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# EXTRACTION OF NEPTUNIUM FROM ACIDIC SOLUTIONS BY ORGANIC NITROGEN AND PHOSPHORUS COMPOUNDS

Boyd Weaver

**OAK RIDGE NATIONAL LABORATORY**
operated by
UNION CARBIDE CORPORATION
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## ABSTRACT

Neptunium distribution coefficients from acid nitrate, chloride, and sulfate solutions by several organic nitrogen and phosphorus compounds were measured as functions of several extraction variables, including neptunium valence, acid and salt concentration, and reagent concentration. Extractability by all the reagents varied in the order $Np(IV) > Np(VI) >> Np(V)$. Except for primary amines, all reagents extracted $Np(IV)$ much more strongly from nitrate than sulfate solutions. Among organonitrogen compounds the order of extractability of $Np(IV)$ was: quaternary > tertiary > primary and secondary from nitrate solutions but primary >> secondary > tertiary from sulfate solutions. Neptunium(IV) nitrate extractions with the different extractants passed through maxima at widely different acid concentrations. In most cases, extraction increased when nitric acid was replaced by nitrate salt. Extraction was usually approximately proportional to the square of the reagent concentration.

CONTENTS

## 1.0 INTRODUCTION

This report describes an experimental survey of the liquid-liquid distribution behavior of neptunium between organic solutions of various organic nitrogen and phosphorus compounds and aqueous mineral acid and salt solutions. The survey is much more nearly complete with respect to Np(IV) than to other valences and to nitric acid solutions than to other acids. Nitrogen compounds used included long-chain primary, secondary, and tertiary amines and quaternary ammonium. Phosphorus compounds tested were dialkylphosphoric acids and neutral phosphates, phosphonates, and phosphine oxides.

The survey was intended to broaden knowledge of the extraction behavior of neptunium, to obtain comparisons between neptunium and plutonium, and to provide a basis for applications to processing of nuclear materials containing neptunium. Some study was made of other associated elements encountered in nuclear processing. The investigation was limited to small-scale single-stage extractions, almost exclusively at tracer levels. Many of the results of this study and a parallel study of plutonium have been published by Weaver and Horner (1). The study of plutonium has been reported in more detail by Horner and Coleman (2).

Acknowledgment is made of the very helpful advice of C. F. Coleman and K. B. Brown and the technical assistance of Janet Bartlett.

## 2.0 EXPERIMENTAL TECHNIQUES AND ANALYSIS

The extraction of neptunium was studied by the use of the 50-hr gamma activity of $Np^{238}$, prepared by neutron irradiation of $Np^{237}$ oxide and kept in nitric acid solution. For the few experiments at higher concentrations $Np^{237}$ nitrate solutions were used and were analyzed by alpha-counting of aliquots. Neptunium(IV) was prepared by reduction with ferrous sulfamate at concentrations up to 0.04 $\underline{M}$. Reduction appeared complete within an hour in nitric acid at least 4 $\underline{N}$ or in concentrated nitrate salt solutions of lower acidity. Neptunium(IV) for use in very dilute acid was usually reduced under more favorable conditions and then adjusted for use by dilution or extraction and backwashing. Neptunium(V) was prepared by boiling a 1 $\underline{N}$ $HNO_3$ solution and Np(VI) by addition of sodium bromate.

Amines were used as solutions in the aliphatic diluent Amsco 125-82, or more often in xylene, sometimes modified by addition of branched primary tridecyl alcohol(TDA) to avoid formation of a third phase. No significant differences in extraction power specifically attributable to diluent composition were observed. The amines were converted to salts by washing with the appropriate acids.

Organophosphorus compounds were used in Amsco 125-82 with little or no modification. Some of them were treated with sodium carbonate solutions or a suspension of chromatographic grade aluminum oxide in a sodium carbonate solution to remove more highly extracting impurities.

