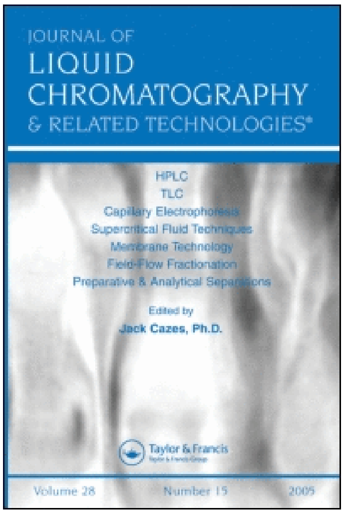

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IMPROVED SEPARATION OF CLOSELY RELATED METAL IONS BY CENTRIFUGAL PARTITION CHROMATOGRAPHY

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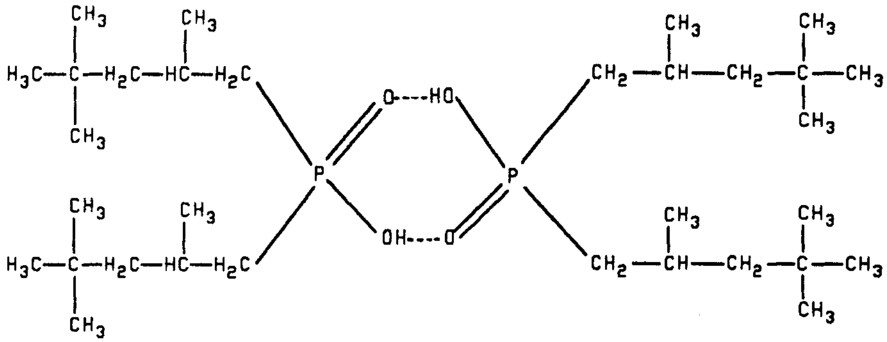
ABSTRACT

Centrifugal Partition Chromatography (CPC) has been used for the analytical scale separations of adjacent trivalent lanthanides. The stationary phase was 0.1 M Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) in heptane and the mobile phase was water at the appropriate pH. Baseline separations of the adjacent lanthanides were achieved with an observed column efficiency of 320 ± 40 theoretical plates. The column efficiency decreased with flow rate, i.e., the normal Van Deemter behavior was observed. The distribution ratios (D) of selected trivalent lanthanides at different pH values were in general in good agreement with the values determined by batch solvent extraction method. The D obtained with CPC differed markedly from the solvent extraction values inn certain cases resulting in a dependence of separation factor (α) of adjacent lanthanides on pH. This anomaly is under further investigation. The number of theoretical plates, selectivity and resolution of adjacent lanthanides obtained with the current system is ssignificantly better than previously reported. We have demonstrated for the first time, that a mixture of light and heavy lanthanides can been efficiently separated in a single run by CPC, by using gradient pH elution.

INTRODUCTION

The efficient separation of trivalent lanthanide ions continues to be an important and challenging problem. The closeness of their properties makes separation of adjacent elements very difficult. We have been investigating this problem for several years using chelate extractants (1). These include 8-quinolinol and its derivatives, several 1-phenyl-3-alkyl-4-acyl-5-pyrazlones, different hydroxamic acids and organophosphorus extractants including pohsphonic acids and phosphinic acids. The extraction constants and separation factors (defined as the differences in the logarithmic values of the extraction equilibrium constants of a pair of metal ions) obtained with these ligand systems could be often improved by mixed complex formation using auxiliary ligand such as 1,10-phenanthroline, bipyridyl and its derivatives, and trioctylphosphine oxide (TOPO). Even with the best ligand or mixed ligand system, it is impossible to obtain complete separation of adjacent lanthanides by batch solvent extraction methods. Multistage methods are necessary for complete separation of adjacent lanthanides. The approaches for the multistage separations of lanthanides include the use of derivatized polymeric supports (2,3), composite supported liquid membranes (4) and centrifugal partition chromatography (CPC) which is a countercurrent distribution technique (5,6). We are developing multistage separation methods for adjacent lanthanides using derivatized polymeric supports and centrifugal partition chromatography. The results of our work using an organophosphorus extractant for the separation of trivalent lanthanides by CPC will be discussed here.

Among the various families of ligands that we have investigated for the separation of lanthanides by solvent extraction, acidic organophosphorus extractants provided the best extraction equilibrium constants and separation factors (7). Bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), a dimeric chelating ligand performed the best among the organophosphorus extractants (8). This ligand whose structure is shown below, was used to obtain analytical scale separations of all adjacent lanthanides except Pr and Nd. A mixture of light and heavy lanthanides was separated, for the first time using CPC, in a single run, by gradient pH elution.



MATERIALS

The extractant Cyanex 272 was kindly supplied by American Cyanamid as a pale yellow liquid. It was purified according to our previously published procedure, by the formation of its copper (II) complex and the decomposition of this complex (8). The purified Cyanex 272 was a clear viscous liquid. Its purity was determined to be 98%, by potentiometric acid base titration . All trivalent lanthanides were obtained from Johnson-Matthey as their chlorides or oxides and were at least 99% pure. Lanthanide stock solutions were 100 ppm in 0.1 M HCl and were appropriately diluted before injection into the CPC. Arsenazo III (Aldrich) for the detection of lanthanides by post-column derivatization, analytical grade n-heptane (EM Science) and HCl (Baker) were used as received.

