Distribution Behavior of Neptunium and Plutonium Between Acid Solutions and Some Organic Extractants

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FOR SEVERAL YEARS a group at Oak Ridge National Laboratory has been studying the extraction properties of a wide variety of organonitrogen and organophosphorus compounds and their applications in nuclear chemistry and engineering. Large-scale applications of this work have been made in the processing of uranium raw materials (*1-5*). Some of these reagents have been studied also at laboratories elsewhere, especially in England (*8*) and at Argonne (*9*), Hanford (*6, 11*), Los Alamos (*12*), and Savannah River (*10*), where applications have been made to reactor fuel processing and recovery of the transuranic elements. The work in this laboratory has now been extended to such problems as waste disposal and the recovery, separation, and purification of the actinide elements (*7*) and fission products. The study presented here treats the behavior of aqueous acid solutions of neptunium and plutonium in relation to some of these reagents and suggests some applications to separations from each other and from other elements encountered in nuclear processing.

In this study most of the work was done with nitric acid solutions; less attention was given to sulfuric and hydrochloric acid solutions. In most cases the valence of the element was adjusted to 4, though brief attention was given to Np(V) and (VI) and to Pu(III) and (VI). Organinitrogen reagents used were salts of long-chained primary, secondary, and tertiary amines and quaternary ammonium salts. Organophosphorus reagents included dialkyl phosphoric acids, neutral phosphates, and phosphine oxides.

EXPERIMENTAL

Preparation of Tracer Solutions. The extraction of neptunium was studied by the use of the 50-hour gamma activity of Np^{238}, prepared by neutron irradiation of Np^{237} oxide and kept in nitric acid solution. Np(IV) was prepared by reduction with ferrous sulfamate, Np(V) by boiling a dilute nitric acid solution, and Np(VI) by addition of sodium bromate.

Plutonium was used as a mixture of long-lived, alpha-active isotopes. It was reduced in nitric acid solution to Pu(III) by hydroxylamine nitrate or by ferrous sulfamate, and oxidized to Pu(IV) by sodium nitrite, and to Pu(VI) by sodium bromate or silver (II) oxide.

Preparation of Organic Solvents. Amines were used as solutions in the commercial paraffinic diluent Amsco 125-82 or more often in xylene, sometimes modified by branched primary tridecyl alcohol to avoid formation of a third phase. The amines were converted to salts by washing with the appropriate acid.

Organophosphorus compounds were used in Amsco 125-82 with little or no modification. Some of them were subjected to special treatment to remove more highly extractable impurities.

Equilibration and Analysis. Prepared aqueous solutions were brought in contact with equal volumes of the organic phase in separatory funnels. Many of the data were obtained by recontact of an organic phase with a prepared aqueous phase. Neptunium distribution coefficients are the ratios of total net gamma activity in 2-ml. samples of the two phases as measured by a well-type scintillation counter. Plutonium distribution coefficients were ratios of alpha activity concentrations in the two phases as measured by standard techniques.

RESULTS

Primary Amines. Table I contains data from one of the primary amines studied, Rohm and Hass Primene JM-T. Extraction of Np(IV) was low from nitrate solutions but increased somewhat with acidity. Extraction of Np(IV) was very high from sulfuric acid solutions; it was nearly independent of acidity up to 5*N* sulfuric acid and was not greatly affected by neutral sulfate. Extraction of Pu(IV) was high but much lower than that of Np(IV) from sulfuric acid solutions; it was decreased by more acid but increased by neutral sulfate.

Table I. Extraction of Np(IV) and Pu(IV) by a Primary Amine from Nitrate and Sulfate Solutions

Primene JM-T[a]	Normality		E^0_a	
Concn., *M*	HNO_3	$NaNO_3$	Np(IV)	Pu(IV)
0.1	1		0.004	
	4		0.15	
	8		0.8	
	1	5	0.03	
0.08	4			0.9
	6			1.0
	8			1.7
	H_2SO_4	$(NH_4)_2SO_4$		
0.001	1.0		≧1000	
	2.0		≧1000	
	5.0		~1000	
	10.0		~20	
	1.0	4.0	600	
0.01[b]	1.0			35
	5.0			8
	1.0	4.0		200

[a] Primene JM-T, mixture of primary amines where nitrogen joins a tertiary carbon atom attached to three 15–21 carbon atom chains.
[b] Diluent is xylene; for all other molarities diluent is Amsco 125-82.

