CONTINUOUS CONCENTRATION OF SINGLE COMPONENT USING AN ANNULAR CHROMATOGRAPH

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A continuous rotating annular chromatograph with rotating inlet and outlet can be used to concentrate a single component by the technique of cycling zone adsorption.

To evaluate the performance of this system, an amino acid (valine) was chosen as the solute and a cation exchange resin as the adsorbent. The adsorption force of valine on the cation exchange resin in the eluent (pH = 4.4 or 7.6) became much weaker than that in the feed (pH = 3.4).

Experimental elution curves were in good agreement with numerical solutions. The two concentration profiles at steady state agreed very well with each other for 8 and 48 hours after starting the operation of the device. When products were collected over a long period, concentrated products with six times the feed concentration could steadily be obtained.

Cycling zone adsorption was first proposed by Pigford *et al.*[6] as a method for concentrating solutes from a feed which was fed continuously to an adsorption column. Cyclic changes in concentrations were produced in a fluid which flowed through a fixed bed due to temperature cycling of the bed. Beaumont *et al.*[1] concentrated a single component of protein (bovine serum albumin or lysozyme) using Cibacron Blue Sepharose CL-6B as adsorbent. The cyclic change of ion strength by potassium chloride was used to concentrate a protein.

Dore *et al.*[3] extended this system to multicomponent separations. Glucose and fructose were separated by cycling feeds with pH values of 8.5, 7.0 and 5.0. DBAE-cellulose was selected as adsorbent. Both glucose and fructose were adsorbed at the highest pH (= 8.5) and desorbed at the lowest pH (= 5.0). At the middle pH (= 7.0), fructose was more strongly adsorbed than glucose. Then glucose could be concentrated at pH = 7.0 and fructose at pH = 5.0.

However, the operation of cycling zone adsorption is periodic and discontinuous. The products should be collected at regular intervals. In this study, cycling zone adsorption is applied to a continuous rotating chromatograph to concentrate a single component.

A continuous rotating chromatograph has been developed for preparative separations. Begovich *et al*[2] operated a rotating annular chromatograph to separate several metal ions. Their device has a rotating annular bed with stationary feed stream and product collection ports. In our previous papers,[4,9] a continuous rotating annular chromatograh (abbrevi-

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ated as CRAC) with rotating feed nozzle and product collectors was proposed. It is the opposite type to that of Begovich *et al.*[2] Sodium chloride and methanol were separated by action of ion exclusion and three amino acids (aspartic acid, glutamic acid and glycine) were separated by the difference of adsorption force using the CRAC. Also, a CRAC with two nozzles was used for non-isocratic elution as reported in the previous paper[7]. Three amino acids (glutamic acid, glycine and valine) could be separated. In the case of isocratic elution, one amino acid (valine) was eluated very late and overlapped with the others (glutamic acid and glycine). For non-isocratic elution, valine appeared earlier and the three amino acids were separated very well.

However, the concentrations at the exit were always lower than those at the feed in the previous works and the products could not be concentrated.

In this work, a single component is concentrated continuously. The principle of the concentrating operation using CRAC is shown schematically in **Fig. 1.** Feed solution containing a dilute solute is supplied into the whole annulus and an eluent fluid is introduced through rotating nozzles. The products are collected by collectors which rotate at the same angular speed as the nozzles. For the feed solution in the annular bed, a feed flow zone is formed and the adsorbent is saturated with solute from the top of the annular bed as shown in Region A of Fig. 1. In this zone, the adsorption force of solute is very strong. On the other hand, when the eluent fluid is introduced from rotating nozzles an eluent flow zone appeares. The adsorption force of solute is weakened in this zone. The solute on the adsorbent is transferred to the eluent fluid at the front of the eluent flow zone and moved down to the exit. Then one dilute component in the feed can be concentrated as shown in Region D of Fig. 1. Contrarily, no solutes are contained in Regions B and C of Fig. 1 for either feed or eluent flow zone.

