QUANTITATIVE ANALYSIS OF SANDWICHING RECYCLE TECHNIQUE IN PREPARATIVE LINEAR CHROMATOGRAPHY

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A new recycling technique named “Sandwiching recycle” is investigated, and its effectiveness in obtaining high recovery yields of the desired component from a multicomponent mixture by means of chromatographic separation is examined. This technique hinders the product from diffusion in such a way that the feed period is sandwiched in between the recycle periods. It is found that sandwiching recycle chromatography is highly effective to increase the yield of the component whose mean retention time is equivalent to its switching time, but that this recycling does not increase the yield of the impure component in the product. Because of the simpleness of its apparatus, this technique can be used for preparative scale separation of mixtures. Detailed features of the recycling method are examined by simulation to recognize what conditions should be taken into consideration to separate the target component from a mixture and to obtain high yield.

Introduction

Recycling of partially separated components is a matter of great concern in liquid chromatography to obtain a sufficiently high yield of products. Several concepts have been proposed (R.M. Nicoud and M. Bailly, 1992) to overcome the difficulties raised by the conventional methods. Crary et al. (1989) paid attention to reinjecting the impure fractions. Bailly and Tondeur (1982) carried out recycling by mixing a certain amount of fresh feed with less purified fractions.

Seko et al. (1982) could increase the concentration of p-Xylene with implementation of a partial recycling process. Heikkila (1983) studied the separation of sugar and amino acids using recycling chromatographic methods. Both of them recycled the impure fraction either together with feed or in between them.

Coq et al. (1981) compared recycling and successive injection techniques for the separation of equimolar binary mixtures and came to a conclusion that the volume of injection could be increased through recycling to yield more products. Their chromatograph was also called a closed-loop or direct pumping type. They have been used originally in the field of gel-permeation chromatography. During recycling, no injection of fresh feed is given.

1. The Sandwiching Recycle Scheme

Suppose that our objective is to separate diethyl phthalate (B) which is the middle component of a three-component system containing di-n-butyl phthalate (A) and dimethyl phthalate (C). Their distribution coefficients and capacity coefficients have been obtained experimentally as shown in Table 1 (Hatanaka and Ishida, 1992). In the present study we assumed that the column was of 40 cm length and that the superficial velocity of the liquid in the column is 10 cm/min. A mixture of hexane and ethyl acetate at a volumetric ratio of 3:2 was considered as an eluent. The column had 400 theoretical plates.

We have examined the effect of the proposed sandwiching recycle by simulation. The equations used in this study are summarized in Table 2, where linear adsorption isotherms were applied as a first-step approximation. These equations are the same as those used in the previous paper (Hatanaka and Ishida, 1992) and it was confirmed that the simulated results agreed with the experimental results quite satisfactorily.

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2. Effect of Sandwiching Recycle for the Target Component

2.1 A typical result

Figure 2 shows a typical example result when we feed only the middle (i.e., target) component B. The concentration of B at the inlet of the column changes as shown in (a), while that at the outlet changes as shown in (b). It is assumed that only eluent is filled in the column.

Step 1. Recycle before feed: The outlet flow shown in (b) is recycled at a constant flow rate during this period. At present, the outlet flow is only eluent.

Step 2. Feed injection and product collection: The feed mixture is injected as a rectangular pulse through a six-port valve into the column, as shown in (a).

Step 3. Recycle after feed: Then the outlet flow shown in (b) is recycled. At this stage, the outlet flow is still only eluent.

Step 4. Eluent flow and withdrawal of waste components: Fresh eluent is supplied into the column. During this eluent supply, the outlet flow in (b) is discharged as waste, as shown in Fig. 1.

These steps are repeated. The time required for a series of these steps is called the switching time $T_s$. This time, $T_s=245$ s, is chosen as the mean retention time of the target component B so that we can obtain a peak in the outlet flow at the middle of the feed period.

Now the second iteration cycle starts:

Step 1. Recycle before feed: This 1st-cycle outlet fraction in step 1 in Fig. 2(b) contains the target component to a considerable extent so it is recycled before the feed pulse as the 2nd-cycle inlet fraction as shown in (a).

Step 2. Feed injection and product collection: The feed mixture is injected into the column as a rectangular pulse in a similar way as in the first cycle. During this period, the outlet flow is collected as the 1st-cycle product, as shown in (c). Thus, in the proposed mode, the feed period is the same as the product collection period. Hence a single six-port valve can be used for both the feed injection and the product collection, as shown in Fig. 1.

