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SEPARATION OF TRANSPLUTONIUMS AND LANTHANIDES BY TERTIARY AMINE EXTRACTION

II. CONTAMINANT IONS

R. D. Baybarz
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Chemical Development Section A

SEPARATION OF TRANSPLUTONIUMS AND LANTHANIDES BY TERTIARY AMINE EXTRACTION

II. CONTAMINANT IONS

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ABSTRACT

The results of laboratory experiments showed that in extraction of transplutonium elements from 10.85 M LiCl by 30% Alamine-336 in DEB, Cr^{3+}, Ce^{3+}, Eu^{3+}, Y^{3+}, Ba^{2+}, and Sr^{2+} in the feed will remain in the aqueous phase. Cd^{2+}, Hg^{2+}, Pd^{2+}, Fe^{3+}, Co^{2+}, Mn^{2+}, Sn^{4+}, Ti^{4+}, Cu^{2+}, TcO_4^-, Zn^{2+}, Zr^{4+}, Ru^{3+}, MoO_4^{2-}, Ni^{2+}, and Pb^{2+} will be extracted, but in the stripping of the transplutoniums from the organic with 5 M HCl, all of these ions except Ni^{2+} and Ti^{4+} will remain in the organic. The presence of Br^-, F^-, and ClO_4^-, and acetate in the extraction feed in concentrations up to 0.1 N does not drastically affect the separation factors of transplutoniums and lanthanides, but I^- and NO_3^- in 0.7 M concentrations decrease the separation factor to 1.

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1.0 INTRODUCTION

A process has been developed (1) for separating transplutonium elements from lanthanides by preferential extraction into 30% Alamine-336 (a mixture of octyl and decyl tertiary amines) in diethyl benzene from 11 M LiCl. This report indicates the extraction and stripping behavior of fission and corrosion product elements and the effect of extraneous anions on lanthanides and actinides as shown by laboratory-scale determinations of distribution coefficients.

The authors gratefully acknowledge the helpful and critical suggestions of R. E. Leuze and Boyd Weaver.

2.0 DISTRIBUTION OF CORROSION AND FISSION PRODUCT ELEMENTS IN EXTRACTION AND STRIPPING

The distribution coefficients for the various ions between 10.85 M LiCl and 30% Alamine-336 in diethyl benzene (Table 1) indicate that Cr^{3+}, Ce^{3+}, Eu^{3+}, Y^{3+}, Ba^{2+}, and Sr^{2+} in the feed will remain mostly in the aqueous phase during extraction. These elements will leave the system in the aqueous waste of the solvent extraction system. The ions Cd^{2+}, Hg^{2+}, Pd^{2+}, Fe^{3+}, Co^{2+}, Mn^{2+}, Sn^{4+}, Ti^{4+}, Cu^{2+}, TcO_4^-, Zn^{2+}, Zr^{4+}, Ru^{3+}, MoO_4^{2-}, Ni^{2+}, and Pb^{2+} in the feed will be extracted into the organic phase along with the transplutoniums.

When the transplutoniums are stripped from the organic phase with 5 M HCl, only Ti and Ni will accompany the product. Distribution coefficients of most of the extracted elements increased with increasing acidity (Table 2, Fig. 1), because of increasing stability of the chloride complex. Distribution of Mn^{2+}, Fe^{3+}, Zr^{4+}, TcO_4^-, and Cd^{2+} increased through the whole acid range, while that of Co^{2+}, Cu^{2+}, and Hg^{2+} showed maximum extraction at ~6 M HCl. The ions Zr^{2+}, Sn^{4+}, and Pb^{2+} showed maxima in ~2 M HCl, while extraction of Ru^{3+} and Pd^{2+} steadily decreased with increasing acidity. Molybdate distribution was minimum in 2 M HCl, but it steadily increased with increasing acidity. The variation in extractibility of the elements with change in acid concentrations is the result of formation of various chloride complexes varying from polyanionic to neutral. The ions Ti^{4+}, Cr^{3+}, and Ni^{2+} were essentially not extracted into Alamine-336 from HCl solution.