Valine, a typical amino acid, is chosen as the solute and a strong cation exchange resin is used as an adsorbent. The adsorption force of valine on cation exchange resin is strongly dependent on pH. Therefore, by changing pH in the eluent the amino acid can be concentrated by this method.

1. Theory

Equations (1)–(5) in the previous paper[4] can be used for the operation of concentrating one component in CRAC. In this work, zero in angular coordinate indicates the leading point to introduce the eluent in which a solute is not included and the angular distance of eluent injection, θ_E, is expressed by $2\pi Q_E/(Q_E+Q_F)$. Feed solution containing a solute is introduced everywhere else.

Then Eqs. (6)–(7) in boundary conditions should

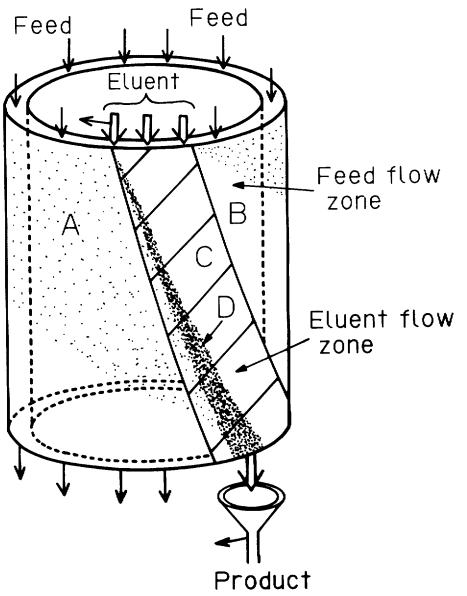


Fig. 1. Principle of continuous concentration using rotating annular chromatograph (CRAC)
Region A: Saturated solute in the feed flow zone
Region B: No solute in the feed flow zone
Region C: No solute in the eluent flow zone
Region D: Concentrated solute in the eluent flow zone

be replaced by the following equations.

$$C=0 \quad \text{at} \quad z=0, \qquad 0<\theta<\theta_E \tag{6}'$$

$$C=C_0 \quad \text{at} \quad z=0, \qquad \theta_E<\theta<2\pi \tag{7}'$$

In the case of linear equilibrium relation, the following equations may be given.

$$\bar{C}=K_f C \text{ in the feed flow zone} \tag{8a}'$$

$$\bar{C}=K_e C \text{ in the eluent flow zone} \tag{8b}'$$

where K_e should be nearly zero or much smaller than K_f.

It is assumed that the angular distance of the eluent flow zone in Fig. 1 is constant at any axial coordinate. Then the eluent flow zone is expressed by

$$\theta_D(z)<\theta<\theta_D(z)+\theta_E \quad \text{at} \quad z>0 \tag{9}$$

where the angular delay θ_D (z) is a function of axial coordinate from the top of the bed and is given by $\omega z\varepsilon_B/u$. The feed flow zone is the whole annular bed except for the eluent flow zone.

Numerical solutions were obtained by the orthogonal collocation method.

2. Experimental

2.1 Apparatus

The continuous chromatographic apparatus for the concentrating operation is shown in **Fig. 2.** This is the same as in our previous paper[4] except for the exchange of feed inlet and eluent inlet. The feed solution containing a dilute solute was supplied everywhere in