Step 3. Recycle after feed: As can be seen from the 1st-cycle outlet concentration profile in (b), the fraction eluted after the product contains considerable amounts of the target component. This fraction is recycled as the 2nd-cycle inlet fraction after the feed pulse.

Step 4. Eluent flow and withdrawal of waste components: The outlet flow that contains the target component at very small concentrations is discharged as waste, and during this waste discharge period, new eluent is supplied into the column. Since the waste discharge period is the same as the eluent supply period, a single six-port valve can be applied for both the waste discharge and the eluent supply, as shown in Fig. 1.

When we look at Fig. 2(c), the concentration of the target component in the product can be increased.
Fig. 3 Quantitative effect in yield with the variation in feed width

tremendously at each successive cycle. This increase is caused by recycling the effluent which contains the target component at high concentration before and after the feed period. By this sandwiching recycle, the spreading of feed pulse by diffusion is hindered, giving rise to the extremely high concentration of the target component in the product.

After the 15th iteration, the concentration profiles reach a steady state, meaning that the increase in the concentration is not observed any more. In addition, the target component which cannot be recovered as product is lost as waste in the waste period.

2.2 Effect of feed period

The increase of yield, i.e., the ratio of the quantity of the obtained target component in the product to that in the feed, can be seen quantitatively in Fig. 3. The abscissa indicates the feed period, $T_f$. It is found that recycling is greatly effective for small as well as large feed width, $T_l$. For lower feed width, increases of more than six fold on its yield are observed. When $T_l$ is 44.0 s (i.e., the case in Fig. 2), the yield without the recycle is 0.744. It is increased to 0.926 at the 15th iteration cycle, nearly reaching the steady state.

2.3 Effect of switching time $T_s$

Figure 4 shows the yields when the switching time $T_s$ is varied from 207 s to 283 s by specifying the target component. The mean retention time of the target component B is 245 s. Also, the values of $T_{t1}$, $T_l$, and $T_{t2}$ are retained. It can be observed that the sandwiching recycle is most significant when $T_s$ is equal to the mean retention time of the target component, i.e., 245 s. Hence, at this switching time, the peak of the target component appears at the middle of the product period as shown in Fig. 2(c).

When the time is measured from the center of the feed period, the product period starts at $T_s-\left(T_l/2\right)$ and ends at $T_s+(T_l/2)$. For $T_s=245$ s and $T_l=44.0$ s, the former is 223 s and the latter is 267 s. When the switching time $T_s$ is chosen at 223 s or 267 s by keeping the retention time of the target component at 245 s, the yield is 0.5 and the sandwiching recycle has no more effect on the increase of the yield. A chromatogram corresponding to $T_{t1}=267$ s is demonstrated in Fig. 5. Figure 5(a) illustrates the feed input as well as inlet concentration profile of the recycled fraction, while (b) represents the outlet concentration profile and (c) is the concentration profile of products collected. For this switching time the peak of the target component appears at the front edge of the product period as shown in (c). Then, the yield is 0.5 and the effect of recycling is insignificantly small. The other half is discharged in the waste period, as shown in (b).

This fact is quite important. It suggests that recycling which can increase the concentration of the target component will not increase the concentration of impure components where their mean retention time is not located in the product period. This will be demonstrated later by considering three components simultaneously.

Further, we have examined the switching effect for the case in which the feed period is doubled, and the result is given in Fig. 6. There is no doubt that the yield is increasing with longer feed period. Also for this case, the yield becomes highest and the most significant effect of the sandwiching recycle is observed when the switching time is equal to the mean retention time of the target component. The yield becomes 0.5 when the switching time $T_s$ is chosen so
that the peak of the target component appears at the edge of the product period. These results show that proper selection of the switching time is quite important.

3. Effect of Impure Components

3.1 A typical example result

Figure 7 is the chromatogram of a three component mixture from which we could separate the middle component of interest. It gives us a clear picture not only regarding the separation of the target component, but also provides information about the possible ways of contamination of impurities in the product.

The rectangular feed input contains A, B and C mentioned in Table 1 with the same concentration. The broken (or dash-dotted) line, the solid line, and the dotted line show the profiles of the less-adsorbed component A, the target component B and component C, respectively. For this rectangular pulse feed for the 1st cycle in Fig. 7(a), the peak of A comes out first, followed by B, and then C, as shown Fig. 7(b).

