

Continuous separation of lanthanides by counter-current fractional extraction

TOSHIFUMI TAKEUCHI^a and YOZO KABASAWA*

Department of Pharmacy, College of Science and Technology, Nihon University, 8 Kanda Surugadai 1-chome, Chiyoda-Ku, Tokyo 101 (Japan)

and

TAKENORI TANIMURA

Laboratory of Analytical Chemistry, Toyama Medical and Pharmaceutical University, 2630 Sugitani, Toyama 930-01 (Japan)

ABSTRACT

The application of a dual counter-current system which involves counter-current fractional extraction with continuous sample feeding is described for the separation of lanthanides. The separation of two model mixtures of samarium and gadolinium and of europium and gadolinium demonstrates the utility of the system. In addition, the column efficiency was determined.

INTRODUCTION

Various types of counter-current chromatography (CCC) have been developed and illustrated for the separation of both organic and inorganic compounds including biological samples and natural products [1]. Most of these techniques, however, involve a one-way elution mode, *i.e.*, one phase of a two-phase system proceeds through a column and the other phase is held stationary. In contrast, if the two phases could be continuously and simultaneously moved in opposite directions, then the system would allow for continuous introduction of the sample. Because CCC does not require a solid support, such a two-solvent counter-current extraction might easily be performed if a suitable column configuration could be devised.

Several dual countercurrent systems have been reported. For example, Ito [2] reported a dual counter-current system based on a foam separation method, which utilized a combined horizontal flow-through coil planet centrifuge with a liquid phase containing surfactant and a gas phase of nitrogen. The system was illustrated for two model mixtures of Rhodamine B–Evans blue and bovine serum albumin–sheep hae-

* Present address: Hawaii Biosensor Laboratory, Department of Chemistry, University of Hawaii at Manoa, 2545 The Mall, Honolulu, HI 96822, U.S.A.

moglobin. Kabasawa [3] reported on a continuous counter-current extraction system termed counter-current fractional extraction with continuous sample feeding (CFE). Fig. 1 shows a schematic diagram of the CFE method. The columns used in CFE are similar to those in rotation locular counter-current chromatography [4], which is segmented by a series of disks with a small hole in each disk. The columns are filled with the two phases, then held at an inclined position and rotated about its longitudinal axis. The lower phase is pumped down to the lower exit and simultaneously the upper phase is forced up the column toward the upper exit. The sample is fed continuously into the middle between the two columns. Recently, DL-valine could be completely separated into its two enantiomers by this device with an *n*-butanol–water system containing a copper(II) complex of *n*-dodecyl-L-hydroxyproline [5].

In this paper, we describe an application of CFE to the laboratory-scale separation of lanthanides. The capability of CFE is demonstrated for the separation of samarium (Sm) and gadolinium (Gd), and of Gd and europium (Eu) utilizing two-phase systems of dilute nitric acid and *n*-hexane containing di(ethylhexyl)phosphoric acid (DEHPA) as the extractant. The column efficiency is determined from the experimental data in conjunction with the theoretical equations of discontinuous dual counter-current distribution processes [6] such as counter double current distribution [7].

EXPERIMENTAL

Materials

Samarium chloride, europium chloride, gadolinium chloride, 2-hydroxyisobutyric acid and di(2-ethylhexyl)phosphoric acid were purchased from Tokyo Kasei (Tokyo, Japan) and were used without further purification. All other chemicals were of analytical-reagent grade and obtained from commercial sources.

Preparation of two-phase system

Equal volumes of *n*-hexane containing 0.5 M DEHPA and 0.55–0.8 M nitric acid were placed in a separating funnel and shaken vigorously. After the mixture was

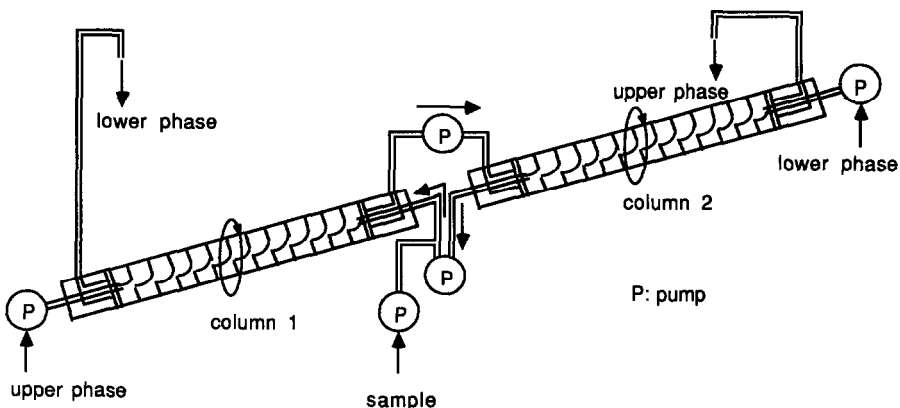


Fig. 1. Schematic diagram of CFE.

