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Simulation of Chromatography: The Relationship between Position Peak and Exit Peak

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菅田節朗

A set of three programs for the simulation of chromatography based on the discrete flow model (one of plate theories) in the linear isotherms were developed. The main of them is that of the relationship between position peak and exit peak (chromatogram). This program represents the elemental processes of column operations and the resulting exit peak by step-by-step operations, and satisfactory results were obtained. The other two, those of position peak and exit peak, were developed for the need of explanations, though these kinds of programs were already reported by other investigators. Using these programs, especially the "tailing" of chromatogram in linear isotherm is discussed.

One of the most simple theories of chromatography is the discrete flow model (one of plate theories). This model has been well-illustrated using counter-current chromatography (CCC), because the theory is simple^{1, 2)}. Programs and/or results for the simulation of chromatography based on the theory for the linear isotherms were already reported^{2, 3)}. Two kinds of chromatographic peaks exist: that are still on a column (position peaks) and for these peaks as they leave the column (exit peaks or chromatograms)²⁾. The reported programs and/or results are for the two kinds of peaks, and they are useful themselves. However, they alone can not give a thorough understanding of chromatographic basis, especially of the relationship between the position and exit peaks. Therefore, the author developed a program to understand the relationship. Further, the programs for the position and exit peaks were also developed for the need of explanations.

Theory

In CCC, column operations consist of two kinds of elemental processes: the equilibration of solute molecules between the stationary and mobile phases in each tube and the subsequent transfer of the series of mobile phases to the next tubes. Alternate repetitions of these two processes transfer the solutes at their intrinsic velocities. Thus, the solutes are separated. Each tube corresponds to a theoretical plate in the plate theory²⁾.

At equilibrium, the solute is partitioned between two phases according to the capacity factor, k' , as follows:

$$k' = n_s/n_m = (C_s V_s)/(C_m V_m) = K (V_s/V_m) \quad \dots\dots (1)$$

In Eq 1, n , C , V and K represent amount of the solute, concentration of the solute, volume of the phase and partition coefficient of the solute, respectively. Subscripts S and M represent the stationary and mobile phases, respectively. If the conditions of CCC remain constant, the phase ratio (V_s/V_m) is to be constant. Solute have their intrinsic values of K ; these values are independent of the concentrations in linear isotherms.

Equations representing the position and exit peaks are derived from the theory mentioned above; they are Eqs. 2 and 3, respectively^{1, 2)}. The exit peak also can be drawn using Eq. 2. In this paper, the presentation of these equations are arranged in my style.

$$Q_{n,j} = Q_0 \frac{n!}{(n-j)!j!} \cdot \frac{k'^{n-j}}{(1+k')^n} \quad (j \leq n) \quad \dots\dots (2)$$

$$Q_n = Q_0 \frac{(n-1)!}{(n-N)!(N-1)!} \cdot \frac{k'^{n-N}}{(1+k')^n} \quad (n \geq N) \quad \dots\dots (3)$$

In these equations, Q_0 , n , j and N represent the total amount of the solute, the number of transfers (start from 0), the plate number (start from 0) and the number of theoretical plates (start from 1), respectively. $Q_{n,j}$ in Eq. 2 denotes the amount of the solute in a given plate, whereas Q_n in Eq. 3 denotes that in a mobile phase which leave the column.

Position peak approaches Gaussian distribution with increasing number of n (see below), then it is also represented as Eq. 4⁴⁾. The exit peak can be drawn using Eq. 4 also.

$$Q_{n,j} = Q_0 \frac{1+k'}{\sqrt{2\pi n k'}} \exp \left\{ - \frac{[j(1+k') - n]^2}{2 n k'} \right\} \quad \dots\dots (4)$$

Results and Discussion

Position Peak

A program for the position peak was developed (Program 1, see the appendix) based on Eq. 2. The peaks are represented stepwise by doing "hit space key". Three stages of them are copied (Fig. 1). At the last stage, Gaussian distribution based on Eq. 4 is also drawn (lines in Fig. 1c). Although the number of n is small, Fig. 1 represents satisfactory results; the peaks approach Gaussian distributions and are separated mutually. Eq. 2 is not usable with large number of n ; in these cases, only Eq. 4 should be used. If G\$ = "N" in line 100 is changed to G\$ = "G", only the peak based on Eq. 4 is drawn. Remark, the symmetry of peak is kept at any stage in the case of $k' = 1$.

