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TECHNICAL NOTE

The Separation of Am from Lanthanides by Purified Cyanex 301 Extraction

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ABSTRACT

Separation factors of tracer amounts of Am from micro lanthanides (La, Ce, Pr, Nd, and Sm) by purified Cyanex 301 extraction in nitrate media have been determined: $SF_{Am/La} \sim 3500$, $SF_{Am/Ce,Pr} \sim 1000$, $SF_{Am/Nd} \sim 1900$, and $SF_{Am/Sm} \sim 4500$, with an average value >2300. The distribution ratio decreases with increasing lanthanide concentration in the aqueous phase. In the presence of a macro amount of Pr + Nd (0.1 ~ 0.6 M) the separation factors $SF_{Am/Eu}$ and $SF_{Am/Pr+Nd}$ are about 4.7×10^3 and 2.1×10^3, respectively. The results of the countercurrent fractional process show that by using three extraction stages and two scrubbing stages, >99.99% Am can be separated from a tracer amount of Eu with <0.1% extraction of Eu. Using six extraction stages, >99.99% Am and <0.6% macro amount of Pr + Nd are extracted into the organic phase.

Key Words. Cyanex 301; Extraction separation; Am; Lanthanides

INTRODUCTION

The separation of Am(III) from trivalent lanthanides (Ln) is one of the difficulties in separation science. Studies in recent years have shown that compounds containing soft donor atoms such as N and S can provide higher selectivity for Am over Ln. The main extraction systems include 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-thione (HBMPPT) with tri-*n*-octylphosphine (TOPO) or 4,7-diphenyl-1,10-phenanthroline as a synergist (1, 2), di-(2-ethylhexyl) dithiophosphoric acid (HDEHDTP) with TBP as a synergist (3, 4), and 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) with dinonylnaphhalene sulfonic acid (HDNNS) as a synergist (4).

Cyanex 301 is a commercial product of Cytec and mainly consists of ~80% bis(2,4,4-trimethylpentyl)dithiophosphinic acid. Cyanex 301 can extract many metal ions including Ag, As, Bi, Co, Ni, Cu, Cr, Fe, In, Pd, Pb, Pt, and Zn (5). The chemical stability in 2 M HNO_3, 6 M HCl, and 3 M H_2SO_4 is satisfactory (6). Recently, the results of Y. Zhu and coworkers demonstrated that Cyanex 301 can separate Am(III) from trivalent lanthanides. Cyanex 301 can separate Am from macro amounts of Ln with a separation factor of >500 when saponified to 16 mol% (7). Purified Cyanex 301 can separate trace amounts of Am from trace amounts of Eu with a separation factor of >5000 (8). In the present work, the separation of Am from Ln by purified Cyanex 301 extraction has been studied.

EXPERIMENTAL

Apparatus

EKCO 700, NaI(Tl) well-type gamma counter for γ-assay of ^{241}Am and $^{152-154}$Eu; ICAP 9000 quantometer for the determination of La, Ce, Pr, Nd, and Sm; PHS-2 pH meter.

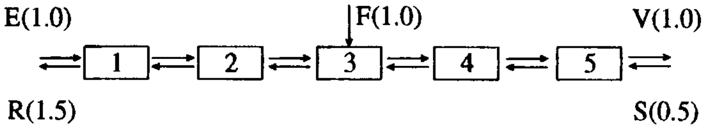
Reagents

Cyanex 301, supplied by Cytec Canada, mainly consists of ~80% bis(2,4,4-trimetylpentyl)dithiophosphinic acid and was purified as described elsewhere (9). A purity of >99% bis(2,4,4-trimentylpentyl)dithiophisphinic acid was found by acid–base titration and ^{31}P-NMR spectroscopy. No. 240 hydrogenated kerosene from Jingzhou Petroleum Refinery, China, was redistilled, and the fraction between 180 and 220°C was used as an organic phase diluent. ^{241}Am was obtained from Institute of Atomic Energy, Beijing, and $^{152-154}$Eu was produced by neutron irradiation at the swimming pool reactor of INET. Both were found to be radionuclide pure. 99.9% Pr + Nd oxide. 99.9% La, Ce, Pr, Nd, and Sm oxide are produced by Yaolong Chemical Factory, Shanghai. All other reagents used were analytical grade.