separated into two stable phases, these upper and lower phases were used in the following experiments.

Measurement of distribution ratios of lanthanides

The lower phase (2.5 ml) containing lanthanides (1 mM for each lanthanide) was agitated with the same volume of the upper phase for 2 min using a vortex mixer. After the phase separation, the lanthanides were determined by high-performance liquid chromatography (HPLC).

HPLC for the determination of lanthanides

A thermostated stainless-steel column (50 cm × 4 mm I.D.) packed with the ion-exchange resin IEX 215 (Tosoh, Japan) was employed. For the separation of Gd and Sm, the column temperature was adjusted to 45°C and 0.25 M 2-hydroxyisobutyric acid (pH 4.5) was used as the eluent. For the separation of Gd and Eu, 0.2 M 2-hydroxyisobutyric acid (pH 4.5) was used at 55°C. The eluent was pumped at 0.4 ml/min with a Kyowa (Japan) minipump. Samples (5 μl) were injected with a Tokyo Rikakikai Model 5010 injector. Lanthanides were detected by post-column derivatization with 0.1 mM 4-(2-pyridylazo)resorcinol dissolved in 3 M ammonium acetate (pH 10), which was fed at 0.8 ml/min by the same pump as that for the eluent. The absorbance was measured at 540 nm with a Uvidec-100-IV UV-VIS detector with a 16-μl flow-through cell (Jasco, Japan) and the data were recorded with a D-2000 data processor (Hitachi, Japan).

CFE

Five pumps (Kyowa, Japan) and two glass columns (both 150 cm × 2 cm I.D.) segmented by PTFE disks with a 6-mm hole were used. The number of cells per column was 130. The columns were equipped with end-caps which contained rotating seals together with an inlet for one phase and an outlet for the other phase, thus allowing for the possibility of dual counter-current separation. The details of the device has been described elsewhere [5]. To begin, the columns were in an upright position. The columns were filled with the upper phase, then fixed at 20° from the horizontal and rotated about the longitudinal axis at 100 rpm. The lower phase was introduced from the upper end of column 2 (Fig. 1) until it reached the lower end of the column 1, then the two phases were fed simultaneously at 0.72 ml/min. The sample feeding pump was also running (0.04 ml/min), however, the lower phase was pumped in. After a steady state had been established, the lanthanide mixture (10 mM of each) dissolved in the lower phase was introduced into the CFE system by the sample pump and eluent fractions were collected at appropriate intervals.

RESULTS AND DISCUSSION

Determination of concentration of nitric acid in the two-phase system of CFE

Although CFE is a continuous process, for theoretical purposes, it can be assumed that columns are divided into theoretical equilibration segments. Each segment gives complete equilibration between the two phases. Based on this assumption, theoretical treatment of the discontinuous counter-current distribution process can be applied to CFE.

In these experiments, our intention was to obtain the same amount per unit time for both components. For the separation of components i and j with the same throughput, the flow-rate ratio, r , can be determined by using the relationship $r = (D_i D_j)^{1/2}$, where D_i and D_j are the distribution ratios for the respective components, defined as the ratio of the concentration of the component in the organic phase to that in the aqueous phase. It has been demonstrated empirically that in the two-phase system of n -hexane and water, the same flow-rate for both phases ($r = 1$) gives the most stable counter-current stream. Therefore, the partitioning behaviours of Sm, Eu and Gd were examined in two-phase systems consisting of n -hexane and various concentrations of dilute nitric acid in order to obtain distribution ratios which gave a value of unity for r .

The distribution ratio was found to decrease with increasing concentration of nitric acid, but no significant change was observed for the separation factor, which is the ratio of the distribution ratios to be separated (Fig. 2). Thus, any nitric acid concentration between 0.55 and 0.8 M can be utilized without a decrease in the separation efficiency. A nitric acid concentration of 0.65 M was selected for the separation of Sm and Gd and 0.75 M for the separation of Gd and Eu.