Exit Peak

A program for the exit peak was developed (Program 2) based on Eq. 3. Two examples of the peaks are shown (Fig. 2). The peaks based on Eq. 4 is also drawn by doing "hit space key" (lines in Fig. 2). If G\$ = "N" in line 100 is changed to G\$ = "G", only the peak based on Eq. 4 is drawn. All the peaks exhibited "tailing" to various extents (Fig. 2). The degree of "tailing" decreases and the peak becomes more Gaussian as the number of N and the value of k' become larger²⁾. Actually a short or an inefficient column is one of the causes of "tailing"⁵⁾. Remark, the peak in the case of $k' = 1$ exhibits "tailing" as a matter of course.

Relationship between Position Peak and Exit Peak

The two kinds of programs mentioned above are useful themselves. However, they alone can not give a thorough understanding of chromatographic basis. For example, these are not so useful to understand instantaneously that the Gaussian (symmetry) distribution in position peak causes the "tailing" of exit peak. Therefore, the author developed a new program (Program 3); the program exhibits the elemental two processes in a column, the equilibration and the transfer (see above), and the resulting exit peak stepwise. Although this program can be used with various values of parameters of course, an example with very small number of N ($N = 6$) and $k' = 1$ (refer to the above remarks) is shown for the simplicity of presentation (Fig. 3). From this, the fact that the symmetry of position peak is not kept in

