

**ACTINIDES(III)-LANTHANIDES GROUP SEPARATION FROM NITRIC ACID USING
NEW AROMATIC DIORGANYLDITHIOPHOSPHINIC ACIDS**

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Abstract

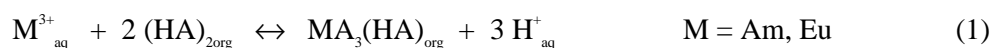
In this paper, extractants are presented which made it possible to separate actinides(III) and lanthanides from strong nitric acid solutions (0.05 - 1 mol/L). For this purpose, new aromatic dithiophosphinic acids were synthesised and characterised, and the distribution ratios of Am(III), Eu(III) and all relevant lanthanides were determined in batch extraction experiments. The extractant used was a mixture of aromatic dithiophosphinic acid + synergist in an aromatic solvent. In particular, the influence of the synergist and solvent is described. With the aid of a 12-step flowsheet it was also possible for the first time to continuously partition actinides/lanthanides at an acid concentration of 0.5 mol/L HNO₃.

Introduction

Isolation of the trivalent Am and Cm actinides from liquid high-level waste is the aim of various partitioning strategies. However, the desirable selective extraction from high-level nitric acid solutions produced by the PUREX process and containing over 30 fission products has not been possible to date. After U, Pu, Np and the majority of undesirable fission products have been separated, an actinide(III) fraction arises in all the partitioning processes so far known (e.g. TRUEX, TRPO, DIDPA and DIAMEX) [1]. The trivalent actinides are so far always accompanied by the trivalent lanthanides, which are abundantly present in HLLW, due to their comparable chemical and physical properties. Since they impair the transmutation of Am and Cm due to their high neutron absorption cross-sections, the two element groups should be partitioned again in a subsequent step. This actinide/lanthanide partitioning is still one of the most difficult operations in any partitioning process.

In the recent past, several interesting extractants have been presented in the literature for actinide/lanthanide partitioning by liquid/liquid extraction. Of particular interest are studies by Chinese scientists [2] who achieved incredibly high Am/Eu separation factors > 5000 with purified Cyanex 301.

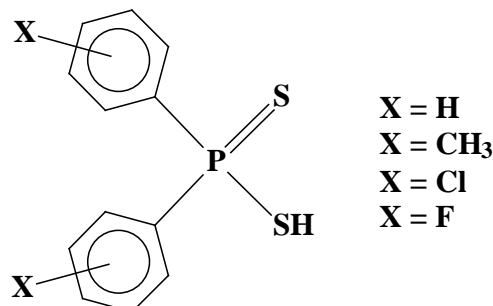
Since we have recently [3] confirmed the excellent results of Zhu et al., we considered that it would be interesting to extend our studies to the selective extraction of trivalent actinides from lanthanides using this class of sulphur-containing extractants. According to Zhu et al. the following extraction mechanism is proposed for the extraction of Am(III) and Eu(III) with Cyanex 301 (HA) where the subscripts aq and org refer to the aqueous and organic phases.



It can be seen from Equation 1 that the extraction equilibrium also depends on acid strength. Three protons are released during extraction. Since previous research on Cyanex 301 indicated that its acidity is too low and that it only becomes an effective extractant in the higher pH regions of aqueous solutions (i.e. pH > 3), it was necessary to attempt to increase the acidity of such ligands as R₂PSSHs by attaching electron-withdrawing substituents (R) so that they could extract in lower pH regions. The ideal acidity of the aqueous phase for the actinide(III) extraction should fall in the range below pH 2. Otherwise the pH value must be controlled or stabilised by a buffer during separation, especially if real waste solutions and Am(III) concentrations > 10⁻³ mol/L are involved.

Recently we have shown that aromatic dithiophosphinic acids (Figure 1) synthesised in our laboratory are more powerful extractants than Cyanex 301 and first results have already been published [4,5]. A detailed description of the synthesis and characterisation of the extractants and the experimental description of batch extraction studies are to be found in reference [6], where studies on the radiolytic stability of the new extractants are also reported, featuring high resistance to gamma radiation. The present paper describes the latest results on actinide/lanthanide partitioning with the aid of aromatic dithiophosphinic acids and, for the first time, also presents the promising results of a continuous extraction procedure.