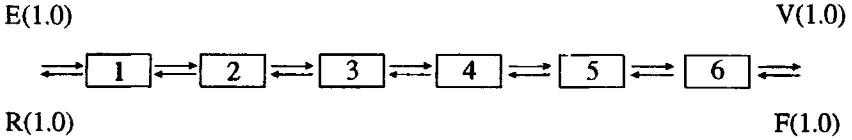
Procedures

For determination of the distribution ratio, equal volumes of the aqueous and organic phases were agitated by magnetic stirrer in glass-stoppered test tubes at 25 ± 0.2°C for 30 minutes. The aqueous phase pH was adjusted with NaOH and HNO_3. After centrifugation and phase separation, the pH of the equilibrated aqueous phase was measured. ^{241}Am and $^{152-154}$Eu in the two phases were measured by gamma counting. La, Ce, Pr, Nd, and Sm in the organic phase were stripped twice into 0.5 M HNO_3. Individual Ln was determined by plasma spectroscopy, and total amount of Ln was determined by EDTA titration. The distribution ratio is defined as D_M = (concentration of M in organic phase)/(concentration of M in aqueous phase). The separation factor is defined as $SF_{M1/M2} = D_{M1}/D_{M2}$.

The countercurrent extraction cascade was carried out with glass test tubes. The process of separating a tracer amount of ^{241}Am from $^{152-154}$Eu is illustrated as follows:



The process of separating ^{241}Am from a macro amount of Ln is illustrated as follows:



Numbers in parentheses refer to relative volumes. F = feed; ^{241}Am, $^{152-154}$Eu + 1 M $NaNO_3$ or ^{241}Am + 0.2 M (Pr + Nd)$(NO_3)_3$. E = extractant; 0.5 M purified Cyanex 301–kerosene. S = scrubbing solution; 0.5 M $NaNO_3$ (pH 3.5). R = aqueous raffinate. V = loaded organic phase.

RESULTS AND DISCUSSION

Extraction of Am and Ln by Purified Cyanex 301

It has been proved (6) that purified Cyanex 301 can effectively separate tracer amounts of Am from tracer amounts of Eu with a separstion factor of >5000. The extraction behavior of other light lanthanides by purified Cyanex 301 has been investigated in the present work. Figure 1 shows that the order in Cyanex 301 extraction is Am $\gg$ Ce $\sim$ Pr > Nd > La > Sm. It can be seen from Table 1 that the separation factors of Am from lanthanides are: $SF_{Am/La} \sim 3500$, $SF_{Am/Ce} \sim 1.0 \times 10^3$, $SF_{Am/Pr} \sim 1.0 \times 10^3$, $SF_{Am/Nd} \sim 1.9 \times 10^3$, and $SF_{Am/Sm} \sim 4.5 \times 10^3$. The average value is higher than 2.3×10^3.