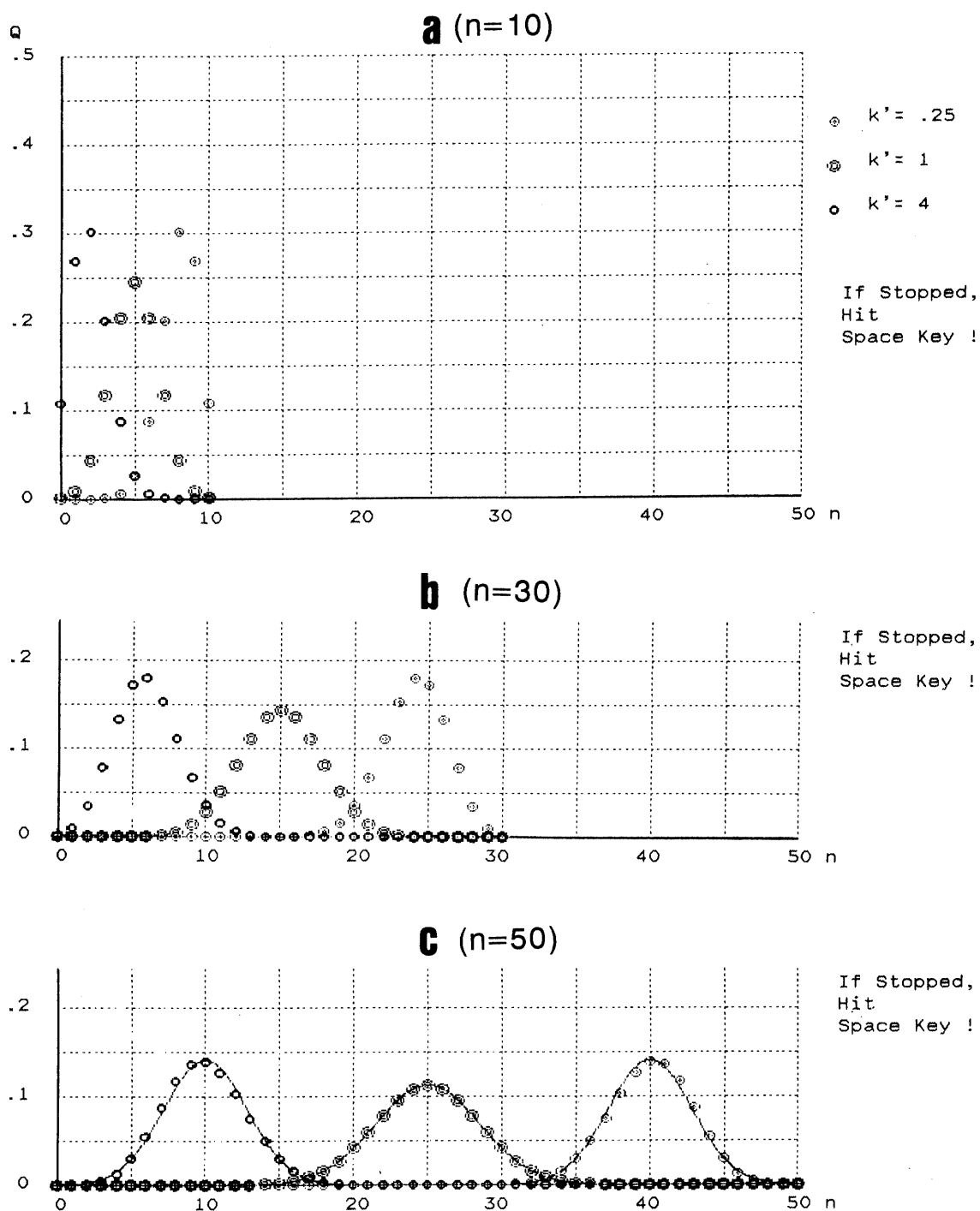


Fig. 1 Three Stages of an Example of the Simulation of "Position Peak" (produced by Program 1)

the exit peak can be grasped confidently.

In conclusion, Program 3 is very useful to understand the elemental two processes, the equilibration