The extraction from various HCl concentrations into 30% Alamine in diethyl benzene is similar to that for the extraction of the first transition series into methyldioctylamine in trichloroethylene from HCl (work done on a tracer level) (2,3).

Table 1. Distribution of Various Ions between 30% Alamine-336-DEB and 10.85 M LiCl

Ion*	D.C. (o/a)
Cd^{2+}	2830
Hg^{2+}	1480
Pd^{2+}	533
Fe^{3+}	408
Co^{2+}	312
Mn^{2+}	263
Ti^{4+}	152
Cu^{2+}	109
Sn^{4+}	71.3
TcO_4^{-}**	53.2
Zn^{2+}	39.4
Zr^{4+}**	15.2
Am^{3+}**	13.9
Ru^{3+}**	9.2
MoO_4^{2-}	6.00
Ni^{2+}	4.27
Pb^{2+}	3.37
Cr^{3+}	0.242
Eu^{3+}**	0.118
Ce^{3+}**	0.102
Y^{3+}**	0.020
Ba^{2+}	0.008
Sr^{2+}**	0.006

*0.1 N concentration in aqueous phase when chloride was soluble to this extent.

**Tracer activity studies.

Table 2. Distribution of Various Elements between 30% Alamine-336-DEB and HCl

Element	Distribution Coefficient						
	0.5 N HCl	1.0 N HCl	2.0 N HCl	4.0 N HCl	6.0 N HCl	8.0 N HCl	10.0 N HCl
Ti^{4+}	0.008	0.009	0.009	0.010	0.011	0.009	0.008
Cr^{3+}	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Mn^{2+}	0.007	0.007	0.042	0.72	2.9	5.9	5.4
Fe^{3+}	76	308	790	1240	1280	1280	1280
Co^{2+}	0.005	0.043	0.37	5.5	40	109	56
Ni^{2+}	0.009	0.009	0.009	0.009	0.009	0.009	0.009
Cu^{2+}	0.40	1.1	3.8	41	143	40	15
Zn^{2+}	1040	1850	3540	2950	1520	720	68
Zr^{4+}	0.10	0.18	0.41	0.91	2.3	72	450
MoO_4^{2-}	12.9	10.2	6.4	25	57	82	85
TcO_4^-	0.97	12.4	27	78	183	311	367
Ru^{3+}	3.5	3.0	2.0	1.8	0.95	0.38	0.029
Pd^{2+}	568	598	574	577	400	33	7
Cd^{2+}	22	82	140	254	300	383	450
Sn^{4+}	242	387	793	410	273	220	193
Hg^{2+}	29	57	131	489	790	167	52
Pb^{2+}	23	39	40	8.4	1.8	0.23	0.03
Eu^{3+}	*	*	*	*	*	*	*
Am^{3+}	*	*	*	*	*	*	*