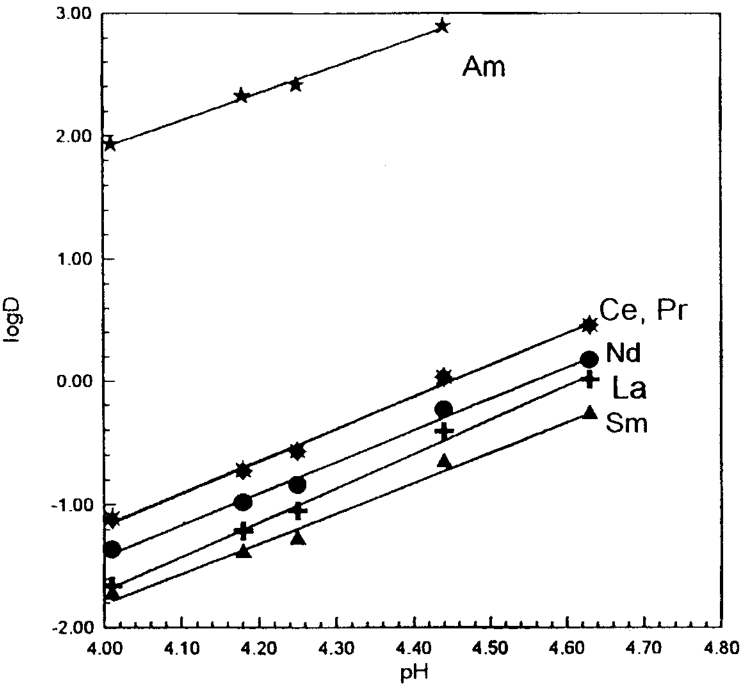


FIG. 1 Plots of log D vs pH. Aqueous phase: ^{241}Am, 460 ppm Ln (~90 ppm for each) + 0.5 M $NaNO_3$. Organic phase: 0.5 M purified Cyanex 301-kerosene. Temperature: 25 ± 0.2°C.

Effects of Ln Concentration on Extraction Separation

Figures 2 and 3 shows the changes of D_{Am}, D_{Eu}, and $SF_{Am/Eu}$ when the Eu concentration in the aqueous phase increases from a tracer amount to a macro amount. The results show that D_{Am} and D_{Eu} decrease with the increase of Eu concentration, and that the decrease of D_{Eu} is more

TABLE 1
The Separation Factors of Am from Ln (experimental conditions are the same as in Fig. 1)

pH	$SF_{Am/La}$	$SF_{Am/Ce}$	$SF_{Am/Pr}$	$SF_{Am/Nd}$	$SF_{Am/Sm}$	Average $SF_{Am/Ln}$
4.01	3.9×10^3	1.1×10^3	1.1×10^3	1.9×10^3	4.6×10^3	2.5×10^3
4.18	3.4×10^3	1.1×10^3	1.1×10^3	2.0×10^3	5.2×10^3	2.6×10^3
4.25	2.9×10^3	9.7×10^2	9.6×10^2	1.8×10^3	4.9×10^3	2.3×10^3
4.44	2.0×10^3	7.3×10^2	7.3×10^2	1.4×10^3	3.6×10^3	1.7×10^3

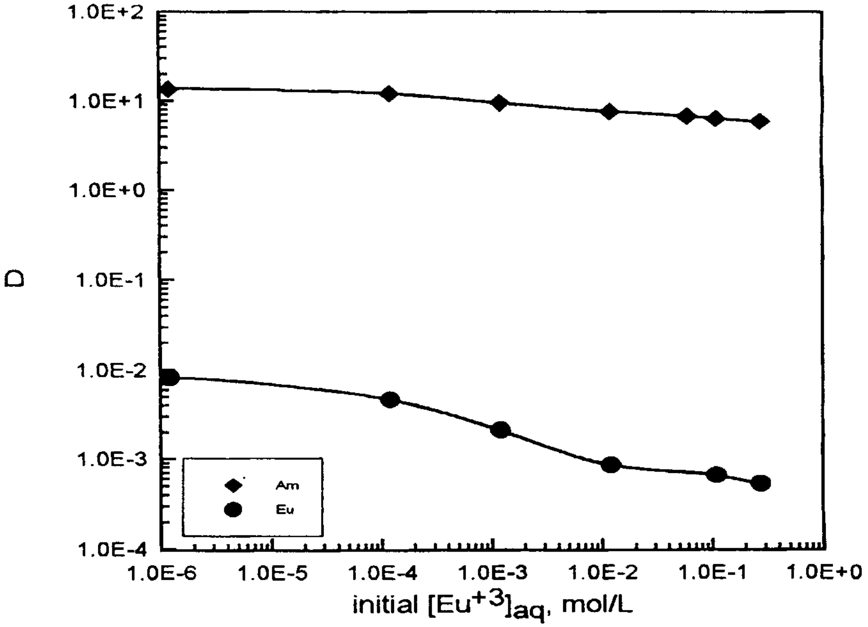


FIG. 2 The effects of Eu concentration on distribution ratios. Aqueous phase: ^{241}Am, Eu, 0.4 M formic acid buffer (pH 3.7), and a suitable content of NaNO$_3$; ion strength ~1.0. Organic phase: 0.5 M purified Cyanex 301-kerosene.