Prepared aqueous solutions were contacted with equal volumes of the organic phases in separatory funnels. Many of the data were obtained by recontact of the organic phase with a prepared aqueous phase, thus aiding in establishing equilibrium under the desired conditions. While all evidence indicated that neptunium extraction was instantaneous, a 10-min period was standard for mechanical shaking of separatory funnels.

Neptunium distribution coefficients were obtained by measuring the relative $Np^{238}$ gamma activities in 2-ml samples of the two phases by means of a well-type scintillation counter or by measuring the $Np^{237}$ alpha activities of small aliquots by standard techniques.

### 3.0 EXPERIMENTAL RESULTS

## 3.1 Extraction by Organonitrogen Compounds

3.1.1 Extraction by Primary Amines. Primene JM-T was used as an example of this class. Extraction of Np(IV) was low from nitrate solutions but increased somewhat with acidity (Table 1). Addition of sodium nitrate to dilute acid increased extraction, but it was still low.

Table 1. Extraction of Np(IV) by a Primary Amine from
Nitrate Solutions.

0.1 $\underline{M}$ Primene JM-T[a] in Amsco 125-82

| Concentration ($\underline{N}$) | | $E_a^o$, Np(IV) |
|---|---|---|
| $HNO_3$ | $NaNO_3$ | |
| 1 | | 0.004 |
| 4 | | 0.15 |
| 8 | | 0.8 |
| 1 | 5 | 0.03 |

[a]Primene JM-T, mixture of primary amines where nitrogen joins
a tertiary carbon atom attached to three 15-21 carbon atom
chains.

Extraction of Np(IV) by very dilute primary amine in Amsco 125-82 from sulfuric acid solutions was very high (Table 2) in $H_2SO_4$ concentrations up to 5 $\underline{N}$ and was not greatly affected by neutral sulfate. In this case the behavior of Np(IV) was distinctly different from that of Pu(IV) (2). The extraction of Pu(IV) was much lower than that of Np(IV) from sulfuric acid and was decreased by increased acidity and increased by neutral sulfate. When a primary amine was present as an impurity in a tertiary amine, the high extractive power of the primary amine interfered with sulfate stripping of Np(IV), which had been extracted by the tertiary amine from nitrate solution.

Table 2.  Extraction of Np(IV) and Pu(IV) by a Primary
Amine from Sulfate Solutions

| Primene (M) | Concentration (N) | | $E_a^o$ | |
|---|---|---|---|---|
| | $H_2SO_4$ | $(NH_4)_2SO_4$ | Np(IV) | Pu(IV)[b] |
| 0.001[a] | 1 | | >1000 | |
| | 2 | | >1000 | |
| | 5 | | ~1000 | |
| | 10 | | ~20 | |
| | 1 | 4 | 600 | |
| 0.01[b] | 1 | | | 35 |
| | 5 | | | 8 |
| | 1 | 4 | | 200 |

[a]Diluent was Amsco 125-82.

[b]Data of Horner and Coleman (2); diluent was xylene.

Extraction by a primary amine from dilute sulfuric acid was used for recovery of neptunium from laboratory residues.  The only difficulty encountered appeared to be from interference by iron.  In subsequent tests the presence of 0.05 M Fe(III) in 1 N $H_2SO_4$ decreased distribution coefficients by a factor of 10.  There was little more effect from 0.5 M Fe(III). The apparent oxidizing effect of Fe(III) has not been explained.

3.1.2  Extraction by Secondary Amines.  Neptunium(III) was only moderately extracted from nitric acid by the two secondary amines tested: 0.3 M ditridecyl amine gave distribution coefficients of 0.5 and 2.2 from 2 N and 8 N $HNO_3$, respectively, while 0.3 M bis(1-isobutyl-3,5-dimethylhexyl) amine gave a coefficient of 1.4 from 8 N $HNO_3$.

Extraction of Np(V) from nitrate solutions by secondary amines was very low, with coefficients of 0.003 and 0.03 by 0.3 M ditridecylamine from 2 N and 8 N $HNO_3$, respectively.