APPARATUS

All pH measurements were performed with Fisher Accumet 925 pH meter and Corning combination glass electrode. Inductively Coupled Plasma Atomic Emission (ICP-AES) analysis of lanthanides from batch solvent extraction experiments and CPC eluents were performed with a Perkin-Elmer 6500 ICP-AES with a micro Babington type nebulizer and Perkin-Elmer a 7300 computer. CPC experiments were performed with a Sanki Co. assembly consisting of a model SPL centrifuge containing 6 analytical/semi-preparative cartridges with 400 channels per cartridge (2400 total channels), model CPC FCU-V loop injector and model LBP-V pump. The lanthanides were analyzed by postcolumn derivatization using Altex 110A HPLC pump and a 100 cm loop for efficient mixing of the eluent and Arsenazo III. A Perkin-Elmer LC-95 analytical uv-vis spectrophotometer detector with 4.9 μL, 1 cm path length cell was set at 654 nm for analysis of the derivatized eluent. The chromatogram was recorded with an Alltech 1200 linear chart recorder.

METHODS

A solution of 0.1 M Cyanex 272 in n-heptane was equilibrated with an aqueous solution at the appropriate pH for 2 hours. Hydrochloric acid at the appropriate concentration was used as the buffer in the pH range 1 - 3 in which the separations were conducted. The equilibrated phases were separated and filtered through a 0.5 micron filter. The CPC cartridges were filled with the equilibrated Cyanex 272 in heptane in the ascending mode. The total internal volume of the CPC system including the cartridges, the sample loop and the tubes was 130 mL. Preliminary experiments indicated that good separation and resolution of the lanthanides could be obtained by using a small heptane/H_2O phase volume ratio. Runs using 20 mL of heptane stationary phase and 110 mL of aqueous mobile phase afforded the best results. This condition was achieved by pumping the aqueous mobile phase in the descending mode through the stationary cartridges until 110 mL of the heptane was removed. The flow of mobile phase was stopped and the cartridges were rotated at 800 rpm. Flow of the mobile phase was resumed in the descending mode after the desired rotational speed was achieved. A flow rate of 1 mL/min was chosen for our experiments in order to optimize the number of theoretical plates and the time required for separating an analyte mixture (see Figure 3 and discussion below).

All CPC experiments were conducted at 20 °C. Analyte solutions (1 mL) containing a mixture of adjacent lanthanides with individual lanthanide concentrations in the range 1 - 20 ppm were used in our experiments. The eluting lanthanides were complexed with 0.01% (w/v) Arsenazo III pumped at 0.6 mL/min and monitored at 654 nm where the absorbance of the lanthanide-Arsenazo III complex has little interference from Arsenazo III (Figure 1). The Arsenazo III was buffered with succinate at pH = 3.5 such that the resulting pH after mixing with the eluting lanthanides was about 3, the value where Arsenazo III has the maximum sensitivity for the detection of lanthanides (9). The eluting lanthanides were individually collected after conditions for their baseline separations were established, concentrated and

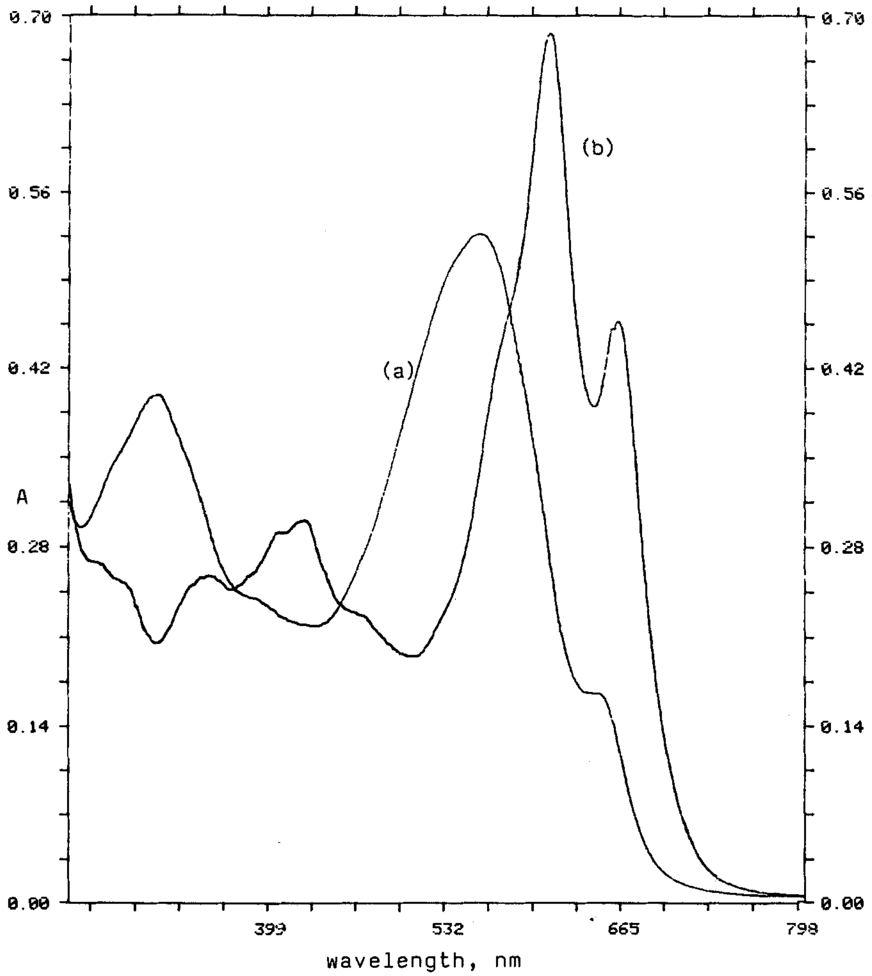


FIGURE 1. Uv-vis spectra of (a) 2.6×10^{-5} M Arsenazo III and (b) a mixture of 2.6×10^{-5} M Arsenazo III and 3.5×10^{-5} M Pr(III) at pH = 3.