and the transfer of mobile phases, and the relationship between the position and exit peaks. If Program 3 is used together with Programs 1 and 2, more effective educational results will be obtained.

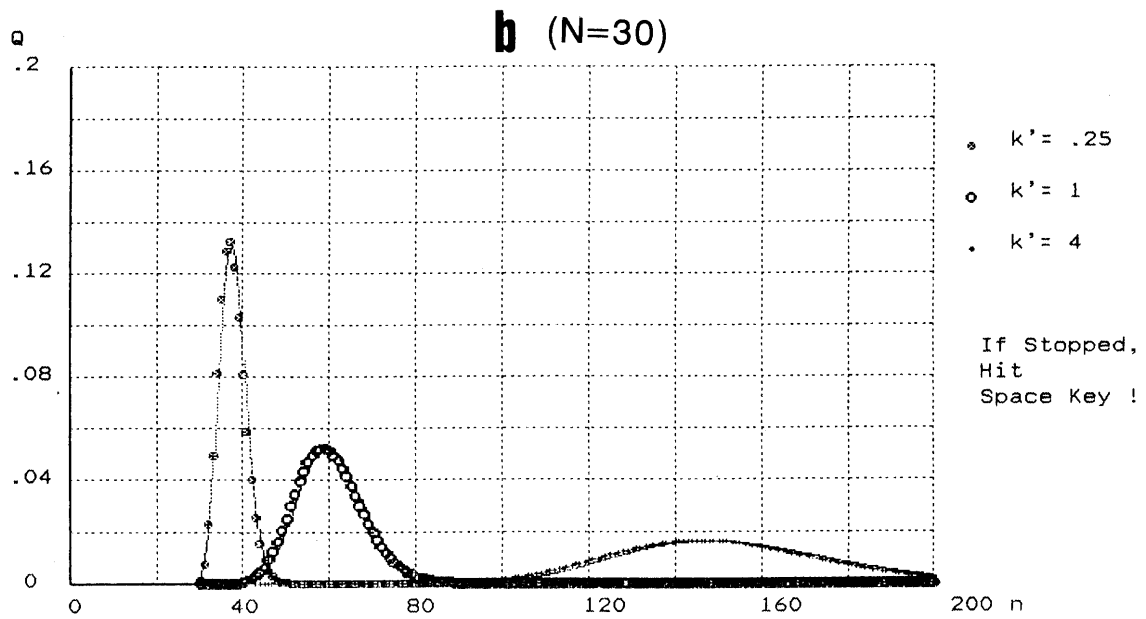
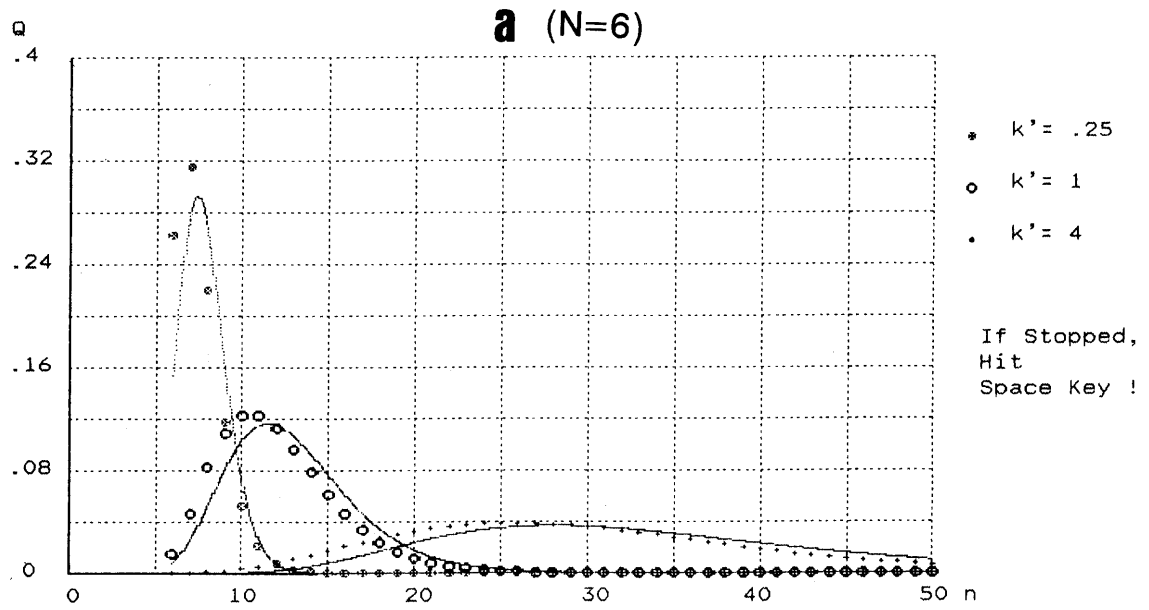


