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PLUTONIUM EXTRACTION FROM NITRATE AND SULFATE SOLUTIONS BY AMINES AND ORGANOPHOSPHORUS COMPOUNDS

D. E. Horner
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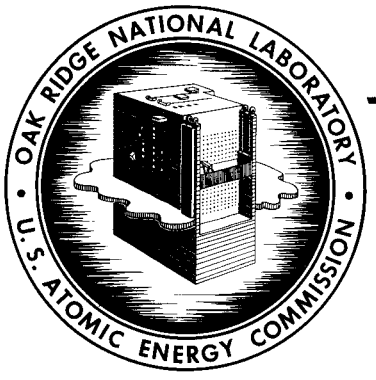

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ABSTRACT

Plutonium extraction coefficients from acid nitrate and sulfate solutions by amines and some neutral and acid organophosphorus compounds were measured as functions of several extraction variables, including plutonium valence, acid and salt concentration, and extractant concentration. Extractability by all the reagents varied in the order Pu(IV) > Pu(VI) > Pu(III); however, several systems showed usefully high extractions of plutonium from stabilized Pu(III) solutions. Primary amines extracted Pu(IV) sulfate much more strongly than the nitrate; most of the other reagents extracted the sulfate much less strongly than the nitrate, but still to a usable extent in some systems. Plutonium(IV) nitrate extractions with the different extractants passed through maxima at widely different nitric acid concentrations. With most, but not all, extraction increased when nitric acid was replaced with nitrate salt.

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1.0 SUMMARY

The extractability of plutonium by amines from both nitrate and sulfate acid solutions varied with oxidation state in the order Pu(IV) > Pu(VI) > Pu(III). Extraction from nitrate solutions was considerably higher with quaternary and tertiary than with secondary and primary amines. From sulfate solutions, it was highest with primary amines.

When no salt was present, Pu(IV) extraction coefficients vs nitric acid concentration went through maxima, near 2 M HNO_3 with the tertiary amines and near 8 M HNO_3 with the quaternary, secondary, and primary amines tested. Most, but not all, systems showed higher extraction coefficients when most of the nitric acid was replaced by nitrate salt. The measured dependences of extraction coefficient on amine concentration varied from first to about fourth power; it is doubted that these dependences correspond directly to the ligand numbers. Plutonium(VI) and Pu(III) extraction coefficients increased with increasing nitric acid concentration to at least 8-9 M HNO_3, but even these were much lower than the corresponding Pu(IV) coefficients. In the presence of ~2 M $Al(NO_3)_3$ (i.e., ~6 N) and <0.5 M HNO_3, however, plutonium extraction coefficients from Pu(III) solution were 10-100 with 0.1 M tertiary amine, suggesting oxidation to Pu(IV) even in the presence of holding reductants.

From sulfate solutions, Pu(IV) extraction coefficients are extremely high with 0.1 M primary amine. The coefficients varied with the third power of the amine concentration, and inversely with the first power of sulfuric acid concentration in unsalted solution. They were increased by replacing sulfuric acid with sulfate salt. Plutonium was also extracted from reduced sulfate solution, even in the presence of much ferrous ion. The extraction probably involves some oxidation.

Extracted plutonium nitrate was stripped with "water" (very dilute nitric acid) only when tertiary amine concentration was low; stripping was more effective with a reductant or a complexer such as sulfate. Extracted plutonium sulfate was stripped by displacement with nitrate.

Extractions by neutral phosphate and phosphonate esters generally paralleled the well-known extractions by TBP. Extractions by trialkylphosphine oxides also showed some parallels, but with a higher order of extraction power. Two of the phosphonates of most interest for potential process use gave Pu(IV) extraction coefficients close to those with TBP, di-*sec*-butyl phenylphosphonate nearly matching TBP and di-*n*-butyl phenylphosphonate being higher by a factor of about 1.5. However, the extraction coefficients measured for both TBP and the phosphonates showed a higher power dependence on nitric acid concentration than is shown in the literature (~2.5 vs ~1.7); this discrepancy has not been explained.

Plutonium(IV) extraction coefficients with tri-n-octylphosphine oxide vs nitric acid concentration showed two maxima, near 1 M and 8 M, with a minimum near 4 M. With 0.1 M tri-n-octylphosphine oxide these coefficients were ~1000 and greater, and at 0.1 M HNO_3 the coefficient was still ~100. They varied with the square of the phosphine oxide concentration. (Coefficients were lower by a factor of ~20 with the highly branched tris-(2-ethylhexyl)phosphine oxide.) Plutonium(VI) extraction coefficients were lower than Pu(IV) coefficients by a factor of ~10. Plutonium(III) coefficients were lower but erratic, suggesting that some oxidation to Pu(IV) readily occurred. Plutonium(IV) extraction coefficients from sulfate solutions were much lower but still usable, e.g., 5 with 0.1 M phosphine oxide from 3 M H_2SO_4.

As expected, the extracted plutonium nitrate could not be stripped from phosphine oxide with "water" (very dilute nitric acid). Water stripping of extracted plutonium sulfate also failed in brief tests (possibly because of colloid formation), although the extraction coefficients suggest that it should be possible. Reductive stripping succeeded under only some of the conditions tested. Sodium carbonate provided the most effective stripping.

Dialkylphosphoric acid extracted Pu(IV) from dilute nitric acid solution with much higher coefficients than did either amines or phosphine oxides, e.g., ~5000 with 0.01 M D2EHPA from 0.3 M HNO_3. The extraction coefficients decreased with increasing acidity (added nitrate salt had little effect), but with slopes over most of the range closer to -2 than to the -4 expected if Pu^{4+} were exchanged for $4H^+$. They varied with the square of the D2EHPA concentration. Since D2EHPA is dimerized, these observations suggest that a divalent plutonium cation---PuO^{++}, or $Pu(NO_3)_2^{++}$, etc.---is extracted to form perhaps $PuO(D2EHP)_4H_2$, in close analogy to the formulations proposed for several other extracted metals.

Plutonium(VI) nitrate extraction coefficients were around three orders of magnitude lower. They were slightly lower than, and generally parallel to, uranyl extraction coefficients, including synergistic enhancement on adding phosphine oxide. Plutonium(III) nitrate coefficients were lower but (even more than in phosphine oxide extraction) appeared to be influenced by oxidation. Plutonium(IV) and Pu(VI) extraction coefficients from 3-5 M H_2SO_4 were low but still usable.

Extracted plutonium was stripped fairly well by the combined action of a reductant and a complexer (sulfate), and by oxalic acid. As with phosphine oxide, sodium carbonate provided the most effective stripping.

2.0 INTRODUCTION

This report describes an experimental survey of the liquid-liquid distribution behavior of plutonium between acidic aqueous solutions and organic solutions with a range of extraction reagents. The objective of this survey was to compare the effectiveness of different extractants for plutonium, and to identify and evaluate quantitatively the important extraction variables, with emphasis on solutions and conditions that could lead to specific process applications. Most of the data are presented as individual extraction (or stripping) coefficients, measured at low plutonium concentrations where there was negligible saturation or loading effects. The extractants were chosen from the classes (amines, phosphorus acids, and phosphine oxides) that have been intensively studied for raw-materials processing, particularly those reagents---di(2-ethylhexyl)phosphoric acid and several amines---which were most successful in the Dapex and Amex raw materials recovery processes.[1] Several neutral phosphonate esters were also examined in comparison with tributylphosphate.

During the course of the raw materials studies, it was observed that the new solvents developed in this program could extract a large number of metals from a wide variety of aqueous compositions, with considerable control of extraction properties being possible through appropriate choice of reagent structure. It was evident that advantage might be taken of these reagents in areas afield from ore processing. Consequently, a systematic experimental survey was initiated at this laboratory to explore their utility in the general field of radiochemical processing, including fuel processing, waste treatment, fission product recoveries, and transuranium recoveries. The work described in the present report is a part of that general program. These classes of reagents, especially the amines, are also being studied intensively for extraction of plutonium and other actinides in many other laboratories,* and in at least one have reached process application (plutonium scrap recovery by amine extraction[2]). In general, the results being obtained with these reagents bear out their early promise.

Most of the analyses for this study were performed by members of the Analytical Chemistry Division under the direction of M. T. Kelley and C. D. Susano. In particular, most of the plutonium determinations were made by J. M. Peele of

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*References 2,7,8,17,19,23 cited in the discussions below provide several examples, but there is no attempt to review or even to list all such related studies.

that Division. Thanks are due to Health Physics Surveyors L. C. Johnson and R. D. Parten for cooperation and advice. R. G. Mansfield of the Chemical Technology Division tested fission-product extraction; M. Janet Debnam gave laboratory assistance.

3.0 EXTRACTION WITH ALKYL AMINES*

The extractability of plutonium by amines from both nitrate and sulfate acid solutions varied with oxidation state in the order Pu(IV) > Pu(VI) > Pu(III). Extraction from nitrate systems was considerably higher with quaternary ammonium and tertiary amine than with secondary and primary amine reagents. From sulfate solutions, in contrast, it varied in the order primary >> secondary > tertiary.

3.1 Nitrate Solutions

The extraction coefficients for Pu(IV) from unsalted nitric acid solutions by all the amines examined increased with increasing nitric acid concentration up to at least 2 M HNO_3. Coefficients with the quaternary, secondary, and primary amines continued to increase almost linearly with nitric acid concentration to maxima near 8 M, dropping sharply on further increase to 10 M (Fig. 3.1). In contrast, the extraction coefficients with the tertiary amine passed through a broader maximum near 2 M HNO_3. This rather surprising difference between the tertiary and the other amines was closely paralleled in the extraction of Np(IV) from nitric acid solutions.[3]** This curve for 0.1 M tri-iso-octylamine and ~10 ppm plutonium also parallels that for 10% tri-n-octylamine and trace Pu from 2-8 M HNO_3 reported by Sheppard.[5] It differs from the gradually rising curves reported by Wilson[6] (0.15 M trilaurylamine, E_a^o = 140 at 2 M and 170 at 4 M HNO_3), and Keder et al.[7] (10% tri-n-octylamine, E_a^o = 210 at 2 M and 260 at 6 M HNO_3) and from the steeper curve reported by Bertocci[8] (0.5 M tris(3,5,5-trimethylhexyl)-amine, E_a^o = 8 at 2 M and 18 at 6 M HNO_3 at plutonium loading of 5 to 10 g/liter). All of the foregoing curves that were carried beyond 6 M HNO_3 agree qualitatively in showing decreasing E_a^o(Pu).

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*See Appendix F for sources, and for identification of arbitrarily named reagents

**Recent extraction tests with a completely symmetrical quaternary, tetra-n-heptylammonium nitrate, showed Np(IV) extraction coefficients maximum near 2 M HNO_3. These coefficients were higher than those with B-104.[4]

The decreased extraction found at 10 M HNO_3 with all classes of amines (Fig. 3.1) differs from the data of Winchester,[2,9] who found almost constant coefficients from 7 to 11 M HNO_3 for 35 vol % Primene JM and 35 vol % Amberlite LA-1 at a plutonium concentration of 50 g/liter (amine/Pu mole ratio ≈ 5/1). It is qualitatively similar to the strong-base resin sorption curve of Durham and Mills,[10] which was nearly constant from 3 to 8 M HNO_3, with a maximum at 7.5 M, and dropped by a factor of ~5 at 10 M.

When the total nitrate concentration was held constant at 6 M by addition of sodium nitrate, the extraction coefficients rose instead of falling with decreasing nitric acid concentration. The secondary N-benzylheptadecylamine was exceptional, showing almost no change with acidity in the 6 M nitrate. The coefficients with the secondary Amberlite LA-1 and the quaternary Aliquat 336 rose in almost inverse proportion to the nitric acid concentration from 6 to 0.3 M. The coefficients with the tertiary rose more steeply, in qualitative conformity to its relatively higher extraction at lower nitric acid concentrations in the salt-free solutions. The resulting coefficients from <1 M HNO_3 in 6 M nitrate salt solution were well over 1000 with both quaternary and tertiary at 0.1 M.

The extraction coefficients from 8 M HNO_3 varied with slightly less than the first power of concentration of the quaternary from 0.01 to 0.3 (Fig. 3.2). The coefficients for the other reagents (from 2 M HNO_3 for the tertiary, 8 M HNO_3 for the others) showed either more scatter or some curvature, with the overall variation being fairly close to the second power of the reagent concentration. Elsewhere the dependence on tertiary amine concentration has been reported to be second power (tracer),[5,7] or slightly higher than first power (macro, amine/Pu ≈ 20/1).[8] Ordinarily, the power dependence of extraction coefficient on extractant concentration corresponds to the ligand number in the resulting organic-phase complex. However, this relation has not held in the U(VI)-amine-sulfate systems;[11] hence interpretation of the extracted plutonium complex has been deferred.

Pu(VI) and Pu(III). The extraction coefficients for Pu(VI) were low, although increasing rapidly with increasing nitric acid concentration from 2 to 8 M (Fig. 3.3). The different amines fell in the same order in their extraction power for Pu(VI) as for Pu(IV) (Fig. 3.1). Of the amines tested, at 0.1 M, only the quaternary B-104 gave extraction coefficients greater than 1. Plutonium(VI) extraction coefficients were not measured as a function of amine concentration. However, it may be predicted from the magnitudes of the coefficients in Fig. 3.3 that, if the dependence is of the order of first or second power, coefficients could be fairly high with quaternary or tertiary at 0.3-0.5 M, but would still be low with secondary and primary.

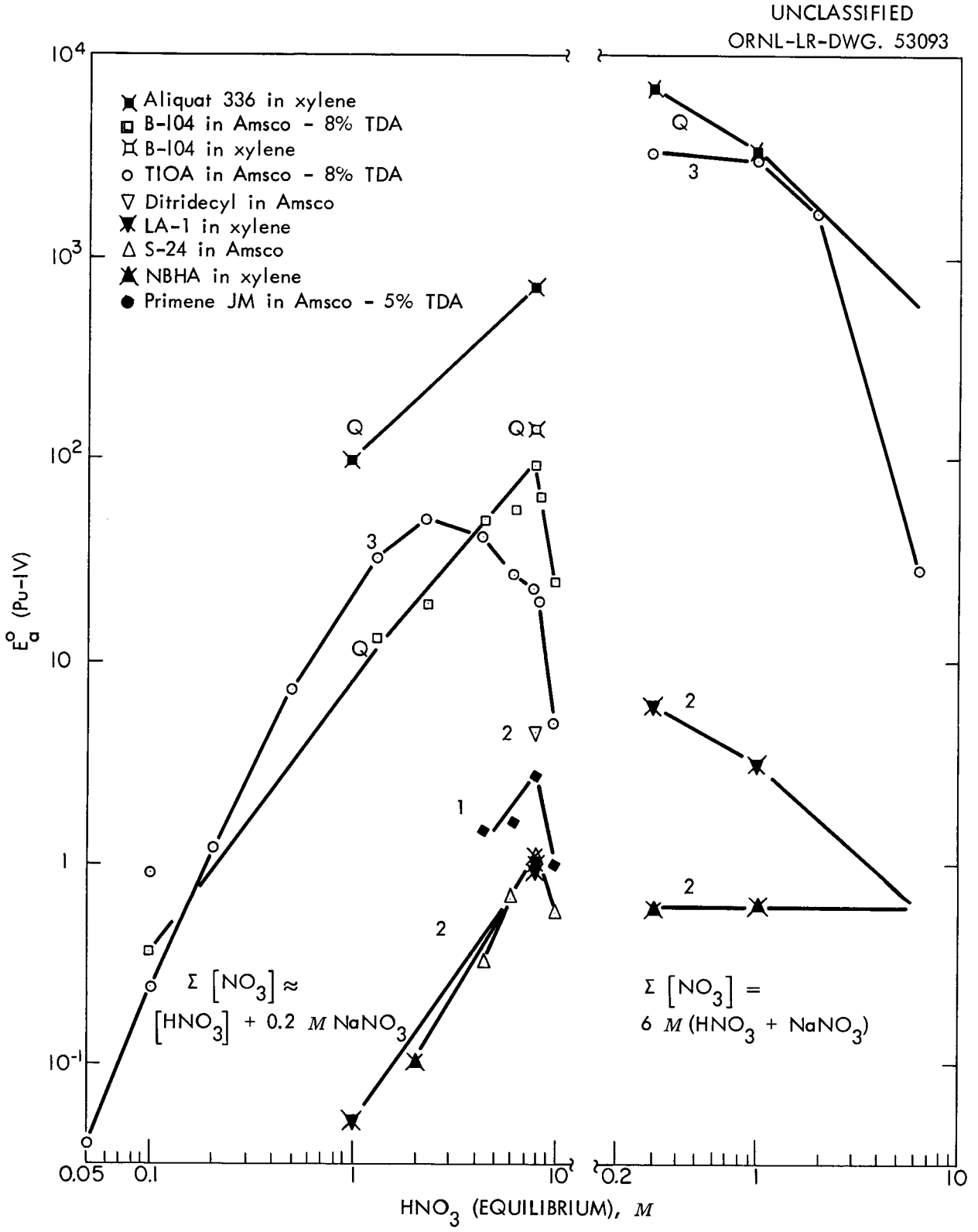

Fig. 3.1. Plutonium(IV) extraction by 0.1 M amines: effect of nitric acid and sodium nitrate concentrations. Amine class: (Q) quaternary ammonium, (3) tertiary, (2) secondary, (1) primary amine. Plutonium(IV) stabilized with 0.04-0.1 M $NaNO_2$. Amsco 125-82, TDA = branched primary tridecanol.

The highest Pu(III) extraction coefficients obtained from unsalted solutions, which were at the highest nitric acid concentrations tested (~6 M), were an order of magnitude lower than the corresponding Pu(VI) coefficients (Fig. 3.3). In contrast, usefully high although variable coefficients for plutonium were obtained with tertiary amines from Pu(III) solutions containing aluminum nitrate at low acidity (Fig. 3.4).* It has not been established whether the Pu(III) was extracted as such, or was oxidized to the more extractable Pu(IV) before or during the transfer in spite of excess ferrous sulfamate in the aqueous solutions and a carbon dioxide atmosphere over the system. If transferred as Pu(III), it appeared to be rapidly oxidized to Pu(IV) in the organic phase, since a 2 M HNO_3 scrub removed only a small amount:

	E_a^o(Pu)		
Amine, 0.3 M	In Extraction (Fig. 3.4)	In 2 M HNO_3 Scrub	% of Pu Removed in Scrub
Tri-iso-octylamine	1	50	2
Trilaurylamine	5	10	10
Alamine 336	2	20	5

The nitric acid scrub contained 0.1 M sulfamic acid to avoid the possibility of oxidizing the plutonium by nitrite during the scrubbing. On the basis of the foregoing extraction coefficients, this scrub was expected to remove Pu(III) essentially completely, but to remove only a trace of Pu(IV). Hence, the removal of $\leq$10% indicates that $\geq$90% of the plutonium in the organic phase was no longer simple Pu(III). The simplest interpretation of this is of course that it had been oxidized to Pu(IV). However, the possibility has not been excluded that a different and nonscrubbable Pu(III) species may have been formed in the organic phase, in some analogy to the "irreversible" extraction of Mo(VI) and V(V) extraction by amine sulfates.[12]

Similarly high and variable extractions of plutonium from Pu(III) solutions are noted below by primary amine sulfate, by phosphine oxide (Sect. 4.2), and by dialkylphosphoric acid (Sect. 5.1).