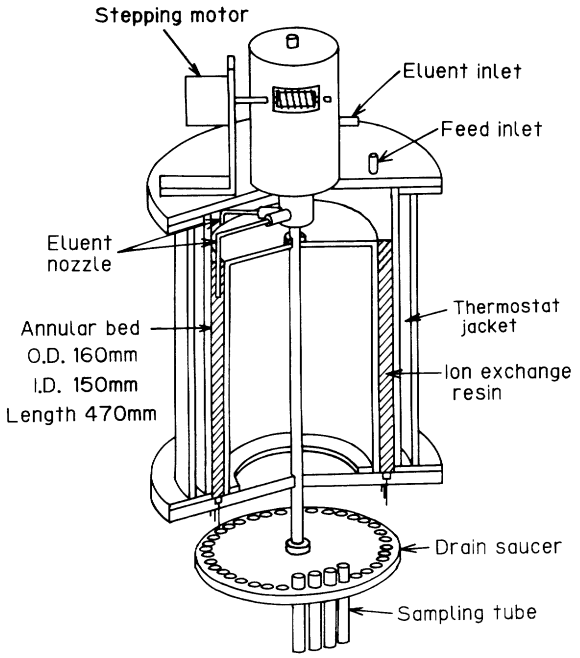


Fig. 2. Continuous rotating annular chromatographic apparatus

the top of the annular bed and the eluent was introduced through two nozzles immersed 45 mm below the top of the fixed bed. Two nozzles were used to avoid the overflow of eluent and its mixing with the feed. The angular distance between the two nozzles was 45 degrees. However, only one nozzle was used when the rate of eluent was low.

The system of products collection shown in Fig. 2 was used to determine the experimental concentration profiles at the bottom of the bed. This device consisted of 60 evenly spaced sampling tubes of 1.5×10^{-6} m^3 on the drain saucer. After steady state was reached the sampling tubes were settled and concentrations of the solution in the tubes were measured. The lower part of the apparatus in Fig. 2 of the previous paper[4] showed the device for continuous product collection.

2.2 Operation

The cation exchange resin Dowex 50W-X8 in the sodium form was packed to a depth of 470 mm. The resin was sieved in the eluent and a portion of average diameter 0.070 mm was adopted. The void fraction in the bed ε_B was 0.374. In this work, 0.1 M sodium citrate buffer solutions was used. A buffer solution of low pH (=3.4) was used as feed solution and one of high pH (=4.4 or 7.6) was used as the eluent.

The feed concentration of valine, C_0, was adjusted to 5.0 mol/m^3. The temperature of the annular bed was held at 303 K by circulating water into the jacket. The exit concentrations of valine were measured by UV-meter (Simadzu Co. Ltd) using the ninhydrin method. The exit pH values were measured by a Compact pH Meter (Horiba Co. Ltd).

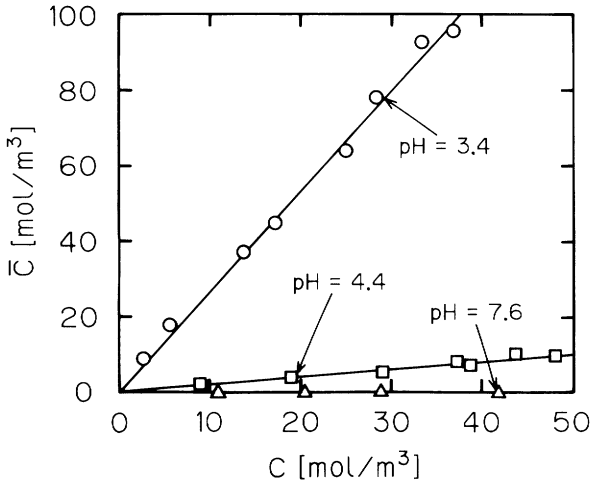


Fig. 3. Adsorption isotherms of valine at 303 K

Table 1. Values of parameter at 303 K

K at pH 3.4	[—]	2.64
K at pH 4.4	[—]	0.211
K at pH 7.6	[—]	0
$\bar{D} \times 10^{11}$	[m^2/s]	3.58
Pe	[—]	0.133

3. Results and Discussion

3.1 Adsorption isotherms and kinetic parameters

Adsorption isotherms were measured in buffer solutions at three levels of pH ($\pm$3.4, 4.4 and 7.6) by a batch method. **Figure 3** shows adsorption isotherms of valine on the strong cation exchange resin Dowex 50W-X8 in the sodium form at 303 K. Since the data are on straight lines through the origin, the adsorption isotherms are linear. From the slopes, the equilibrium constrants, K, could be calculated at pH = 3.4 and pH = 4.4. However, valine in the buffer solution with pH 7.6 was not adsorbed on the ion exchange resin and thus K was nearly zero. The values of K at pH = 4.4 was much sampller than that at pH 3.4, and buffer solutions with pH = 4.4 and 7.6 could be used as eluents to desorb valine, which was adsorbed in the solution with pH = 3.4.