Table II. Extraction of Np(IV) and Pu(IV) by Secondary Amines from Nitrate Solutions

	Normality		E^0_a
Amine	HNO_3	$NaNO_3$	Np(IV)
0.3*M* ditridecyl	2		0.5
	8		2.2
0.3*M* amine S-24[a]	8		1.4
			Pu(IV)
0.1*M* *N*-benzylheptadecyl	1		0.003
	8		1.0
	0.3	5.7	0.6
	1	5	0.6
0.1*M* amine S-24[b]	4		0.3
	6		0.6
	8		1.0
0.1*M* Amberlite LA-1[c]	1		0.05
	8		0.9
		NH_4NO_3	
	1	5	3
	0.3	5.7	6

[a] Bis(1-isobutyl 3,5-dimethylhexyl)amine (Union Carbide experimental).
[b] Diluent is Amsco 125-82; for all other molarities diluent is xylene.
[c] *N*-Dodecenyl trialkylmethylamine (Rohm and Haas).

Secondary Amines. Experimental data for secondary amine extraction from nitrates are given in Table II. Extractive power for Np(IV) and Pu(IV) from nitric acid was only moderate but increased with nitrate concentration. Extractions from sulfate solutions were low except with *N*-benzyl branched secondary alkyl amines—e.g., coefficients of 6 and 20 were obtained for Pu(IV) from $3M$ sulfuric acid and $3M$ sulfate, pH 0.7, with $0.1M$ *N*-benzylheptadecylamine.

Tertiary Amines. The tertiary amines studied include tri-*n*-octyl, triiso-octyl, trilauryl, and General Mills Alamine 336, a mixture of octyl and decyl straight-chain tertiary amines. Their chief observed differences were in physical properties and compatibility with diluents and aqueous solutions. Most of the work was done with triiso-octylamine (TIOA) in xylene or Amsco 125-82 with tridecyl alcohol modifier. These organic solutions separate readily from most aqueous solutions.

Data from extraction of Np(IV) by $0.1M$ and $0.3M$ TIOA in xylene from nitric acid and mixtures of nitric acid and metallic nitrates are shown in Figure 1. Maximum extraction occurred at about $2N$ nitric acid. Extraction was approximately proportional to the cube of the acidity below $1N$ nitric acid and had an increasing inverse acid dependency above $2N$ nitric acid. In the more acid range, extraction was approximately proportional to the square of the reagent concentration.

Sodium nitrate effectively increases extraction from dilute nitric acid, and aluminum nitrate is considerably more effective. Decreasing acidity of strong nitrate salt solutions increases extraction even at acidities less than $1N$, giving coefficients several orders of magnitude higher than those from nonsalted solutions of the same acidity.

Extraction of Pu(IV) by TIOA was greater than that of Np(IV) by a factor of about 10 under all conditions observed.

Extraction of Pu(IV) was very low from sulfuric acid, 1×10^{-4} from $3M$ sulfuric acid with $0.1M$ TIOA. The low extractability of Np(IV) is indicated by the ease with which it can be stripped from TIOA by either dilute sulfuric acid or sodium sulfate.

Extraction of Np(IV) from hydrochloric acid solutions is highly dependent on the acid concentration. Thus $0.3M$ TIOA gave coefficients ranging from 0.03 for $1N$ hydrochloric acid to 400 for $8N$ hydrochloric acid, with most of the increase above $6N$ hydrochloric acid.

In Figure 2 are data on the reagent concentration dependence of extractions of Pu(IV) from nitric acid by TIOA and the primary amine, Primene JM-T. Extraction was approximately proportional to the square of the primary amine

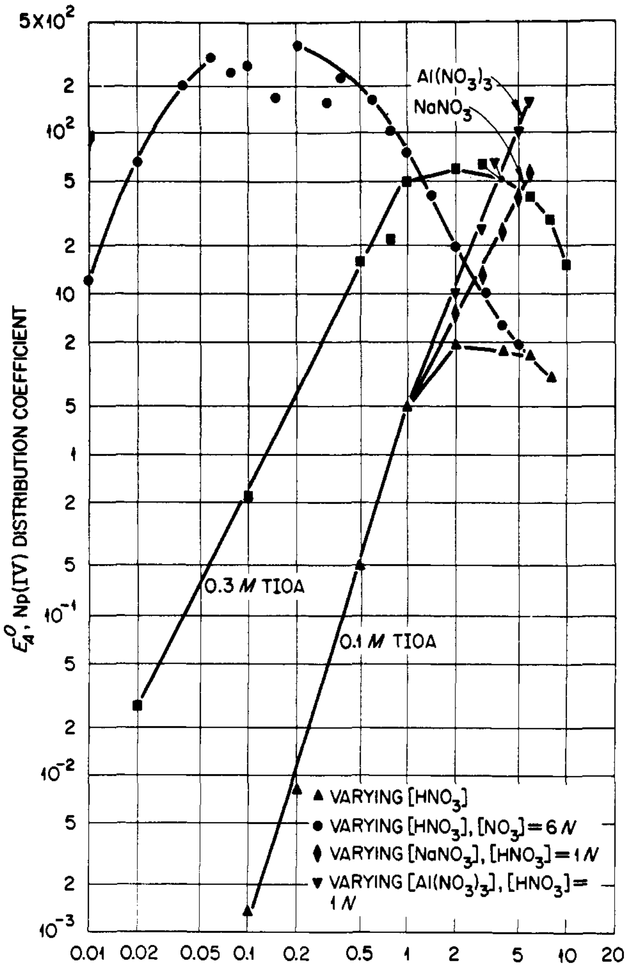

Figure 1. Extraction of Np(IV) by a tertiary amine from nitric acid and nitrate solutions

