

In contrast, suppose that for some reason or another a particular liquid-chromatographic system were represented by the relation (cf. eqn. 1 of preceding paper):

$$\log k'_{(M)} = \log k'_{(S)} - S \phi_A \quad (9)$$

where  $S$  is an empirical constant and where it is assumed that  $t_A$  can be determined unambiguously. In order to identify the appropriate quantities for " $t_{R(A)}$ " and " $t_{R(S)}$ ", eqn. 6 is rearranged to the form:

$$\frac{1}{t_{R(M)}} = \frac{1}{t_{R(S)}} - \phi_A \left( \frac{1}{t_{R(S)}} - \frac{1}{t_{R(A)}} \right) \quad (10)$$

Comparison of coefficients hence yields the identities:

$$"t_{R(S)}" = \frac{1}{\log k'_{(S)}} \quad (11a)$$

$$"t_{R(A)}" = \frac{1}{\log k'_{(S)} - S} \quad (11b)$$

Entry of these values for " $t_{R(A)}$ " and " $t_{R(S)}$ " would then yield a separation factor defined by:

$$10^{S f} + k'_{(M)1} k'_{(M)2} = \frac{k'_{(M)1}}{k'_{(M)2}} = \alpha_{1/2} \quad (12)$$

for which a program statement could easily be added to retrieve the correct window-diagram boundary, here,  $\alpha$  as a function of mobile-phase composition.

In the cases considered above, it was assumed that the example relations were linear. If this were not so, the program could still be made to function with appropriate (fitted) values of  $B_1$  and  $B_2$  defined analogous to those of eqn. 1. It appears, therefore, that the algorithm is likely to be useful in virtually any situation in chromatography wherein retentions can be described as a function of the parameter(s) to be optimized.

**Commands Indigenous to APPLE BASIC**

The only three commands used here which may not be compatible with other versions of BASIC are PR#1, PR#0, and HOME. The first two of these specify the hard-copy printer and the display unit, respectively, while the third command causes the display to clear and the cursor to be positioned in the upper left-hand corner of the screen. These commands appear in the following statements:

<u>Command</u>	<u>Statement Nos.</u>
PR#1	1210, 1910, 3205
PR#0	1010, 1350, 3010, 3270
HOME	1010, 1110, 1165, 1910, 3010, 3050, 3210, 3250, 3300

There may also be difficulty with multiple TAB statements depending upon the printer employed (here, an Epson MX-70). We have found that substitution of POKE (36,nn) for TAB (nn) solves this problem.

**ACKNOWLEDGMENT**

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