Figure 1. Structure of the synthesised aromatic dithiophosphinic acids

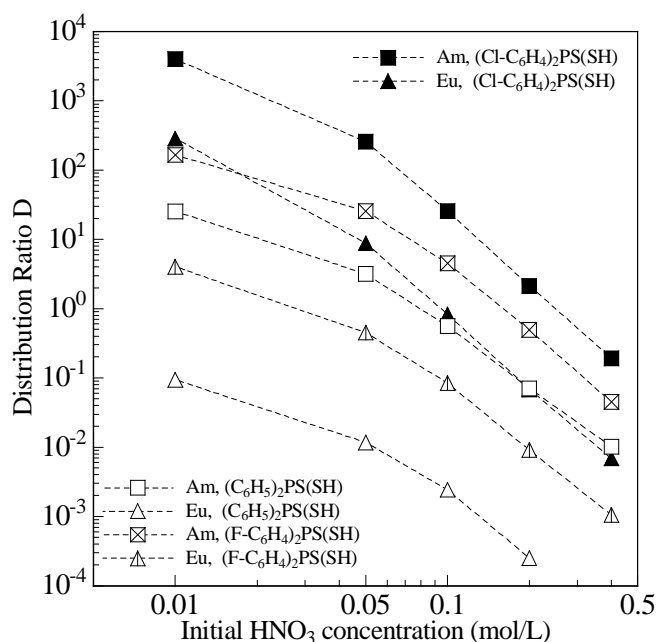


Results and discussion

Effect of the synergist

The extraction results with bisphenyl-, bis(chlorophenyl)- and bis(fluorophenyl)-dithiophosphinic acid using TBP as the synergist from 0.01 to 0.4 mol/L nitric acid are shown in Figure 2. It can be seen that the extraction ratios of Am(III) and also Eu(III) increase strongly in the order $(\text{C}_6\text{H}_5)_2\text{PS}(\text{SH}) < (\text{F-C}_6\text{H}_4)_2\text{PS}(\text{SH}) < (\text{Cl-C}_6\text{H}_4)_2\text{PS}(\text{SH})$. However, the selectivity in the investigated acidity range decreases in the same order with Am/Eu separation factors of 230 - 280, 41 - 57 and 28 - 31. This suggests that the extraction can be improved by incorporating even stronger electron-attracting groups (such as NO_2 or two Cl groups), whereas selectivity decreases inversely. The influence of TBP and the extractant concentration on the extraction of Am and Eu has also been examined. The results of a slope analysis are reported in reference [6]. It was found that the optimum extractant concentration was 0.5 mol/L and that of the TBP synergist ranged between 0.1 and 0.25 mol/L. No extraction has been observed without TBP.

Figure 2. Extraction of Am(III) and Eu(III) with different 0.5 M dithiophosphinic acids + 0.25 M TBP in toluene from HNO_3



The influence of the synergist on the extraction of Am(III) and Eu(III) with the dithiophosphinic acid $(\text{Cl-C}_6\text{H}_4)_2\text{PS}(\text{SH})$ was studied. We tested various neutral triorganylphosphates and phosphine oxides. The results are shown in Table 1. For comparison, the data with TBP are listed in the first line of Table 1. Using mixtures of trimethyl- or triphenylphosphate + bis(chlorophenyl)dithiophosphinic acid, for example, no extraction of Am(III) and Eu(III) ($D_{\text{Am, Eu}} < 10^{-3}$) from 0.2 M HNO_3 was observed. On the other hand, we observed a selective extraction of Am(III) with a distribution ratio D_{Am} of 2 and a high Am/Eu separation factor of > 200 under the same conditions using trioctyl- or tris(2ethylhexyl)phosphate as the synergist.

Obviously, the selectivity is caused by steric hindrance. At the phase boundary, however, a white voluminous precipitate was observed, which made phase separation difficult and was presumably caused by co-extracted HNO_3 or H_2O . Therefore, no further investigations were carried out.

The best results so far have been achieved with the synergistic combination of bis(chlorophenyl)dithiophosphinic acid + trioctylphosphine oxide (TOPO). Similar results were obtained with tributylphosphine oxide (TBPO). As can be seen from Table 1, the Am(III) distribution ratios increase by approx. two orders of magnitude compared to TBP (e.g. $D_{\text{Am, TOPO}} = 152$ and $D_{\text{Am, TBP}} = 2$, respectively, for 0.2 M HNO_3) with comparable Am/Eu separation factors of approx. 30.