By the moment method described in the previous papers,[5,8] the values of intraparticle duffusivity, $\bar{D}$, and Peclet number, Pe, were obtained only from data at pH = 3.4 because adsorption capacities at pH = 4.4 or 7.6 were too small to determine these value. The Pe of valine was assumed to be independent of the flow rate because the particle Reynolds number was less than 0.5 this work.

The equilibrium constants and kinetic parameters are listed in **Table 1.**

3.2 Comparison between experimental and calculated elution curves

The experimental conditions in this work are summarized in **Table 2.** **Figures 4–8** show both profiles

Table 2. Experimental conditions in CRAC

Run No.	Feed rate $Q_F \times 10^7$ [m³/s]	Eluent rate $Q_E \times 10^8$ [m³/s]	Number of nozzles	Rotating speed ω [deg/s]	pH of eluent
1	4.7	12.0	2	0.060	4.4
2	4.7	12.0	2	0.090	4.4
3	4.7	12.0	2	0.132	4.4
4	4.7	6.0	1	0.090	7.6
5	3.0	5.8	1	0.045	7.6

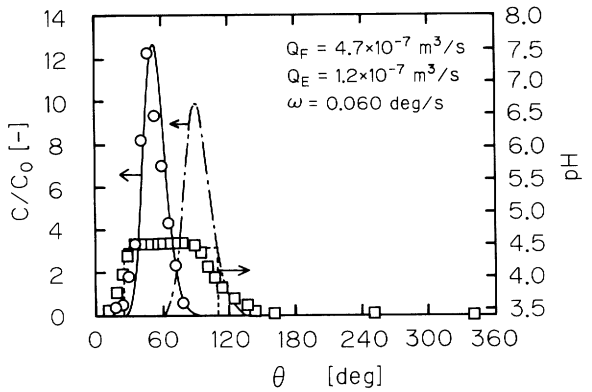


Fig. 4. Elution curves in CRAC for Run No. 1

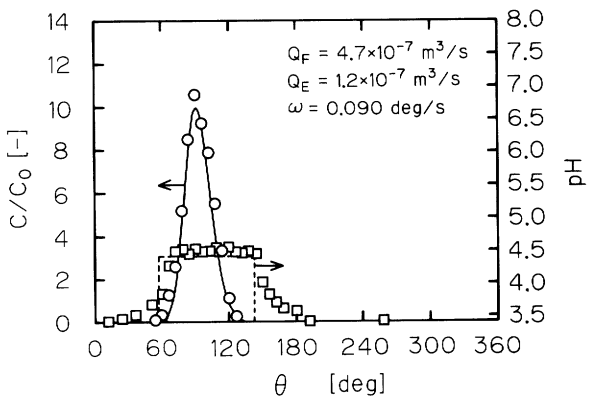


Fig. 5. Elution curves in CRAC for Run No. 2

of valine concentration and pH for each run in Table 2.

Square marks in these figures are experimental values of pH at the exit. The thick dotted lines are rectangular profiles of pH calculated from Eq. (9) for the eluent flow zone.

The experimental profiles become broader than ideal profiles. This difference may be explained as follows. The sudden change of pH between feed and eluent at the top of the bed might be buffered by the reaction of ion exchange between Na^+ and H^+ on the ion exchange resin in the annular bed.

The ratios of experimental concentrations of valine at the exit to the feed concentration are indicated by circles. Valine could not be detected at the exit in angular ranges of low pH (=3.4). This means that Region A of valine did not appear at the bottom of the annular bed as illustrated in Fig. 1.