3.1.3  Extraction by Tertiary Amines.  The tertiary amines studied included tri-n-octyl, tri-iso-octyl, trilauryl, and General Mills Alamine 336, a mixture of octyl and decyl straight-chain amines.  Their chief observed differences were in physical properties and compatability with diluents and aqueous solutions.  Most of the work was done with tri-iso-octylamine (TIOA) in xylene or Amsco 125-82 with 5% tridecyl alcohol as modifier.  These organic solutions separated readily from most aqueous solutions.

3.1.3.1  Extraction from Nitric Acid.  Maximum extraction of Np(IV) by TIOA from nitric acid was at ~2 N $HNO_3$.  Extraction was approximately proportional to the cube of the acidity below 1 N $HNO_3$, and the inverse acid dependency increased above 2 N $HNO_3$ (Fig. 1).  In the more acid range
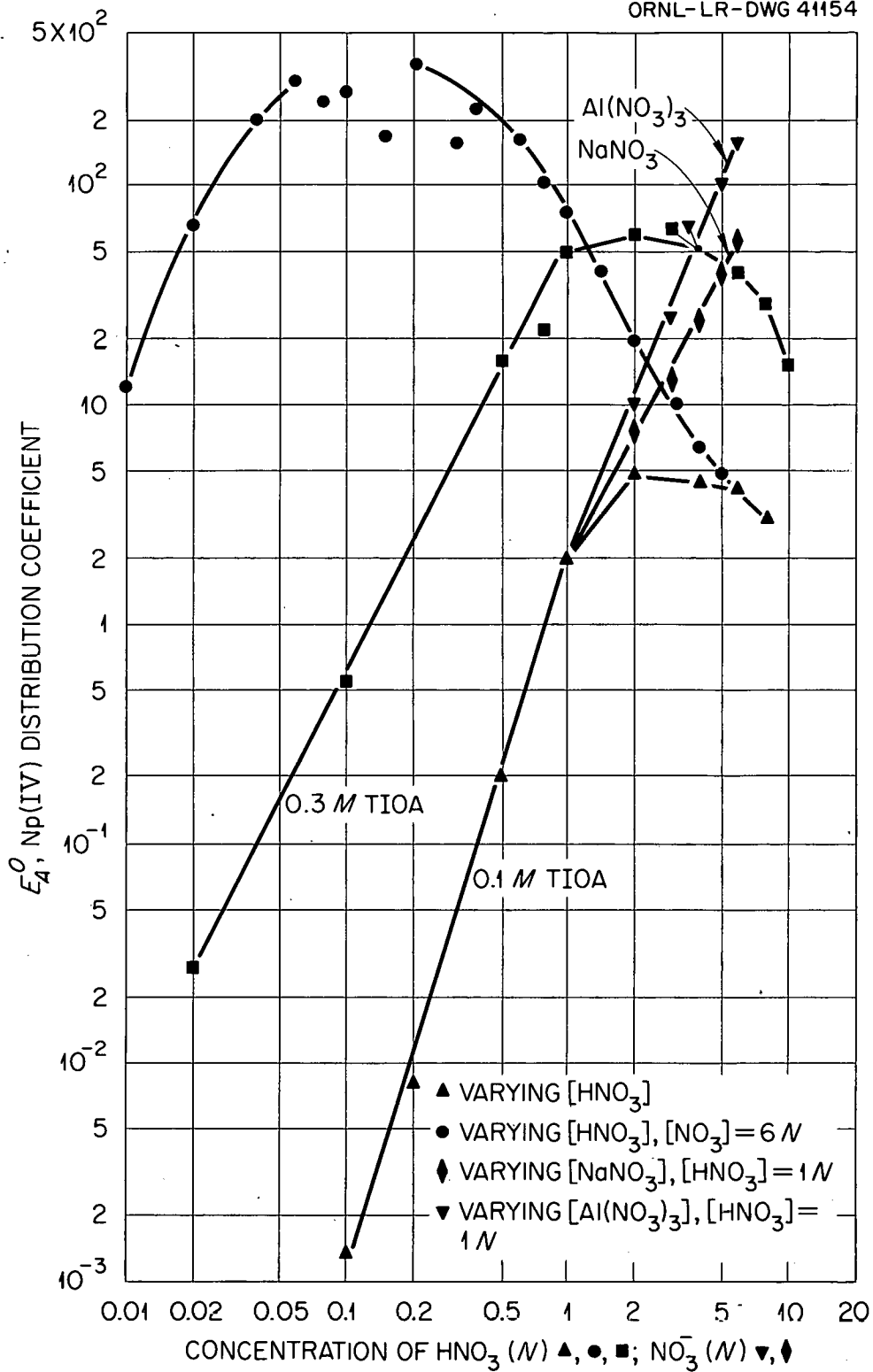
Fig. 1. Neptunium (IV) extraction from nitrate solutions by tri-iso-octyl amine.