Continuous separation of lanthanides

The continuous separation of Gd and Sm by CFE showed a satisfactory performance. Sm and Gd were obtained continuously over a 2-week period with purities of higher than 99.5% (Fig. 3). Purity is defined as the ratio of the component concentration to the total concentration of all components multiplied by 100. The complete separation of Gd and Eu could not be achieved. At steady state, the separation gave a 97% purity of Gd in the upper phase, whereas the lower phase was only 93% pure in Eu (Fig. 4).

If CFE consists of theoretical equilibration segments in series, the number of theoretical equilibration segments on the left side of the sample feed segment (m for

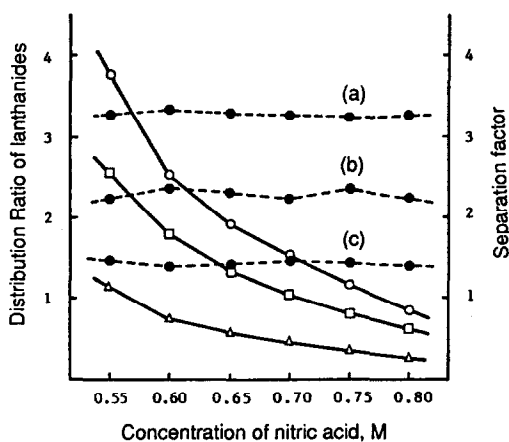


Fig. 2. Effect of nitric acid concentration on distribution ratios and separation factors of Sm, Eu and Gd. Solid lines, distribution ratios of (Δ) Sm, (\square) Eu and (\circ) Gd; dashed lines, separation factors of (a) Gd/Sm (b) Eu/Sm and (c) Gd/Eu.

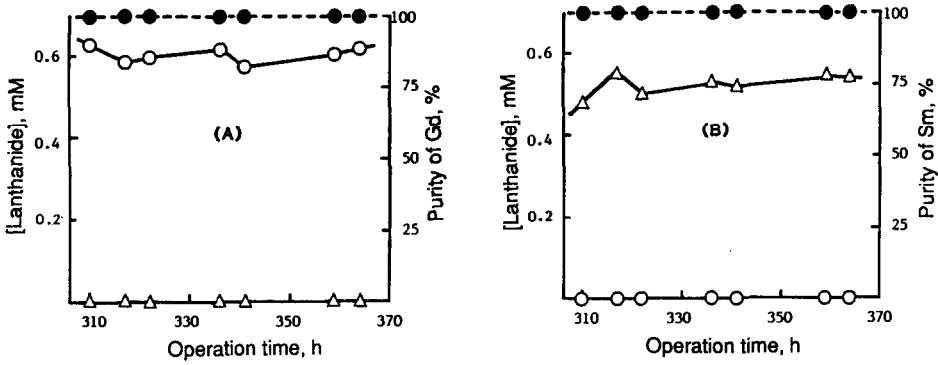


Fig. 3. Concentration and purity of Sm and Gd obtained with continuous separation: (A) upper phase; (B) lower phase. (Δ) Sm concentration; (\circ) Gd concentration; (\bullet) purity. The two-phase system used was 0.5 M DEHPA in *n*-hexane and 0.65 M nitric acid.

column 1) and that on the right side (*n* for column 2) is approximated by solving the equation below using the experimental data. The feed segment is counted twice, hence the total number of segments is $m + n - 1$. The extraction factor (*e*) of a component is defined as the ratio of the amount of component in the aqueous phase to that in the organic phase; e_1 is the extraction factor in the column 1 and e_2 is that in the column 2. Because the ratio of flow-rates of the two phases (*r*) is equal to the ratio of the volumes of the two phases, $e = r/D$.

$$\psi = \frac{\text{amount of a component in the upper phase (mol/min)}}{\text{initial amount of a component fed (mol/min)}}$$

$$= \frac{(e_1 - 1)(e_2^m - 1)}{(e_1^{n+1} - 1)(e_2 - 1)e_2^{m-1} + (e_2^{m-1} - 1)(e_1 - 1)}$$

if *m* and *n* are assigned values of 21 and 16, respectively, the calculated values were consistent with the experimental data (Table I). Hence it is estimated that the CFE