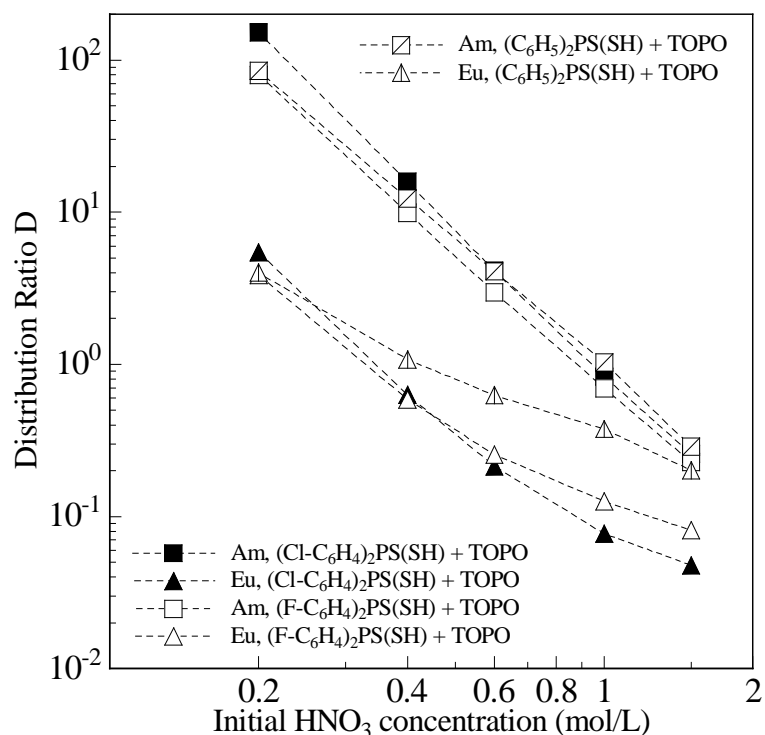
Table 1. The influence of the synergist on the extraction of Am(III) and Eu(III) with 0.5 M bis(chlorophenyl)dithiophosphinic acid + synergist in toluene from nitric acid

Synergist (0.25 mol/L)	0.2 mol/L HNO_3			0.4 mol/L HNO_3		
	D_{Am}	D_{Eu}	$\text{SF}_{\text{Am/Eu}}$	D_{Am}	D_{Eu}	$\text{SF}_{\text{Am/Eu}}$
Tributylphosphate	2.13	0.068	31.2	0.19	0.0068	28.1
Trimethylphosphate	0.0046	0.00037	12.3	0.0012	0.00056	2.3
Triphenylphosphate	0.0017	0.00022	8.1	0.00051	0.00026	2.0
Trihexylphosphate	25.54	21.25	1.2	3.25	3.31	0.9
Trioctylphosphate*	2.11	0.0088	237.9	0.165	0.0013	122.5
Tris(2-ethylhexyl)phosphate*	1.98	0.00165	1199.8	0.169	0.00072	235.1
Tributylphosphine oxide	121.07	5.89	20.5	11.54	0.588	19.6
Trioctylphosphine oxide	152.25	5.46	27.9	15.85	0.632	25.1
Cyanex 925	4.17	1.54	2.7	0.456	0.167	2.7

* precipitate formed after extraction

Figure 3 shows a comparison of the three dithiophosphinic acids + TOPO as the synergist. Surprisingly, a different pattern is found here compared to that with the synergist TBP (cf. Fig. 2). At an acid concentration of 0.2 mol/L HNO_3 the extraction results with different dithiophosphinic acids are even almost comparable to each other. This also applies to the Am distribution ratios at higher HNO_3 concentrations. However the Eu distribution ratios increase in the order $(\text{Cl-C}_6\text{H}_4)_2\text{PS}(\text{SH}) < (\text{F-C}_6\text{H}_4)_2\text{PS}(\text{SH}) < (\text{C}_6\text{H}_5)_2\text{PS}(\text{SH})$ with increasing acidity so that the selectivity also decreases in the same order (inversely for TBP).

Figure 3. Extraction of Am(III) and Eu(III) with different 0.5 M dithiophosphinic acids + 0.25 M TOPO in toluene from HNO₃



Influence of the diluent

In previous extraction studies toluene was used as the solvent because the aromatic dithiophosphinic acids are poorly soluble in nonpolar solvents such as n-dodecane. A disadvantage of toluene, however, is that it is very aggressive towards Plexiglas, the material of our mixer-settlers which will be used in the near future for the continuous counter-current tests, and therefore cannot be used.