Fig. 2 Two Examples of the Simulation of "Exit Peak" (produced by Program 2)

Appendix

Programs developed in this paper are as follows, and they are written by N₈₈-BASIC using an NEC Model PC-9801 personal computer.

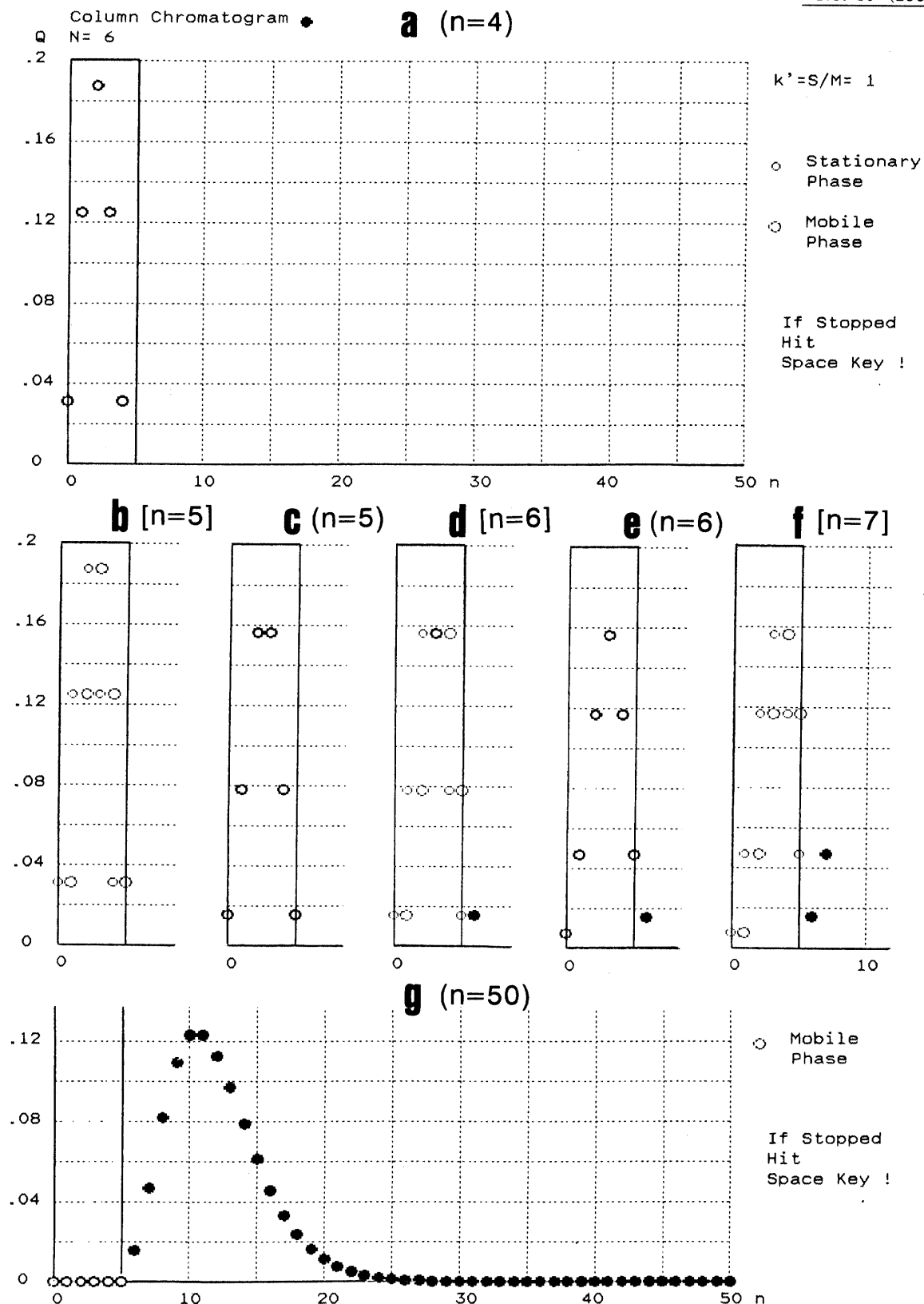


Fig. 3 Seven Stages of an Example of the Simulation of "Relationship between Position Peak and Exit Peak" (produced by Program 3)

The numbers n in () represent the equilibrated states and those in [] represent the instants of transfers of mobile phases.