The switching time, $T_s=245$ s, is chosen as the mean retention time of the target component B. The fractions before and after the product period are recycled. For the target component B, the composite inlet profile in (a) has only a single peak for each cycle. On the other hand, the less-adsorbed component A has a peak in the recycle period before feed and a rectangular pulse in the feed period. Similarly the more adsorbed component C also has the same kind of pulse in the feed period and a peak in the recycle period after feed. Such double peaks of impure components in the inlet stream leads to the same double peaks in the outlet stream too, as shown in (b). This chromatogram clearly shows that the sandwiching recycle increases the yield of the target component significantly but it has an insignificantly small effect on the impurity components. This is the important advantage of the sandwiching recycle.
Fig. 8 Effect of feed period on impurities, $T_i = 245 \text{ s}$, $T_{r1} = T_{r2} = 52.3 \text{ s}$

For this case, the yield of the target component B is increased to 0.926, as demonstrated in Fig. 2.

3.2 Effect of feed period

The extent of impurities in the product and the effect of the feed width on it at the steady state are shown in Fig. 8. When the feed period is 44.0 s, the impurity, i.e., $A/(A+B+C)$ or $C/(A+B+C)$, is less than 0.02 for both the less- and more-adsorbed components.

When high levels of impurities are present, a smaller feed width should be chosen, giving rise to the decrease in productivity, i.e., the decrease in the amount of feed in the switching period. On the other hand, for mild purity requirements, larger feed widths can be used, increasing the productivity. Hence, the width of the feed period is determined mainly by the requirement on the impurities.

3.3 Effect of recycle period from the impurities viewpoint

Figure 9 illustrates the effect of the recycle periods at the steady state from the viewpoint of impurities. When the recycle periods are short, the impurity is limited. However, after $T_{t1} + T_{r2} = 104.6 \text{ s}$, impurities caused by the more-adsorbed component begin to increase significantly. After $T_{t1} + T_{r2} = 120 \text{ s}$, the impurity of the less-adsorbed component also increases.

A typical chromatogram for a larger recycle period, say at $T_{t1} + T_{r2} = 167 \text{ s}$, is shown in Fig. 10. Let us look first at the 1st cycle. For a rectangular feed input in (a), we obtain a single peak of each component shown in (b). The inlet stream in the 2nd cycle has two peaks for the impure components as stated earlier in 3.1. Then look at the 15th cycle. To be noted is the fact that the more adsorbed component (C) appears in the recycle before feed and that the less adsorbed component (A) appears in the recycle after feed. These fractions are of course unfavorable and increase the impurities in the

Fig. 9 Effect of recycle period from the viewpoint of impurities, $T_i = 245 \text{ s}$ and $T_r = 44.0 \text{ s}$

A typical chromatogram for a larger recycle period, say at $T_{t1} + T_{r2} = 167 \text{ s}$, is shown in Fig. 10. Let us look first at the 1st cycle. For a rectangular feed input in (a), we obtain a single peak of each component shown in (b). The inlet stream in the 2nd cycle has two peaks for the impure components as stated earlier in 3.1. Then look at the 15th cycle. To be noted is the fact that the more adsorbed component (C) appears in the recycle before feed and that the less adsorbed component (A) appears in the recycle after feed. These fractions are of course unfavorable and increase the impurities in the

product. This is caused by too long a recycle period, in other words, too short a waste period, because the impure components must be discharged during the waste period.

4. Overall Consideration of Sandwiching Recycle Process

A collective effect due to recycle periods for the feed pulse of 44 s on yield at the steady state is shown
Conclusion

An effective sandwiching recycle technique with two six-port valves has been proposed for separation of the middle component from a multicomponent system with the following conclusions:

1. Sandwiching Recycle is most effective for the component of which mean retention time is equal to the switching time. Hence, a proper selection of the switching time is required.
2. The proper selection of feed period should be done based on the purity requirement, i.e., the leakage of impure components.
3. The proper selection of recycle period is made so that additional impurities are caused by recycling.
4. Sandwiching recycle can reduce the consumption of eluent significantly.

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Nomenclature

- $a_r$ = specific surface area [m$^2$/m$^3$ bed]
- $C$ = concentration in the mobile phase [mol/m$^3$]
- $C^*$ = concentration in equilibrium with the stationary phase [mol/m$^3$]
- $K_f$ = overall mass transfer coefficient [m/s]
- $m$ = distribution coefficient [-]
- $T_t$ = feed period [s]
- $T_{t1}$ = recycle before feed [s]
- $T_{t2}$ = recycle after feed [s]
- $T_i$ = switching period [s]
- $T_w$ = waste discharge period [s]

Literature Cited