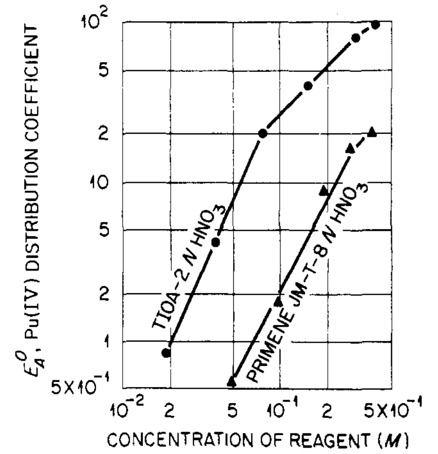

Figure 2. Extraction of Pu(IV) by primary and tertiary amines from nitric acid

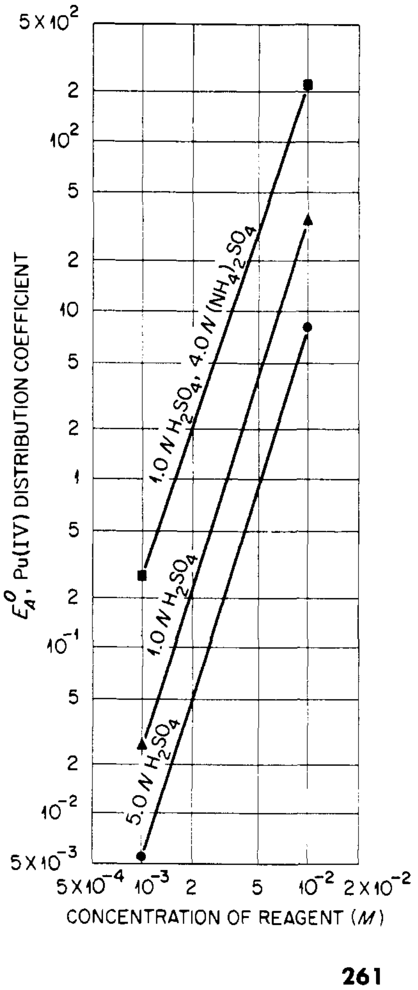

Figure 3. Extraction of Pu(IV) by a primary amine from sulfuric acid

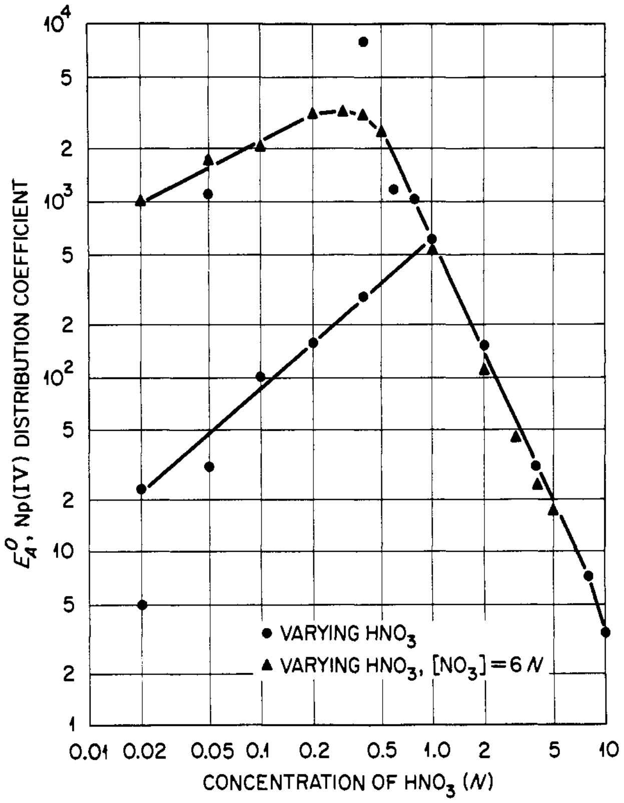

Figure 4. Extraction of Np(IV) by 0.01*M* bis(2-ethylhexyl)-phosphoric acid from nitric acid and nitrate solutions

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Table III. Extraction of Np(IV) and Pu(IV) by Quaternary Ammonium Nitrates

Reagent	HNO_3, *N*	E_a^0 Np(IV)	E_a^0 Pu(IV)
0.1*M* B-104[a]	1		≧10
	2		≧20
	4		≧50
	6		≧50
	8		≧100
	10		≧25
0.2*M* B-104	2	380	
	4	620	
	6	670	
	8	760	
0.1*M* Aliquat 336[b]	1		100
	8		700
	1[c]		~3200
	0.3[d]		~6700

[a] Didodecenyl dimethyl ammonium nitrate.
[b] Mixed trioctyl and tridecyl methyl ammonium nitrate.
[c] Extracted from 5*N* $NaNO_3$.
[d] Extracted from 5.7*N* $NaNO_3$.

concentration up to at least 0.3*M*, and to the square of the tertiary amine concentration up to about 0.1*M*.