For this reason, other aromatic hydrocarbons were tested, e.g. Plexiglas is very resistant to tert.-butyl benzene. Surprisingly, the extraction properties also changed when changing the solvent. The results are compiled in Table 2.

It can be seen that the distribution ratio D_{Am} increases with rising molecular magnitude of the solvent and that the Am/Eu separation factors also increase in the order toluene < xylene < tert.-butyl benzene < tri-isopropylbenzene. With tri-isopropylbenzene, for example, a $D_{Am} = 4.75$ and a separation factor of 30 is obtained for HNO₃ = 1 mol/L. Increasing the size and number of substituent on the benzenic ring seems to decrease the interaction between the diluent and the extractants, and consequently, let the extractant exert a more direct interaction with the M(III) ions.

Table 2. The influence of the diluent on the extraction of traces of Am(III) and Eu(III) with 0.5 M bis(chlorophenyl)dithiophosphinic acid + 0.25 M TOPO from nitric acid (without macro concentrations of lanthanides)

Diluent	HNO ₃ (mol/L)	D _{Am}	D _{Eu}	SF _{Am/Eu}
Toluene	0.5	7.19	0.306	23.5
	1.0	0.794	0.0732	10.8
	2.0	0.113	0.0329	3.4
	3.0	0.0263	0.0158	1.7
Xylene	0.5	8.83	0.385	22.9
	1.0	0.927	0.0805	11.5
	2.0	–	–	–
	3.0	–	–	–
Tert.-butylbenzene	0.5	19.18	0.615	31.2
	1.0	1.768	0.0988	17.9
	2.0	0.193	0.0393	4.9
	3.0	0.0476	0.0219	2.2
Tri-isopropylbenzene	0.5	55.8	1.23	45.6
	1.0	4.76	0.159	29.8
	2.0	0.416	0.0570	7.3
	3.0	0.106	0.0461	2.3

Distribution ratios of ²⁴¹Am and all relevant Lanthanides

Prior to the continuous counter-current experiments, the distribution ratios of all relevant lanthanides present in the feed of an An(III)/Ln(III) fraction from the DIAMEX process had to be determined. Table 3 shows the compositions of the four simulated feed solutions with different HNO₃, which were used in the subsequent extraction studies. Table 4 show the results of the extraction of ²⁴¹Am and ¹⁵²Eu and of the other Ln(III) (determined by ICP-MS) with 0.5 M bis(chlorophenyl)dithiophosphinic acid + 0.25 M TOPO in tert.-butyl benzene. The results with tert.-butyl benzene as the solvent show that the planned counter-current tests can be carried out at a HNO₃ feed concentration of about 0.5 - 1 mol/L. However, it can also be seen that the distribution ratios D_{Am} and D_{Eu} are smaller by a factor of 2 in comparison to those determined from pure HNO₃ (cf. Table 2).

Table 3. Composition of the simulated An(III)/Ln(III) feed solutions generated from DIAMEX process for the extraction tests

	HNO ₃			
	0.50 mol/L	0.99 mol/L	2.06 mol/L	3.09 mol/L
Element	Concentration in g/L determined by ICP-MS ¹⁾			
Y	0.2372	0.2345	0.2380	0.2261
La	0.7446	0.7200	0.7409	0.7064
Ce	1.4595	1.3830	1.4470	1.4070
Pr	0.6832	0.5993	0.6715	0.6447
Nd	2.4823	2.4550	2.4948	2.4045
Sm	0.4806	0.4685	0.4796	0.4603
Eu	0.0939	0.0878	0.0907	0.0900
Gd	0.0751	0.0765	0.0813	0.750

¹⁾ rel. Error ± (4-10)%

Table 4. Extraction of Am(III) and lanthanides(III) with 0.5 M bis(chlorophenyl)dithiophosphinic acid + 0.25 M TOPO in tert.-butylbenzene from simulated An/Ln feed solution.