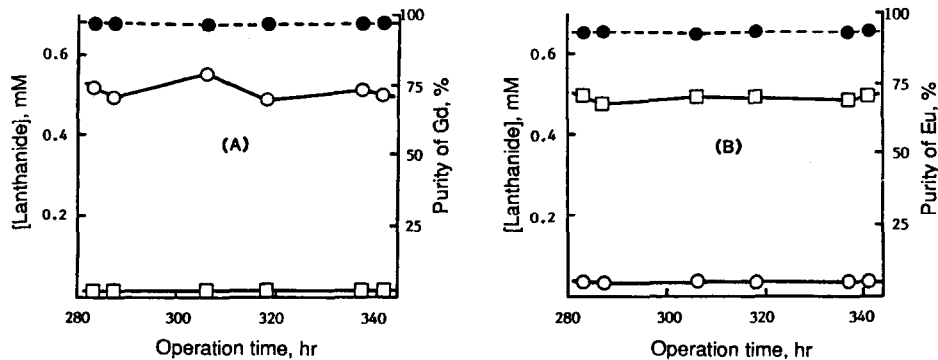


Fig. 4. Concentration and purity of Eu and Gd obtained with continuous separation: (A) upper phase; (B) lower phase. (\square) Eu concentration; (\circ) Gd concentration; (\bullet) purity. The two-phase system used was 0.5 M DEHPA in *n*-hexane and 0.75 M nitric acid.

TABLE I

COMPARISON OF EXPERIMENTAL VALUES WITH CALCULATED RESULTS FOR THE SEPARATION OF EUROPIUM AND GADOLINIUM BY CFE

Calculation condition: $m = 21$, $n = 16$, $r_1 = 1$, $r_2 = 1.06$, $D_{Eu} = 0.81$, $D_{Gd} = 1.17$, $\psi_{Eu,obs.} = 0.025$, $\psi_{Gd,obs.} = 0.925$, feed amount of each lanthanide = $4.0 \cdot 10^{-7}$ mol/min.

| | Experimental (mol/min) | | Calculated (mol/min) | |
|--------------------|------------------------|---------------------|----------------------|---------------------|
| | Gd | Eu | Gd | Eu |
| Upper phase outlet | $3.7 \cdot 10^{-7}$ | $1.0 \cdot 10^{-8}$ | $3.7 \cdot 10^{-7}$ | $1.0 \cdot 10^{-8}$ |
| Lower phase outlet | $2.7 \cdot 10^{-8}$ | $3.7 \cdot 10^{-7}$ | $3.0 \cdot 10^{-8}$ | $3.9 \cdot 10^{-7}$ |

consists of 36 theoretical equilibration segments with each segment being about seven cells of the CFE column. The discrepancy in m and n could be explained by the difference in the flow-rate of lower phase between columns 1 and 2; the flow-rate of the lower phase in the column 1 was 0.76 ml/min because the sample was introduced into the lower phase.

The counter current process consists of two concurrent sub-processes: extraction and washing. For a component to be extracted, one of two solvents involved is used for extraction and the other is used for washing. The component is extracted between the feed point and the inlet of the extraction solvent, and concurrently the undesirable component is washed (back-extracted) between the feed point and the washing solvent inlet. For the other component, the situation is reversed. A given component with $e > 1$ is recovered in the aqueous phase and a component with $e < 1$ is recovered in the organic phase. Because e is a function of r and D , such extraction behaviour is controllable. Unlike conventional CCC, these processes occur simultaneously in the columns. Therefore, a reasonably high purity of extracts can be obtained with a limited number of theoretical equilibration segments. It is obvious from the nature of CFE that a sample can only be separated into two fractions. Thus, for the separation of multiple components in a sample, the number of sets of CFE needed to isolate each component is one less than the number of components.

CFE employs rotation of columns to promote the partitioning of components and the two phases completely fill the columns. This design prevents both the formation of emulsions and the oxidation of sample components, which often happen in discontinuous counter-current systems involving phase dispersion by vigorously mixing to reach equilibrium. The throughput of lanthanides in our experiments was $4 \cdot 10^{-7}$ mol/min. Although further experiments are necessary for preparative-scale separations, this preliminary application demonstrated certain advantages of CFE. Other factors which influence the column efficiency are currently being investigated and further applications of CFE are in progress.

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