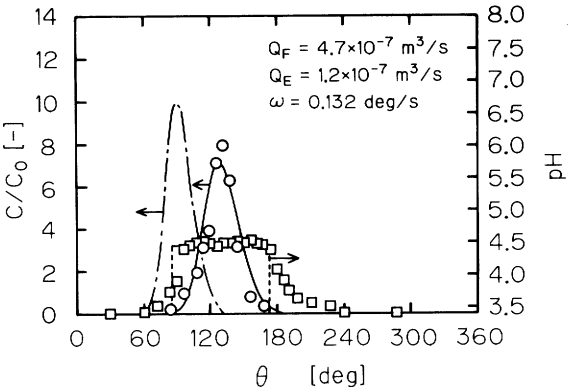


Fig. 6. Elution curves in CRAC for Run No. 3

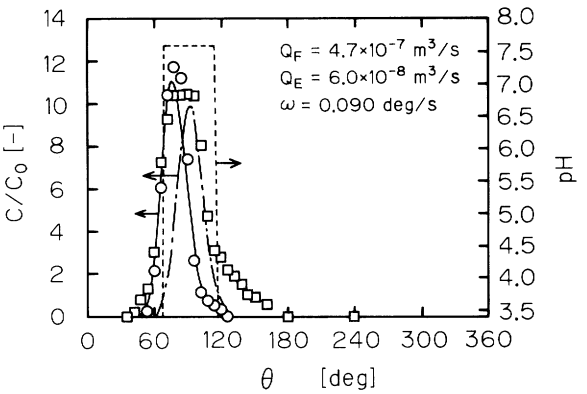


Fig. 7. Elution curves in CRAC for Run No. 4

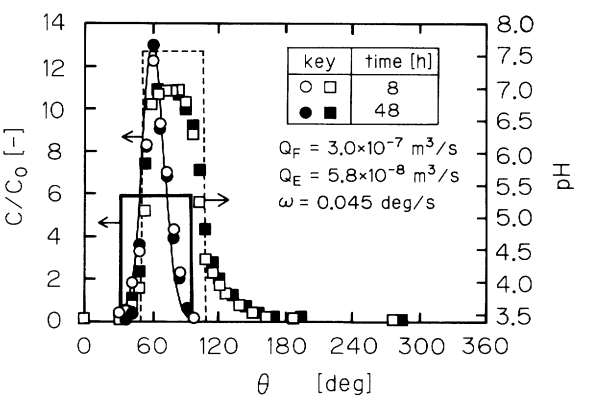


Fig. 8. Elution curves in CRAC for Run No. 5

The solid lines in these figures are numerical solutions calculated from theory in Section 1. The equilibrium constants and kinetic parameters in Table 1 were used to obtain numerical solutions. The values of k_f were calculated from a correlation.[10]

The agreement between experimental results and numerical solutions is excellent in Figs. 4–8.

The dot-dash lines in Figs. 4–7 illustrate the calculated results of valine concentration profiles for Run No. 2 as the standard condition with which the results of other conditions were compared.

3.3 Effect of rotating speed

As shown in Figs. 4, 5 and 6 (Runs No. 1, 2 and 3 in Table 2), the rotating speed, ω, is varied from

0.060 to 0.132 deg/s, while the feed rate, Q_F, and the eluent rate, Q_E, and kept constant. As the rotating speed is increased, the peak position of valine appears later, the maximum concentration becomes lower, and the bandwidth becomes wider.

Therefore, the rotating speed should be decreased to recover a higher concentration of valine and to save power. However, if the rotating speed is too small, the eluent flow zone may not be formed effectively. There is thus a lower limit of rotating speed to form the eluent flow zone. In this work, it was about 0.03 deg/s.

3.4 Effect of pH

The value of pH in the eluent for Run No. 4 increased from 4.4 (the standard condition) to 7.6 as shown in Fig. 7 and the eluent rate was decreased by half the standard contition (Run No. 2), while Q_F and ω were identical. Since the eluent rate was low, a single nozzle was enough to pass down the eluent.