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*The extraction coefficients of ~10^{-4} from the nitric acid solutions before the aluminum nitrate was added (Fig. 3.4) confirm that the plutonium was essentially completely reduced to Pu(III) in the feed solution, since coefficients ~10^{-1} would be expected for Pu(IV) with 0.1 M TIOA from unsalted 0.2 and 0.3 M HNO_3.

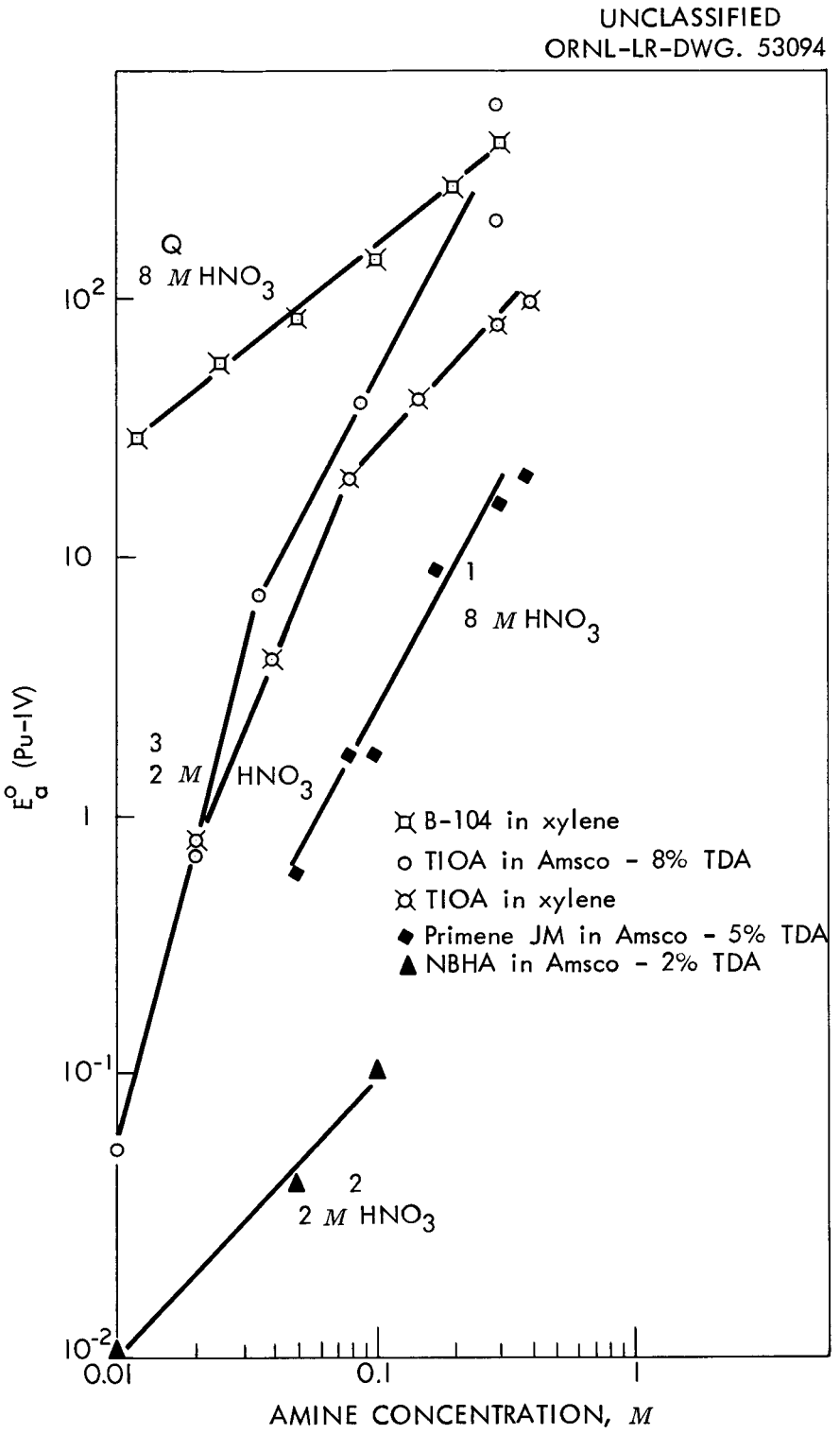

Fig. 3.2. Plutonium extraction by amines from nitric acid solutions: effect of amine concentration. Amine class: (Q) quaternary ammonium, (3) tertiary, (2) secondary, (1) primary amine. Plutonium(IV) stabilized with 0.04-0.1 *M* $NaNO_2$.

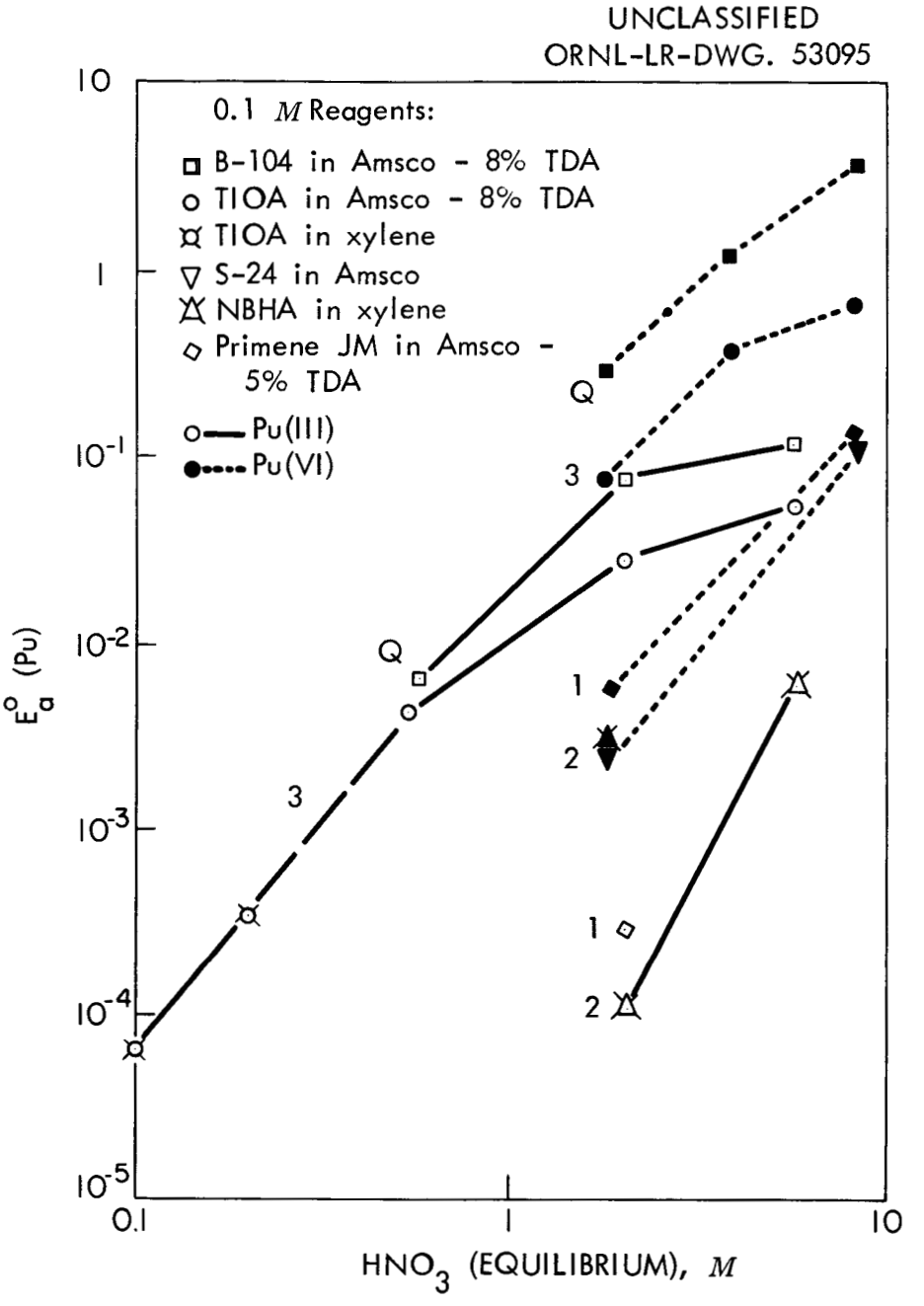

Fig. 3.3 Plutonium(III) and Pu(IV) extraction by 0.1 *M* amines: effect of nitric acid concentration. Amine class: (Q) quaternary ammonium, (3) tertiary, (2) secondary, (1) primary amine. Plutonium reduced with 0.03 *M* ferrous sulfamate plus 0.05 *M* excess sulfamic acid, or oxidized with AgO.

3.2 Sulfate Solutions

Extraction coefficients for Pu(IV) from sulfate solutions were highest with primary amine and much lower with secondary and tertiary (Fig. 3.5). The extraction coefficients varied with the third power of concentration of the primary amine Primene JM-T between 0.001 and 0.01 M. The coefficient of ~8000 with 0.4 M Primene JM-T (different diluent and slightly higher acidity) is also in fair alignment, probably as close as should be expected in view of the analytical difficulty in measuring extremely high coefficients. The extraction coefficients decreased in almost inverse proportion to the sulfuric acid concentration when it was increased from 0.5 to 2.5 M, but increased by an order of magnitude when the solution was made 2.5 M in total sulfate by adding 2 M $(NH_4)_2SO_4$ to the 0.5 M H_2SO_4.

Extraction coefficients with the primary amines 1-(3-ethylpentyl)-4-ethyloctylamine and 1-undecyllaurylamine were similar to those with Primene JM-T in preliminary extraction tests. Those tests are not included in Fig. 3.5 because the absolute values of the high extraction coefficients were affected by the presence of americium in the plutonium stock (see Appendix B). Of those, only the tests with Primene JM-T were repeated with the effect of americium eliminated.

Extraction coefficients with the secondary amines tested were less than a hundredth as high as with the primary amine. Extraction was much lower with the highly branched amine S-24 than with the slightly branched ditridecylamine, in parallel to their relative extractions of several other tri- and tetravalent metal sulfates, e.g., thorium.[11] Here the highest extractions, giving usefully high coefficients at > 0.1 M amine, were obtained with the N-benzyl secondary-alkyl amines, N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine (NBHA) and N-benzyl-1-undecyllaurylamine. These are amines of the type that has shown exceptionally high extraction power for uranyl sulfate.[13] The extraction coefficients varied with close to the first power of NBHA concentration between 0.1 and 0.4 M. The extraction coefficients were higher from 3 M $(NH_4)_2SO_4$ at pH ~0.7 than from 3 M H_2SO_4 by a factor of ~3, in the same direction as but much smaller than the difference found with primary amine between 2 M $(NH_4)_2SO_4$--0.5 M H_2SO_4 (pH ~0.5) and 2.5 M H_2SO_4.

The extraction coefficient with the tertiary amine was very low, lower by a factor of at least 10^6 than the corresponding coefficient with the primary amine. This is in accord with the previously reported high selectivity of the tertiary amine for uranyl sulfate over such tetravalent sulfates as U(IV) and thorium.[11]

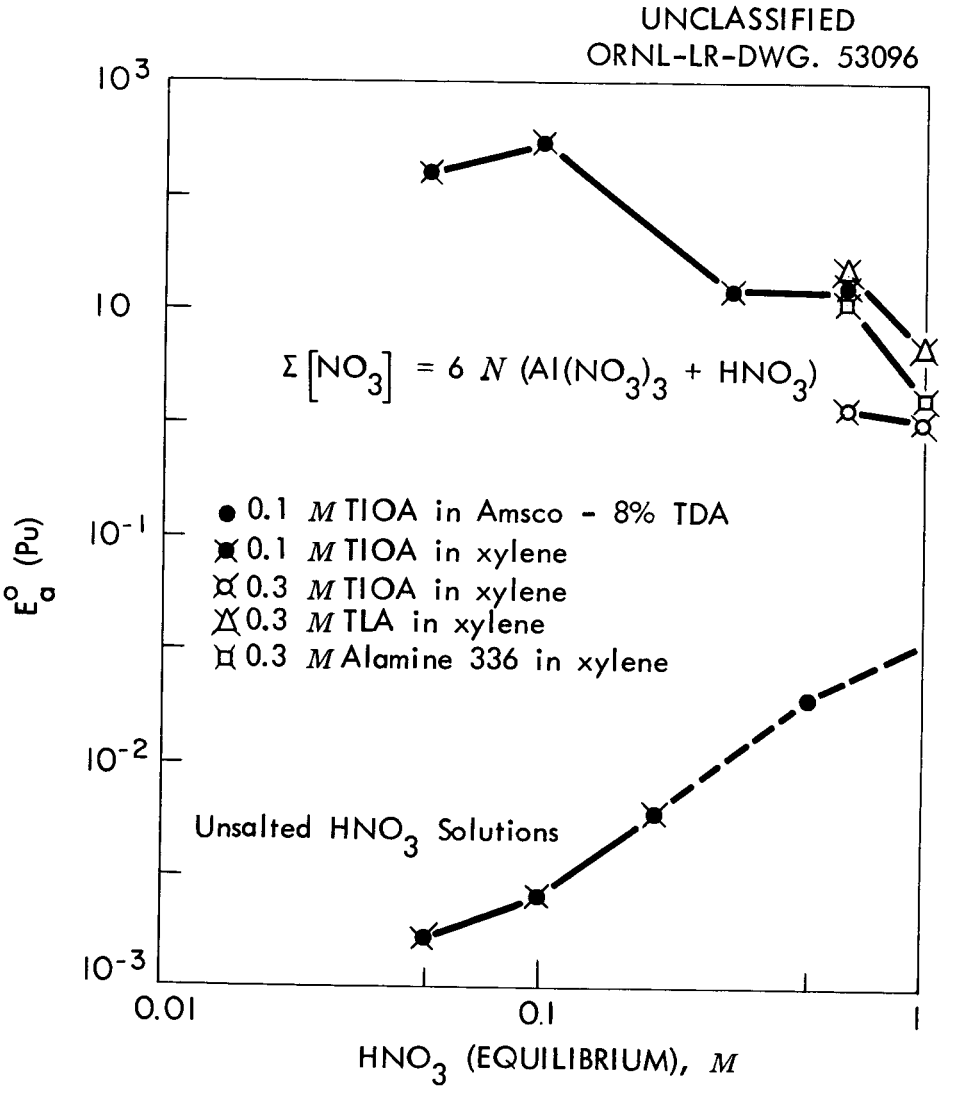

Fig. 3.4. Extraction by tertiary amines from solutions of Pu(III) in nitric acid with and without aluminum nitrate salting. Plutonium reduced with 0.03 *M* ferrous sulfamate plus 0.05 *M* excess sulfamic acid.

Plutonium extraction coefficients with primary amines from solutions of Pu(III) in 3 M H_2SO_4 were highly variable, typically ranging from ~5 to >>100 with 0.1 M amines (cf. extractions with tertiary amines from Pu(III) nitrate solutions, above). This is attributed to enhanced oxidation of Pu(III) to Pu(IV), in spite of the presence of holding reductants. This explanation is supported by the observation that the plutonium extraction is increased by addition of a small amount of ferric sulfate to a feed solution containing a much larger amount of ferrous sulfate; e.g., 0.1 M $Fe_2(SO_4)_3$, 1 M $FeSO_4$, ~10^{-5} M Pu.[14] Although variable, this means of extracting Pu(III) with a primary amine appears sufficiently dependable for use in a process proposed for scavenging uranium and plutonium from sulfuric acid stainless steel decladding solutions.[14]

3.3 Selectivity

The parallels between amine extraction and anion exchange sorption, borne out by the general aspects of plutonium nitrate extraction, also suggest that Pu(IV) nitrate should be extracted with high selectivity over most other metal nitrates. Experience so far reported supports this expectation, at least with respect to the important contaminants encountered in uranium-plutonium dissolver solution[5,6] and metallurgical scrap plutonium solutions.[2,9]

A study is in progress in the Department of Nuclear Engineering, Massachusetts Institute of Technology, on the amine extraction characteristics of a range of fission-product and corrosion-product metals of interest in radiochemical nitrate systems.[15] Molybdenum, zirconium, ruthenium, and samarium have been examined at various concentrations in extraction from nitric acid and acidic sodium nitrate solutions, with Aliquat 336, trilaurylamine, Amine S-24, ditridecylamine, and Primene JM-T. The results, showing low extractions of the last three metals under all conditions tested, suggest that ruthenium is more likely than zirconium or rare earths to be the first limitation reached in using amine extraction for very high decontamination of plutonium. Extraction coefficients for ruthenium (fresh or aged nitrosylruthenium nitrate) rose rapidly with contact time for several hours and then more slowly for at least several days. As measured at 24 hr, the extraction coefficients were directly proportional to the amine concentration and inversely proportional to the nitric acid concentration; e.g., E_a^o = 0.08 from 2 M HNO_3 with 0.4 M trilaurylamine in toluene. Extraction coefficients for zirconium (zirconyl nitrate refluxed and aged in 8 M HNO_3) were very low from dilute nitric acid. They increased rapidly with increasing nitric acid concentration, in proportion to about the fourth power, but still reached only ~0.01 from 10 M HNO_3 with 0.3 M amine. The results over the entire range were rather well summarized by the expression