Program 1

```

10 ' ***** Position Peak *****
20 '
30 CLS 3 :CONSOLE ,,0,1 :SCREEN 3 :COLOR 6
40 PRINT "***** Position Peak *****":COLOR 7:PRINT
50 '
60 ' ----- PARAMETERS -----
70 INPUT "Parameter Change (Y/N)";Z$:CLS 3
80 IF Z$="Y" GOTO 90 ELSE 100
90 LIST 100-150
100 N1=5 :N2=50 :ST=5 :FX=50 :FY=.5 :G$="N"
110 K1=.25 :K2=1 :K3=4 :Q1=1 :Q2=1 :Q3=1
120 C10=1 :C11=3 :C20=2 :C22=4 :C30=2 :C33=3
130 ' Step-by-step Presentation(N1,N2,ST), Only Gaussian distribution(N -> G)
140 ' Full scales of X-axis( FX ) and Y-axis( FY )
150 ' Capacity Factor,k'(K), Amount of Substance(Q), Scales of Circles(C10..)
160 CLS 3
170 ' ----- PRESENTATION OF THE BACKGROUND -----
180 '
190 LINE(40,40)-(40,360) :LINE(40,360)-(510,360)
200 FOR I=1 TO 10 :LINE(40+47*I,40)-(40+47*I,360),7,,&HCCCC
210 LINE(40,360-32*I)-(510,360-32*I),7,,&HCCCC :NEXT I
220 LOCATE 1,2 :PRINT "Q" :LOCATE 2,23 :PRINT "0"
230 FOR I=2 TO 6 :LOCATE 0,27-4*I :PRINT .2*FY*(I-1) :NEXT I
240 LOCATE 5,25:PRINT "0" ;".2*FX;" ;".4*FX;" ;".6*FX;"
";.8*FX;" ;FX;"n"
250 CIRCLE(530,90),C10,5 :CIRCLE(530,90),C11,5 :LOCATE 69,5:PRINT "k'=";K1
260 CIRCLE(530,122),C20,2:CIRCLE(530,122),C22,2 :LOCATE 69,7:PRINT "k'=";K2
270 CIRCLE(530,154),C30,4:CIRCLE(530,154),C33,4 :LOCATE 69,9:PRINT "k'=";K3
280 LOCATE 67,13 :PRINT "If Stopped," :LOCATE 67,14 :PRINT "Hit"
290 LOCATE 67,15 :PRINT "Space Key !"
300 '
310 ' ----- CALCULATION -----
320 IF G$="G" GOTO 540 ELSE 330
330 FOR N=N1 TO N2 STEP ST
340 Q10=Q1*(K1/(1+K1))^N :Q20=Q2*(K2/(1+K2))^N :Q30=Q3*(K3/(1+K3))^N
350 NN=N-ST :Q11=Q1*(K1/(1+K1))^NN :Q22=Q2*(K2/(1+K2))^NN
360 Q33=Q3*(K3/(1+K3))^NN
370 FOR X=0 TO N
380 XX=40+470*X/FX
390 M=N-ST :IF M<0 GOTO 450
400 IF X=0 GOTO 420
410 Q11=Q11*(M-X+1)/(X*K1):Q22=Q22*(M-X+1)/(X*K2):Q33=Q33*(M-X+1)/(X*K3)
420 CIRCLE(XX,360-320*Q11/FY),C10,0 :CIRCLE(XX,360-320*Q11/FY),C11,0
430 CIRCLE(XX,360-320*Q22/FY),C20,0 :CIRCLE(XX,360-320*Q22/FY),C22,0
440 CIRCLE(XX,360-320*Q33/FY),C30,0 :CIRCLE(XX,360-320*Q33/FY),C33,0
450 M=N
460 IF X=0 GOTO 480
470 Q10=Q10*(M-X+1)/(X*K1):Q20=Q20*(M-X+1)/(X*K2):Q30=Q30*(M-X+1)/(X*K3)
480 CIRCLE(XX,360-320*Q10/FY),C10,5 :CIRCLE(XX,360-320*Q10/FY),C11,5
490 CIRCLE(XX,360-320*Q20/FY),C20,2 :CIRCLE(XX,360-320*Q20/FY),C22,2
500 CIRCLE(XX,360-320*Q30/FY),C30,4 :CIRCLE(XX,360-320*Q30/FY),C33,4
510 NEXT X
520 IF INKEY$="" THEN GOTO 520
530 NEXT N
540 FOR X=0 TO N2 STEP FX/1000
550 DM1=1+K1 :DM2=1+K2 :DM3=1+K3 :PI=3.14159 :XX=40+470*X/FX
560 Q10=Q1*DM1/((2*PI*N2*K1)^.5)*EXP(-(X*DM1-N2)^2/(2*N2*K1))
570 Q20=Q2*DM2/((2*PI*N2*K2)^.5)*EXP(-(X*DM2-N2)^2/(2*N2*K2))
580 Q30=Q3*DM3/((2*PI*N2*K3)^.5)*EXP(-(X*DM3-N2)^2/(2*N2*K3))
590 PSET(XX,360-320*Q10/FY),5 :PSET(XX,360-320*Q20/FY),2
600 PSET(XX,360-320*Q30/FY),4
610 NEXT X
620 IF INKEY$="" THEN GOTO 620
630 GOTO 30
640 END