extraction was approximately proportional to the square of the reagent concentration.

3.1.3.2 <u>Extraction from Nitrate Salts</u>. Sodium nitrate effectively increased extraction from dilute nitric acid, and aluminum nitrate was considerably more effective. Decreasing the acidity of concentrated nitrate solutions increased extraction even at acidities $< 1$ $\underline{N}$, giving coefficients several orders of magnitude higher than those from nonsalted solutions of the same acidity. Apparently the salt hinders hydrolysis of Np(IV) over a considerable range of acidity. At acidities $< 0.1$ $\underline{N}$ extraction decreased with acidity. There were some irregularities at low acidities, probably caused by variation in the degree of hydrolysis of Np(IV).

3.1.3.3 <u>Loading Experiments</u>. Attempts were made to determine the ratio of amine to neptunium when a tertiary amine was loaded with neptunium. Organic phases were 0.4 ml 0.1 $\underline{M}$ amine nitrates in xylene. Aqueous phases were 1.0 ml 0.025 $\underline{M}$ $Np^{237}$ in 1 $\underline{N}$ $\overline{HNO_3}$-5 $\underline{N}$ $Al(NO_3)_3$-0.04 $\underline{M}$ $Fe(NH_2SO_3)_2$. The aqueous contained enough neptunium to load at least 1 vol of organic, assuming a ratio of 2 moles of amine per mole of neptunium. In the case of TIOA, analysis showed less than 0.001 $\underline{M}$ neptunium in the organic phase. A very small volume of third phase was observed in one experiment and was probably present in others. With Alamine 336 there were various degrees of extraction in different experiments. In at least one experiment there was a definite third phase, which disappeared reversibly on heating to $70^\circ C$. Trilaurylamine (TLA), 0.3 $\underline{M}$ in xylene, gave no third phase, and the loaded organic contained 1 mole of neptunium for each 5-6 moles of amine. The use of TIOA or Alamine 336 in a process would require a diluent other than pure xylene. Alamine 336 in Amsco 125-82 plus 10% tridecanol has been used successfully in an application to the recovery and separation of neptunium, uranium, and technetium (3).

3.1.3.4 <u>Extraction from Hydrochloric Acid</u>. Extraction of Np(IV) from hydrochloric acid solutions was highly dependent on the acid concentration. Thus 0.3 $\underline{M}$ TIOA in xylene gave coefficients ranging from 0.03 for 1 $\underline{N}$ HCl to 400 for $\overline{8}$ $\underline{N}$ HCl, with most of the increase above 6 $\underline{N}$ HCl.

3.1.3.5 <u>Comparative Extraction of Neptunium and Thorium</u>. A comparative extraction of thorium from 8 $\underline{N}$ HCl gave a coefficient less than 0.01, indicating a method for a very high degree of separation between these elements. They could be coextracted from nitrate solution and separated by stripping out the thorium with 8 $\underline{N}$ HCl.

From nitrate solutions, Np(IV) was extracted preferentially to thorium by factors of 10-20. Thorium extraction is high enough from concentrated nitrate salt solutions to give good recovery by reasonably concentrated amine solutions but different enough from neptunium extraction to permit separation of these elements by a multistage countercurrent amine-nitric acid system.