Figure 7 shows a very sharp peak of valine, and the maximum concentration at the exit becomes about 12 times the feed concentration.

Although the value of pH at the top of bed changed from 3.4 (in the feed) to 7.6 (in the eluent), the maximum pH at the bottom was 6.8 in the eluent flow zone and the experimental profile of pH was very different from the ideal one as indicated by the thick dotted line in Fig. 7. This may be due to the buffer interaction to the sudden change of pH from 3.4 to 7.6 on the ion exchange resin.

The leading part in the peak of valine was almost overlapped with that in the peak of pH. This means that the driving force for desorption is strong and valine can be desorbed rapidly with increase in pH. A sharp peak of valine could then be obtained although the eluent rate was half the standard condition.

When the eluent of pH = 4.4 is used, the eluent rate has to be increased to form the eluent flow zone effectively. However, when Q_E increased over a certain limit (about 9.0×10^{-8} m^3/s through one nozzle in this case), the eluent could not flow down the column. In such cases, most parts of the eluent rose upward from the nozzle and mixed with the feed over the top of the bed as indicated in the previous paper.[7] Then it is required to increase the number of nozzles. But using the eluent of pH = 7.6, the number of nozzles could be decreased.

Therefore, pH in the eluent should be as high as possible in this case.

3.5 Elution curves over a long period

From experimental results where each operating condition was changed, the optimum conditions were found to be slower rotating speed, lower feed rate and higher pH in the eluent. Also, one nozzle was enough to pass down the eluent due to the lower flow rate.

Operation at optimum conditions (Run No. 5 in Table 2) continued for more than two days to check the time deviation.

Figure 8 shows both profiles of valine concentration and pH at both 8 and 48 hours after starting operation of the device. It is seen from the excellent agreement between the two periods that the operation is stable and the adsorption capacity of valine does not change with time.

The peak of valine was very sharp and the maximum concentration at the exit was about 13 times the feed concentration. The numercal solution (thin solid line in Fig. 8) agrees with the experimental elution curve.

To obtain the concentrated product for practical purposes, a portion of peak was continuously collected by a funnel as shown in Fig. 1.

The rectangular thick solid line in Fig. 8 indicates the average concentration of valine collected between 35 and 95 degrees from the feed nozzle. The concentration at the exit did not change with time during two days and was six times the feed solution in any time. The concentration ratio can be calculated from the total angle of the annular bed divided by the angular range of collection (360/60 = 6 in this work) when the solute is not contained in the other angular range.

Conclusion

The continuous rotating annular chromatograph (CRAC), utilizing the cycling zone adsorption technique, was used to concentrate a amino acid (valine).

Experimental elution curves agreed well with numerical solutions.

The optimum conditions were found to be slower rotating speed, lower feed rate and higher pH in the eluent. The average concentration of valine collected at the exit was six times that of the feed solution at the optimum condition.

Acknowledgement

The authors would like to thank Mr. H. Ito for his help in the design of the apparatus.

Nomenclature

C	=	concentration of valine in liquid phase	[mol/m^3]
$\bar{C}$	=	concentration of valine in resin phase	[mol/m^3]
C_0	=	feed concentration	[mol/m^3]
$\bar{D}$	=	intraparticle diffusivity	[m^2/s]
D_L	=	axial dispersion coefficient	[m^2/s]
K	=	adsorption equilibrium constant	[—]
Pe	=	Peclet number ($=2uR_P/\varepsilon_B D_L$)	[—]
Q_E	=	eluent rate	[m^3/s]
Q_F	=	feed rate	[m^3/s]
R_P	=	radius of adsorbent particle	[m]
u	=	superficial velocity	[m/s]
z	=	axial coordinate	[m]

ε_B	=	interparticle void fraction in the bed	[—]
θ	=	angular coordinate	[deg or rad]
ω	=	rotating speed	[deg/s or rad/s]

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