```

Program 2

```

10 ' ***** Exit Peak (Chromatogram) *****
20 '
30 CLS 3 :CONSOLE ,,0,1 :SCREEN 3 :COLOR 6
40 PRINT "***** Exit Peak (Chromatogram) *****":COLOR 7:PRINT
50 '
60 ' ----- PARAMETERS -----
70 INPUT "Parameter Change (Y/N)";Z$:CLS 3
80 IF Z$="Y" GOTO 90 ELSE 100
90 LIST 100-150
100 CLM=20 :NL=100 :FY=.2 :FX=NL :G$="N"
110 K1=.25 :K2=1 :K3=4 :Q1=1 :Q2=1 :Q3=1
120 C10=1 :C11=3 :C20=2 :C22=4 :C30=2 :C33=3
130 ' Number of theoretical plates(CLM), Last number of transfers(NL)
140 ' Only Gaussian derived(N -> G), Full scales of X- and Y-axis(FX,FY)
150 ' Capacity Factor,k'(K), Amount of Substance(Q), Scales of Circles(C10..)
160 CLS 3
170 ' ----- PRESENTATION OF THE BACKGROUND -----
180 '
190 LINE(40,40)-(40,360) :LINE(40,360)-(510,360)
200 FOR I=1 TO 10 :LINE(40+47*I,40)-(40+47*I,360),7,,&HCCCC
210 LINE(40,360-32*I)-(510,360-32*I),7,,&HCCCC :NEXT I
220 LOCATE 1,2 :PRINT "Q" :LOCATE 2,23 :PRINT "0"
230 FOR I=2 TO 6 :LOCATE 0,27-4*I :PRINT .2*FY*(I-1) :NEXT I
240 LOCATE 5,25:PRINT "0" :PRINT ".2*FX;" :PRINT ".4*FX;" :PRINT ".6*FX;"
:PRINT ".8*FX;" :PRINT "FX;" :PRINT "n"
250 CIRCLE(530,90),C10,5 :CIRCLE(530,90),C11,5 :LOCATE 69,5:PRINT "k'=";K1
260 CIRCLE(530,122),C20,2:CIRCLE(530,122),C22,2 :LOCATE 69,7:PRINT "k'=";K2
270 CIRCLE(530,154),C30,4:CIRCLE(530,154),C33,4 :LOCATE 69,9:PRINT "k'=";K3
280 LOCATE 67,13 :PRINT "If Stopped," :LOCATE 67,14 :PRINT "Hit"
290 LOCATE 67,15 :PRINT "Space Key !"
300 '
310 ' ----- CALCULATION -----
320 IF G$="G" GOTO 480 ELSE 330
330 Q10=Q1/((1+K1)^CLM) :Q20=Q2/((1+K2)^CLM) :Q30=Q3/((1+K3)^CLM)
340 FOR N=CLM TO NL
350 IF N=CLM GOTO 390
360 Q10=Q10*((N-1)/(N-CLM))*(K1/(1+K1))
370 Q20=Q20*((N-1)/(N-CLM))*(K2/(1+K2))
380 Q30=Q30*((N-1)/(N-CLM))*(K3/(1+K3))
390 XX=40+470*N/FX
400 CIRCLE(XX,360-320*Q10/FY),C10,5
410 CIRCLE(XX,360-320*Q10/FY),C11,5
420 CIRCLE(XX,360-320*Q20/FY),C20,2
430 CIRCLE(XX,360-320*Q20/FY),C22,2
440 CIRCLE(XX,360-320*Q30/FY),C30,4
450 CIRCLE(XX,360-320*Q30/FY),C33,4
460 NEXT N
470 IF INKEY$="" THEN GOTO 470
480 FOR N=CLM TO NL STEP FX/2000
490 PI=3.14159 :IF N=0 GOTO 570
500 Q10=Q1/((2*PI*N*K1)^.5)*EXP(-(CLM*(1+K1)-N)^2/(2*N*K1))
510 Q20=Q2/((2*PI*N*K2)^.5)*EXP(-(CLM*(1+K2)-N)^2/(2*N*K2))
520 Q30=Q3/((2*PI*N*K3)^.5)*EXP(-(CLM*(1+K3)-N)^2/(2*N*K3))
530 XX=40+470*N/FX
540 PSET(XX,360-320*Q10/FY),5
550 PSET(XX,360-320*Q20/FY),2
560 PSET(XX,360-320*Q30/FY),4
570 NEXT N
580 IF INKEY$="" THEN GOTO 580
590 GOTO 30
600 END