analyzed by ICP-AES at the appropriate wavelength for cross-contamination. Typically the cross-contamination was below the detection limit of ICP-AES, which varied between 1.7 ppm (401.2 nm) for Nd, and 0.01 ppm (381.96 nm) for Eu. Concentrations of the injected samples were increased or several batches of eluting analytes were collected and concentrated for proper check of cross-contamination. A mixture of light and heavy lanthanides were separated in a single run using gradeint pH elution. The initial pH of the mobile phase was 3.0 and was gradually stepped down by the addition of 0.5 M HCl. Aliquots of the mobile phase were removed from time to time and its pH determined by titration with 0.1 M NaOH. The pH at which the lanthanides were eluting were determined by their peak widths which were very sensitive to pH.

RESULTS AND DISCUSSION

We had previously demonstrated that Cyanex 272 is a dimeric chelating ligand and determined its dimerization constant in $CHCl_3$ (184 M^{-1}), its K_{DR} for $CHCl_3/H_2O$ (43.8) and pK_a in H_2O (3.18) by ICP-AES (10). It was also shown that the extraction equilibrium was as written in equation 1, by solvent extraction experiments in $CHCl_3/H_2O$ system (8).

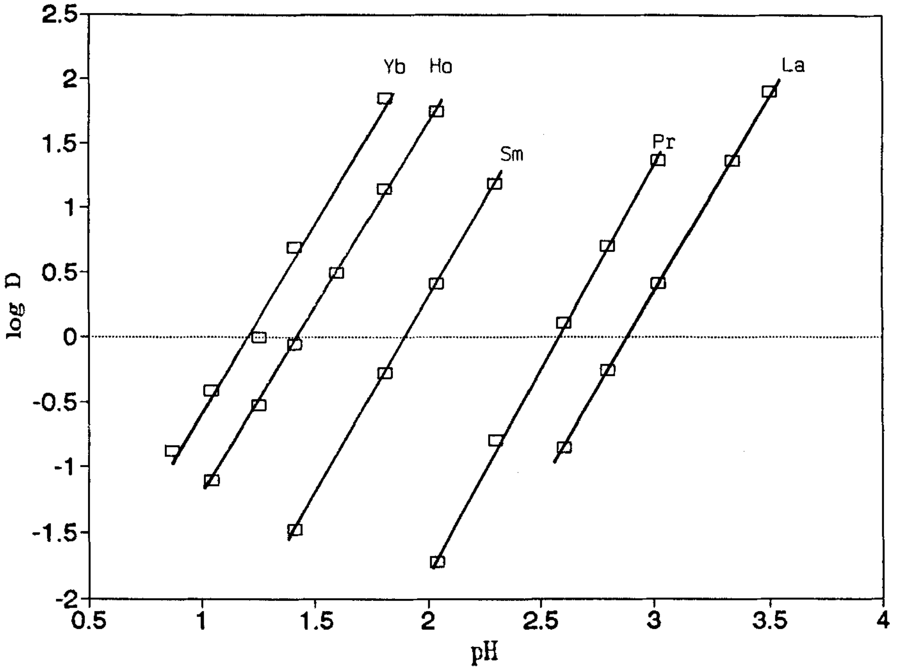


FIGURE 2. log D vs pH for Yb, Ho, Sm, Pr and Nd by batch solvent extraction with equal heptane and H_2O phase volumes.

$$M^{3+}_{aq} + 3(HL)_{2,org} \rightleftharpoons M(HL_2)_{3,org} + 3H^{+}_{aq} \qquad (1)$$

The corresponding extraction equilibrium expression is equation 2.

$$K_{ex} = \frac{[M(HL_2)_3]_{org}[H^+]^3_{aq}}{[M^{3+}]_{aq}\ [(HL)_2]^3_{org}} \qquad (2)$$

Batch solvent extraction experiments in heptane/H_2O with selected individual lanthanides with equal phase volume ratios confirmed the stoichiometry in equation 1. A plot of log D vs. pH (D = distribution ratio of the trivalent lanthanide measured by ICP-AES) for Yb, Ho, Sm, Pr and Ln for heptane/H_2O is shown in Figure 2. The slopes of these lines is 2.93 ± 0.08.

The CPC chromatograms were characterized in terms of the number of theoretical plates, distribution ratios of the respective lanthanides, and the separation factor and resolution of a given lanthanide pair as previously defined (11). The dependence of the number of theoretical plates on the flow rate was determined with 4 ppm Sm at pH = 2.1 which showed the number of theoretical plates decreasing with flow rate, i.e., the normal Van Deemter type behavior and the opposite of Armstrong's observation (Figure 3) (12). A flow rate of 1 mL/min was found to optimize the number of plates and the time for the separation of an analyte mixture.