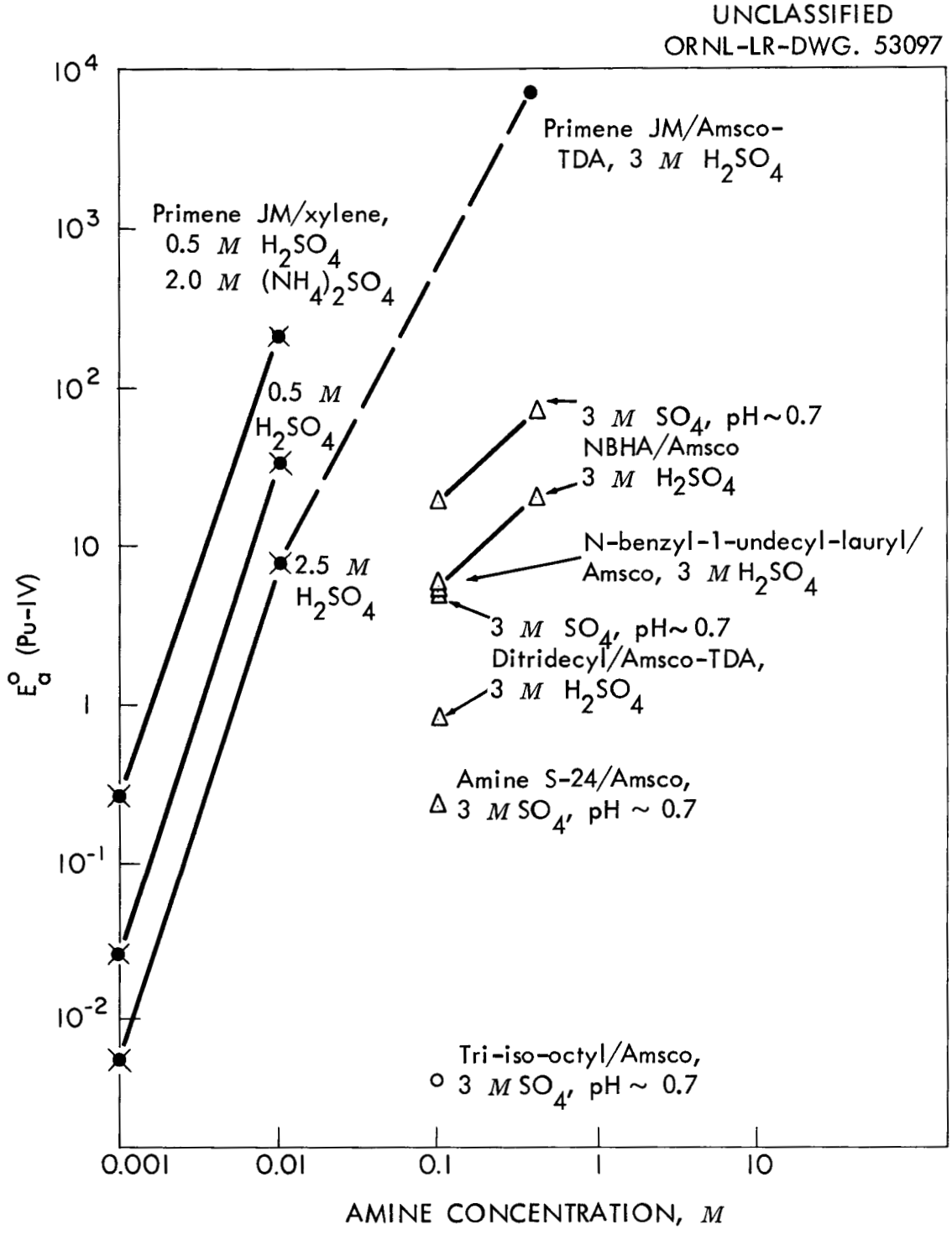

Fig. 3.5. Extraction of Pu(IV) from sulfuric acid and acidic sulfate solutions by primary, secondary, and tertiary amines. Diluents: xylene, Amsco 125-82, or 95% Amsco 125-82—5% tridecanol. For primary amine extraction, plutonium reduced with hydroxylamine sulfate, reoxidized and stabilized at (IV) with 0.5 *M* $NaNO_2$. Others stabilized at (IV) with 0.1 - 0.5 *M* $NaNO_2$.

$$E_a^o(Zr) = K(\underline{M}_{amine})^2(\underline{M}_{H^+})^2(\underline{M}_{NO_3^-})^2$$

with $K \approx 6 \times 10^{-6}$ for trilaurylamine and for Primene JM-T and $\approx 2 \times 10^{-5}$ for Aliquat 336 (toluene diluent). Extraction coefficients for samarium, taken as a representative rare earth(III) ion, were all below $\sim 10^{-4}$ with 0.3 M amines in toluene. There was no obvious systematic change either with nitric acid concentration (2-9 M) or with amine class.

The fission product extractions with control and irradiated amines described in Appendix C appear consistent with the foregoing, although their sensitivity was limited by dilution of the dissolver solution spike to a rather low activity level. They also provided a "shotgun" test that no other activity in the mixed fission products was extracted to any great extent, besides demonstrating that the selectivity was not much affected by irradiation doses of 400 watt-hr/liter.

Two metals capable of being extracted as oxygenated anions rather than as complex nitrate anions, molybdenum(VI) and technetium(VII),[4,16] were strongly extracted when the competing nitrate concentration was fairly low.[15] Extraction coefficients for Mo(VI) (ammonium molybdate dissolved in nitric acid) with 0.1 M amines in toluene were of the order of 100 and higher at nitric acid concentrations below 0.1 M, dropping rapidly to $\sim 10^{-4}$ at 2-8 M HNO_3 and to $< 10^{-5}$ at 10 M HNO_3. They were appreciably higher at 6 M than at 2 or 8 M HNO_3 but still near 10^{-4}. Extraction coefficients for Tc(VII) (Tc-95m tracer) with 0.3 M trilaurylamine in Amsco 125-82 were of the order of 1000 and higher at nitric acid concentrations below 0.1 M, dropping to ~100 at 1 M HNO_3 and then more steeply to ~0.2 at 10 M HNO_3.

Neptunium(IV) nitrate extraction coefficients are about an order of magnitude lower than those for Pu(IV) under similar conditions, while those for thorium and uranium are still lower.[3,5,7,8,15,17]

Sulfates. The relative extractions of a range of metal sulfates by different classes of amines has been reported.[11] Plutonium(IV) falls in the group of sulfates, including zirconium, thorium, and U(IV), that are extracted with extremely high coefficients by primary amines. This group is readily separated from other less extractable groups, including the rare earths. Separations within this group may also be feasible, but cannot be predicted from the extraction coefficients so far measured because usually only limiting values have been obtained of these very high coefficients.

3.4 Stripping of Extracted Plutonium

Several different methods are available for stripping extracted plutonium from the amines, including (1) hydrolysis of the extractant to free-base molecular amine, (2) displacement of the extracted metal complex by a competing anion, (3) destruction of the extractable complex, and (4) formation of a competing nonextractable complex. The nitrate complex can be stripped with dilute acid ("water stripping" with acidification to prevent trouble from hydrolysis of the Pu(IV) cation),* and the stripping is aided by addition of a reductant or an aqueous complexing agent. The sulfate complex can be stripped by displacement with dilute nitrate. Alkaline stripping was not tested, but sodium carbonate stripping can be expected to be applicable, since it has proved suitable for stripping Pu(IV) from an acid extractant (Sect. 5.3) and experience has shown alkaline stripping generally effective for the amines.

Dilute Acid Stripping. The extraction curves of Fig. 3.1 indicate that stripping by dilute nitric acid, through dissociation of the extractable plutonium nitrate complex, should be marginal for the tertiary tri-iso-octylamine and the quaternary B-104 at 0.1 M. With these the plutonium distribution begins to favor the aqueous phase at about 0.2 M HNO_3 (equilibrium concentration). The reciprocals of these extraction curves are in fair agreement with directly measured stripping coefficients S_o^a (Fig. 3.6). The stripping coefficients fell farther below the line when 5% tridecanol was used instead of 8% in the diluent, reflecting higher extraction power at the lower alcohol concentration. With these extractants at 0.1 M, stripping by this method calls for use of the lowest acidity that can give a stable solution. At lower extractant concentrations, somewhat higher acidities should be tolerable, while at much higher concentrations of these extractants simple dilute-acid stripping will not apply.

Stripping should be effective at acidities even approaching 1 M from the primary and secondary amines at 0.1 M (Fig. 3.1), and at the lower acidities from considerably higher concentrations of these amines. (Stripping with 0.1 M HNO_3 from ~1 M Amberlite LA-1 in halogenated hydrocarbon diluent has been used in plutonium recovery operations at Los Alamos.[19])

Stripping by Reduction. Extracted plutonium was effectively stripped from 0.1 M tri-iso-octylamine and 0.1 M B-104 (in 92% Amsco 125-82--8% tridecanol) by 2 M HNO_3

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*The amine nitrates can extract significant concentrations of excess nitric acid (Appendix A), which must be taken into account in adjusting the nitric acid concentration of a "water" strip.

solution containing 0.1 M $Fe(NH_2SO_3)_2$ + 0.1 M NH_2SO_3H:

	S_o^a(Pu)	
Extractant	1st Stage	2nd Stage
0.1 M TIOA	60	65
0.1 M B-104	40	100

Each extract was stripped twice at A/O = 1/1, 10 min contact at room temperature. With lower nitric acid, 0.05-0.1 M, and addition of 0.1 M H_2SO_4 (instead of sulfamic acid) to the ferrous sulfamate, stripping coefficients were much higher, >>1000 from 0.1 M TIOA. Others have also reported reductive stripping of plutonium nitrate from tertiary amine with ferrous sulfamate[6] and from secondary amine with hydroxylamine nitrate.[2,9]

Reductive stripping of plutonium sulfate from secondary amines is probably feasible, but was not tested. However, reductive stripping of plutonium sulfate from primary amines is not feasible, at least with the usual reductants. Pu(IV) is stabilized in the amine-sulfate system, and, as described above, the primary amines can extract plutonium from sulfate solutions containing high concentrations of ferrous ion.

Displacement Stripping. Dilute to moderately concentrated nitric acid or acidic nitrate solution is effective in stripping plutonium sulfate from primary amines. For example, in four stage countercurrent stripping of plutonium (and uranium) from 0.3 M Primene JM-T, 5 M HNO_3 at A/O = 1/10 stripped >99.9% of the plutonium into a product solution containing 2.5 M sulfate and 0.25 M nitrate.[14]

3.5 Choice of Diluent

A primary consideration in choice of diluent is phase stability and good physical performance. In addition, the nature of the diluent can influence the effects of amine class and structure on extraction power and selectivity.

The compatability of amines and diluents was previously discussed with emphasis on sulfate systems.[11] The molecular or free-base forms of all the amines considered here are soluble in many organic diluents, but some of their salts show limited organic solubilities, typically decreasing in the order sulfate, bisulfate, chloride, nitrate. Class and structure of the amine and type of the diluent are both important in determining the solubilities. Salts of all the long straight-chain primary amines tested were insufficiently soluble in ordinary hydrocarbon diluents. Salts of straight chain secondary and tertiary amines are sufficiently soluble (>0.1 M) for use in aromatic hydrocarbons at ordinary

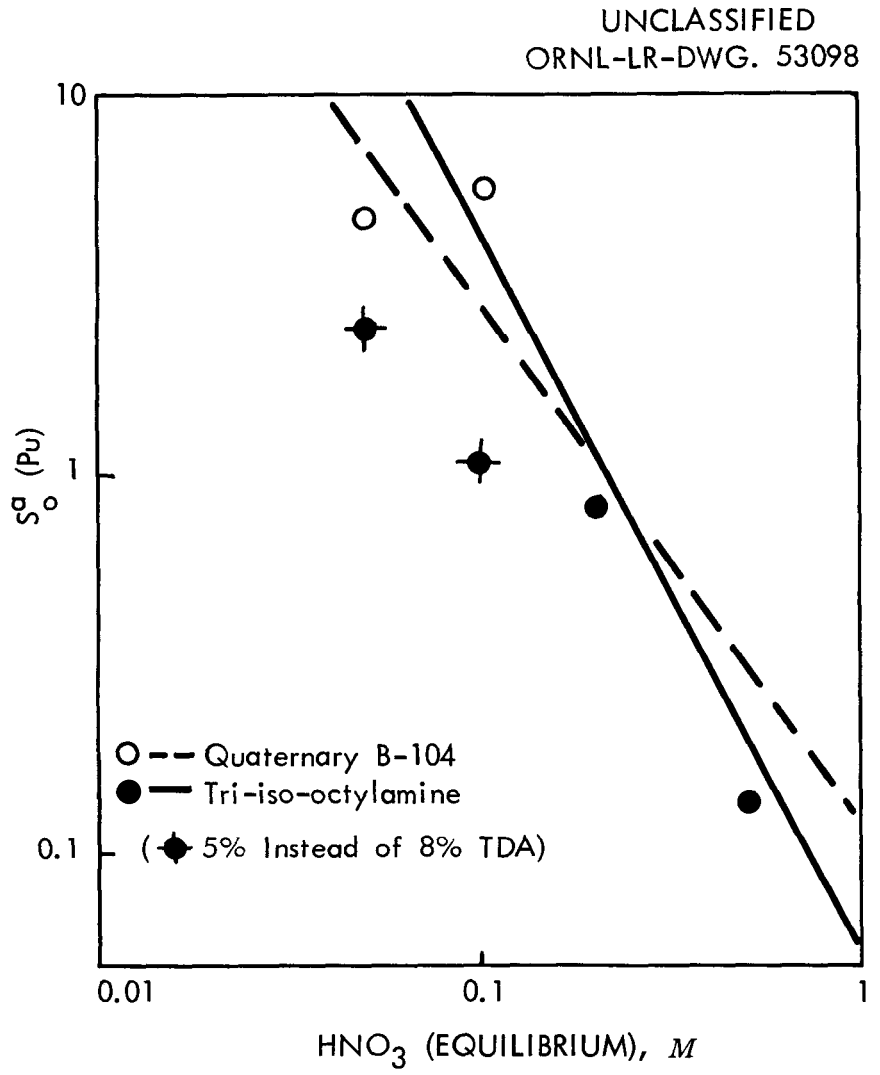

Fig. 3.6. Stripping of extracted Pu(IV) with dilute nitric acid from amines in 92% Amsco 125-82 - 8% tridecanol. Points are 10-min stripping equilibrations; the lines are the reciprocals of the extraction curves in Fig. 3.1.

temperatures. Their normal sulfates are also soluble in aliphatic hydrocarbons like kerosene and Amsco 125-82, but the bisulfates, chlorides, and nitrates of the straight-chain secondaries separate out as a precipitate or as a third liquid phase. The bisulfates and nitrates of the straight-chain tertiaries are borderline, the solubility increasing somewhat with chain length. The solubilities of all these salts in kerosene increase on addition of high molecular weight alcohols, e.g. oxo-process decanol or tridecanol. The solubilities also increase with branching of the alkyl groups in the amines. Where tested, solubilities increased either slightly or considerably (none were found to decrease) with increasing temperature in the range 0-50°C.

Most of the tests described in this report used either xylene or Amsco 125-82, the latter frequently modified with tridecanol. Trilaurylamine did not require modification of the Amsco 125-82 to maintain solubility of its nitrate in contact with nitric acid solutions up to 10 M.[16] Alamine 336 (mixed n-octyls and n-decyls), tri-n-octylamine, and tri-iso-octylamine required 5-10% tridecanol for consistent behavior. The branched secondaries did not require modification. Primene JM-T required about 5% tridecanol.

Another limitation that may be encountered is separation (at high loading) of a third phase containing the extracted metal ion. In the uranyl sulfate system this was seldom if ever encountered when sufficient solubility of the amine bisulfate had been ensured. It has not been tested in the plutonium extractions reported here, since these used only low plutonium levels. Wilson[6] reported miscibility up to 0.8 g of plutonium per liter of 0.15 M TLA--98% Amsco--2% n-octyl alcohol but >5.2 g of plutonium per liter of 0.15 M TLA--90% Amsco--10% n-octyl alcohol,* and miscibility limits from 0.1 to 26 g of plutonium per liter of 0.22 M tri-n-octylamine in a range of diluents. Amberlite LA-1 (20%, in a heavy halogenated diluent) has been loaded to ~30 g of plutonium per liter in processing of metallurgical scrap.[19] In direct measurement of neptunium loading, a third phase separated at ~ 1 g of neptunium per liter of 0.025 M tri-iso-octylamine in either xylene or 95% xylene--5% tridecanol, but there was no separation at the maximum extractable neptunium concentrations, i.e., ~ 1.5 g of neptunium per liter of 0.025 M TLA(EK) or Alamine 336 and ~ 6 g of neptunium per liter of 0.1 M Alamine 336, each in xylene.[20]

As mentioned in Sect. 3.3, the chemical nature of the diluent can combine with the amine class and structure in

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*Although not specified, the "Amsco" was probably Amsco 125-82 or a near equivalent, and the TLA was presumably technical grade.

affecting extraction power and selectivity. However, diluent effects on the plutonium extraction coefficients have been compared only incidentally in this report (e.g., slightly lower extractions with tri-iso-octylamine in xylene than in 95% Amsco 125-82--5% tridecanol, Fig. 3.2). Diluent effects are included in the program of fission-product and corrosion-product extraction studies at MIT[15] (Sect. 3.3).

4.0 EXTRACTION WITH NEUTRAL PHOSPHORUS ESTERS AND WITH PHOSPHINE OXIDES

Extractions by neutral phosphate and phosphonate esters generally parallel those by the intensively studied tri-n-butyl phosphate (TBP). Extractions by trialkylphosphine oxides also parallel these to some extent, but with extraction power so much higher that the phosphine oxides effectively provide a different type of extractant. In addition to the well-established gradation of extraction power $(RO)_3PO < (RO)_2RPO < (RO)R_2PO < R_3PO$,[21,22] the extraction power also shifts with the structure of the alkyl (or aryl) groups, giving some overlapping between the foregoing classes, and also giving different ratios of extraction coefficients for specific metal ions, i.e., different selectivities.[23,24]

4.1 Esters

Plutonium(IV) extractions from nitric acid solutions by several phosphates and phosphonates were compared with extraction by TBP, with emphasis on di-n-butyl phenylphosphonate (DnBPP) and di-sec-butyl phenylphosphonate (DsBPP), two reagents that show potential advantages over TBP in Thorex- and Purex-type processes.[24] The curves of plutonium extraction coefficient vs nitric acid concentration for these three reagents were nearly straight on a log plot and closely parallel from ~2 M HNO_3 down to at least 0.4 M HNO_3, with slopes close to 2.5 (Fig. 4.1). The coefficients with DsBPP were close to those with TBP, while those with DnBPP were higher by a factor of about 1.5.