*<0.001

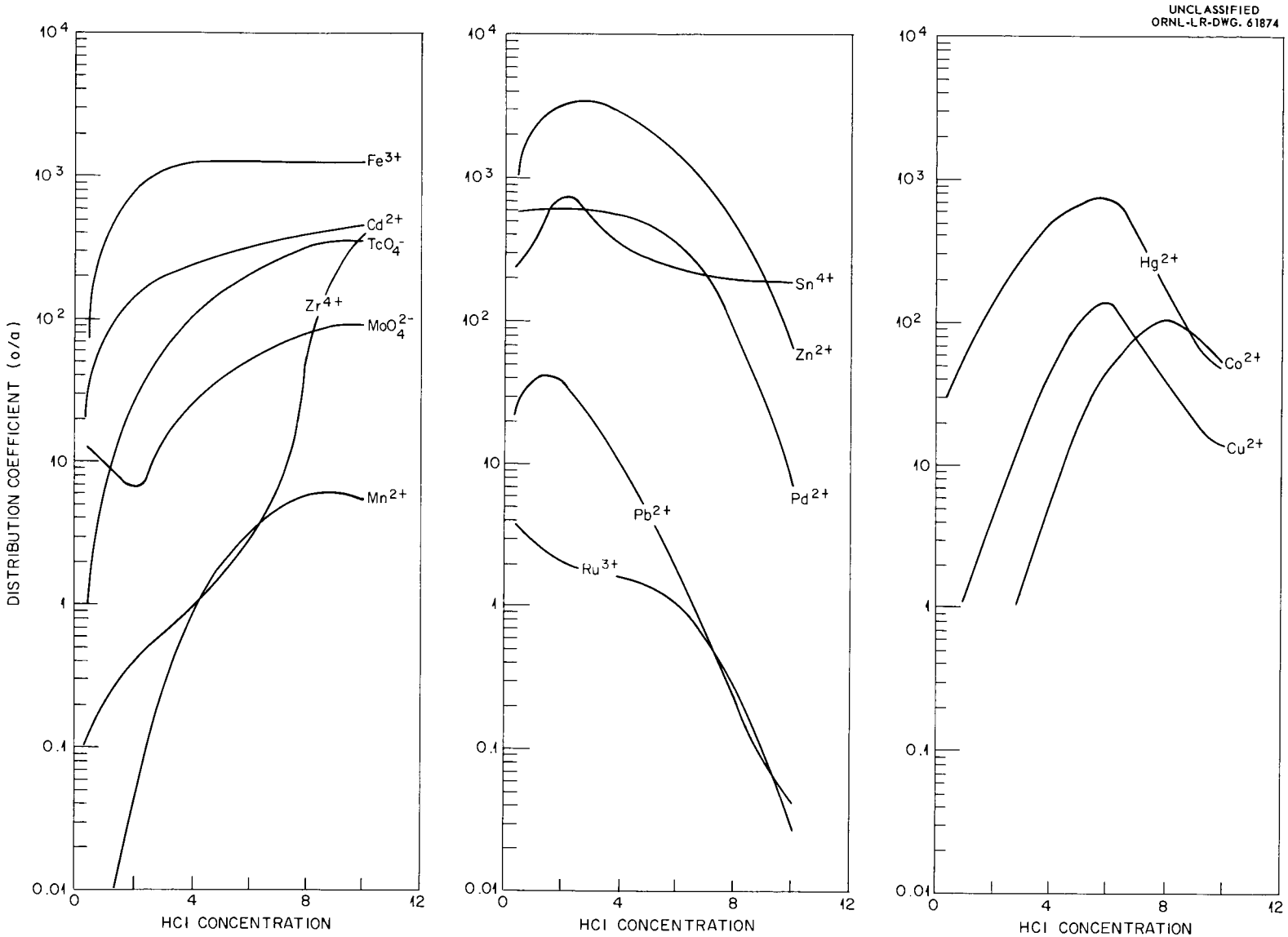

Fig. 1. Distribution coefficients of various ions between 30% Alamine-336 in diethyl benzene and HCl solutions as a function of HCl concentration.

The extraction of HCl into 30% Alamine-336 in diethyl benzene from aqueous hydrochloric acid solution increased directly as a function of the HCl concentration (Fig. 2).

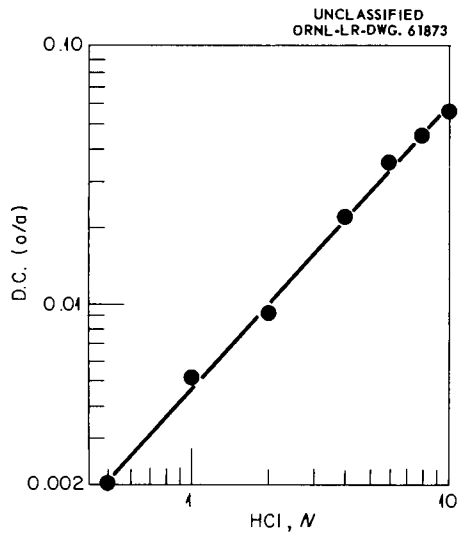

Fig. 2. Distribution coefficient of HCl between 30% Alamine-336 in diethyl benzene and aqueous HCl.

3.0 EFFECT OF EXTRANEOUS ANIONS ON ACTINIDE AND LANTHANIDE DISTRIBUTION COEFFICIENTS

The presence in the feed of up to 0.1 N perchlorate, fluoride, or bromide ion did not greatly affect the distribution coefficients of the actinides and lanthanides as represented by americium and europium, respectively (Fig. 3, Table 3). The distribution coefficient of both elements began to decrease rapidly at 0.01 N acetate. At 0.1 N iodide ion the d.c. of americium decreased sharply but that of europium began to increase. Increasing nitrate ion increased both distribution coefficients rapidly, with a crossover point of the two curves at 0.7 N nitrate.