Baseline separations of all adjacent lanthanides except Pr and Nd were obtained. The chromatograms for the separation of La, Pr and Nd at pH = 2.8 is shown in Figure 4. The effect of pH on the separation of Nd, S, and Eu is shown in Figure 5. Figure 6 contains the the separation of Gd, Dy and Tb as a function of heptane/H_2O phase volume ratio. The separation of Ho and Er at pH = 1.65 and the separation of Tm and Yb at pH = 1.36 are shown in Figure 7. The selectivity (α) and resolution (R_s) values of the adjacent lanthanide pairs separated are collected in Table 1.

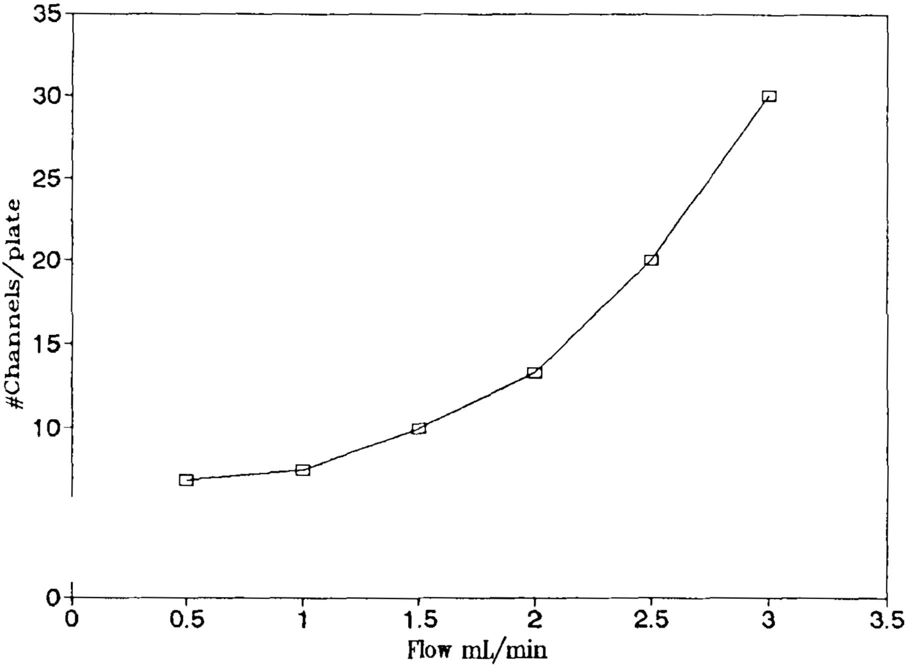


FIGURE 3. Dependence of the number of channels per theoretical plate on flow rate (mL/min) determined for 4 ppm Sm at pH = 2.1.

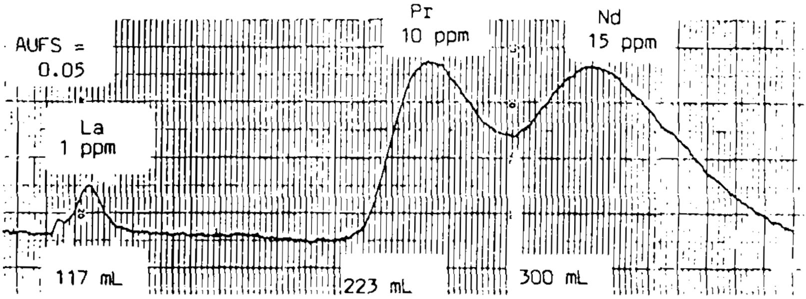


FIGURE 4. CPC separation of La (1 ppm), Pr(10 ppm) and Nd (15 ppm) at pH = 2.8.