Figure 3 shows a third-power dependence of Pu(IV) extraction on concentration of Primene JM-T from sulfate solutions. A coefficient of 8000 for extraction of Pu(IV) from 3*M* sulfuric acid by 0.4*M* Primene is in fair alignment with these data.

Quaternary Ammonium Compounds. Quaternary ammonium nitrates differ considerably in physical properties, but in general they require modification in paraffin, and sometimes in aromatic diluents, and they form emulsions with dilute nitric acid. However, they are strong extractants of Np(IV) and Pu(IV) from nitric acid solutions. Table III contains data from extractions with xylene solutions of a commercial reagent, General Mills Aliquat 336, and a Rohm

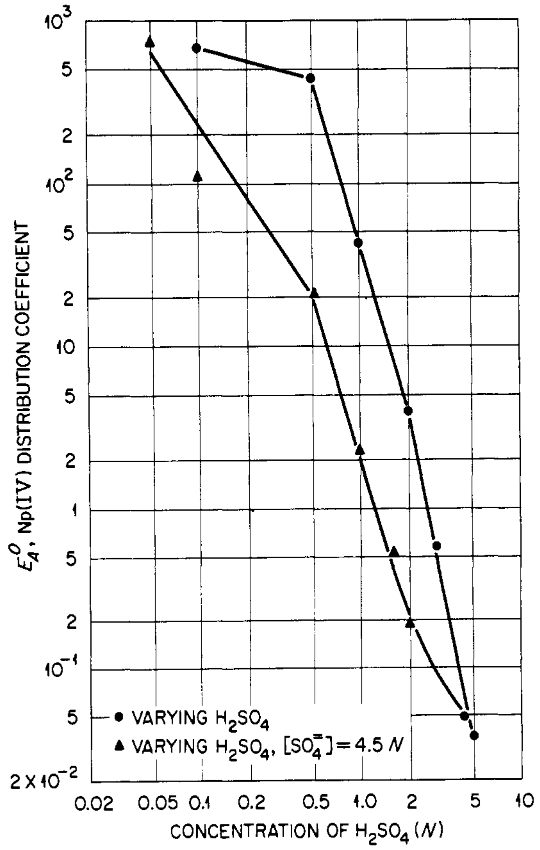

Figure 5. Extraction of Np(IV) 0.1*M* bis(2-ethylhexyl)-phosphoric acid from sulfuric acid and sulfate solutions

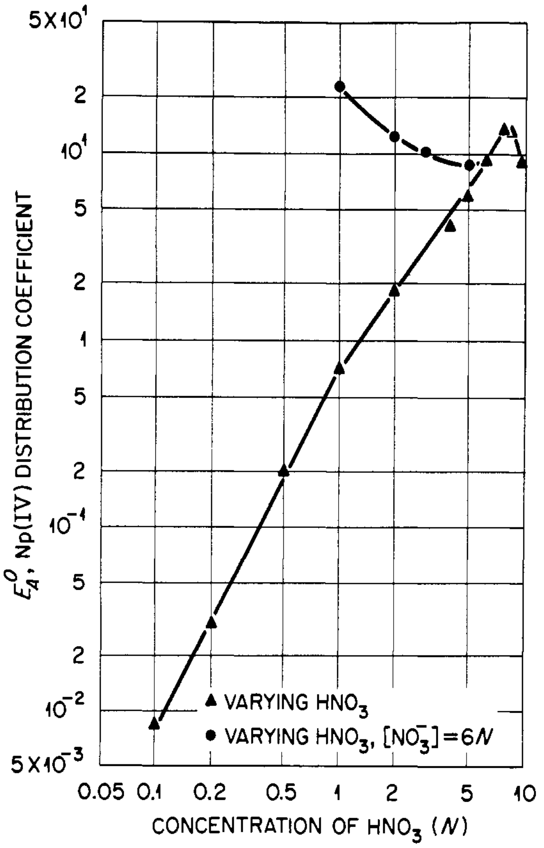

Figure 6. Extraction of Np(IV) by 1*M* tributyl phosphate from nitric acid and sodium nitrate solutions

and Haas experimental product, B-104, which had unusually good physical properties. Extraction was increased by increasing acidity up to 8*N* nitric acid and still more by increasing the neutral nitrate concentration.