The TBP extraction curve (Fig. 4.1), however, does not agree with corresponding data previously reported by Best et al.,[25] and hence these TBP and phosphonate extractions were rechecked in different ways. The equilibrations are summarized, separately for each of the three reagents, in Fig. 4.2. The solid black points represent independent direct extraction equilibrations at the equilibrium aqueous nitric

acid concentrations shown.* While there was noticeable scatter, especially with TBP, these data definitely show parallel, nearly straight lines of slope ~2.5 from ~0.1 to ~2 M HNO_3, shifting toward slope ~1 at ~4 M HNO_3. For TBP, these extraction coefficients agree fairly well with those of Best at 4 M HNO_3, but not at concentrations below 1 M HNO_3. The discrepancy at low acidities is considerably greater than the scatter. (For this comparison, Best's coefficients were normalized from 19% TBP to 1 M TBP using $E_a^o \propto \underline{M}^2_{TBP}$, Fig. 4.2d. The slope of a smooth curve through Best's data shifts from ~1.7 above 2.5 M toward ~1.0 at 0.2 M HNO_3.)

One possibility considered in attempting to resolve this discrepancy was that the extraction coefficients in the present work might be erroneously low at the low acidities because of polymerization or other hydrolysis reaction rendering a large fraction of the plutonium inextractable.** If that explanation were correct, back extractions by barren nitric acid solutions should involve less or none of the inextractable species, and hence should show higher distribution coefficients. Instead, the back extractions corroborated the direct extractions down to 0.4 M HNO_3 (Figs. 4.2a-c). At lower acidities the back extractions neither confirmed nor contradicted the direct extractions (see below).

At the same time, it is difficult to suggest that Best's extraction coefficients might be high by more than a small amount, i.e., by a factor of ~2 at the lowest acidity, and less at the higher acidities. The basis for this statement is that the most likely cause for erroneously high extraction

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*For some of the equilibrations in Fig. 4.2 (marked ▲, △, ■) the equilibrium aqueous nitric acid was calculated from the initial concentration by means of independently-measured acid extraction coefficients (Appendix B). For the others the reagent was pre-equilibrated to avoid acid transfer, or the final acidity was measured by titration. Chronologically, the equilibrations requiring calculation of the final acidity were the first ones run. These were rechecked first with individual direct extractions using pre-equilibrated reagents or titration of the final acidity, and finally by the back-extraction series.

**From published measurements at macro plutonium concentrations,[26] the plutonium at these low concentrations would not be expected to polymerize at acidities above 0.1 M. However, the possibility was still considered that hydrolysis short of actual polymerization might impair extraction at acidities somewhat higher than was indicated by the polymerization studies.

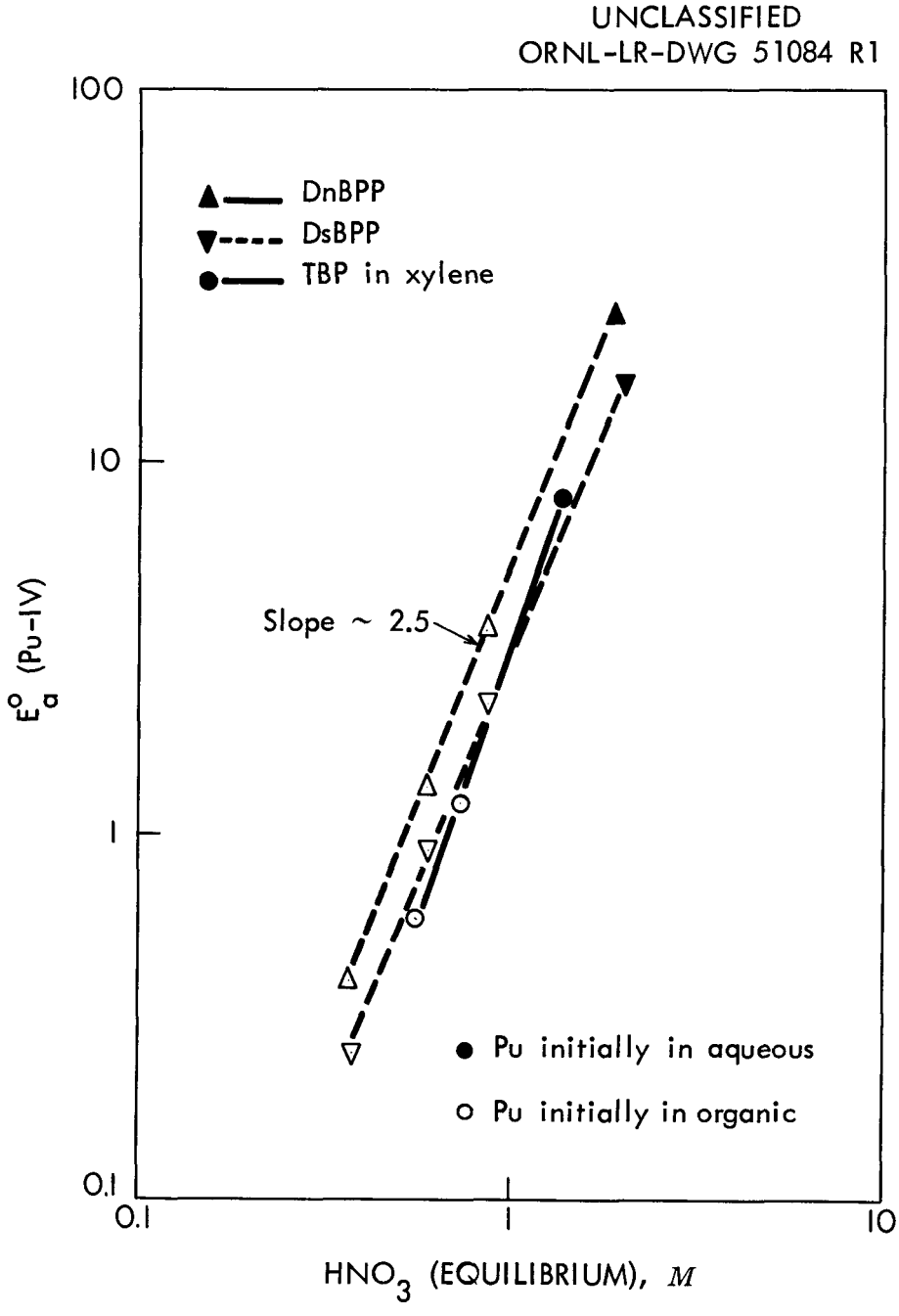

Fig. 4.1. Plutonium (IV) extraction from nitric acid solutions by 1 M di-n-butyl phenylphosphonate, di-sec-butyl phenylphosphonate, and tributyl phosphate. Plutonium reduced with hydroxylamine nitrate, reoxidized with $NaNO_2$.

coefficients in the direct extraction of trace Pu(IV) would be the presence of a trace contaminant with much higher extraction power than TBP, whose effect would be completely masked in extraction of plutonium at macro concentrations. Best's macro extractions are in fairly good agreement* with the dashed line in Fig. 2d, which is the extension of the straight upper portion of the trace extraction curve, slope 1.7, and is only a little closer than that curve to the slope 2.5 line found in the present measurements. This internal evidence does not exclude the possibility of high coefficients due to a large amount of contaminant of only moderately higher extraction power than TBP, but this seems considerably less likely than trace contamination. Thus, as stated above, the discrepancy between Best's and the present work remains unresolved.

Extraction coefficients for trace Np(IV) with 1 M TBP in xylene[3] are also included in Fig. 4.2d. Np(IV) extractions generally parallel Pu(IV) extractions closely. Here the slope between 0.1 and 1 M HNO_3 is ~2.0, in between the slopes from the two plutonium studies.

Returning to the back-extraction series in Figs. 4.2a-c, the behavior in these series changed abruptly when the acidity fell much below 0.4 M. Instead of continuing to decrease with decreasing acidity, the distribution coefficients in back-extractions leveled off and then rose, eventually exceeding unity in one case in which five successive scrubs with 0.1 M HNO_3 (Fig. 4.2c, □) were used. In each of the other three series the last scrub was with 1 M HNO_3, which gave coefficients almost back in line with the other high-acid equilibrations. The tentative explanation offered for this behavior is that significant hydrolysis occurred at acidities not much below 0.4 M, at least in the organic phase, to produce a difficultly stripped plutonium species that was probably nontransferable rather than highly extractable. It is tempting to suggest that it was nontransferable because it had polymerized. However, if polymer were involved it differed from that studied in the aqueous phase[26] in at least

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*The actual macro extraction coefficients reported were somewhat higher than the trace extraction coefficients, which Best et al. attributed to the significant contributions of plutonium nitrate to the total nitrate salting concentration. They state that normalization using $E_a^o \propto \underline{M}_{NO_3}^3$ (rather than $E_a \propto \underline{M}_{NO_3}^4$) makes the macro extraction coefficients agree with the trace extraction coefficients. However, a plot of all their reported macro extractions (Fig. 4.3) shows that normalization using either $E_a^o \propto \underline{M}_{NO_3}^4$ or $E_a^o \propto \underline{M}_{NO_3}^3$ makes the macro data, within considerable scatter, agree better with the extended slope of 1.7 than with the trace extraction curve.

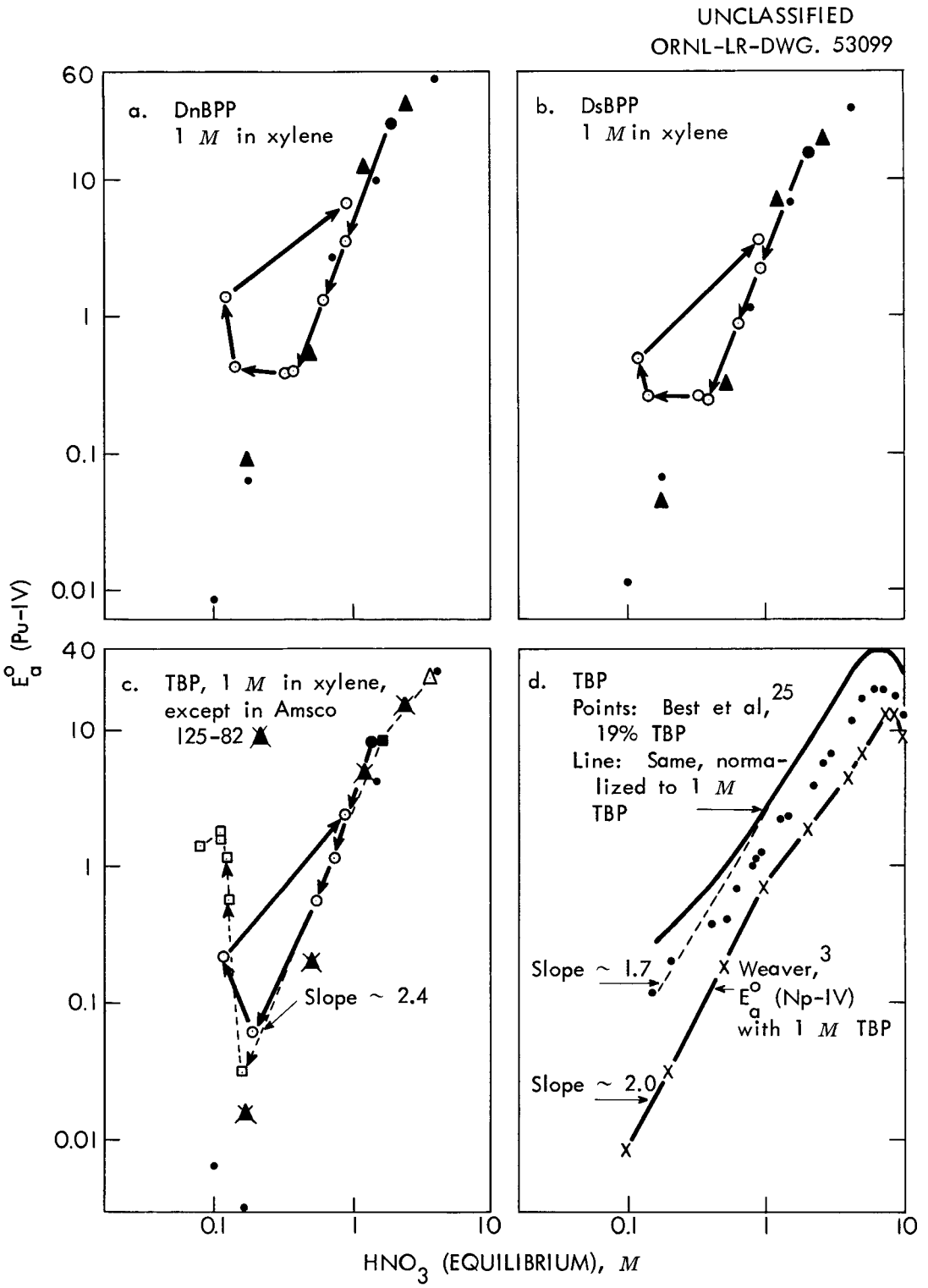

Fig. 4.2. Anomalous stripping of Pu(IV). ● ■ Direct extraction of plutonium initially in aqueous phase; ○ □ △ stripping of extracted plutonium; arrows show successive equilibrations. Reagents scrubbed with (▲) 2% NaOH or (■ ●) 2% Na_2CO_3 and alumina, 2 *M* HNO_3, and water. Plutonium reduced with hydroxylamine nitrate, reoxidized with $NaNO_2$.

two respects: in being formed at acidities above 0.3 M, and in rather readily reverting to a transferable species at 1 M acidity.* The initial scrub acidities, equilibrium acidities, and initial plutonium concentrations for these back-extraction series are summarized with the distribution coefficients in Table 4.1. Both phases were analyzed after each equilibration, with good material balances.

Plutonium extraction from nitric acid--aluminum nitrate solution was higher with tri-sec-butyl phosphate (TsBP) and tri(octyl-2) phosphate (TCP) than with TBP, and did not drop quite so much in competition with uranium and thorium extraction:

Reagent, 0.3 M in Amsco 125-82	E_a^o(Pu-IV) in 0.5 M HNO_3--0.5 M $Al(NO_3)_3$	
	U and Th Absent	10 g U + 10 g Th/liter
TBP	1.3	0.8
TsBP	5	3
TCP	4	2

(17 mg Pu/liter, stabilized with 0.1 M, $NaNO_2$, A/O phase ratio = 1/1, 10 min equilibration at room temperature). There was a smaller difference, still in the same direction, when the extraction coefficients were depressed to low levels by approximately saturating the extractants with uranium:

Reagent 0.3 M, in xylene	Extracted U(VI), M	E_a^o(U-VI)	E_a^o(Pu-IV)	Ratio
TBP	0.17	0.10	0.028	0.28
TsBP	0.16	0.10	0.038	0.38
DAAP	0.18	0.11	0.060	0.55
DnBPP	0.19	0.12	0.034	0.28
DCPP	0.16	0.10	0.036	0.26

(extraction from 1 M HNO_3--1.8 M $UO_2(NO_3)_2$ solution). The last three reagents listed are phosphonates---diamyl amylphosphonate, di-n-butyl phenylphosphonate, and di(octyl-2) phenylphosphonate. The uranium extraction coefficients were forced by saturation to be close to 0.1. While the ratio E(Pu)/E(U) was below unity with all the reagents, it was higher with TsBP than with TBP. It was still higher with the alkylphosphonate, but essentially the same as TBP with the two phenylphonates.

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*The extraction coefficients after the 1 M HNO_3 scrubs are higher than the indicated straight lines by factors of 1.1 to 1.5, suggesting 10 to 30% unstrippable plutonium still present.

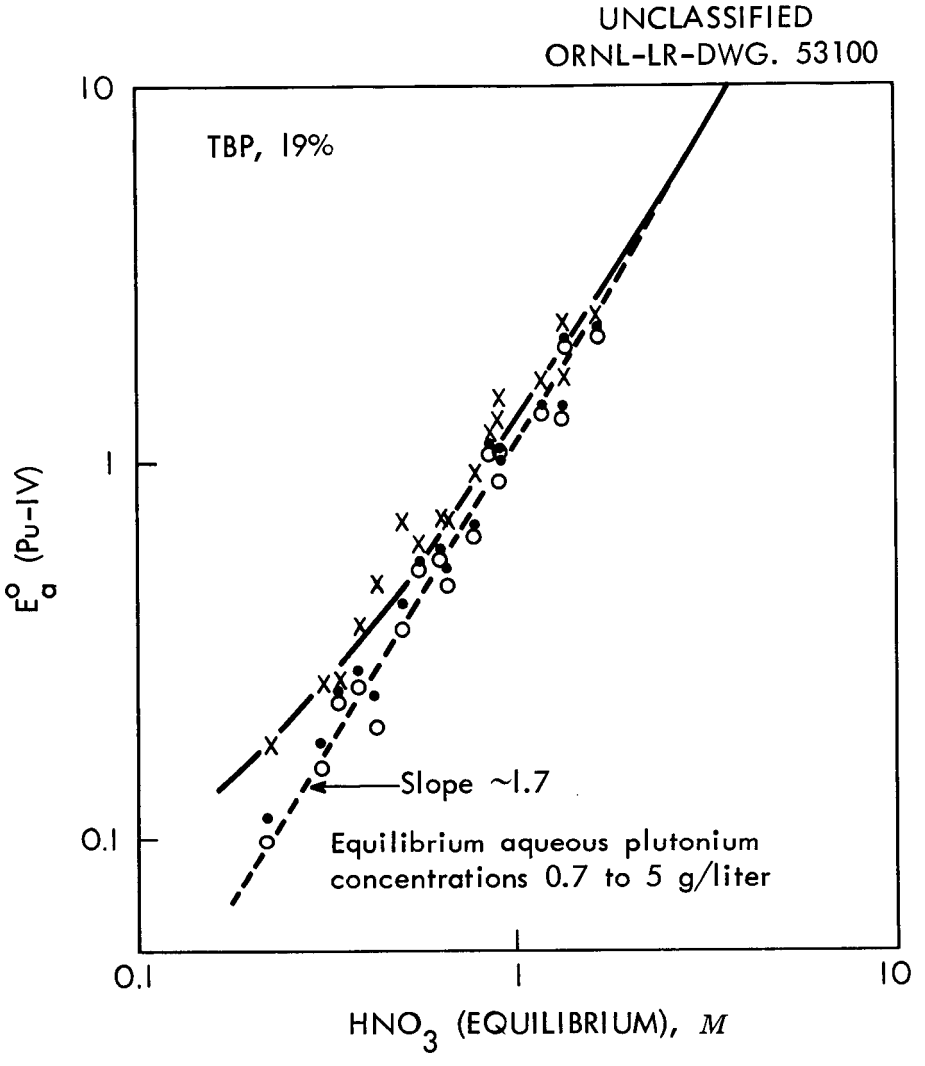

Fig. 4.3. Extraction of macro plutonium with 19% TBP, Best et al.[25] Points x normalized to $\Sigma [NO_3] = [HNO_3]$ using ● , E $\propto [NO_3]^3$, o , E $\propto [NO_3]^4$. The solid line is the smoothed curve fitted to the trace plutonium extractions of Best et al. (cf. Fig. 4.2-d).