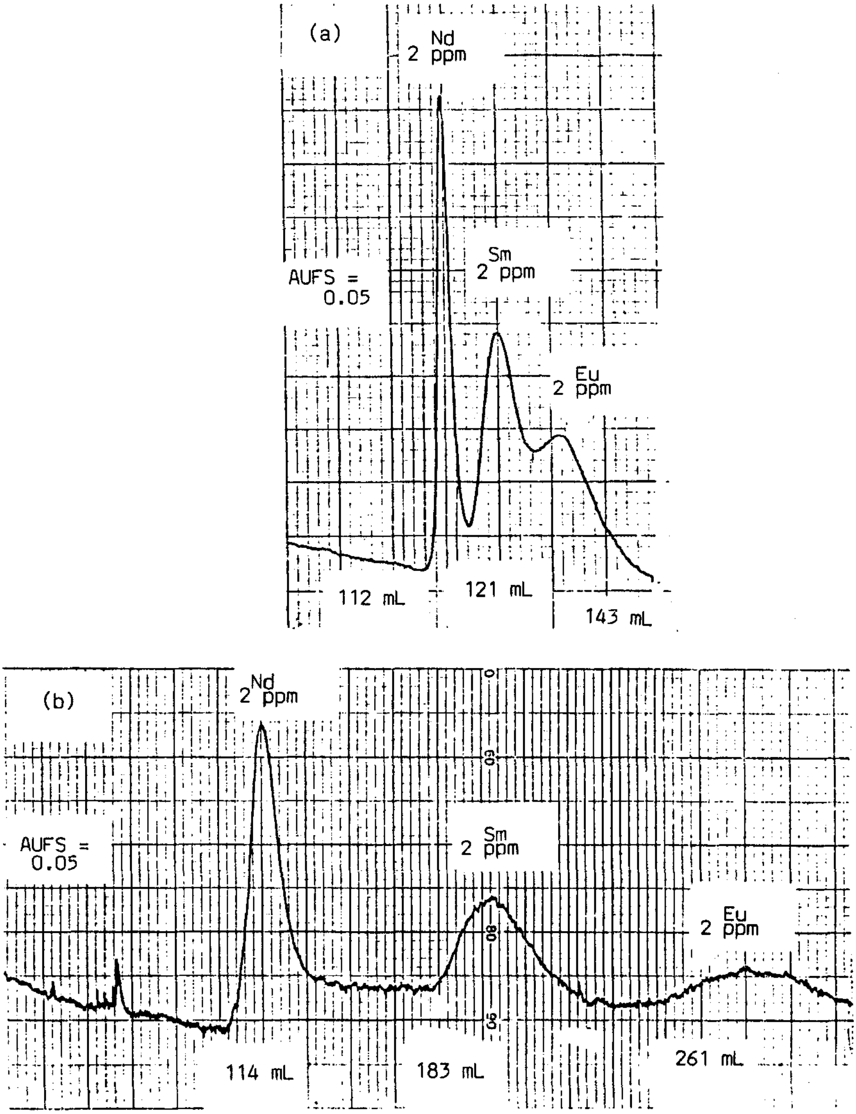


FIGURE 5. Separation of 2 pppm each of Nd, Sm and Eu at (a) pH = 1.9 and (b) pH = 2.1.

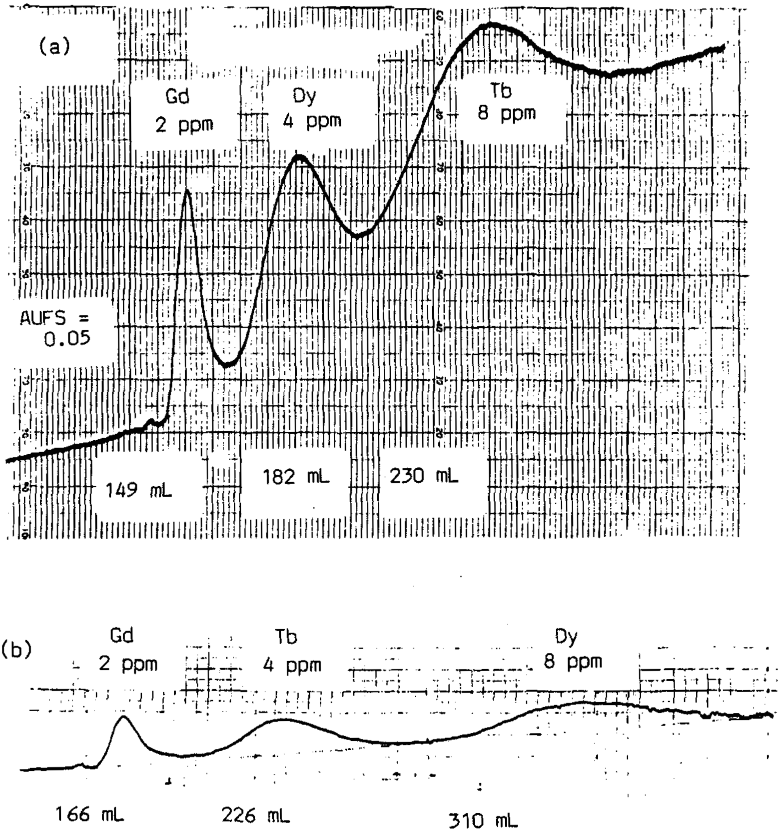


FIGURE 6. Separation of Gd (2 ppm), Dy (4 ppm) and Tb (8 ppm) at pH = 1.8 (a) heptane/H_2O ratio = 0.18 and (b) heptane/H_2O ratio = 0.26.

The retention volumes (V_r) and distribution constants (D) of the lanthanides studied here are given in Table 2. The D values from batch solvent extraction (SX) experiments for Yb, Ho, Sm, Pr and La at the pH values the CPC experiments were conducted are also included in this table.