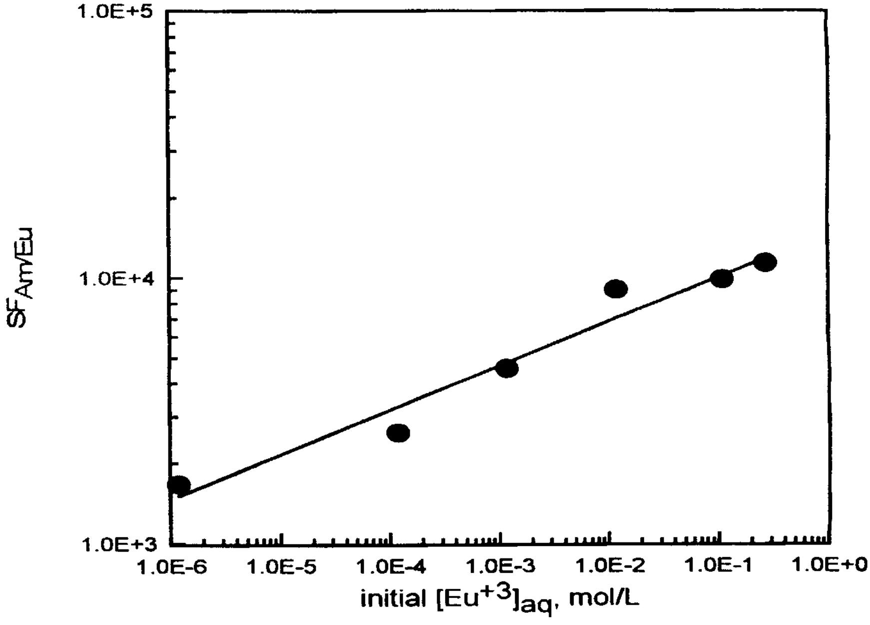


FIG. 3 The effect of Eu concentration on the separation factor SF$_{Am/Eu}$. The experimental conditions are the same as in Fig. 2.

TABLE 2

The Results of Separating Am from Ln with Purified Cyanex 301 Extraction in the Presence of a Macro Amount of Pr + Nd (aqueous phase: ^{241}Am, $^{152-154}$Eu and (Pr + Nd)$(NO_3)_3$, initial pH 5.0; organic phase: 0.5 M purified Cyanex 301-kerosene, saponified to 3 mol%, temperature 25 ± 0.2°C)

Initial [Pr + Nd] in aqueous phase (M)	0.1	0.2	0.3	0.4	0.5	0.6
Equilibrium pH	4.02	4.01	3.92	3.91	3.92	3.90
D_{Am}	97.1	72.9	38.8	34.5	33.6	27.8
D_{Eu}	0.0199	0.0144	0.00782	0.00780	0.00740	0.00615
D_{Pr+Nd}	0.0505	0.0346	0.0199	0.0155	0.0126	0.0130
$SF_{Am/Eu}$	4.9×10^3	5.1×10^3	5.0×10^3	4.4×10^3	4.9×10^3	4.5×10^3
$SF_{Am/Pr+Nd}$	1.9×10^3	2.1×10^3	2.0×10^3	2.2×10^3	2.7×10^3	2.2×10^3