Table 4.1 Acid and Plutonium Concentrations in Extraction and Stripping Equilibrations

1 M extractants in xylene
A/O phase ratio = 1/1

Plutonium reduced at 1 g/liter in 2 M HNO_3 by 0.1 M $NH_2OH \cdot HNO_3$, 2 hr at room temperature, and then oxidized by 0.5 M $NaNO_2$, 10 min at 50°C; aliquots pipetted into nitric acid solutions as indicated

Extractant	Nitric Acid, M		Initial Pu, mg/liter	D_a^o(Pu)
	Initial	Equilibrium		
DnBPP	2.0	1.9	170	25
	0.5	0.87		3.5
	0.5	0.60		1.3
	0.3	0.37		0.40
	0.3	0.33		0.39
	0.1	0.14		0.43
	0.1	0.12		1.4
	1.0	0.90		6.6
DsBPP	2.0	2.0	170	16
	0.5	0.88		2.2
	0.5	0.61		0.90
	0.3	0.38		0.25
	0.3	0.33		0.27
	0.1	0.14		0.27
	0.1	0.12		0.51
	1.0	0.88		3.6
TBP	1.7	1.4	100	8.0
	0.50	0.73		1.2
	0.50	0.55		0.59
	0.10	0.19		0.06
	0.10	0.12		0.22
	1.0	0.88		2.4
	2.0	(1.6)[b]	86	8.3
	4.0[a]	(3.6)[b]		24
	H_2O[a,c]	0.16		0.03
	0.1	0.13		0.58
	0.1	0.12		1.1
	0.1	0.11		1.6
	0.1	0.11		1.7
	0.1	0.08		1.4

[a] Organic from initial extraction split; one portion scrubbed with 4 M HNO_3 only, the other scrubbed with water and then 0.1 M HNO_3.

[b] Equilibrium acidity calculated from independently measured nitric acid extraction coefficients

[c] A/O phase ratio = 2/1 instead of 1/1.

4.2 Phosphine Oxides

Nitrate Solutions. Plutonium(IV) extraction from unsalted nitric acid solutions by tri-n-octylphosphine oxide (TOPO) reached a maximum at around 1 M HNO_3 (Fig. 4.4). It was lower at 4 M HNO_3, and high again at 8 M HNO_3. With 0.1 M TOPO in Amsco 125-82, the extraction coefficient was 100 at 0.1 M HNO_3* and >3000 at the maximum. (Parallel extraction of Np(IV)[3] by 0.01 M TOPO is included in Fig. 4.4 for comparison, showing a maximum at around 1 M, a minimum at 4 M, and a second maximum near 8 M HNO_3.) The extraction coefficient varied with nearly the square of the TOPO concentration (Fig. 4.5). The plutonium extraction coefficients with 0.01 M TOPO were higher than neptunium coefficients (Fig. 4.4) by a factor of about 2. This is similar to the difference in plutonium and neptunium extractions with TBP, and in the same direction but smaller than the difference in extractions with tertiary amine, which was by a factor of about 10.[3]

Extraction coefficients with the highly branched reagent tris(2-ethylhexyl)phosphine oxide (T(2EH)PO) at 0.1 M were lower by a factor of about 20 than with 0.1 M TOPO, only a little higher than with 0.01 M TOPO. In comparison, coefficients were lower with T(2EH)PO than with TOPO by factors of around 40 in extraction of uranyl nitrate and sulfate[27] and 10 in extraction of Np(IV) nitrate,[3] showing large changes in selectivity as well as in magnitude of extraction power with the change in structure.

The plutonium extraction coefficient with 0.01 M TOPO increased on addition of nitrate salt to nitric acid, from ~80 at 1 M HNO_3 to 1000 at 1 M HNO_3 + 5 M $NaNO_3$ (Fig. 4.4).

The extraction coefficient for Pu(VI) with 0.1 M TOPO from ~2 M HNO_3 was 320, lower by a factor of 10 than the coefficient for Pu(IV). The extraction coefficients for Pu(III) were still lower, but were highly variable in repeated tests. The lowest coefficients obtained consistently with 0.1 M TOPO were a little above unity, i.e., ~3 from 0.5 M and 2 M HNO_3 and ~2 from 6 M HNO_3. Hence, this is tentatively accepted as the level of extraction coefficients for Pu(III) as such. The much higher coefficients found in other tests, 20 to >100, are attributed to oxidation, strongly enhanced by the presence of the extractant. Similarly high and variable extractions of plutonium from Pu(III) solutions are noted above by amines---Pu(III) sulfate by primary amine (Sect. 3.2) and Pu(III) nitrate

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*The reproducibility of extraction from 0.1 M HNO_3 was not checked, and might be questioned because of possible interference by hydrolysis; cf. TBP and phosphonates, above. However, it is likely that the high complexing power of the phosphine oxide can stabilize Pu(IV) even at the low acidity.

by tertiary amine (Sect. 3.1)---and below by dialkylphosphoric acid (Sect. 5.1).

Sulfate Solutions. Plutonium(IV) extraction coefficients from sulfuric acid solutions containing little or no salt are fairly high, although several orders of magnitude lower than the coefficients from nitric acid solutions:

TOPO Concn., M	E_a^o(Pu-IV) 5 M H_2SO_4	3 M H_2SO_4	3 M H_2SO_4 -- 0.5 M Na_2SO_4	0.5 M H_2SO_4 -- 2.5 M $(NH_4)_2SO_4$
0.1		5		<0.01
0.3	20	30	20	0.1

(diluent Amsco 125-82). These extraction coefficients resemble those for uranyl sulfate.[27] However, while the uranyl extraction was markedly increased by adding small concentrations of nitrate to sulfate solution, the plutonium extraction was not increased by adding 1 M or 2 M $NaNO_3$ to the 3 M H_2SO_4.

The extraction coefficient for Pu(VI) from 5 M H_2SO_4 with 0.3 M TOPO was 4, compared with 20 for Pu(IV).

In some of the tests with 5 M H_2SO_4, but not with 3 M H_2SO_4, the 0.3 M TOPO solution in Amsco 125-82 separated into two organic phases. The possibility of modifying the diluent to prevent this was not examined.

4.3 Stripping of Extracted Plutonium

Esters. Stripping from the phosphate and phosphonate esters was not examined in this study. Since they show about the same order of extraction power, the methods used to strip plutonium (and uranium) from TBP should apply to the others with some shift in operating conditions, e.g., a change of flow ratio A/O from 1.4/1 to 2/1 for stripping uranium from DnBPP with ~0.01 M HNO_3.[24]

Phosphine Oxide. Neither plutonium nitrate nor uranyl nitrate[27] can be stripped from 0.1 M phosphine oxide with "water," i.e., dilute nitric acid.* The much lower extraction coefficients from sulfuric acid solution suggest that water should strip the extracted plutonium or uranyl sulfate. However, neither uranium nor plutonium was stripped in the few

*At some much lower TOPO concentration, probably <0.001 M, its extraction and stripping coefficients should match those of 1 M TBP, so that "water" stripping should be feasible. This was not tested, and is not likely to be of practical importance.

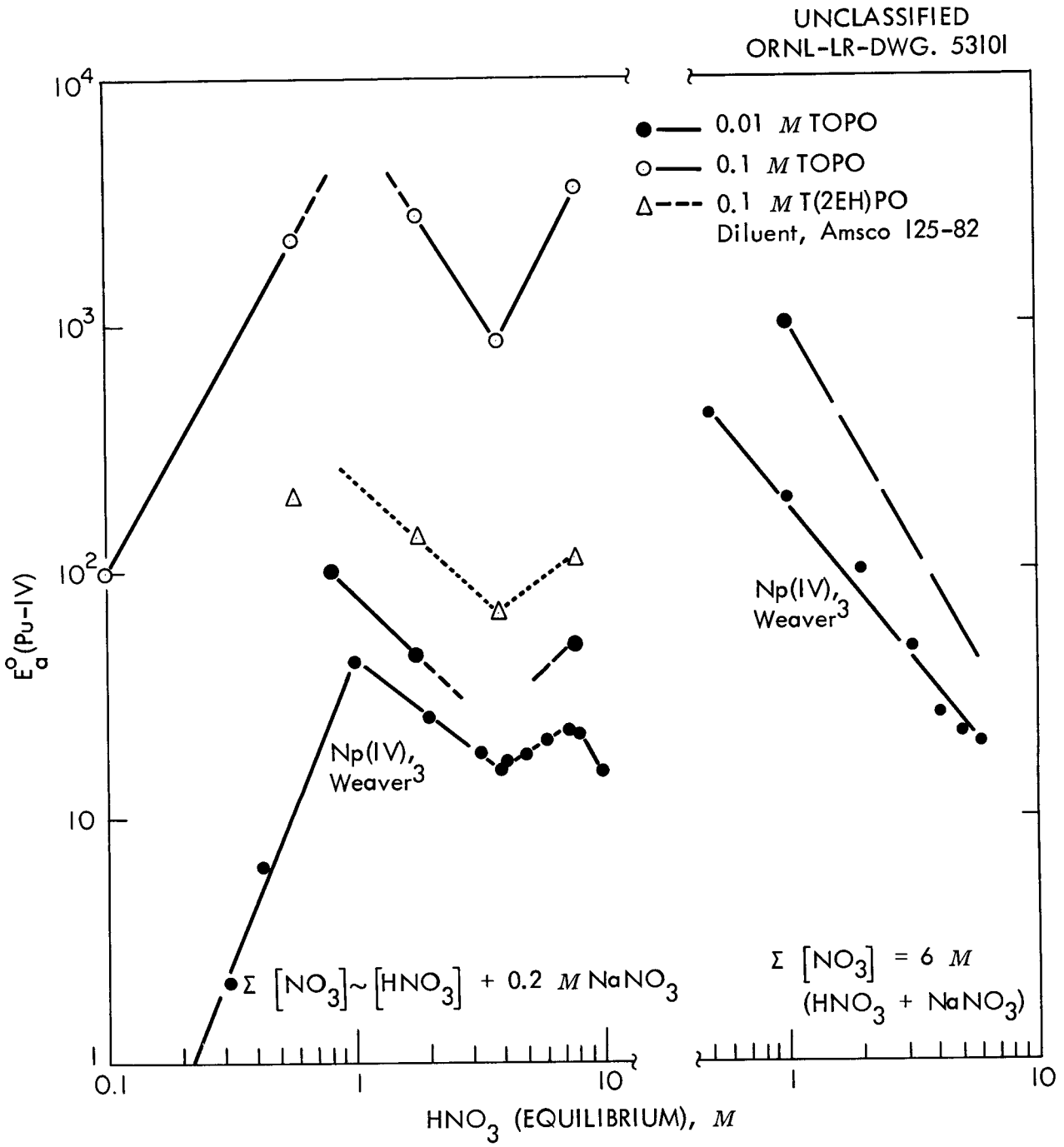

Fig. 4.4. Plutonium(IV) extraction by tri-n-octylphosphine oxide and tri-(2-ethylhexyl)phosphine oxide: effect of nitric acid and sodium nitrate concentrations. Plutonium(IV) stabilized with 0.04 - 0.1 M $NaNO_2$.

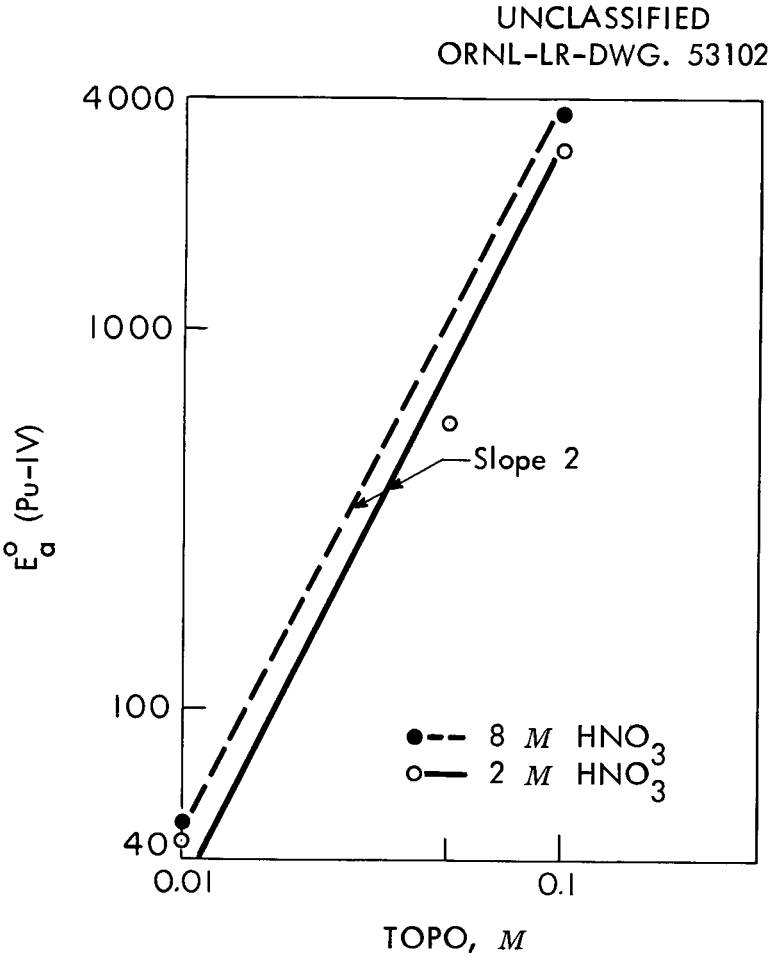

Fig. 4.5. Variation of Pu(IV) extraction coefficients with tri-n-octylphosphine oxide concentration from nitric acid solutions. Diluent, Amsco 125-82.

tests made.* Plutonium was tested only once: $S_o^a(Pu) = 0.03$ at phase ratio A/O = 1/1, after extraction into 0.3 M TOPO from 3 M H_2SO_4 at 20 mg/liter.

Reductive stripping of plutonium nitrate from 0.1 M TOPO in Amsco 125-82 succeeded under some but not all of the conditions tested. Plutonium was stripped by a mixture of ferrous sulfamate with dilute nitric and sulfuric acids:

HNO_3, M	H_2SO_4, M	$Fe(NH_2SO_3)_2$, M	$S_o^a(Pu)$ 1st	$S_o^a(Pu)$ 2nd
0.05	0.1	0.1	1.8	16
0.1	0.1	0.1	1.2	-

(phase ratio A/O = 1/1 for each of two successive contacts, 10 min each; plutonium ~20 mg/liter). The low stripping coefficient in the first contact is attributed mainly to increase in the aqueous nitric acid concentration from stripping of the excess nitric acid (not measured) originally extracted with the plutonium. Stripping failed at a higher nitric acid concentration: $S_a^o = 0.1$ and 0.3 in successive contacts with 2 M HNO_3 containing 0.1 M $Fe(NH_2SO_3)_2$ and 0.1 M NH_2SO_3H. The stripping coefficient of 0.3 matches the extraction coefficient of 3 for Pu(III) (Sect. 4.2) found when enchanced extraction due to oxidation was believed to be at a minimum. Stripping also failed with hydroxylamine hydrochloride: $S_o^a = 0.03$ to 0.01 with 0.1 M $NH_2OH \cdot HCL$ in 0.05 to 0.2 initial M HNO_3 (phase ratio A/O = 1/1, 10 min at room temperature). Addition of sulfate might aid this stripping agent, but was not tested.

From the extraction data, a dilute sulfate solution should strip plutonium in a countercurrent system, which would effect displacement of the nitrate. This was not tested.

Both uranium[27] and plutonium can be stripped with sodium carbonate solution: $S_o^a(Pu) > 1000$ in stripping with 1 M Na_2CO_3

*The only explanation that can as yet be offered to account for the failure to water-strip plutonium sulfate and uranyl sulfate from phosphine oxide solution is that the extracted complex is somehow prevented from effective contact with the aqueous phase, perhaps by forming a colloid. A similar and perhaps parallel retention of a small amount of uranium during carbonate stripping was previously encountered,[27] which appeared to be a physical effect due to a degradation product of the phosphine oxide or the diluent. In that case the "protection" of the residual uranium was destroyed by addition of ethanol or acetone to the system, and some analogous treatment might prove sufficient to permit water stripping of the nitrate-free uranyl and plutonium sulfates.

from 0.3 M TOPO after extraction from 3 M H_2SO_4. The plutonium concentration was only 20 mg/liter in this test, and higher loadings have not been tested with phosphine oxides. Plutonium concentrations of 2 g/liter were obtained in stripping dialkylphosphoric acid with 1 M Na_2CO_3 (Sect. 5.3), without any evidence of precipitation.

5.0 EXTRACTION WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID

Plutonium(IV) is extracted from dilute nitric acid solutions much more strongly by di(2-ethylhexyl)phosphoric acid (D2EHPA) than by either amines or phosphine oxides. While the mechanism of extraction must be different, i.e., extraction of a simple cation or cationic complex instead of a neutral or anionic complex, the extractability varies in the same order with the plutonium oxidation state, Pu(IV) > Pu(VI) > Pu(III), as it does with the other reagents.

5.1 Nitrate Solutions

As expected on the basis that the extraction is plutonium-hydrogen cation exchange, Pu(IV) extraction coefficients decreased with increasing acidity over most of the nitric acid concentration range (Fig. 5.1). The slope, presumably corresponding to the charge of the plutonium cation and the number of hydrogen ions exchanged, changed with increasing acidity from ~1/2 near 1 M HNO_3 to ~2, and then to >4 above 6 M HNO_3.* The slopes lower than ~4 suggest extraction of an oxygenated or a nitrate-complexed Pu(IV) cation (more likely the former since the slope increased with increasing nitric acid concentration). However, this cannot be taken as more than a suggestion at this point, for the measurement of these slopes depended on the accuracy of the extraction coefficients measured at >>1000, where the raffinates were approaching analytical limits. At ~0.1 M HNO_3 (the only acidity below 0.3 M tested), the extraction coefficient dropped by a factor of 10, suggesting major interference by plutonium hydrolysis. Addition of sodium nitrate to the nitric acid (total nitrate = 6 M) had little effect on the extraction from 1-6 M HNO_3. It increased the extraction from 0.3 M HNO_3, bringing that point more nearly into line with the points at the higher acidities.

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*At high nitric acid concentrations, D2EHPA extracts U(VI)[28] and probably Pu(VI) (below) like a neutral ester in addition to cation-exchange extraction. While that may well be true here too, TBP-like extraction could hardly contribute a discernable increase to these high Pu(IV) extraction coefficients.