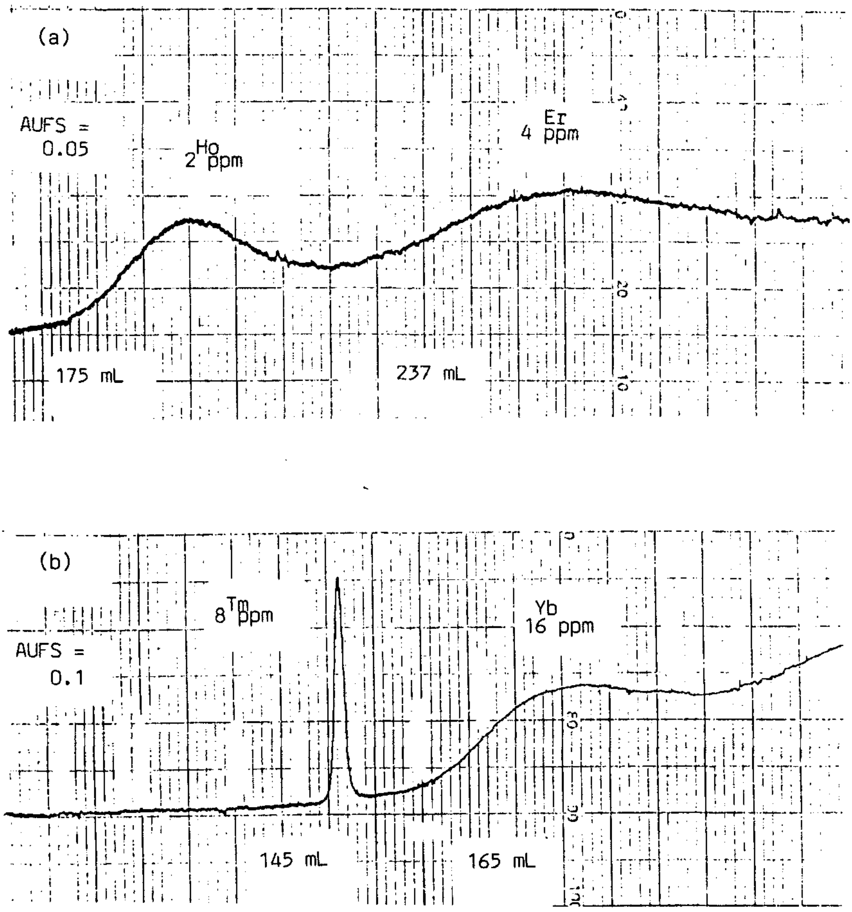


FIGURE 7. Separation of (a) Ho (2 ppm) and Er (4 ppm) at pH = 1.65 and (b) Tm (8 ppm) and Yb (16 ppm) at pH = 1.36.

The dependence of the retention volumes and the resolution factors on pH in the case of Nd, Sm, and Eu is evident from Table 1, Table 2 and Figure 5. It can also be noted from Table 2 that in general the D values determined from CPC and solvent extraction experiments agree well. The case of Nd is peculiar in that

TABLE 1. α and R_s Values for Adjacent Lanthanides.

Lanthanide Pair	pH	α	R_s
La - Pr	2.8	9.8	2.7
Pr - Nd	2.8	1.7	1.2
Nd - Sm	2.1	11.2	2.1
Sm - Eu	2.1	2.0	1.5
Nd - Sm	1.9	2.4	0.7
Sm - Eu	1.9	2.4	1.1
Gd - Tb	1.8	1.8	0.94
Tb - Dy	1.8	1.66	1.13
Ho - Er	1.65	1.86	0.96
Tm - Yb	1.36	1.5	0.7

TABLE 2. V_r and D Values of Lanthanides from CPC and Solvent Extraction.

Lanthanide	pH	V_r, mL	D	D(SX)
La	2.8	117	0.6	0.56
Pr	2.8	223	5.9	5.1
Nd	2.8	300	9.8	
Nd	2.1	114	0.35	
Sm	2.1	183	3.9	3.7
Eu	2.1	260	7.8	
Nd	1.9	112	0.33	
Sm	1.9	121	0.79	0.82
Eu	1.9	143	1.9	
Gd	1.8	149	2.4	
Tb	1.8	182	4.4	
Dy	1.8	230	7.2	
Gd[a]	1.8	166	2.5	
Tb[a]	1.8	226	4.7	
Dy[a]	1.8	310	7.9	
Ho	1.65	175	3.4	3.1
Er	1.65	237	6.3	
Tm	1.36	145	2.0	
Yb	1.36	165	2.9	3.2

a. Heptane = 27 mL and H_2O = 103 mL. All others, heptane = 20 mL and H_2O = 110 mL.

the retention volumes and hence the D values at pH 1.9 and 2.1 are almost identical which seems to violate the stoichiometry in equation 1. These data together with the data at pH = 2.8 yield an average slope for log D vs. pH of 1.75 and not 3. This is manifested in the dependence of α on pH for Nd - Sm and Nd - Eu pairs. It is also manifested in the number of theoretical plates for Nd at pH = 1.9 being 700 as opposed to 378 at pH = 2.1 and 300 at pH = 2.8. Batch solvent extraction experiments clearly show that kinetics of extraction of lanthanides by Cyanex 272 in heptane/H_2O is very rapid and possibly is not the source of this anomaly. The source of this anomaly in the CPC experiments is under further investigation. It has, however, worked to our practical advantage in this particular instance.

In the case of Gd, Tb and Dy we find that the retention volumes and resolution factors are very sensitive to the phase volume ratios. Increasing the ratio of heptane to water from 0.18 to 0.26 improves the resolution and hence the separation of these three adjacent lanthanides. The D values are unaffected as expected (Table 2). Table 3 contains the α values, the experiemntal and calculated resolution factors, R_s and R'_s respectively. The experiemtal and calculated resolution factors agree well.

The column efficiency obtained in this work is about ten times that obtained by Araki, and three times that obtained by Akiba, taking the highest number of plates from their experiments

TABLE 3. Experimental and Calculated Resolution Factors.