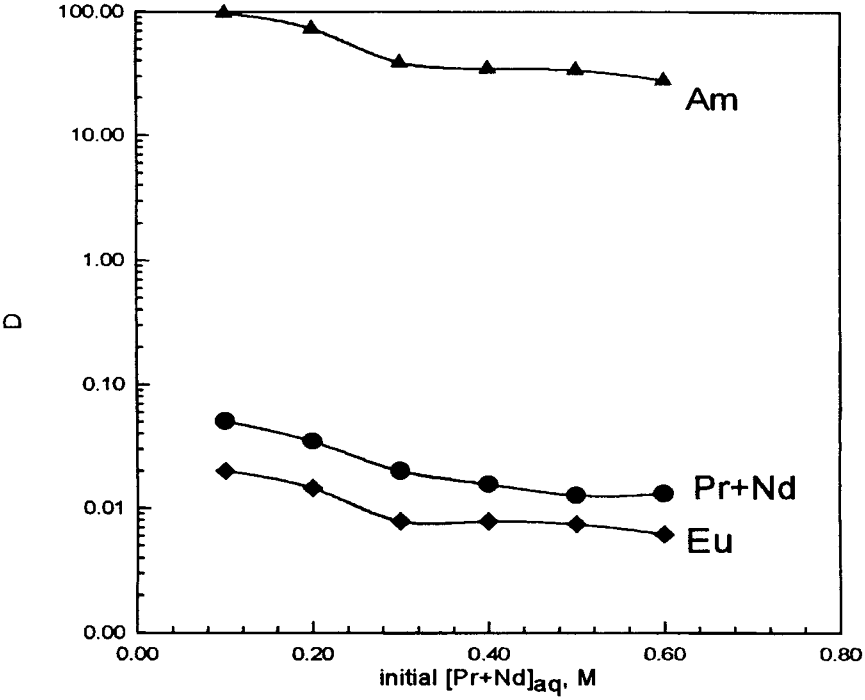


FIG. 4 The effects of a macro amount of Pr + Nd on distribution ratios. The experimental conditions are the same as in Table 2.

obvious. The decrease of D_{Am} and D_{Eu} in the concentration range of 1.0 × 10^{-4} to 0.01 M Eu is apparent. The separation factor $SF_{Am/Eu}$ increases with increasing Eu concentration in the aqueous phase and reaches a value of 1 × 10^4 at >0.25 M Eu. The results demonstrate that purified Cyanex 301 can separate Am from a macro amount of Eu and that a suitable increase of Eu concentration in the aqueous phase is beneficial for the separation.

Table 2 gives the results of separating Am from Ln with purified Cyanex 301 extraction in the presence of a macro amount of Pr + Nd (0.1 ~ 0.6 M). Figure 4 shows the effects of Pr + Nd concentration in the aqueous phase on the distribution ratios D_{Am}, D_{Eu}, and D_{Pr+Nd}. The distribution ratios decrease slightly when Pr + Nd concentration increases. It can be seen from Table 2 that in the presence of a macro amount of Pr + Nd, purified Cyanex 301 can effectively separate Am from Ln with $SF_{Am/Eu}$ ~ 4.7 × 10^3 and $SF_{Am/Pr+Nd}$ ~ 2.1 × 10^3 when saponified to 3 mol%.

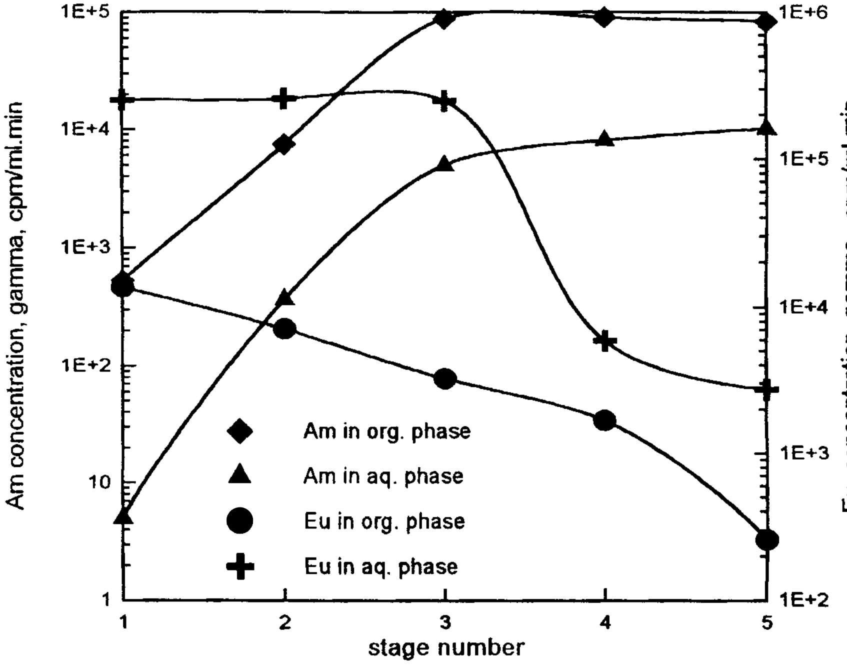


FIG. 5 ^{241}Am and $^{152-154}Eu$ concentration profiles in two phases. Feed: ^{241}Am, $^{152-154}Eu$ + 1 M $NaNO_3$, pH 4.0. Extractant: 0.5 M purified Cyanex 301-kerosene. Scrubbing solution: 0.5 M $NaNO_3$ (pH 3.5). Temperature: 25 ± 0.2"C.