Dialkyl Phosphoric Acids. An organophosphorus reagent which is widely used for extraction is bis(2-ethylhexyl)-phosphoric acid (D2EHPA). Data for extraction of Np(IV) by 0.01*M* D2EHPA from nitrate solutions are given in Figure 4. Extraction from nitric acid was inversely proportional to the square of the acidity above about 1*N* nitric acid. Below that point it was directly proportional to the acidity. The addition of neutral nitrates did not affect extraction above 1*N* nitric acid. Below this point coefficients from salted solutions increased to a maximum at about 0.3*N* nitric acid.

Extraction of Pu(IV) from nitrate solutions is somewhat similar to that of Np(IV) but several times as high. Thus 0.01*M* D2EHPA gave a coefficient of 1000 from 2*N* nitric acid and ~10,000 from 0.3*N* nitric acid and 5.7*N* sodium nitrate. In the range from 10^{-4} to $10^{-2}M$ reagent, extraction from 1*N* nitric acid was proportional to the square of the free reagent concentration.

Figure 5 contains data from extraction of Np(IV) by D2EHPA from sulfate solutions. Extractions were strong from very dilute sulfuric acid but decreased with approximately an inverse fourth power dependence as acidity was increased from 0.5*N* to 5.0*N*. Addition of sodium sulfate decreased extraction. Pu(IV) extractions, on the other hand, increased with sulfuric acid concentration from 4*N* to 10*N*. This is the second case where opposite behavior of Np(IV) and Pu(IV) in sulfate solution was observed.

Trialkyl Phosphates. Of the neutral phosphate reagents, only tri-*n*-butyl phosphate (TBP) has been studied as an extractant for Np(IV). Data from extraction by 1*M* TBP from nitrate solutions are given in Figure 6. With this reagent extraction shows a maximum at 8*N* nitric acid. Addition of sodium nitrate or replacement of nitric acid by sodium nitrate increased extraction.

Three neutral phosphates were compared as extractants for Pu(IV). Tri-*n*-butyl, tri-*sec*-butyl and tricapryl phosphates, 0.3*M* in Amsco 125-82, gave coefficients of 1.3, 4.8, and 4.3, respectively, from 0.5*N* nitric acid with 0.5*M* aluminium nitrate.

Alkyl Phosphine Oxides. Tri-*n*-octyl phosphine oxide (TOPO) has been given the most attention of this group. Data obtained for Np(IV) with 0.01*M* TOPO are given in Figure 7. There are extraction maxima at 1*N* and 8*N* nitric acid. Below 1*N* nitric acid extraction was approximately proportional to the cube of the acidity. Coefficients were greatly increased by replacement of nitric acid by neutral nitrate.

A tenfold higher concentration (0.1*M*) of the branched tris(2-ethylhexyl)phosphine oxide gave approximately the same coefficient as 0.01*M* TOPO.

Pu(IV) was extracted by 0.01*M* TOPO from 1*N* nitric acid and 8*N* nitric acid coefficients of 100 and 50, respectively. Addition of 5*N* sodium nitrate to 1*N* nitric acid increased the coefficient to 1200.

Table IV has data for extraction by TOPO from various sulfate solutions. Both Np(IV) and Pu(IV) were less strongly extracted by TOPO from sulfate than from nitrate solutions. Replacement of sulfuric acid by neutral sulfates decreased coefficients considerably.

Extraction of Neptunium and Plutonium in Valences Other than (IV). Several reagents of the various types have been examined for extraction or separation of Np(V) and (VI) and Pu(III) and (VI). Data from nitric acid systems are in Tables V and VI. Extractions by primary and secondary amines were very low for all the species. Tertiary amines and quaternary ammonium compounds gave significant extraction of the sexivalent species from highly acidic solutions. The phosphorus compounds also extracted the sexivalent species, and TOPO gave extraction of Pu(III) from dilute nitric acid.

Coextraction of neptunium and plutonium, followed by selective stripping, would be useful in processes for the recovery and separation of these elements. However, the conditions which give extractable Np(IV) in nitric acid solutions usually give unextractable Pu(III), while Pu(IV) is usually coexistent with Np(V). In concentrated aluminium nitrate solutions containing 1 to 2*N* nitric acid, the addition of nitrite, which oxidizes Pu(III) to the extractable

Table IV. Extraction of Np(IV) and Pu(IV) by Trioctyl Phosphine Oxide from Sulfate Solutions

Normality			E_a^0
TOPO	H_2SO_4	Na_2SO_4	Np(IV)
0.1	4.5		1.1
	2.0	2.5	0.06
	0.10	4.4	0.004
	1.0		0.34
	1.0	1.0	0.13
	1.0	3.5	0.013
	2.0		0.46
		$(NH_4)_2SO_4$	Pu(IV)
	6.0		4.8
	1.6	4.4	0.01
0.3	6.0		17
	1.6	4.4	0.1