Lanthanide Pair	$V_m/V_s = 6.4$			$V_m/V_s = 3.6$		
	α	R_s	R'_s	α	R_s	R'_s
Gd - Tb	1.8	0.94	0.88	1.9	1.4	1.3
Gd - Dy	3.0	2.05	1.84	3.1	2.82	2.6
Tb - Dy	1.66	1.13	0.94	1.65	1.44	1.26

(5,6). The conditions in their experiments are such that each analyte mixture yielded a different number of theoretical plates. We have established conditions that yield a uniform number of theoretical plates, irrespective of the adjacent lanthanide mixture chosen. The only deviation observed is in the case of Nd where the separation factor showed a dependence on pH. The number of theoretical plates obtained for the separation of lanthanides is considerably smaller than the theoretical plates obtained for the separations of organic molecules.

The major objective of the work outlined here was to demonstrate that counter current distribution methods like CPC can separate adjacent lanthanides efficiently. We can use the equations for countercurrent distribution and the D values derived from CPC experiments to simulate the chromatogram from CPC experiments. The fraction f_o of a given lanthanide with a distribution constant D in the organic phase where the ratio of

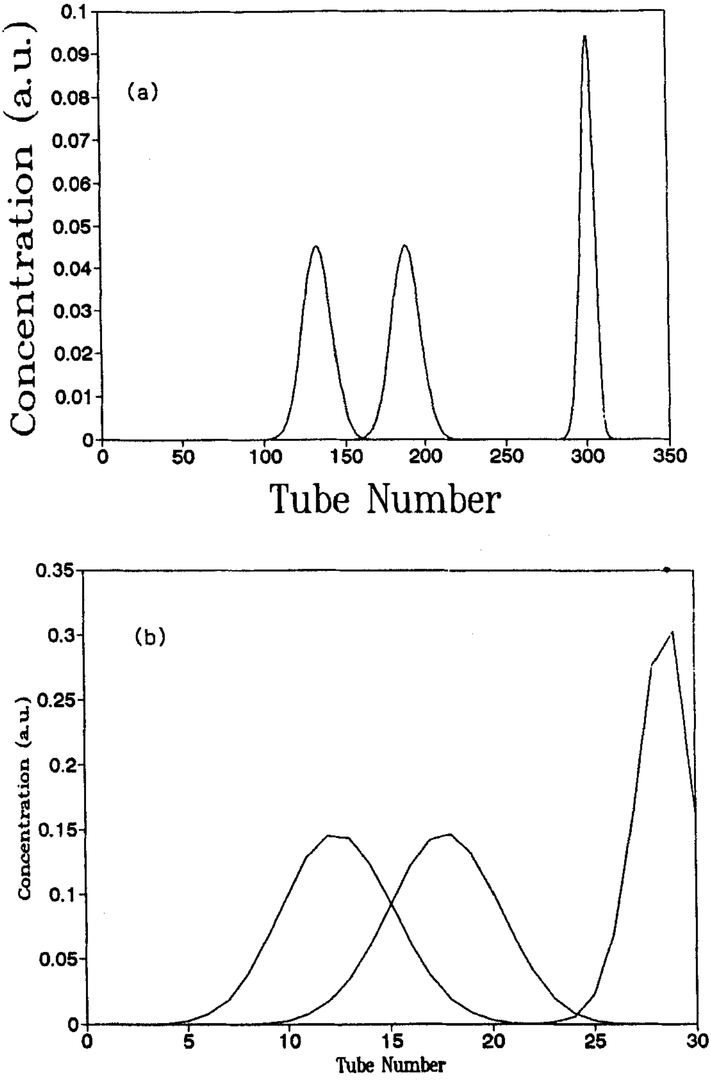


FIGURE 8. Simulation of the CPC chromatogram for 2 ppm each of Nd, Sm, and Eu at pH = 2.1 for (a) 320 stages and (b) 30 stages using the D values from CPC experiment.