3.1.3.6 <u>Extraction of Higher Valences.</u>  Extractions of Np(V)
by tertiary amines were very low, with coefficients of 0.01 and 0.1 by
0.3 $\underline{M}$ TIOA from 2 $\underline{N}$ and 8 $\underline{N}$ HNO$_3$, respectively.  Extractions of Np(VI),
however, were usefully high, with coefficients of 2 and 5 by 0.3 $\underline{M}$ TIOA
from 2 $\underline{N}$ and 8 $\underline{N}$ HNO$_3$.

3.1.3.7 <u>Stripping.</u>  Extraction of Np(IV) by 0.3 $\underline{M}$ tertiary
amines free of primary amines from very dilute sulfuric acid gave co-
efficients of the order of 0.01.  Thus Np(IV) extracted by pure tertiary
amine nitrate can be stripped out very readily by 0.05 $\underline{N}$ H$_2$SO$_4$.  Nep-
tunium(IV) can also be stripped readily from 0.1 $\underline{M}$ amine nitrate by
nitric acid somewhat more dilute than 1 $\underline{N}$, but not from 0.3 $\underline{M}$ amine.
Dilute oxalic acid was even more effective than sulfuric acid for strip-
ping.  The poor extraction of Np(V) indicates the possibility of stripping
by an oxidizing aqueous solution.  However, sodium nitrite and sodium
bromate in 2 $\underline{N}$ HNO$_3$ were both completely ineffective in oxidizing Np(IV)
in tertiary amines or other extractants to Np(V) or Np(VI).  Hydrogen
peroxide in dilute nitric acid did strip neptunium from tertiary amines.

3.1.4 <u>Extraction by Quaternary Ammonium Compounds.</u>  Quaternary
ammonium nitrates differ considerably in physical properties, but in
general they require modification by an alcohol in aliphatic diluents and
sometimes in aromatics, and they form emulsions with dilute nitric acid.
However they are strong extractants of Np(IV) from nitric acid solutions.
Two reagents tested which had favorable physical properties were tetra-n-
heptyl ammonium nitrate (THA) and a Rohm and Haas experimental product,
B-104, dimethyl-didodecenyl ammonium.  Their responses to aqueous conditions
were very different (Fig. 2).  Both extracted more strongly from salted
solutions than from acid; but, while the B-104 extraction increased with
acidity from 2 $\underline{N}$ to 8 $\underline{N}$ HNO$_3$, extraction by THA reached a very high peak at
~1 $\underline{N}$ HNO$_3$.  Extraction by THA was very low from dilute sulfuric acid, pro-
viding a means of stripping after extraction from nitrate.

3.2 <u>Extraction by Organophosphorus Compounds</u>

3.2.1 <u>Extraction by Dialkyl Phosphoric Acids.</u>  Di-(2-ethylhexyl)-
phosphoric acid (D2EHPA) is a very strong extractant for Np(IV) from nitrate
solutions (Fig. 3).  At acidities from 1 to 10 $\underline{N}$ HNO$_3$, extraction was
inversely proportional to the square of the acidity; below 1 $\underline{N}$ HNO$_3$ it was
directly proportional to the acidity.  Addition of neutral nitrate as alumi-
num nitrate did not affect extraction above 1 $\underline{N}$ HNO$_3$ but extended the range
of inverse proportionality to the square of the acidity at least down to
0.5 $\underline{N}$ HNO$_3$, probably by protection of the Np(IV) against hydrolysis.  Even
without salting, there were some instances of very high extraction at low
acidities.

Neptunium(V) was extracted poorly by D2EHPA, 0.1 $\underline{M}$ reagent giving a
coefficient of only 0.1 from 8 $\underline{N}$ HNO$_3$.  Neptunium(VI) was extracted under
the same conditions with a coefficient of 14.

A concentration isotherm was obtained for extraction of Np(IV) by
D2EHPA from nitric acid (Fig. 4).