As with the other extractants discussed above, this extraction pattern resembles that found for Np(IV).[3]*

Extraction with a concentration of D2EHPA higher than 0.01 M was measured at 6 M and higher HNO_3, since trials at lower acidity indicated extraction coefficients too high to measure.

Extractions over a range of D2EHPA concentrations (Fig. 5.2) showed the extraction coefficient varying with close to the square of the D2EHPA concentration. This concentration was corrected for the amount tied up by the plutonium, calculated on the basis (explained below) of four organophosphorus anions per plutonium. (While some of the corrections were appreciable, up to 30% at 10^{-4} M D2EHPA, ignoring them would have shifted the apparent slope only to ~2.4, with still nearly as close a fit to linearity. Hence, the conclusion of second power dependence does not depend strongly on the correctness of the assumed 4:1 ratio, and conversely the resulting good fit gives only a little additional support to that assumption.)

Since D2EHPA is dimeric in hydrocarbon solutions,[29,30] second power dependence on its concentration indicates complexing at a mole ratio of D2EHPA to metal ion of 4:1. As both neptunium and plutonium results indicated two hydrogen ions exchanged per metal ion, the complex formed is probably $PuOX_4H_2$ (or possibly $Pu(OH)_2X_4H_2$, $Pu(NO_3)_2X_4H_2$, etc.), where X represents the dialkylphosphate anion. This is analogous to the proposed formulations at low loading, $UO_2X_4H_2$ for uranyl, $Fe(OH)X_4H_2$ for iron(III), REX_6H_3 for rare earths, and ThX_8H_4 for thorium.[30,31]

The extraction coefficient for Pu(VI) with 0.1 M D2EHPA from ~4 M HNO_3 was ~12 (Fig. 5.3), nearly three orders of magnitude lower than for Pu(IV). As generally found in the extraction of U(VI),[28,32] the Pu(VI) extraction coefficient was lower with an alcohol (tridecanol) and higher with phosphine oxide added to the extractant.** With the

*The reproducibility of the neptunium extractions[3] was checked by many equilibrations, taking advantage of the ready analysis of Np-238 tracer. The Np(IV) extraction coefficients were well reproducible from 1-10 M HNO_3 solutions, slope ~2 between 1 and 8 M HNO_3. Below ~1 M HNO_3 they were scattered, which was attributed to variable hydrolysis of the neptunium. In the presence of sodium nitrate to keep the total nitrate at 6 M, the same extraction coefficients were found at 1-10 M HNO_3, while below 1 M HNO_3 a reproducible smooth curve was found that fell in the higher part of the range of scatter of the acid-only solutions.

**When the extracted plutonium is to be stripped with a carbonate solution, a diluent like Amsco 125-82 needs a modifier such as an alcohol, TBP, phosphonate, or phosphine oxide to maintain miscibility of the organophosphate salt. Cf. Sect. 5.3.

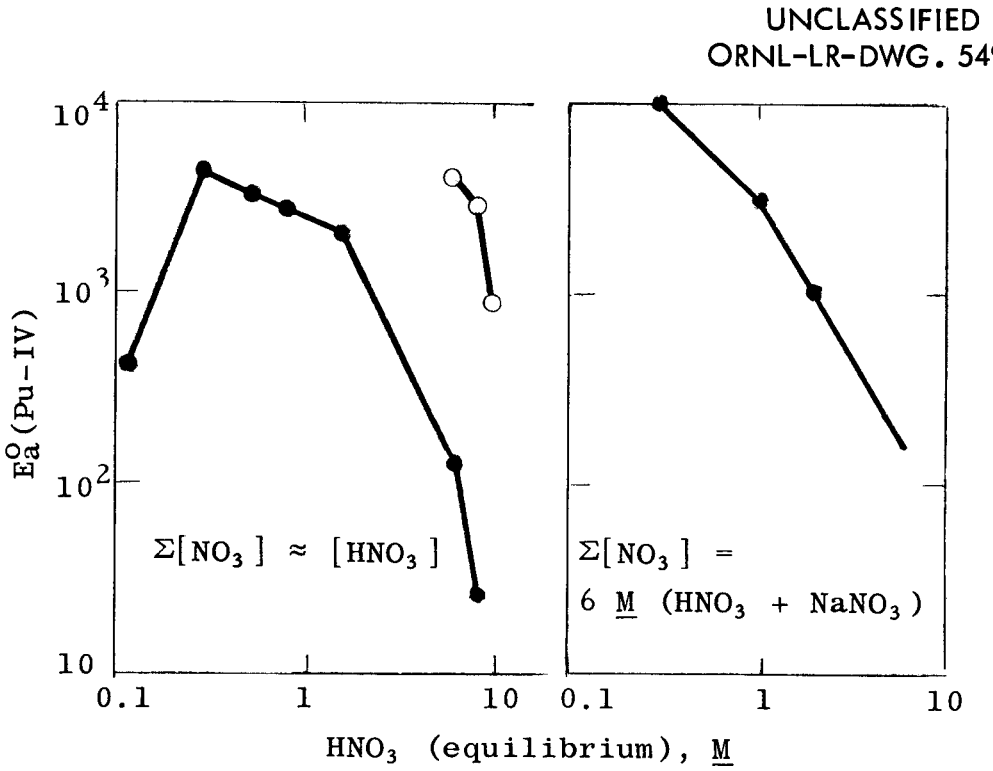


Fig. 5.1. Plutonium(IV) extraction by di(2-ethylhexyl)-phosphoric acid: effect of nitric acid and sodium nitrate concentration. ● 0.01 M D2EHPA; ○ 0.1 M D2EHPA; diluent, Amsco 125-82. Plutonium reduced with hydroxylamine nitrate, reoxidized and stabilized with 0.1-0.5 M $NaNO_2$.

Amsco-alcohol diluent, the extraction coefficients rose with increasing nitric acid concentration from 2 to 8 M, parallel to U(VI) extraction.[28] (This suggests that in the Pu(VI) extraction, as previously shown in the U(VI) extraction, a TBP-like extraction mechanism becomes important at high nitrate concentrations in addition to the cation-exchange extraction mechanism.) With phosphine oxide present, the extraction coefficients were much higher, although dropping sharply from 2 to 4 M HNO_3. This is qualitatively similar to, but steeper than, the curve for U(VI) extraction with D2EHPA plus TBP.[32] At ~2 M HNO_3 the Pu(VI) extraction coefficient with 0.05 M TOPO <100 (estimated from 320 with 0.1 M TOPO). Since the coefficient with 0.1 M D2EHPA alone is 4 (Fig. 5.3), the coefficient of 360 with 0.1 M D2EHPA + 0.05 M TOPO shows a synergistic enhancement of plutonium extraction corresponding to that in uranium extraction.

The extraction coefficients for Pu(III) with 0.1 M D2EHPA from nitric acid are much lower than for Pu(IV), but it has not been possible to measure exactly how low. Direct extraction under a carbon dioxide atmosphere from solutions reduced with ferrous sulfamate in the presence of excess sulfamic acid gave extraction coefficients ranging around 10^{-1} from nitric acid solutions 0.5 to 6 M and >1 from 8 M (Fig. 5.4). However, these extractions were suspected to involve some Pu(IV), in view of (1) very low extraction coefficients with D2EHPA for the analogous RE(III) and Am(III) (Appendix E), and (2) the experience encountered in extracting reduced plutonium with amines (Sects. 3.1, 3.2) and phosphine oxide (Sect. 4.2). To test this, some of the extracts were scrubbed with 1 M HNO_3, containing sulfamic acid to avoid oxidation by nitrite. A small fraction of the plutonium was removed, as shown by the triangles in Fig. 5.4, indicating that most of the plutonium in the extract was Pu(IV)* at the time of the scrub. However, it was not indicated to be all Pu(IV), for which the expected distribution coefficient would have been ~10^5. The extreme assumption that the plutonium removed by the scrub was all that had been originally extracted as Pu(III) permitted calculation of the extraction coefficients shown at the bottom of Fig. 5.4, which lie between 10^{-3} and 10^{-4} over the acid range.

This entire extraction-scrub test series was repeated, using hydrazine instead of excess sulfamic acid with the ferrous sulfamate reductant. This combination has been reported to be particularly effective in reducing and stabilizing Pu(III).[18] The results (Fig. 5.4) were similar to the previous results. Again, the extreme assumption that all plutonium originally extracted as Pu(III) was removed in the scrub led to calculated extraction coefficients for Pu(III) lying between

*An alternative possibility cannot yet be ruled out, that some new and nonstrippable species of Pu(III) might have been formed in the organic phase.

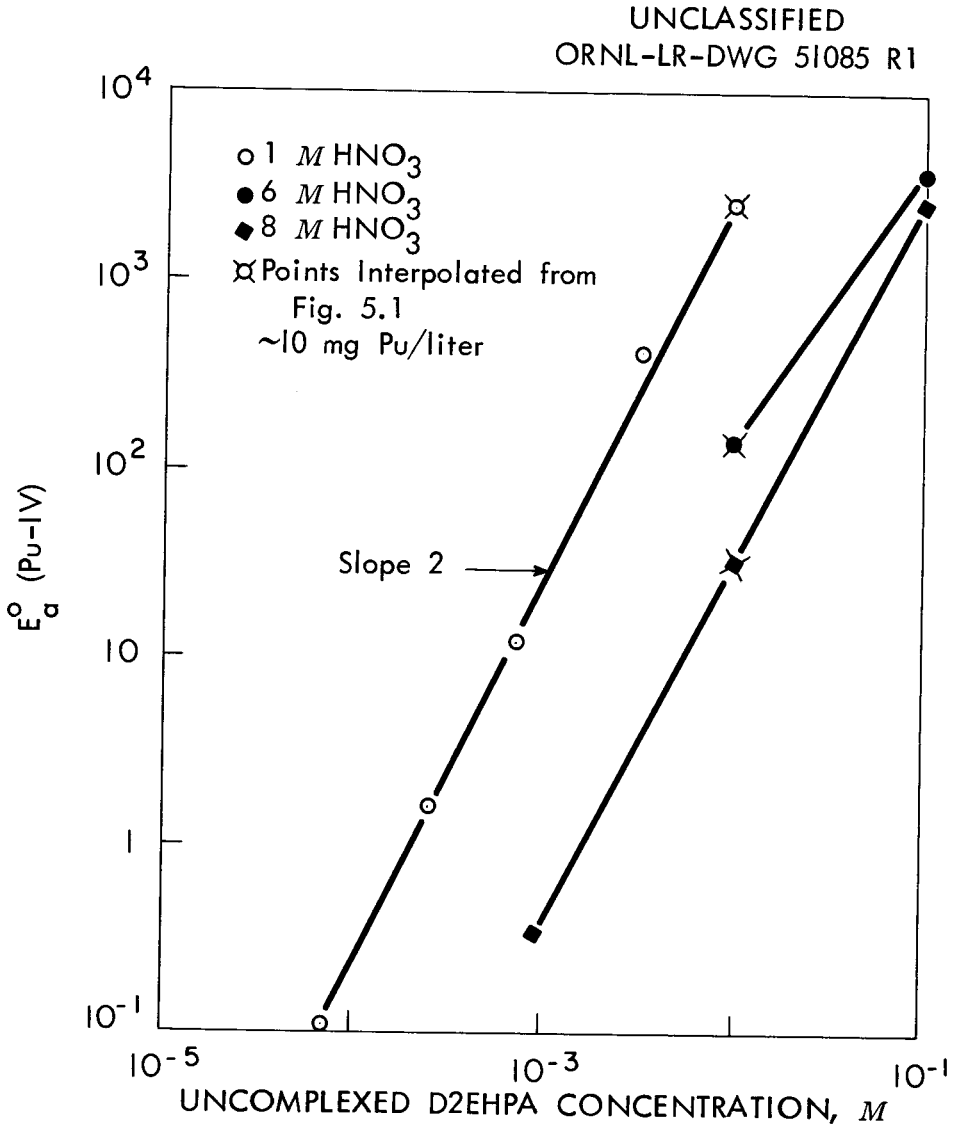


Fig. 5.2. Variation of plutonium(IV) extraction coefficient with di(2-ethylhexyl) phosphoric acid concentration from nitric acid solutions. Diluent, Amsco 125-82; plutonium reduced with hydroxylamine nitrate, reoxidized and stabilized with 0.1 - 0.5 *M* $NaNO_2$.

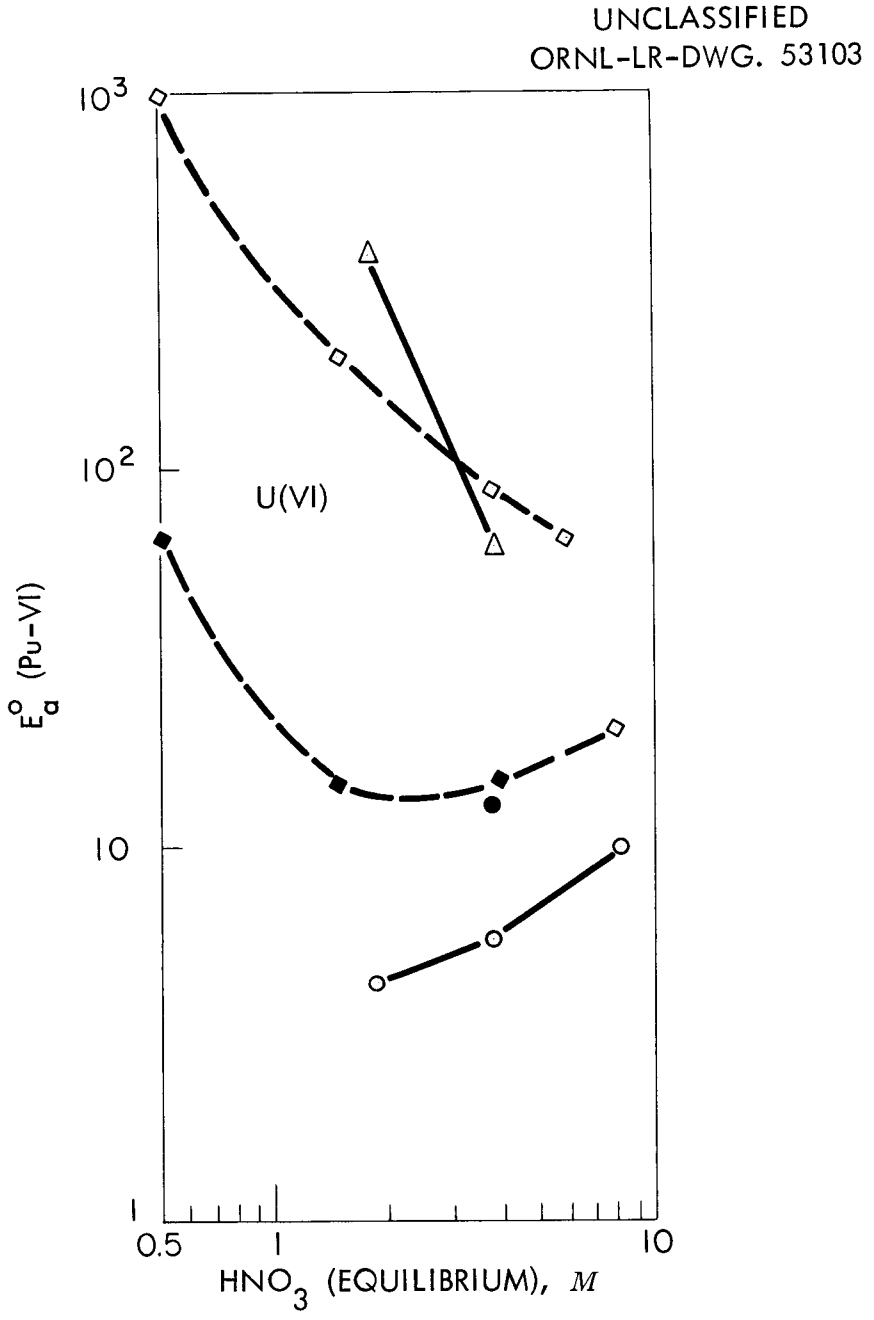


Fig. 5.3. Plutonium(VI) extraction from nitric acid solution by 0.1 M D2EHPA in Amsco 125-82 plus ● no modifier, o 2 V % tridecanol, Δ 0.05 M TOPO. ◆ Uranium(VI) extraction with 0.1 M D2EHPA in kerosene plus 3% 2-ethylhexanol.[28] ◇ Uranium(VI) extraction with 0.1 M D2EHPA in kerosene plus 0.1 M TBP.[32] Plutonium oxidized with AgO.

10^{-3} and 10^{-4}. Since it is more likely that some Pu(IV) was present before or during the extraction and some more was formed after the extraction, the actual Pu(III) extraction coefficients probably lie between the limits indicated in Fig. 5.4, i.e., somewhere around the order of 10^{-2}.

5.2 Sulfate Solutions

Plutonium extraction from sulfate solutions with D2EHPA was examined briefly, primarily to scout its possible utility in scavenging plutonium and uranium lost to sulfuric acid fuel-decladding solutions.* Plutonium(IV) extraction coefficients from 3 and 5 M H_2SO_4 solutions were relatively low, not much above unity even with 0.4 M D2EHPA (Table 5.1). With 0.5 M Na_2SO_4 added to the 3 M H_2SO_4, the extraction coefficients were an order of magnitude higher. Addition of TBP decreased the extraction, while addition of TOPO had little effect.

Plutonium(VI) extraction from 5 M H_2SO_4 was still lower, except that the extraction coefficient with TOPO added was of the same order as the Pu(IV) coefficients. Like the extractions of U(VI), and of Pu(VI) nitrate, the Pu(VI) extraction coefficient from sulfuric acid was lowered by the addition of an alcohol and raised by the neutral organophosphorus reagents, TBP < DAAP < TOPO. The extraction coefficient with 0.1 M TOPO alone is considerably less than 5 (since it is 4 with 0.3 M TOPO, Sect. 4.2), so that the increase from 0.4 to 5 on adding 0.1 M TOPO to 0.4 M D2EHPA showed synergistic enhancement.