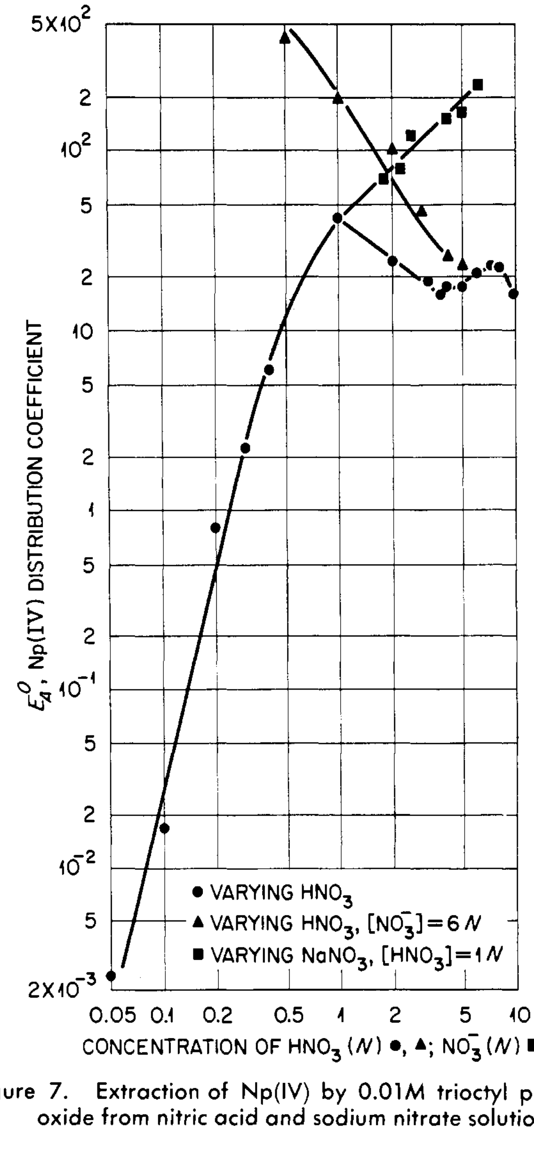

Figure 7. Extraction of Np(IV) by 0.01*M* trioctyl phosphine oxide from nitric acid and sodium nitrate solutions

Table V. Extraction of Np(V), Pu(III), and Pu(VI) by Primary and Secondary Amines from Nitric Acid

Reagent	HNO_3, *N*	Species		E_a^0
		Np	Pu	
0.01*M* Primene JM-T	2		Pu(III)	0.003
	6		Pu(III)	<0.02
	2		Pu(VI)	0.006
	8		Pu(VI)	0.13
0.3*M* ditridecylamine	2	Np(V)		0.003
	8	Np(V)		0.03
0.1*M* *N*-benzyl-heptadecylamine	0.6		Pu(III)	0.0003
	2		Pu(III)	0.0001
	6		Pu(III)	0.006
	2		Pu(VI)	0.003
0.1*M* Amine S-24	2		Pu(VI)	0.002
	8		Pu(VI)	0.1
	2		Pu(III)	<0.0002
	6		Pu(III)	<0.0002

Table VI. Extraction of Np(V), Np(VI), Pu(III), and Pu(VI) by Organophosphorus Compounds, Tertiary Amine, and Quaternary ammonium Nitrates from Nitric Acid

Reagent	HNO_3, *N*	Species		E_a^0
		Np	Pu	
0.3*M* TIOA	2	Np(V)		0.01
	8	Np(V)		0.1
	2	Np(VI)		2
	8	Np(VI)		5
0.1*M* TIOA	0.6		Pu(III)	0.004
	2		Pu(III)	0.03
	6		Pu(III)	0.06
	2		Pu(VI)	0.07
	4		Pu(VI)	0.3
	8			0.6
0.1*M* B-104	0.6		Pu(VI)	0.007
	2		Pu(III)	0.08
	6		Pu(III)	0.12
	2		Pu(VI)	0.3
	4		Pu(VI)	1.2
	8		Pu(VI)	3.7
0.1*M* D2EHPA	0.6		Pu(III)	1.0
	2		Pu(III)	0.04
	2		Pu(VI)	5
	4		Pu(VI)	6
	6		Pu(VI)	14
	8		Pu(VI)	10
	8	Np(V)		0.1
	2	Np(VI)		14
	8	Np(VI)		14
0.3*M* TOPO	2	Np(V)		≦1.5
	8	Np(V)		≦1.0
	2		Pu(III)	4
0.1*M* TOPO	4		Pu(VI)	17

Pu(IV), left Np(IV) unchanged and extractable. High concentrations of sodium nitrate, ammonium nitrate, and even nitric acid were sometimes, but not always, effective in protecting the Np(IV).

Plutonium, reduced to Pu(III) in high nitrate salt concentrations and below 1*N* nitric acid, has been found to be extracted well by a tertiary amine. The valence of the extracted species is uncertain as yet, but it appears feasible to coextract the two elements with or without addition of nitrite and then to separate them by stripping out the plutonium with a reducing solution.