	HNO ₃							
	0.5 mol/L		1.0 mol/L		2.0 mol/L		3.0 mol/L	
Element	D _{M(III)}	SF _{Am/Ln}	D _{M(III)}	SF _{Am/Ln}	D _{M(III)}	SF _{Am/Ln}	D _{M(III)}	SF _{Am/Ln}
Y	0.325	36.7	0.0384	43.6	<0.0005	-	<0.0004	-
La	0.254	46.9	0.0353	47.4	0.0053	33.8	0.0015	29.2
Ce	0.551	21.6	0.0741	22.6	0.0060	29.8	0.0025	17.0
Pr	0.527	22.6	0.0844	19.9	0.0135	13.3	0.0044	9.8
Nd	0.296	40.3	0.0527	31.8	0.0099	18.1	0.0031	14.2
Sm	0.373	31.9	0.0672	24.9	0.0099	18.0	0.0039	11.2
Gd	0.303	39.4	0.0515	32.5	0.0082	21.8	0.0026	16.3
Eu	0.357	33.4	0.0688	24.4	0.0122	14.8	0.0066	6.6
¹⁵² Eu	0.352	33.8	0.0931	18.0	0.0377	4.8	0.0216	2.0
²⁴¹ Am	11.926		1.677		0.180		0.0436	

Determination of the M(III) Transfer Kinetic

In order to obtain information about the transfer kinetics of the dithiophosphinic acid/TOPO/tert.-butyl benzene and An(III)/Ln(III) feed simulate extraction system, the dependence on the mixing time (0.5 - 12 min) was determined. After mixing, both phases were immediately separated by centrifugation at 4200 rpm (1 min), aliquots were sampled and analysed by γ -spectrometry. Table 5 shows the results of the simple kinetics studies. It can be seen that the equilibrium state is only obtained after 10 min mixing time.

Table 5. Am(III) and Eu(III) extraction kinetics for 0.5 M bis(chlorophenyl)dithiophosphinic acid + 0.25 M TOPO in tert.-butylbenzene from simulated An(III)/Ln(III) feed solution (0.5 M HNO₃)

Contact time (min)	D _{Am}	D _{Eu}	SF _{Am/Eu}
0.5	0.795	0.184	4.3
1	1.55	0.263	5.8
2	1.64	0.316	5.2
5	4.31	0.357	12.1
6	7.21	0.352	20.2
10	9.66	0.380	25.4
12	9.18	0.392	23.4

Continuous An(III)/Ln(III) Separation with the aid of Centrifugal Extractors

An 8-stage miniature centrifugal extractor battery (two batteries with four stages each) of the same design as installed at ITU, Karlsruhe, was acquired from INET Beijing, China. A first continuous extraction test was carried out for An(III)/Ln(III) separation at 0.5 mol/L HNO₃. The aim of this experiment was to determine in the first place the efficiency and hydraulic properties of the centrifugal extractors. At the same time, however, we expected that the extraction kinetics, especially of Am(III) (see Table 5), would exert a great influence on the process parameters initially determined empirically. On the basis of the results so far obtained, a flowsheet was proposed by P. Baron, CEA, France, which is shown in Figure 4.

Figure 4. Flowsheet of the counter-current test with centrifugal-contactors for the An(III)/Ln(III) separation