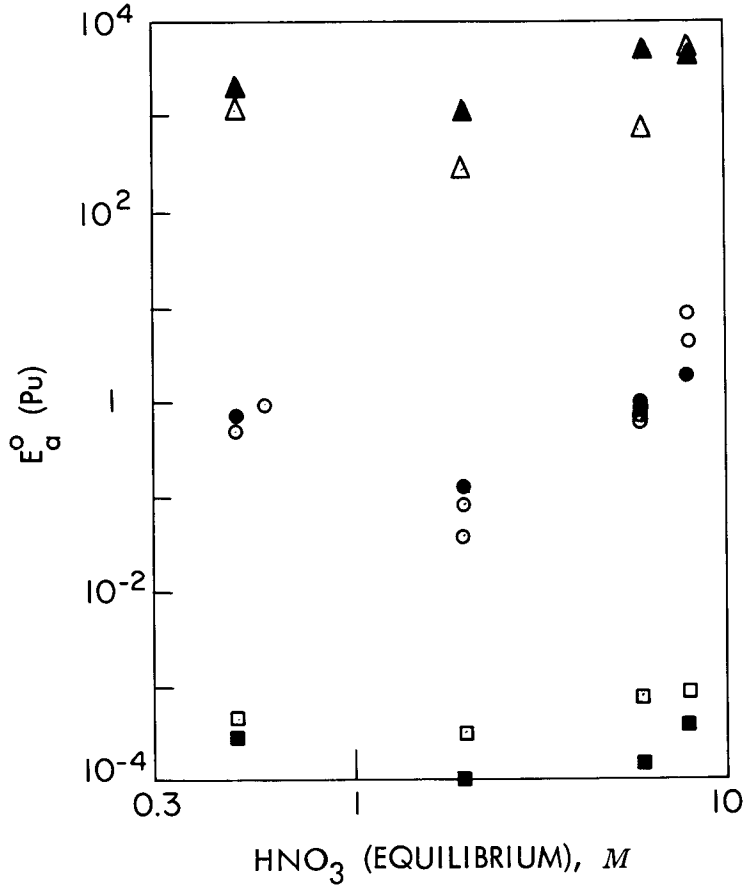
5.3 Stripping of Extracted Plutonium

Methods available for stripping extracted metals from D2EHPA include (1) reversal of the metal ion-hydrogen ion exchange by concentrated acid, (2) oxidation or reduction of the metal ion to a nonextractable valence, (3) formation of a competing nonextractable complex of the metal.

It is obvious from the extraction curves in Fig. 5.1 and 5.2 that nitric acid at up to ~10 M cannot strip plutonium from D2EHPA at 0.01 M or higher. Extrapolations of these data indicate that stripping coefficients S^a_o >10 could be reached with 10 M HNO_3 from 0.001 M D2EHPA and with 8 M HNO_3 from 0.0004 M D2EHPA, etc.

While the calculated Pu(III) extraction coefficients in Fig. 5.4 suggest that reduction should provide stripping from 0.1 M D2EHPA, the actual (mixed) extraction coefficients from reduced solutions shown in the same figure warn that reduction

*This was not developed into a process, as primary amine extraction appeared more promising for scavenging plutonium. A chemical flowsheet using D2EHPA extraction was developed for scavenging uranium (and thorium) from enriched uranium-thorium fuel decladding.[14]



o Distribution in direct extraction

Δ Distribution in subsequent scrub with 1 N HNO_3, containing 0.5 M NH_2SO_3H

□ Calculated distribution of Pu(III) in the original extraction

Original aqueous solutions reduced with:

o 0.1 M $Fe(NH_2SO_3)_2$ + 0.5 M NH_2SO_3H

● 0.1 M $Fe(NH_2SO_3)_2$ + 0.1 M N_2H_4

Fig. 5.4. Extraction from reduced Pu(III) solution by 0.1 M D2EHPA in Amsco 125-82.

Table 5.1 Plutonium Extraction from Sulfate Solutions by D2EHPA Alone and in Combinations

Initial plutonium concentration: 10-20 mg/liter
Organic diluent: Amsco 125-82
Phase ratio: 1/1
Room temperature

D2EHPA M	Modifier	E_a^o(Pu-VI)[a] 5 M H_2SO_4	E_a^o(Pu-IV)[b] 5 M H_2SO_4	3 M H_2SO_4	3 M H_2SO_4 0.5 M Na_2SO_4
0.4	None	0.4	~10	4	50
0.4	0.16 M decanol[c]	0.2	~3	-	-
0.4	0.15 M TBP	0.6	~2	3	20
0.4	0.15 M DAAP[d]	1	~3	-	-
0.4	0.1 M TOPO	5	~8	3	70
0.1	0.05 M TOPO	-	0.5	0.4	10

[a] Oxidized to Pu(VI) with AgO.
[b] Adjusted to Pu(IV) with 0.5 M $NaNO_2$.
[c] Mixed primary decyl alcohols from the oxo process.
[d] Diamyl amylphosphonate.

of the extracted plutonium will be difficult. This was confirmed by direct stripping tests (Table 5.2) with ferrous sulfamate plus excess sulfamic acid, which failed to strip much plutonium from 0.1 or 0.01 M D2EHPA. It stripped the plutonium essentially completely from 0.001 and 0.0001 M D2EHPA, indicating that a threshold for protection of the Pu(IV) by complexing with D2EHPA lies between 0.001 and 0.01 M D2EHPA.*

Addition of 0.1 M H_2SO_4 as an aqueous complexing agent to the ferrous sulfamate reductant and decrease of the nitric acid concentration to <0.1 M gave stripping coefficients approaching 10 from 0.1 M D2EHPA. Dilute (0.01 and 0.1 M) oxalic acid stripped the plutonium effectively from 0.01 M D2EHPA (not tested with 0.1 M D2EHPA). It was not determined whether the oxalic acid reduced the plutonium in these tests, or acted only as a complexing agent.

In uranium recovery,[28] the most useful stripping agent for D2EHPA has been sodium carbonate in, e.g., 1 M solution. Extracted ions are removed from the D2EHPA by carbonate

*The mole ratio of plutonium to D2EHPA in the loaded extract probably also influences this protection against reduction, at least on approaching saturation loading. However, the plutonium/D2EHPA ratio was still fairly low even in the 0.001 and 0.0001 M extracts, ~1/15.

Table 5.2 Stripping Plutonium from D2EHPA

Extracts loaded by extracting Pu(IV) from 1-6 M HNO_3 solutions, 10-20 mg Pu/liter

Diluent: Amsco 125-82

Phase ratio: 1/1

Stripping contact: 10 min shaking at room temperature

D2EHPA, M	HNO_3, M	Reductant,[a] M	Complexer,[b] M	S_o^a 1st Contact[c]	S_o^a 2nd Contact[c]
0.1	2	0.1 FS + 0.1 SA	-	0.05	0.07
0.1	1	0.1 FS + 0.1 SA	-	0.14	-
0.01	1	0.1 FS + 0.1 SA	-	0.3	-
0.001	1	0.1 FS + 0.1 SA	-	400	-
0.0001[d]	1	0.1 FS + 0.1 SA	-	800	-
0.1	0.1	0.1 FS	0.1 H_2SO_4	5	10
0.1	0.05	0.1 FS	0.1 H_2SO_4	4	7
0.01	-	-	0.01 H_2Ox	100	-
0.01	-	-	0.1 H_2Ox	2000	-

[a] FS = ferrous sulfamate; SA = sulfamic acid

[b] H_2Ox = oxalic acid.

[c] First and second contacts of the same organic solution with successive equal volumes of the aqueous solution.

[d] 2 mg Pu/liter.

complexing, precipitation, or exchange with sodium ion, and the D2EHPA is converted to its sodium salt. (Kerosene-type diluents, including Amsco 125-82, require addition of a modifier, usually a long chain alcohol, TBP, or a phosphonate, etc., to prevent separation of the sodium dialkylphosphate as a separate phase.[28,32] Sodium carbonate stripped plutonium effectively, after extraction from either sulfate or nitrate solution. Plutonium at 20 mg/liter, extracted from 3 M and 5 M H_2SO_4, was stripped from 0.4 M D2EHPA in Amsco 125-82 modified with decanol, TBP, DAAP, or TOPO (cf. Table 5.1) by 1 M Na_2CO_3 solution, A/O = 1/1, with stripping coefficients $S_o^a \approx 20$. Plutonium at ~200 mg/liter and at 1.1 g/liter, extracted from 2 M HNO_3 (cf. Appendix E), was stripped from 0.1 M D2EHPA in Amsco 125-82 modified with 2 vol % tridecanol by 1 M Na_2CO_3 with S_o^a = 80 (A/O = 1/1) and 70 (A/O = 1/2), respectively. The latter strip solution contained 2.3 g of plutonium per liter, with no evidence of precipitation. A second contact at A/O = 1/2 decreased the plutonium remaining in the extract from 35 to 1.6 mg/liter, S_o^a = 60.

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Appendix A. Extraction of Excess Nitric Acid by Amine Nitrates

Amine nitrates in hydrocarbon solution extract excess nitric acid to a considerable extent, enough to be of importance in process design calculations (especially if an aqueous phase of low acidity is to be contacted after one of high acidity) as well as in setting up conditions for laboratory tests. This extraction of excess nitric acid was first shown implicitly by the data of Winchester[9] (Amberlite LA-1 and Primene JM-T) and Wilson[6] (trilaurylamine). Bertocci[8] correlated the nitric acid extraction by tri-isononylamine in xylene with the amine nitrate and the aqueous acid concentrations, arriving at the expression

$$(HNO_3 \text{ free})_{org}/(TNA)_{org}(HNO_3)_{aq} = 0.17$$

which is equivalent to

$$E_a^o(\text{xs } HNO_3) = 0.17(\underline{M} \text{ amine nitrate})$$

Carswell and Lawrance[17] published extraction curves for excess nitric acid from ~1-7 $\underline{M}$ HNO_3 solutions by 0.1-0.4 $\underline{M}$ tri-iso-octylamine in benzene. These can be fitted to Bertocci's correlation, with values of the constant between 0.16 and 0.17. Unpublished measurements by Mason and Vaughen (MIT)[15] with trilaurylamine, ditridecylamine, and Primene JM-T in toluene show the same correlation as Bertocci's with the tertiary amine, with values of the constant between 0.16 and 0.18, but the extraction coefficients with the secondary and primary amine varied with the absolute nitric acid concentration.

With some assumptions, nitric acid distribution coefficients can be calculated from the published data of Winchester and of

Wilson. From Wilson's data, two scrub equilibrations with fairly low uranium (0.04 and 0.02 M uranium, ~4 M HNO_3) both indicate E_a^o(xs HNO_3) ≈ 0.25(M TLA nitrate). Winchester's data indicate a self-consistent extraction curve, but it is not linearly proportional to the amine nitrate concentration (the effect of aqueous nitric acid concentration could not be separated):

$$E_a^o(\text{xs } HNO_3) \approx 0.7(\underline{M} \text{ amine nitrate})^{1.4}$$

This fits closely the individual calculated extraction coefficients with both Amberlite LA-1 and Primene JM-T, but its validity, of course, depends on the assumptions used in those calculations.

Nitric acid extractions by trilaurylamine, Amine S-24, Amberlite LA-1, ditridecylamine, and Primene JM-T in xylene were measured in this laboratory (Table A-1), primarily for use in setting up metal nitrate extraction test conditions. With each, two amine concentrations and two nitric acid concentrations were tested, plus an extraction from sodium nitrate--nitric acid solution with one amine concentration. Only one measurement was made at each point, so that these must be held subject to revision; however, they are supported by good material balance and by the fairly close self-consistency. While two values each of the two variables are not sufficient to establish the form of correlation, they all show significant agreement with Bertocci's correlation,

$$E_a^o(\text{xs } HNO_3) \approx k(\underline{M} \text{ amine nitrate})$$

with k = 0.16-0.18 for TLA, 0.13-0.14 for S-24, 0.10-0.13 for LA-1, 0.06-0.08 for DTDA, and 0.07-0.11 for Primene JM-T. Thus there is close agreement among all the evaluations of extraction by tertiary amines. The MIT extractions with DTDA and Primene JM-T were of the same magnitude as those in Table A-1 at acidities near 8 M, but were considerably lower at low acidities. This discrepancy may be resolved by further tests to be made at MIT, and possibly also in this laboratory.

Appendix B. Extraction of Nitric Acid by Phosphate and Phenylphosphonate Esters

Estimates of nitric acid extraction in some of the plutonium extraction tests, Sect. 4.1, were based on unpublished extraction data of Blake and Schmitt.[33] As these data can also be useful in setting up tests and in estimating process behavior, they are quoted in full in Table B-1.

Table A-1. Nitric Acid Extraction by Amine Nitrates

Phase ratio A/O = 1/1, room temperature

Amine[a] (in xylene)		HNO_3 at Equilibrium, M						E_a^o(xs HNO_3)/M(amine nitrate)		
		~1 M HNO_3[b]		~8 M HNO_3[c]		~1 M HNO_3 -- 5 M $NaNO_3$[d]		~1 M HNO_3	~8 M HNO_3	~1 M HNO_3 -- 5 M $NaNO_3$
	M	Aq	Org	Aq	Org	Aq	Org			
TLA	0.089	0.957	0.104	7.78	0.201	0.887	0.140	0.18	0.16	0.65
	0.358	0.673	0.399	7.37	0.788			0.17	0.16	
S-24	0.100	0.948	0.113	7.78	0.204	0.875	0.135	0.14	0.13	0.40
	0.518	0.522	0.556	7.20	1.01			0.14	0.13	
LA-1	0.095	0.962	0.105	7.80	0.194	0.877	0.125	0.11	0.13	0.36
	0.561	0.467	0.595	7.09	0.974			0.13	0.10	
DTDA	0.107	0.949	0.113	7.81	0.175	0.877	0.126	0.06	0.08	0.20
	0.403	0.655	0.418	7.41	0.604			0.06	0.07	
PrJM	0.051	1.004	0.056	7.88	0.078	0.928	0.071	0.10	0.07	0.42
	0.523	0.532	0.554	7.48	0.862			0.11	0.09	

[a] Trilaurylamine, Amine S-24, Amberlite LA-1, ditridecylamine, Primene JM-T. Prescrubbed with dilute nitric acid to remove appreciably soluble fractions.

[b] 1.05 M HNO_3 initial.

[c] 7.96 M HNO_3 initial.

[d] 1.00 M HNO_3, 5.0 M $NaNO_3$ initial.

Table B-1. Nitric Acid Extraction by Phosphate and Phosphonate Esters

Phase ratio A/O = 1/1, room temperature

Reagent (0.1 M)	Diluent	HNO_3 at Equilibrium, M: Initial Aq 0.201 M HNO_3 Aq	Org	Initial Aq 2.01 M HNO_3 Aq	Org	Initial Aq 5.64 M HNO_3 Aq	Org	Initial Aq 10.05 M HNO_3 Aq	Org
TBP	Amsco[a]	0.193	0.0084	1.67	0.34	4.82	0.82	9.01	1.04
TBP	Xylene	0.191	0.010	1.66	0.35	4.77	0.87	8.97	1.08
$(2EH)_3PO_4$[b]	Amsco[a]	0.192	0.0090	1.67	0.34	4.78	0.86	8.99	1.06
DBBP[c]	Amsco[a]	0.179	0.022	1.57	0.44	4.74	0.90	8.97	1.08
DnBPP[d]	Xylene	0.191	0.010	1.64	0.37	4.76	0.88	8.95	1.09
DsBPP[e]	Xylene	0.189	0.012	1.61	0.40	4.74	0.90	8.95	1.10

[a]Amsco 125-82.

[b]Tris(2-ethylhexyl)phosphate.

[c]Di-n-butyl n-butylphosphonate.

[d]Di-n-butyl phenylphosphonate.

[e]Di-sec-butyl phenylphosphonate.

Appendix C. Uranium and Fission Product Extraction by Irradiated Amines

Samples of five amines irradiated to 200-400 watt-hr/liter at Stanford Research Institute [34] and of the corresponding unirradiated controls were compared with respect to titratable base content, and to extraction of uranium and fission products from nitric acid solution. Changes were small in titratable base content (4-8% decrease), and in uranium distribution. There was little change in fission product extraction by two tertiary amines with straight alkyls, but up to 10-fold increase in extraction by a tertiary, a secondary, and a primary amine, each with branched alkyls. The amine samples were:

Primene JM-T (commercial primary amine). Stock purchased by SRI from vendor.

N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine, NBHA (research secondary amine). Stock supplied from this laboratory (Batch 228B): neutral equivalent = 347 (2.88 eq/kg); 4% primary, 95% secondary, < 1% tertiary amine.

Tri-iso-octylamine, TIOA (commercial tertiary amine). Stock purchased by SRI from vendor.

Alamine 336 (commercial tertiary amine). Stock purchased by SRI from vendor.

Trilaurylamine, TLA (commercial tertiary amine). Stock supplied from this laboratory (Batch 86D, after fractionation by removal of solids precipitated at ~10°C): neutral equivalent = 570 (1.75 eq/kg); 4% primary, 5% secondary, 91% tertiary amine.

Weighed samples of the undiluted amines were assayed by nonaqueous titration.[35] The results (Table C-2) show small decreases in the titratable base content, between 4 and 8%, after irradiation. (The NBHA sample, 4% loss, was irradiated only to 200 watt-hr/liter. If linear with dose, the loss at 400 watt-hr/liter would be 8%, which is still in the same range.)

A 0.10 M solution of each amine in xylene, prepared on the basis of the foregoing assays, was used to extract uranium (0.2 M) from an ~8 M HNO_3 solution spiked with irradiated uranium dissolver solution to a level of ~10^6 gross γ counts/min ml (Table C-1). The volumes used were 80 ml of extractant and 16 ml of feed. After equilibration, 10 ml of the organic phase was removed for analysis. The 70 ml of loaded extractant was scrubbed twice in the same separatory funnel with 14-ml volumes of ~8 M HNO_3 already containing 0.05 M uranium; 20 ml of the organic phase, after the second scrub stage only, was removed for analysis. The 50 ml of scrubbed extract was

Table C-1. Extraction Test Conditions

Extractant/Feed/Scrub/Strip = 5/1/1/1

Extractant: 0.10 M amine in xylene

80 ml in extraction, 70 ml in scrubbing, 50 ml in stripping

Feed: ~8 M HNO_3

0.214 M U(VI)

7.74×10^5 c/min ml	gross γ
1.21×10^6	gross β
5.26×10^5	Zr-Nb γ
7.68×10^5	TRE β
6.78×10^4	Ru γ

16 ml

Scrub: 7.6 M HNO_3

0.052 M U(VI)

14 ml each in two stages

Strip: 0.01 M HNO_3

10 ml each in two stages

Mixing: 10 min by interface stirrer in cylindrical separatory funnel, room temperature

stripped twice with 10-ml volumes of 0.01 M HNO_3. All the final organic solution and all the aqueous solutions were submitted for analysis.