Comparative Extraction of Some Elements Other than Neptunium and Plutonium. Experiments were performed with several of the reagents to determine extractability of some potentially competing or desirable elements. In Table VII are data for the fission product elements ruthenium, mixed zirconium-niobium, the rare earth europium, and the transuranic americium. Because in the first two cases the elements may be present in various forms with different extractabilities, the data represent only the particular tracer solution and first-stage extractions. Some data from extraction of zirconium on a macroscale are included. In addition, zirconium is highly extractable by D2EHPA. Tertiary amines appear to be preferable for separation of neptunium from fission products, while some of the latter can be recovered by organophosphorus compounds.

The possibility of separating neptium from thorium with tertiary amines was studied. Np(IV) was extracted perferentially to thorium from nitric acid. Separation factors remained between 10 and 20, as loading of the amine with thorium decreased the coefficients for both elements. This is not sufficient for a batch process but would be useful in a multistage partitioning system.

A possible batch process with nearly complete recovery of neptunium and high decontamination from thorium consists of extraction of Np(IV) and some thorium from nitrate solutions by a tertiary amine, followed by stripping thorium from the amine with 8*N* hydrochloric acid. Thorium coefficients with 0.3*M* TIOA and 8*N* hydrochloric acid are less than 0.01; Np9IV) coefficients are greater than 100.

Stripping. Neptunium and plutonium may be recovered from extractants by adjustment of the aqueous conditions or the valence or chemical state of the element. The simplest stripping method is contacting with water or very dilute acid. The third-power dependence of Np(IV) extraction on nitric acid concentration indicates easy stripping of neptunium from 0.1*M* TIOA by 0.1*N* nitric acid, while several stages would be required for complete stripping from 0.3*M* TIOA. The high extracting power and low acid dependency on Np(IV) extractions by D2EHPA preclude water stripping of this reagent, while neptunium in TBP and TOPO should be strippable by only a few stages of water or very dilute nitric acid. The higher extractability of Pu(IV) by these reagents is reflected in more difficult stripping.

Plutonium—extracted along with Np(IV) from a strong nitrate solution by a tertiary amine—may be stripped by ferrous sulfamate in 2*N* nitric acid, while the neptunium remains in the solvent. Thus, this reagent is useful for the coextraction and separation of the two elements.

Extracted elements may be removed from organic solvents by contact with aqueous solutions of reagents which form nonextractable complexes with the elements. For

Table VII. Extraction of Reactor Products by Various Reagents

Reagent	HNO_3, *N*	Element	E_a^0
0.3*M* TIOA	2	Zr	<0.01
	8	Zr	≦0.02
	1 + 5*N* NH_4NO_3	Zr	<0.01
	2	Ru	0.027
	8	Ru	0.006
0.5*M* Amberlite LA-1	8	Zr	<0.01
	1 + 5*N* NH_4NO_3	Zr	<0.01
0.3*M* TOPO	0.1	Zr-Nb	11
	2	Zr-Nb	11
	8	Zr-Nb	1.2
	2	Ru	<0.001
	8	Ru	<0.001
0.1*M* Primene JM-T[a]		Am	0.04
0.3*M* *N*-benzyl-heptadecylamine	8	Eu	<0.001
0.3*M* TIOA	2–8	Eu	<0.001
0.3*M* trilaurylamine	2	Am	0.2
0.1*M* D2EHPA	8	Eu	<0.01
0.4*M*	2	Am	<0.01
0.3*M* TOPO	0.1	Eu	5
	0.5	Eu	10
	1	Eu	5
	2	Eu	1.5
	8	Eu	0.02
	0.2	Am	17
	2.0	Am	~1.0

[a] Extracted from 3*N* H_2SO_4.

example, Np(IV) and Pu(IV) are readily removed from tertiary amines by dilute sulfuric acid or sulfate solutions. Conversely, nitrates may be used for stripping Np(IV) and Pu(IV) extracted by primary amines from sulfate solutions. Stripping Np(IV) from 0.1*M* D2EHPA by sulfuric acid requires an acid concentration of at least 2*M*, while plutonium cannot be stripped in this way. Dilute oxalic acid is much more effective than sulfuric acid in stripping neptunium from D2EHPA.

Numerous attempts to strip neptunium from various solvents by oxidation to Np(V) with solutions containing sodium nitrite were unsuccessful, indicating that oxidation in the organic phase by nitrite is very slow. Adjustment of plutonium valence for stripping invloves reduction to Pu(III). Plutonium has been effectively stripped from TIOA and Quaternary B-104 by 0.1*M* ferrous sulfamate plus 0.1*M* sulfamic acid in 2*N* nitric acid with stripping coefficients approaching 100. Stripping from D2EHPA and TOPO by the same means was unsuccessful. Both neptunium and plutonium may be stripped from organophosphorus extractants by sodium carbonate or ammonium carbonate solutions without valence adjustment. Concentrations of Pu(IV) up to 2 grams per liter have been obtained in 1*M* sodium carbonate without precipitation.