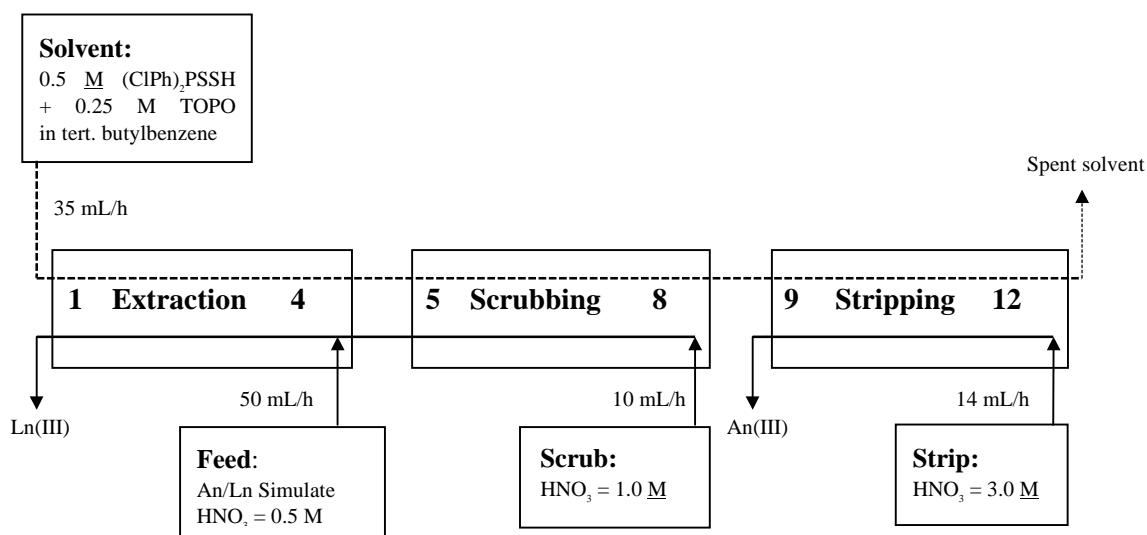


Table 6 shows the composition of the feed solution. The extraction scheme contains eight stages for extraction + scrubbing and four stages for stripping. Since only eight stages were available, however, the loaded organic phase coming from stage 8 was collected and stripping was carried out with four steps in a subsequent second test after previous cleaning of the extraction battery. The attainment of the steady state (after approx. 3 h) was checked by sampling at the outlets (raffinate stage 1, product stage 8). Subsequently, the samples were taken, the organic phase was separated from the aqueous phase by centrifuging, and aliquots were first measured with the aid of gamma spectrometry.

Table 6. Composition of the simulated An(III)/Ln(III) feed solutions generated from DIAMEX process. The HNO₃ concentration was 0.5 Mol/L

Element	Concentration (g/L)	Activity (Bq/mL)	γ-Activity (Cps/mL)
Am		²⁴¹ Am, 1850	148.912
Cm		²⁴⁴ Cm, 500	
Y	0.235		
La	0.787		
Ce	1.535	¹³⁹ Ce, 2500	75.719
Pr	0.722		
Nd	2.627		
Sm	0.517		
Eu	0.0975	¹⁵² Eu, 1850	81.638
Gd	0.0725	¹⁵³ Gd, 1850	46.377

The following main results were obtained and are summarised in Table 7. The mass balances for ²⁴¹Am, ¹⁵²Eu, ¹⁵³Gd and ¹³⁹Ce were good for the extraction and scrubbing part (100 - 103 %), less satisfactory for the stripping part (67 - 81 %). The decontamination factor $DF(Am)_{raf/feed}$ was 28.2. In the case of Am(III)/Ln(III) separation the DFs in column 6 of Table 3 were obtained, which increase in the order Ce < Eu < Gd. As was to be expected, the extraction efficiency obtained with the aid of the centrifugal extractors was not good. The distribution ratios of ²⁴¹Am determined in stages 1 and 8, for example, were clearly (by a factor of 3 - 4) below those obtained in batch experiments. This reflects the influence of the slow extraction kinetics of Am(III). In contrast, the extraction kinetics of the lanthanides is clearly better.

The concentration profiles of the γ-active radionuclides ²⁴¹Am, ¹⁵²Eu, ¹⁵³Gd and ¹³⁹Ce are shown in Figures 5 and 6. The experiment remains to be complemented by the α-analyses for the determination of the Cm concentration profiles and the ICP-MS analyses for quantifying the inactive lanthanides. Moreover, the H⁺ concentration profile remains to be determined. Based on the results obtained here, further experiments are planned for An(III)/Ln(III) separation in the centrifugal extractors.

Table 7. Distribution ratios, mass balance and decontamination factors in the extraction-scrubbing stages obtained in the counter-current test

Element	D _{M(III)} stage 1	D _{M(III)} stage 8	Extract (%) stage 8	Raffinat (%) stage 1	DF (Am/Ln)	DF (Am) raf /feed
Am	2.88	2.153	99.35	3.55		28.18
Ce	0.293	0.144	4.20	96.27	33.76	
Eu	0.208	0.134	2.32	101.20	61.24	
Gd	0.164	0.119	1.49	101.85	94.69	

Figure 5. Concentration profile of ^{241}Am , ^{152}Eu , ^{153}Gd and ^{139}Ce in the extraction-scrubbing bank