```


Program 3 (1)

```

10 ' ***** Relationship between Position Peak and Exit Peak *****
20 ' (Chromatogram)
30 CLS 3 :CONSOLE ,,0,1 :SCREEN 3 :COLOR 6
40 PRINT "***** Relationship between Position Peak and Exit Peak *****"
50 COLOR 7:PRINT
60 '
70 ' ----- PARAMETERS -----
80 '
90 CLM=6 :N1=4 :N2=50 :FY=.2 :K=1 :Q=1 :CS=3 :CM=4 :ST=1
100 INPUT "Parameter Change (Y/N)";Z$:IF Z$="Y" GOTO 110 ELSE 170
110 PRINT :INPUT "Number of theoretical plates, N( 1 - ab. 50 )";CLM :PRINT
120 PRINT "Range of Step-by-step Presentation (from n1 to n2 )"
130 INPUT " n1 ( 0 - smaller than N )";N1
140 INPUT " n2 ( 50, 100, 150 or 200 etc. larger than N )";N2
150 PRINT :INPUT "Full Scale of Y-axis ( 0.1, 0.2, 0.25, 0.5, 1 etc.)";FY
160 PRINT :INPUT "k'( ab. 0.2 -10 )";K
170 FX=N2 :KS=K/(K+1) :KM=1/(K+1)
180 CLS 3
190 ' ----- PRESENTATION OF THE BACKGROUND -----
200 '
210 LINE(40,40)-(40,360) :LINE(40,360)-(510,360)
220 X1=40+470*(CLM-1)/FX
230 LINE(40,39)-(X1,39),4
240 LINE(40,40)-(X1,40),4:LINE(X1,40)-(X1,360)
250 FOR I=1 TO 10
260 LINE(40+47*I,40)-(40+47*I,360),7,,&HCCCC
270 LINE(40,360-32*I)-(510,360-32*I),7,,&HCCCC
280 NEXT I
290 COLOR 4:LOCATE 5,1:PRINT "Column"
300 LOCATE 5,2 :PRINT "N=";CLM :COLOR 5
310 LOCATE (6+58.8*(CLM-1)/FX),1:PRINT "Chromatogram":COLOR 7
320 CIRCLE (156+470*(CLM-1)/FX,9),CM,5
330 PAINT (156+470*(CLM-1)/FX,9),5,5
340 LOCATE 2,2 :PRINT "Q" :LOCATE 2,23 :PRINT "0"
350 FOR I=2 TO 6
360 LOCATE 0,27-4*I :PRINT .2*FY*(I-1)
370 NEXT I
380 LOCATE 5,25:PRINT "0 " ;.2*FX;" " ;.4*FX;" " ;.6*FX;"
";.8*FX;" " ;FX;"n"
390 LOCATE 66,3 :PRINT "k'=S/M=";K
400 CIRCLE(530,122),CS,2
410 LOCATE 69,7 :PRINT "Stationary" :LOCATE 69,8 :PRINT "Phase"
420 CIRCLE(530,170),CM,5
430 LOCATE 69,10 :PRINT "Mobile" :LOCATE 69,11 :PRINT "Phase"
440 LOCATE 67,15 :PRINT "If Stopped" :LOCATE 67,16 :PRINT "Hit"
450 LOCATE 67,17 :PRINT "Space Key !"
460 '
470 ' ----- CALCULATION -----
480 FOR N=N1 TO N2 STEP ST
490 Q0=Q*KS^N
500 IF N>CLM-1 GOTO 520

```

Program 3 (2)

```

510  NO=N :GOTO 530
520  NO=CLM-1
530  FOR X=0 TO NO
540    IF X=0 GOTO 560
550    Q0=Q0*(N-X+1)/(X*K)
560    QS=Q0*KS:QM=Q0*KM
570    CIRCLE(40+470*X/FX,360-320*QS/FY),CS,2
580    CIRCLE(40+470*X/FX,360-320*QM/FY),CM,5
590  NEXT X
600  IF INKEY$="" THEN GOTO 600
610  IF N=N2 GOTO 1000
620  Q0=Q*KS^N
630  IF N>CLM-1 GOTO 650
640  NO=N :GOTO 660
650  NO=CLM-1
660  FOR X=0 TO NO
670    IF X=0 GOTO 690
680    Q0=Q0*(N-X+1)/(X*K)
690    QM=Q0*KM
700    CIRCLE(40+470*X/FX,360-320*QM/FY),CM,0
710  NEXT X
720  Q0=Q*KS^N
730  IF N>CLM-1 GOTO 750
740  NO=N :GOTO 760
750  NO=CLM-1
760  FOR X=0 TO NO
770    IF X=0 GOTO 790
780    Q0=Q0*(N-X+1)/(X*K)
790    QM=Q0*KM
800    IF X=(CLM-1) GOTO 820
810    CIRCLE(40+470*(X+1)/FX,360-320*QM/FY),CM,5
820  NEXT X
830  IF N<CLM-1 GOTO 860
840  CIRCLE(40+470*(N+1)/FX,360-320*QM/FY),CM,5
850  PAINT(40+470*(N+1)/FX,360-320*QM/FY),5,5
860  IF INKEY$="" THEN GOTO 860
870  Q0=Q*KS^N
880  IF N>CLM-1 GOTO 900
890  NO=N :GOTO 910
900  NO=CLM-1
910  FOR X=0 TO NO
920    IF X=0 GOTO 940
930    Q0=Q0*(N-X+1)/(X*K)
940    QS=Q0*KS:QM=Q0*KM
950    CIRCLE(40+470*X/FX,360-320*QS/FY),CS,0
960    IF X=(CLM-1) GOTO 980
970    CIRCLE(40+470*(X+1)/FX,360-320*QM/FY),CM,0
980  NEXT X
990 NEXT N
1000 END

```

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