The separation of the actinides and lanthanides will be affected by the presence of extraneous ions as follows:

The presence of 0.1 N fluoride, bromide, perchlorate, or acetate will have no effect on the separation factor of ~100 between americium and europium. Acetate at higher concentrations decreases the separation factor to ~30 at 0.5 N. Iodide and nitrate at 0.1 N gave a separation factor of ~50 and 10, respectively, between americium and europium. At higher anion concentrations the separation factor decreased to 1 (0.7 N for acetate and nitrate), with the europium being more extractable than americium at greater anion concentrations.

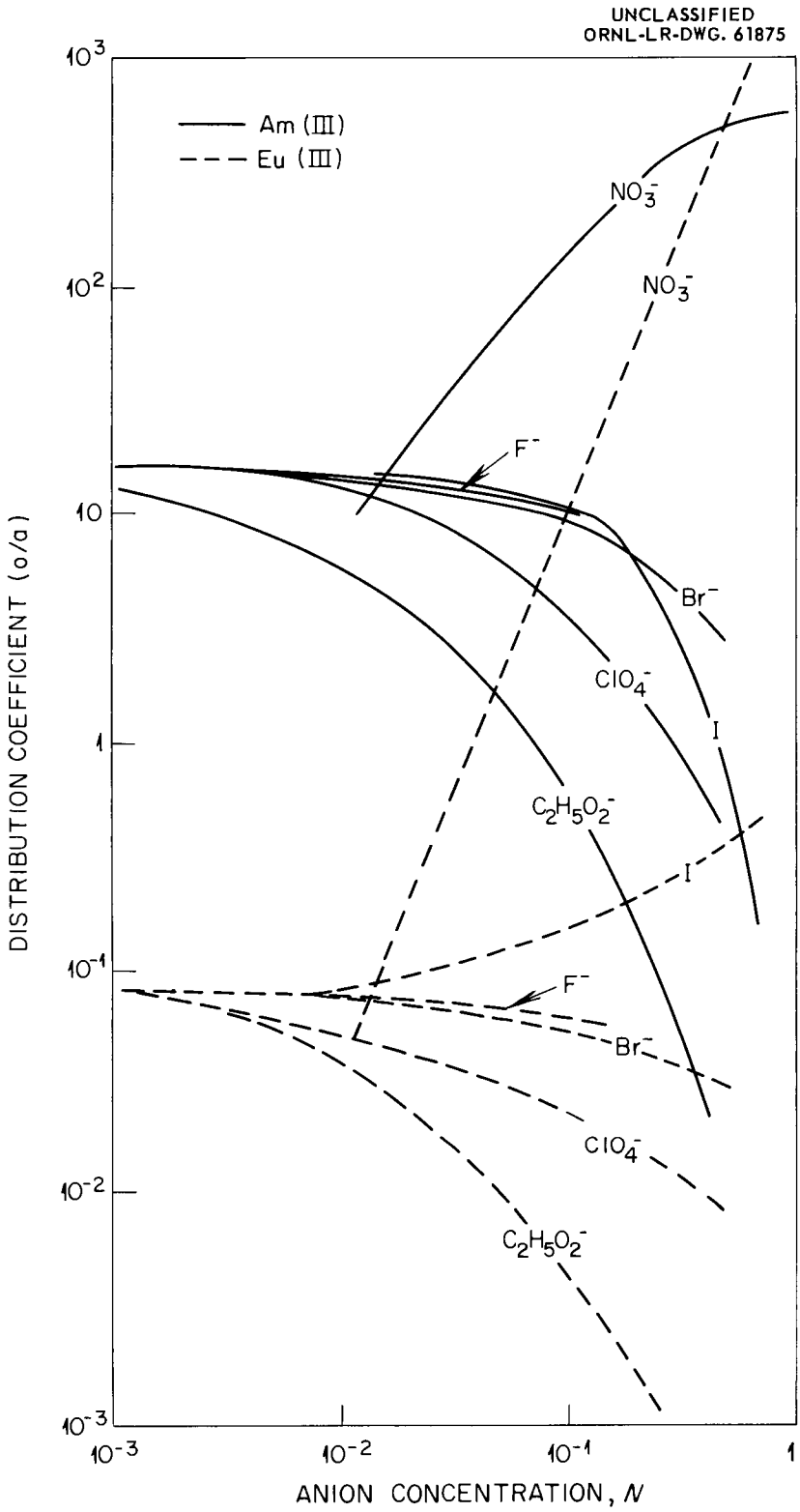

Fig. 3. Effect of various anions on distribution coefficients of trivalent americium and europium between 10.85 M LiCl and 30% Alamine-336 in diethyl benzene.

Table 3. Effect of Various Anions on Distribution of Am and Eu between 30% Alamine-336-DEB and 10.85 M LiCl

Element	Distribution Coefficient 0.001 N Anion	0.005 N Anion	0.01 N Anion	0.05 N Anion	0.1 N Anion	0.25 N Anion	0.50 N Anion	0.75 N Anion
				ClO_4^-				
Am	15.5	11.5	12.0	8.00	4.80	1.08	0.47	
Eu	0.084	0.061	0.046	0.035	0.025	0.018	0.009	
				I^-				
Am			13.9	13.2	10.0	7.0	0.86	0.16
Eu			0.10	0.12	0.18	0.26	0.33	0.45
				F^-				
Am	16.2	15.5	14.9	11.8	10.9			
Eu	0.090	0.086	0.080	0.078	0.060			
				$C_2H_5O_2^-$				
Am	11.0	8.38	4.42	1.74	0.80	0.084	0.024	
Eu	0.085	0.054	0.040	0.012	0.005	0.0013	0.0008	
				Br^-				
Am	16.6	15.6	13.4	12.7	10.0	5.49	2.78	
Eu	0.089	0.073	0.074	0.057	0.051	0.041	0.031	
				NO_3^-				
Am			9.1	49	95	300	490	590*
Eu			0.083	1.4	9.2	62	210	1030*

*1.0 N

4.0 EXPERIMENTAL PROCEDURE