Cascade Countercurrent Extraction

Figure 5 describes ^{241}Am and $^{152-154}$Eu concentration profiles in two phases in a countercurrent extraction cascade. 99.994% ^{241}Am and 0.07% $^{152-154}$Eu are extracted into the organic phase. The separation coefficient of $^{152-154}$Eu from ^{241}Am [defined as (extraction percentage of Am)/(extraction percentage of Eu)] is 1.4 × 10^3 and that of ^{241}Am from $^{152-154}$Eu [defined as (percentage of Eu in raffinate)/(percentage of Am in raffinate)] is 1.7 × 10^4. A tracer amount of Am has been separated effectively from a tracer amount of Eu with three extraction stages and two scrubbing stages.

Figure 6 describes ^{241}Am and Pr + Nd concentration profiles in two phases in a countercurrent extraction cascade. 99.993% ^{241}Am and 0.54% Pr + Nd are extracted into the organic phase. The separation coefficient of Pr + Nd from ^{241}Am and of ^{241}Am from Pr + Nd are 185 and 1.4 × 10^4, respectively. Am can be separated effectively from a macro amount of Pr + Nd without a scrubbing stage.

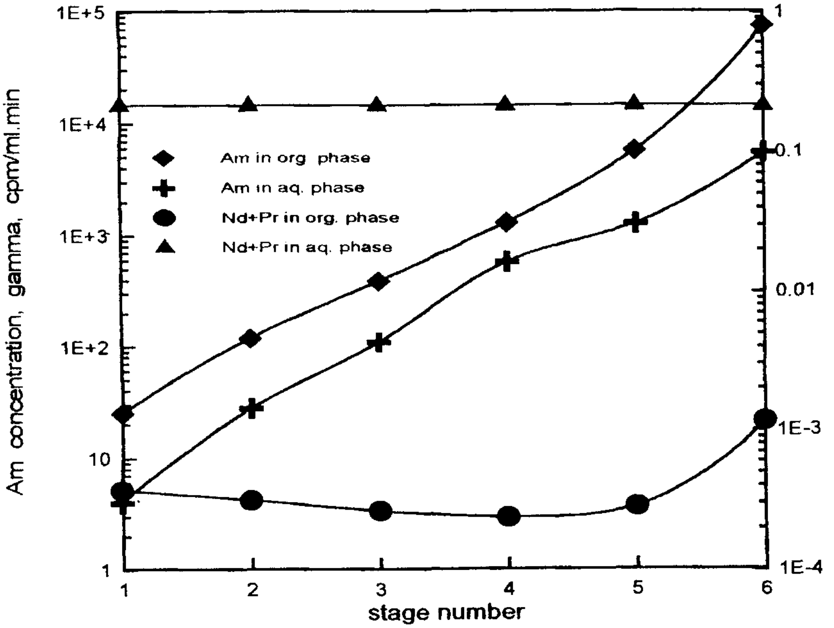


FIG. 6 ^{241}Am and Pr + Nd concentration profiles in two phases. Feed: ^{241}Am + 0.2 M (Pr + Nd)$(NO_3)_3$, pH 5.0. Extractant: 0.5 M purified Cyanex 301-kerosene, saponified to 0.2 mol%. Temperature: 25 ± 0.2°C.

CONCLUSION

Due to the presence of the soft donor atom "S" in the Cyanex 301 molecule, the covalent bonding tendency of the extractant to Am(III) increases and high selectivity toward Am(III) over Ln(III) appears. The results in the present work demonstrate that Am can be separated effectively from tracer and macro amounts of Ln with purified Cyanex 301 extraction.

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