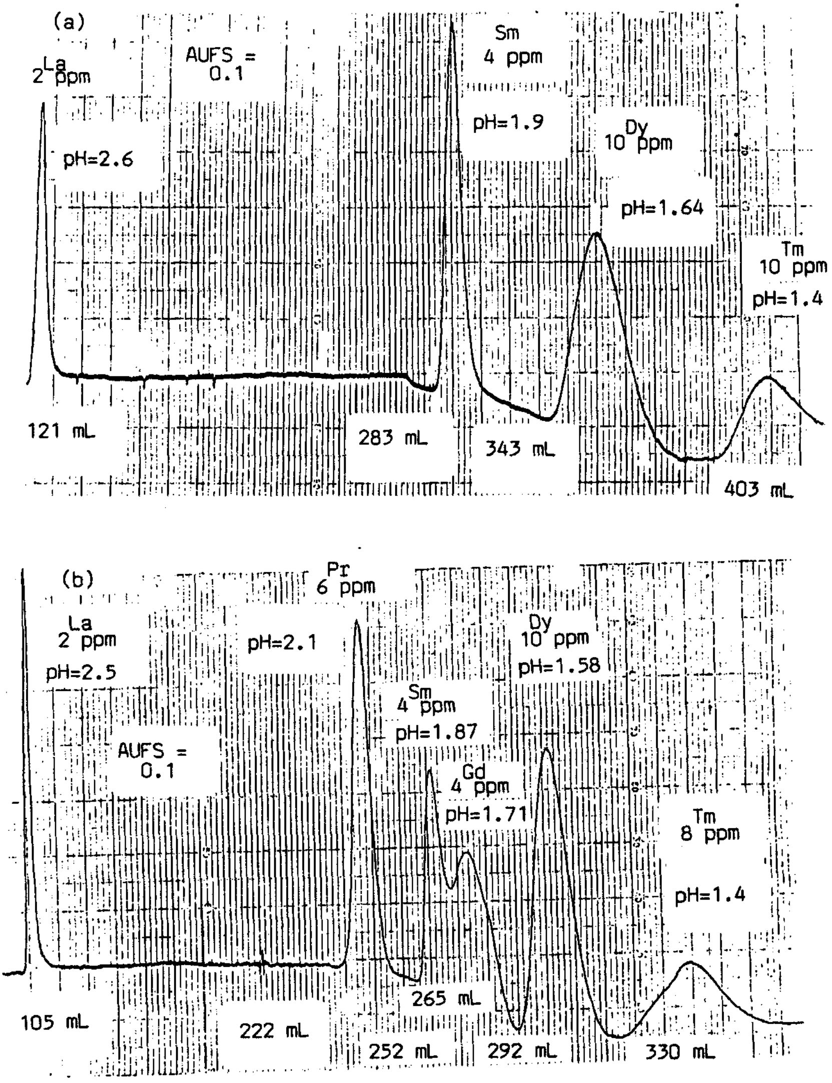


FIGURE 9. Gradient pH separation of (a) La (2 ppm), Sm (4 ppm), Dy (10 ppm) and Tm (10 ppm) and (b) La (2.5 ppm), Pr (6 ppm), Sm (4 ppm), Dy (10 ppm), and Tm (8 ppm).

the volume of the organic phase to the volume of the aqueous phase is R_v is given by equation 3.

$$f_o = \frac{D\,R_v}{D\,R_v + 1} \qquad (3)$$

In a counter current distribution involving N stages,

$$(f_o + f_w)^N = 1 \qquad (4)$$

where f_w is the fraction of the lanthanide in the aqueous phase. The concentration of the lanthanide in the m th stage of the separation is given by

$$\frac{N!}{m!\,(N-m)!}\, f_o^{N-m}\, f_w^{m} \qquad (5)$$

The simulations of the separation of Nd, Sm and Eu at pH = 2.1 using equation 5 for 30 and 320 stages is shown in Figure 8. It is evident from these simulations that with the D values normally obtained in solvent extraction techniques, adjacent lanthanides can be only separated by multistage methods. Their D values would have to differ by three to four orders of magnitude to be separated by single stage batch extraction.

A further advantage of CPC can be well illustrated by the ability to separate a mixture of light and heavy lanthanides in a single run by the use of gradient pH elution. It is evident from Figure 2 that complete separation and recovery of each lanthanide in a mixture of light and heavy lanthanides cannot be achieved with an eluent at a constant pH. We have successfully separated a mixture of light and heavy lanthanides by using a pH gradient (Figure 9).

REFERENCES

1. Freiser H., Solvent Extraction of Tervalent Lanthanides as Chelates. A Systematic Investigation of Extraction Equilibria, Solvent Extr. Ion. Exch., 6, 1093, 1988.

2. Alexandratos, S. D., Wilson, D. L., Strand, M. A., Quillen, D. R., Walder, A. J. and McDowell, W. J., Metal Ion Extraction Capability of Phosphinic Acid Resins: Comparative Study of Phosphinic, Sulfonic and Carboxylic Resins using Zinc Ions, Macromolecules, 18, 835, 1985.

3. Freiser, H., Unpublished Observations.

4. Danesi, P. R., Yinger, L. R., Cianetti, C. and Rickert, P. G., Solv. Extr. Ion Exchange, 2, 781, 1984.

5. Araki, T., Okazawa, T., Kubo, Y., Ando, H. and Asai, H., Separation of Lighter Rare Earth Metal Ions by Centrifugal Counter-Current Type Chromatography with Di-(2-ethylhexyl)phosphinic Acid, J. Liquid Chromatogr., 11, 267, 1988.

6. Akiba, K., Sawai, S., Nakamura, S. and Murayama, W., Mutual Separation of Lanthanoid Elements by Centrifugal Partition Chromatography, J. Liquid Chromatogr., 11, 2517, 1988.

7. Motomizu, S. and Freiser, H., Extraction of Tervalent Lanthanides with Acidic Organophosphorus Compounds, Solv. Extr. Ion Exch., 3, 637, 1985.

8. Komatsu, Y. and Freiser, H., Extraction Separation of Tervalent Lanthanide Metals with Bis(2,4,4-trimethylpentyl)phosphinic Acid, Anal. Chim. Acta, 227, 397, 1989.

9. Savvin, S. B., Analytical use of Arsenazo III, Talanta, 8, 673, 1961.

10. Ke-an, L., Muralidharan, S. and Freiser, H.,Determination of the Equilibrium Constants of Organophosphorus Liquid-Liquid Extraction by Inductively Coupled Plasma Atomic Emission Spectroscopy, Solv. Extr.. Ion Exch, 3, 895, 1985.

11. Berthod, A. and Armstrong, D. W., Centrifugal Partition Chromatography II. Selectivity and Efficiency, J. Liquid Chromatogr., 11, 567, 1988.

12. Armstrong, D. W., Bertrand, G. L. and Berthod, A., Study of the Origin and Mechanism of Band Broadening and Pressure Drop in Centrifugal Countercurrent Chromatography, Anal. Chem., 60, 2513, 1988.