DISCUSSION AND SUMMARY

Neptunium and plutonium in the quadrivalent state are parallel in many respects in their extraction behavior. Their chief difference is a generally much greater extractability of Pu(IV). Np(IV) shows an abrupt change in extractability at about 1*N* nitric acid with most reagents, indicating that hydrolysis begins at this point. The high complexing power of sulfate and nitrate salts apparently suppresses hydrolytic behavior. Extractions of Np(IV) and Pu(IV) are greater from nitric acid than from sulfuric acid except with primary amines. In general, the order of extraction is: Pu(IV) $>$ Pu(VI) $\gg$ Pu(III) and Np(IV) $>$ Np(VI) $\gg$ Np(V).

Among the organonitrogen compounds extractability is: quaternary $>$ tertiary $>$ primary and secondary from nitrate solutions, but primary $\gg$ secondary $>$ tertiary from sulfate solutions. Extractions of Np(IV) and Pu(IV) show maxima at 2*N* nitric acid by tertiaries and at 8*N* nitric acid by the other amines. Increasing nitrate concentration at constant acidity increases extractability by amines. Extraction of Np(IV) from sulfuric acid by a primary amine increases with acidity, while the reverse is true of Pu(IV).

Extraction of Np(IV) and Pu(IV) by organophosphorus reagents from nitric acid varies in the order: dialkyl phosphoric acid$>$ phosphine oxide $\gg$ neutral phosphate. Of examples studied, D2EHPA extraction is inversely proportional to the square of the acidity above 1*N* nitric acid; TOPO extraction has maxima at 1*N* and 8*N* nitric acid; TBP has a maximum only at 8*N* nitric acid.

Extractions of Pu(III) from nitric acid TOPO and D2EHPA have been obtained only by reagent concentrations considerably higher than necessary to extract Np(IV) well. Coextraction of Pu(III) and Np(IV) from a highly salted nitrate solution by a tertiary amine has been indicated.

Extraction coefficients of some fission products indicate possible selections of reagents for decontamination.

Neptunium and plutonium may be recovered and concentrated separately from nitric acid process solutions by separate adjustment to the quadrivalent state followed by extraction with dilute solutions of tertiary amines, quaternary ammonium nitrates, or dialkylphosphoric acids, or more concentrated solutions of trialkyl phosphates. High nitrate salt concentrations usually improve neptunium recovery and may be used in some cases for coextraction of neptunium and plutonium.

Neptunium and plutonium can be recovered effectively from high nitric acid concentrations by D2EHPA and tertiary amines, though distribution coefficients are decreased by the acid.

Table VIII. Estimated Extraction of Np(IV) by 0.1*M* Reagents

Reagent Type	E_a^0 from Aqueous Solutions 2*N* HNO_3	6*N* HNO_3	8*N* HNO_3	1*N* H^+, 6*N* (NO^3)
Primary amine	0.05	0.4	0.5	0.03
Secondary amine	0.05	0.1	0.2	. . .
Tertiary amine	5	4	3	100
Quaternary ammonium	100	170	200	. . .
D2EHPA	10,000	1500	500	50,000
TBP	0.02	0.1	0.15	0.2
TOPO	2000	20000	2500	20,000

Methods indicated for recovery and concentration of extracted values from the organic solvents include washing with water, dilute acid, aqueous reducing agents, aqueous complexing agents, or alkaline carbonates.

Pu(IV) is highly extractable from strong sulfuric acid solutions by primary amines and usefully extractable by more concentrated solutions of D2EHPA and TOPO. *N*-Benzyl secondary heptadecylamine also extracts Pu(IV) well from highly salted solutions, and replacement of acid by salt improves extraction by primary amines. Np(IV) is highly extractable from sulfuric acid solutions by primary amines and from very dilute sulfuric acid by D2EHPA. There is considerably more difference between extraction behavior of Np(IV) and Pu(IV) in sulfate than in nitrate systems.

The extractive powers of these reagents vary over so wide a range that no experimental comparison of reagents at a common concentration can be made. However, calculations from observed distribution coefficients and assumed second-power reagent dependencies allow some rough estimations. Table VIII shows a comparison of estimated extractabilities of Np(IV) from various kinds of nitrate solutions by 0.1*M* reagents. The reagents would not all be used at this concentration for any one purpose.

ACKNOWLEDGMENT

The authors gratefully acknowledge the large amount of helpful advise by C.F. Coleman and the laboratory work by Janet Debnam.

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RECEIVED for review July 1, 1959. Accepted September 28, 1959. Division of Industrial and Engineering Chemistry, 135th Meeting, ACS, Boston, Mass., April 1959. ORNL is operated by Union Carbide Corp. for the U. S. At. Energy Comm.