Stock solutions for the series of studies were made up in large quantities so that the same solution could be used for all runs. The 10.85 M LiCl solution was made by dissolving LiCl in distilled water, and the amine by diluting Alamine-336 to 30% by volume with diethyl benzene. The alamine solution was scrubbed, volume for volume, with three passes of 1 M Na_2CO_3 to convert the amine to the basic form and remove contaminating materials. After one pass with distilled water, two passes with 3 M HCl were made to produce the tertiary amine hydrochloride salt. Finally, two passes with 2 M LiCl were made to remove the excess HCl from the amine. Titration of the 30% Alamine-336 solution showed a normality of 0.584 for the tertiary amine.

In the extractions of the macro runs the chloride of the cation (all except those listed under tracer studies) was dissolved in 10.85 M LiCl or the desired HCl solution at a concentration of ~0.1 N. In the tracer studies for Tc, Zr, Am, Ru, Ce, Eu, Y, and Sr, the cation was introduced in a few microliters directly into the solution being used to give an activity of $\sim 10^6$ alpha, beta, or gamma counts per minute per milliliter. Extractions were carried out with equal volumes of aqueous and organic phase. The two phases were shaken together vigorously by hand and allowed to separate before being sampled.

In the determination of the effect of extraneous anions, the anions were added to the 10.85 M LiCl as the lithium salt, except in the case of acetate where the sodium salt was used. Tracer Am-241 and Eu-152 were introduced into the aqueous solution and the same procedure for extraction was used as described for the tracer activity studies.

The tracer studies were evaluated by counting the activity in the aqueous and organic phases, alpha activity with proportional counters, beta with Geiger-Müller counters, and gamma with scintillation counters. In runs with Am-241 and Eu-152 in the same solution, the Am-241 alpha activity was counted separately, and the Eu-152 gamma activity was counted through lead absorbers to shield the Am-241 0.060-Mev gamma rays.

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