Uranium extractions (Table C-2) were nearly the same with the irradiated amines as with the corresponding controls. The very low extraction coefficients with the primary and secondary amines increased slightly after irradiation. The extraction coefficients with the tertiary amines decreased slightly. The extraction coefficients with the tertiary amines are considerably depressed by high uranium loading; hence, the mole ratio of amine to uranium is a more significant measure of extraction performance. These ratios also showed only a slight decrease in uranium extraction after irradiation.

Fission product extraction (Table C-3) increased after irradiation of Primene JM-T, NBHA, and TIOA. They were for the most part little changed by irradiation of Alamine 336 and TLA. It may also be noted that fission product extractions by the irradiated TIOA and Primene JMT were about the same,

Table C-2. Effect of Irradiation on Amine Assay and Uranium Extraction

Test conditions: Table 1

Extractant	Base Assay, eq/kg	Losses, %			U Extraction by 0.1 M Amine			
		Weight Loss[a]	Decreased Assay	Total Loss of Base	E_a^o(U) Extrn	E_a^o(U) 2nd Scrub	Mole Ratio Amine/U Extrn	Mole Ratio Amine/U 2nd Scrub
Primene JM-T								
Control	3.27				0.012	0.013	40	150
Irradiated[b]	3.02	0.45	7.5	8.0	0.014	0.014	35	130
NBHA								
Control	2.82				0.017	0.019	30	100
Irradiated[c]	2.71	-	4.0	-	0.020	0.025	25	75
TIOA								
Control	2.75				0.18	0.21	5.0	7.5
Irradiated[b]	2.62	0.22	4.6	4.8	0.17	0.20	5.0	7.9
Alamine 336								
Control	2.72				0.19	0.22	4.8	7.2
Irradiated[b]	2.60	0.12	4.1	4.2	0.18	0.21	5.0	7.3
TLA								
Control	1.76				0.17	0.20	5.0	7.7
Irradiated[b]	1.66	0.14	5.6	5.7	0.16	0.18	5.2	8.6

[a]Estimated from gas produced.

[b]Irradiated to 400 watt-hr/liter.

[c]Irradiated to 200 watt-hr/liter.

Table C-3. Comparisons of Uranium and Fission Product Extraction

Test conditions: Table C-1

Extractant	Distribution Coefficients, O/A, with 0.1 M Amines					
	Extraction		2nd Scrub		2nd Strip	
	Control	Irrad.[a]	Control	Irrad.[a]	Control	Irrad.[a]
Primene JM-T						
Uranium	0.012	0.014	0.013	0.014		
Gross γ	0.0012	0.0012	<0.05	0.2		
Gross β	0.0016	0.0055				
Zr-Nb γ	0.0010	0.0037	<0.05	0.07		
Ru γ	0.0052	0.011				
TRE β	0.0020	0.0065				
NBHA						
Uranium	0.017	0.020	0.019	0.025	0.2	0.4
Gross γ	0.00032	0.0024	0.07	0.15	1	2
Gross β	0.00031	0.0027	0.05	0.09		
Zr-Nb γ	0.00006	0.0026		0.07	0.4	0.8
Ru γ	0.0036	0.0022				
TRE β	0.00023		0.10	0.08		
TIOA						
Uranium	0.18	0.17	0.21	0.20	0.011	0.017
Gross γ	0.00030	0.0034	0.05	0.05	0.4	0.6
Gross β	0.00063	0.0064	0.22	0.08	<0.1	0.1
Zr-Nb γ	0.00032	0.0034	0.02	0.03		
Ru γ		0.017				
TRE β		0.012	0.13	0.06		
Alamine 336						
Uranium	0.19	0.18	0.22	0.21	0.016	0.014
Gross γ	0.00045	0.00066	0.09	0.04	0.9	0.4
Gross β	0.00082	0.00009	0.14	0.05	0.3	0.02
Zr-Nb γ	<0.00024	0.00050	<0.06	0.01	0.4	0.2
Ru γ	0.0053	0.0048				
TRE β	0.00091	0.00050	0.03	0.01		
TLA						
Uranium	0.17	0.16	0.20	0.18	0.022	0.014
Gross γ	0.0047	0.00060	0.11	0.03	0.3	0.07
Gross β	0.00084	0.00072	0.23	0.07	0.09	0.06
Zr-Nb γ	0.00034	0.00012	0.05	<0.03	<0.1	<0.1
Ru γ	0.0027	0.0065				
TRE β	0.00068	0.00067	0.17	0.04		

[a]NBHA irradiated to 200 watt-hr/liter, the others to 400 watt-hr/liter.

whereas with the control samples the extractions by TIOA and NBHA were similar to those with Alamine 336 and TLA, considerably lower than with the primary amine. Fission product extractions by the irradiated NBHA (200 instead of 400 watt-hr/liter) were a little lower than by the irradiated TIOA and Primene JM-T.

The fission product distributions in the second scrub stage appeared more variable than in the extraction, reflecting the less dependable analyses at the lower activity levels. The scrubbing was much less effective than the original extraction in rejection of fission products. There was little systematic effect shown of irradiation on scrubbing, except that scrubbing of the tertiary amines, especially TLA, appeared to be slightly improved after irradiation.

Little if any systematic shift appeared in the stripping coefficients (shown as extraction coefficient = 1/stripping coefficient in Table C-3). The significance of these fission product coefficients in stripping are limited even more than the coefficients in scrubbing, by the analytical uncertainty due to low activity levels.

Phase separation was good, and no systematic difference was noticed between control and irradiated amines.

The decrease in concentration of titratable base in the irradiated amines was small but definite. Degradation of tertiary to secondary and primary amines was not measured on these samples, but cannot have been extensive since there was only a slight decrease in the uranium/amine mole loading ratio obtained with the 0.1 M amines. Fission product extraction coefficients with the two straight-chain alkyl tertiary amines from 8 M HNO_3-0.2 M $UO_2(NO_3)_2$ solution, $<10^{-3}$ for ruthenium γ and generally $<10^{-4}$ for the others, showed no systematic change on irradiation. However, the coefficients with the branched-alkyl tertiary and secondary amines (initially similar to the foregoing) and with the primary amine (initially 1 to 5×10^{-3}) were higher (10^{-3} to 10^{-2}) after irradiation. This decrease of selectivity thus does not appear to be a function of amine class. It might result from formation of organic molecules with appreciable extraction power by radiolysis of the branched but not the straight-chain alkyls. The ease or difficulty of recovering the higher extraction selectivity, e.g. by washing the extractant, was not examined. The impaired selectivity did not carry through into the scrubs, which were considerably less efficient than the extractions in rejecting fission products, but which appeared slightly better rather than worse after irradiation of the tertiary amines.

Appendix D. Fission Product Extraction by D2EHPA

In connection with studies by Gresky et al.[36] of the selectivity of several extractants, including D2EHPA, the extraction of plutonium, uranium, and fission products from ~ 2 M $UO_2(NO_3)_2$--1 M HNO_3 solution was measured as a function of D2EHPA concentration. The extraction coefficient for plutonium (Table D-1) was much higher than that for uranium, and higher than those for cerium and zirconium-niobium at 0.1 M D2EHPA but lower at < 0.001 M D2EHPA. It should be noted that each organic phase was highly loaded with uranium, so that the free D2EHPA concentration in each test was much lower than the total concentration shown, and not necessarily proportional to that total concentration.

It should also be noted that the uranium loading was higher than the stoichiometric limit for cation-exchange extraction, i.e., mole ratio D2EHPA/U = 2/1, showing that these equilibrations with ~3.7 M total nitrate are in the region where TBP-like extraction of uranium by the D2EHPA is important in addition to the cation-exchange extraction.[28] As this may be true also of the extraction of the plutonium and/or fission products, the separation factors found here cannot be assumed to apply to extraction from solutions of much different composition.

Appendix E. Removal of Americium from Plutonium Stock

Measurements of the high plutonium extraction coefficients encountered with many of the extractants described in this report are affected by contamination of the plutonium with even a small amount of a less extractable α emitter. In principle, such effects can be eliminated by a sufficiently extended series of back extractions. However, that technique has limitations, and it is of real advantage to eliminate such impurities before use.

About 3% of the α activity was due to americium-241 in the plutonium-239 stock that was the source for most of the plutonium head solutions used in this investigation. This was effectively eliminated by extracting the plutonium with 0.1 M D2EHPA from 2 M HNO_3, E_a^o(Pu-IV) $\approx 10^4$ and E_a^o(Am-III) $< 10^{-2}$. The extracted plutonium was scrubbed twice with 2 M HNO_3, and stripped twice with 1 M Na_2CO_3. The diluent was 98% Amsco 125-82--2% tridecanol. The phase ratios were feed/extractant/scrub/strip $\approx$ 1/2/1/1. Plutonium concentrations were 0.2 and 2.2 g/liter (Table E-1) in the feeds for two successive separations. In the second of these, it was 2.3 g/liter in the first strip solution (before combination with the second), with no evidence of precipitation. The combined strip solution was acidified to give a stock solution containing ~ 1 g Pu/liter, 2 M HNO_3, and 1 M $NaNO_3$. Americium-241 in this purified solution was too low for detectable effect on direct extractions,

Table D-1 Plutonium and Fission-product Extraction by D2EHPA Loaded with Uranium

Aqueous: 1.83 M U, 1.0 M HNO_3, 0.001 M Pu, spiked with mixed fission products (dissolver solution) to 1.3 x 10^7 γ counts/min ml

Organic: D2EHPA in Amsco 125-82

Phase ratio A/O = 1/1, 10 min equilibration, room temperature

D2EHPA, M	D2EHPA/U, Mole Ratio	Extraction Coefficients, o/a					Separation Factors, Pu/X			
		Pu(IV)	U(VI)	Gross γ	Ce[a]	Zr-Nb[b]	U	Gross γ	Ce	Zr-Nb
0.1	1.7	12	0.03	0.6	0.2	2	400	20	50	6
0.05	1.6	6	0.02	0.6	0.2	2	300	10	25	3
0.01	1.8	0.8	0.003	0.4	0.2	1	250	2	4	0.7
0.001	1.6	0.04	0.0003	0.2	0.1	0.4	125	0.2	0.5	0.1
0.0001	-	0.002	-	0.02	0.01	0.02	-	0.1	0.2	0.1

[a]Cerium as measured by γ emission at 0.10-0.20 Mev

[b]Zr-Nb as measured by γ emission at 0.56-0.95 Mev

Table E-1 Removal of Americium from Plutonium Stock

0.1 M D2EHPA in 98% Amsco 125-82--2% tridecanol

		α activity, counts/min ml[a]			
		A/O	Aqueous	Organic	$D_a^o(\alpha)$
Extraction	2 M HNO_3	~1/2	$\sim 5 \times 10^6$	1.7×10^8	~30
Scrub	2 M HNO_3	1/2	-	1.7×10^8	-
		1/2	2.6×10^3	1.7×10^8	4×10^4
Strip	1 M Na_2CO_3	1/2[b]	1.7×10^8	2.5×10^6	0.015
		1/2[b]	6.5×10^6	1.2×10^5	0.018

[a] 1.6×10^8 α counts/min ml before extraction. Pulse analysis indicated ~3% due to americium-241; analysis of changing α distribution coefficients in multiple equilibrations indicated 2.7% due to a nonextractable α emitter, attributed to americium.

[b] Phase ratio in terms of initial volumes. The volumes change appreciably in carbonate stripping because of water extraction accompanying conversion of D2EHPA to its salt.

with extraction coefficients up to at least 3000 (Pu(IV) sulfate extraction by primary amine), i.e., <0.03% of the α activity was due to americium.

The raffinates from the foregoing extractions provided americium stock solutions with activity of ~4 x 10^5 and ~5 x 10^6 α counts/min ml. Brief tests of americium extraction indicated E_a^o(Am) $\approx$ 1 from 2 M HNO_3 with 0.3 M TOPO, but << 1 with 0.4 M D2EHPA, 0.4 M D2EHPA + 0.1 M TOPO, 0.3 M TIOA, and 0.3 M TLA. From 3 M H_2SO_4, E_a^o(Am) $\approx$ 0.04 with 0.4 M Primene JM-T.

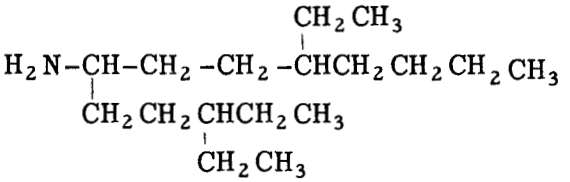
Addition of thiocyanate to the 2 M HNO_3 solution did not increase the americium extraction by 0.3 M TOPO, E_a^o(Am) = 1.2 without and 1.0 with 0.1 M KCNS. With 1 M and 5 M KCNS there were heavy precipitates, presumably thiocyanate polymer or decomposition product.

Appendix F. Reagent List

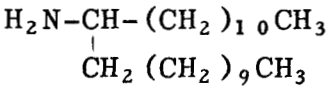
Primary Amines:

Primene JM-T (Rohm and Haas Co.) $H_2N-C(R)(R')R''$
trialkylmethylamine; R + R' + R'' = 17-23 carbon atoms.

1-(3-Ethylpentyl)-4-ethyloctylamine (Union Carbide Chem. Co.)



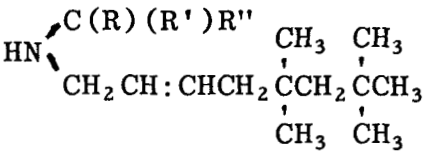
1-Undecyllaurylamine (Armour Chemical Division)



Secondary Amines:

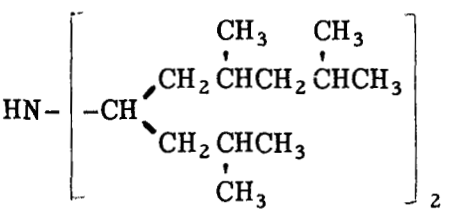
"DTDA," Ditridecylamine (Union Carbide Chem. Co.)
$HN-[-CH_2CH_2CH_2-C_{10}H_{21}]_2$
"tridecyl" = mixture of 13-carbon alkyls from tetrapropylene.

"LA-1," Amberlite LA-1, previously Amine 9D-178 (Rohm and Haas Co.)

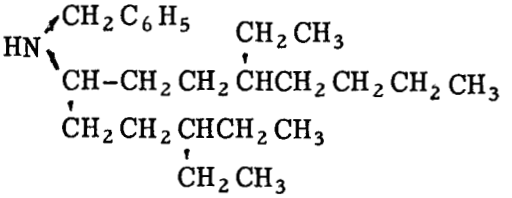


N-dodecenyl(trialkylmethyl)amine; R + R' + R'' = 11-14 carbon atoms.

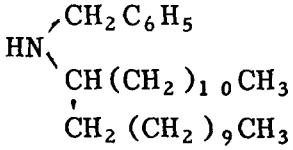
"S-24," Amine S-24 (Union Carbide Chem. Co.)
bis(1-isobutyl-3,5-dimethylhexyl)amine.



"NBHA," N-benzylheptadecylamine (Union Carbide Chem. Co.)
N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine.

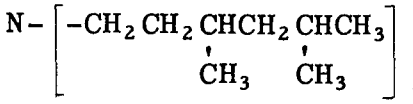


N-Benzyl-1-undecyllaurylamine (Armour Chemical Division)



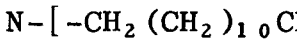
Tertiary Amines:

"TIOA," Tri-iso-octylamine (Union Carbide Chem. Co.)



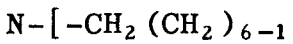
"iso-octyl" = mixture of dimethylhexyls and methylheptyls, etc., principally 3,5-, 4,5-, and 3,4-dimethylhexyl.

"TLA," Trilaurylamine (Archer-Daniels-Midland Co.)



(technical grade)

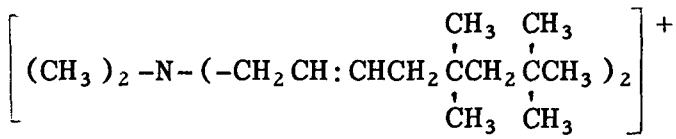
Alamine 336 (General Mills, Inc.)



straight chain alkyls, principally octyl and decyl.

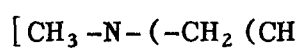
Quaternary Ammoniums:

"B-104," Experimental Quaternary B-104 (Rohm and Haas Co.)



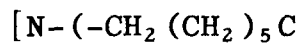
Dimethyl-didodecenylammonium.

Aliquat 336 (General Mills, Inc.)



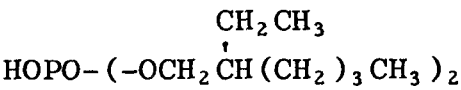
Trialkylmethyl ammonium, straight chain alkyls, principally octyl and decyl.

Tetra-n-heptylammonium (Eastman Organic Chemicals, No. 7630)



Dialkylphosphoric Acid:

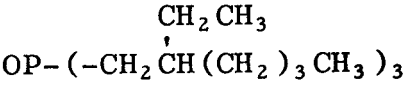
"D2EHPA," (Union Carbide Chem. Co.)
di(2-ethylhexyl)phosphoric acid



Phosphine Oxides:

"TOPO" (Eastman Organic Chemicals)
tri-n-octylphosphine oxide

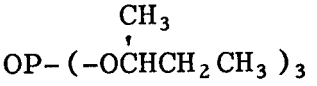
"T(2EH)PO" (ORNL)
tris(2-ethylhexyl)phosphine oxide



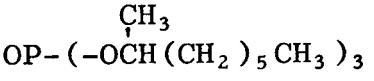
Phosphorus Esters:

TBP (Commercial Solvents Corp.)
tri-n-butylphosphate

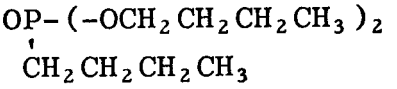
"TSBP" (ORNL)
tri-sec-butylphosphate



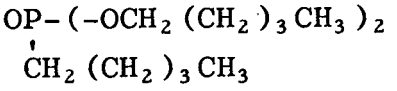
"TCP" (ORNL)
tri-2-octylphosphate



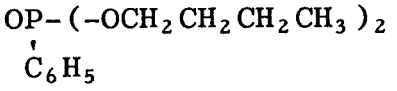
"DBBP" (Shea Chemical Corp.)
di-n-butyl n-butylphosphonate



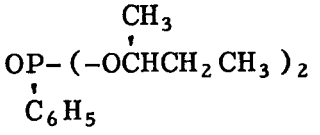
"DAAP" (Shea Chemical Corp.)
diamyl amylphosphonate



"DnBPP" (Virginia-Carolina Chemical Corp.)
di-n-butyl phenylphosphonate



"DSBPP" (ORNL)
di-sec-butyl phenylphosphonate



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