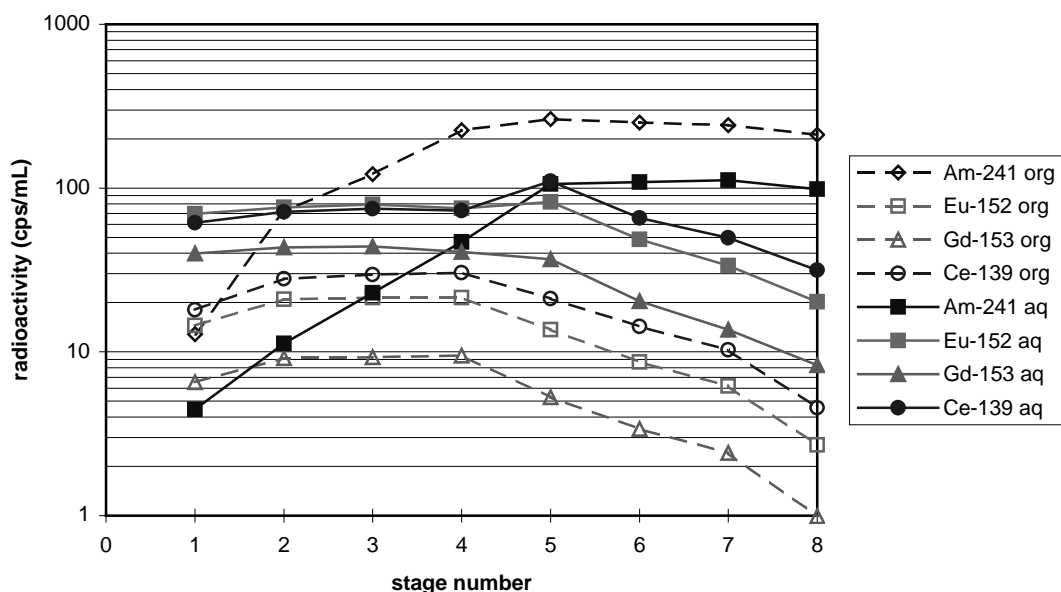
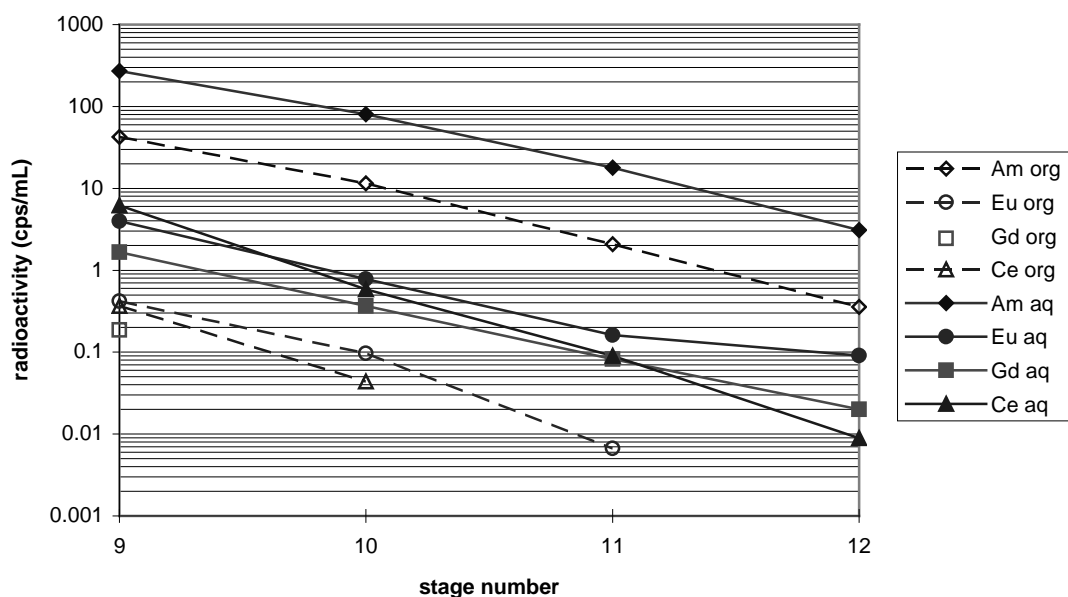


Figure 6. Concentration profile of ^{241}Am , ^{152}Eu , ^{153}Gd and ^{139}Ce in the stripping bank



Conclusions

The results of this study show that actinide(III)/lanthanide(III) partitioning is possible with high efficiency using the newly developed S-containing extractants. By variation of the synergist and solvent it is now possible to carry out group separation at 1.0 mol/L HNO_3 with Am(III) distribution ratios > 1 and Am(III)/Ln(III) separation factors > 20 . The results of the continuous test clearly show that it will be possible in future to successfully reprocess real An(III)/Ln(III)-containing process solutions arising from HLLW partitioning.

Acknowledgements

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