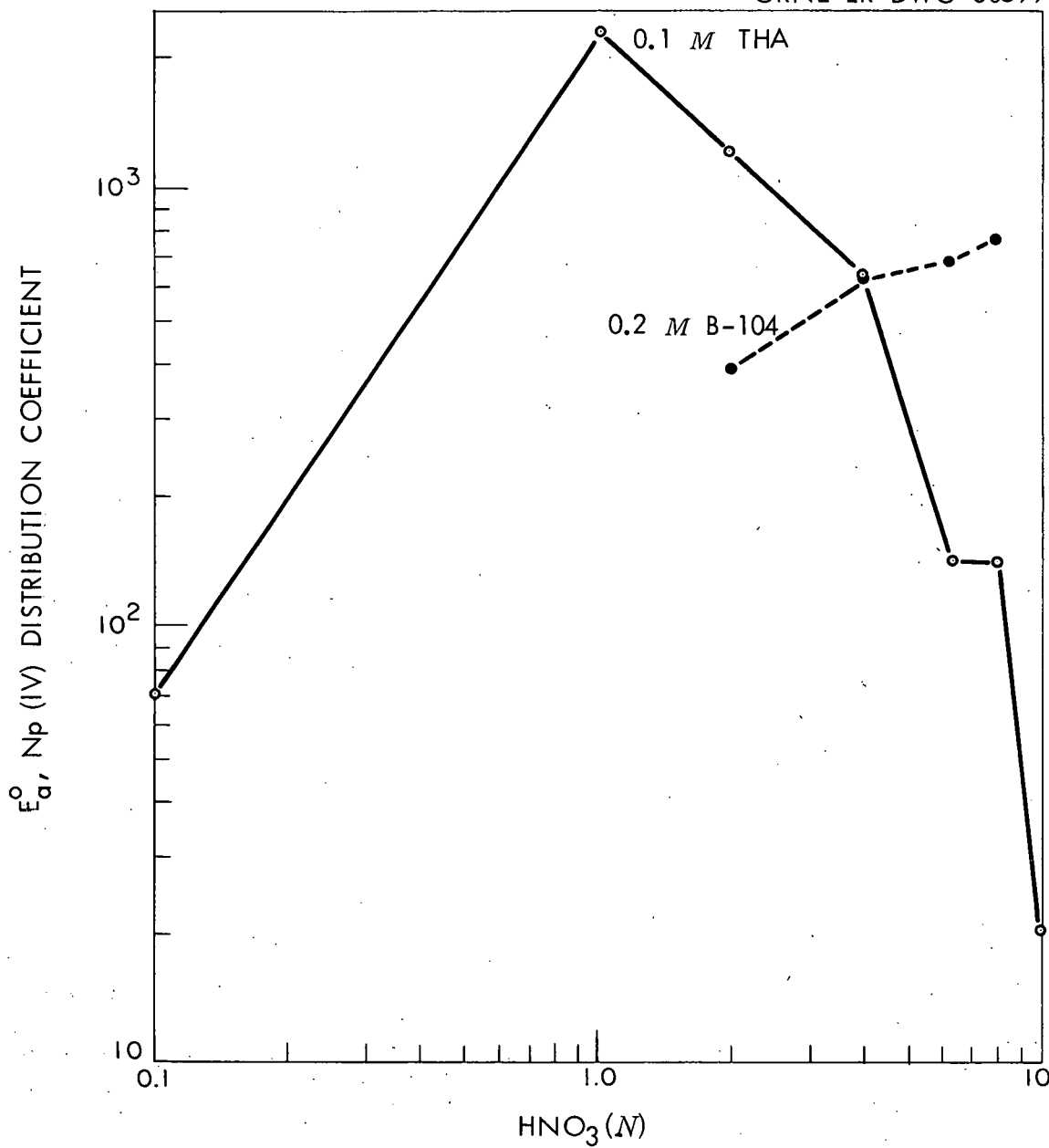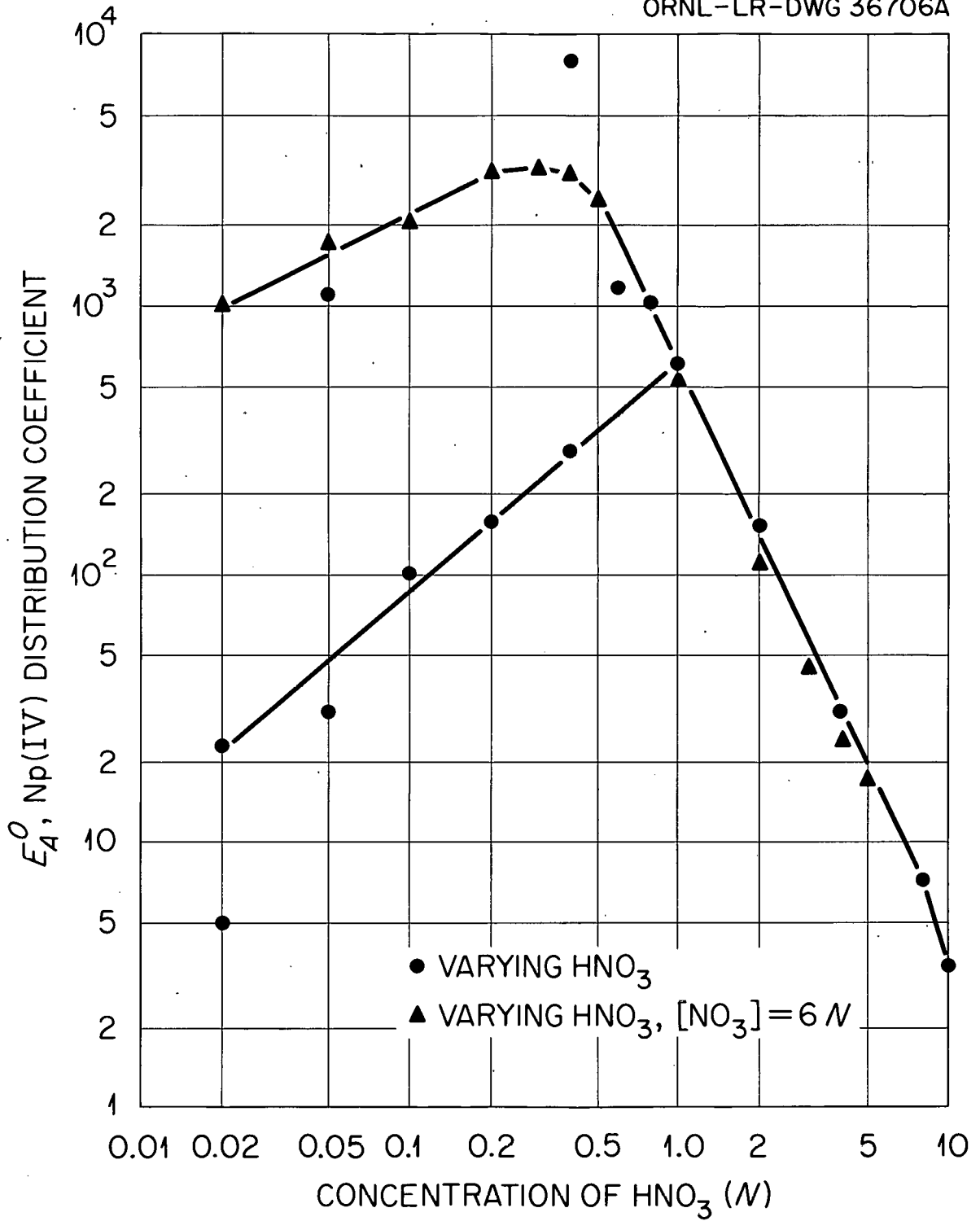Fig. 2. Neptunium (IV) extraction from nitric acid by quaternary ammoniums.

Fig. 3. Neptunium (IV) extraction from nitrate solutions by 0.01 $M$ di-(2-ethyl-hexyl) phosphoric acid.

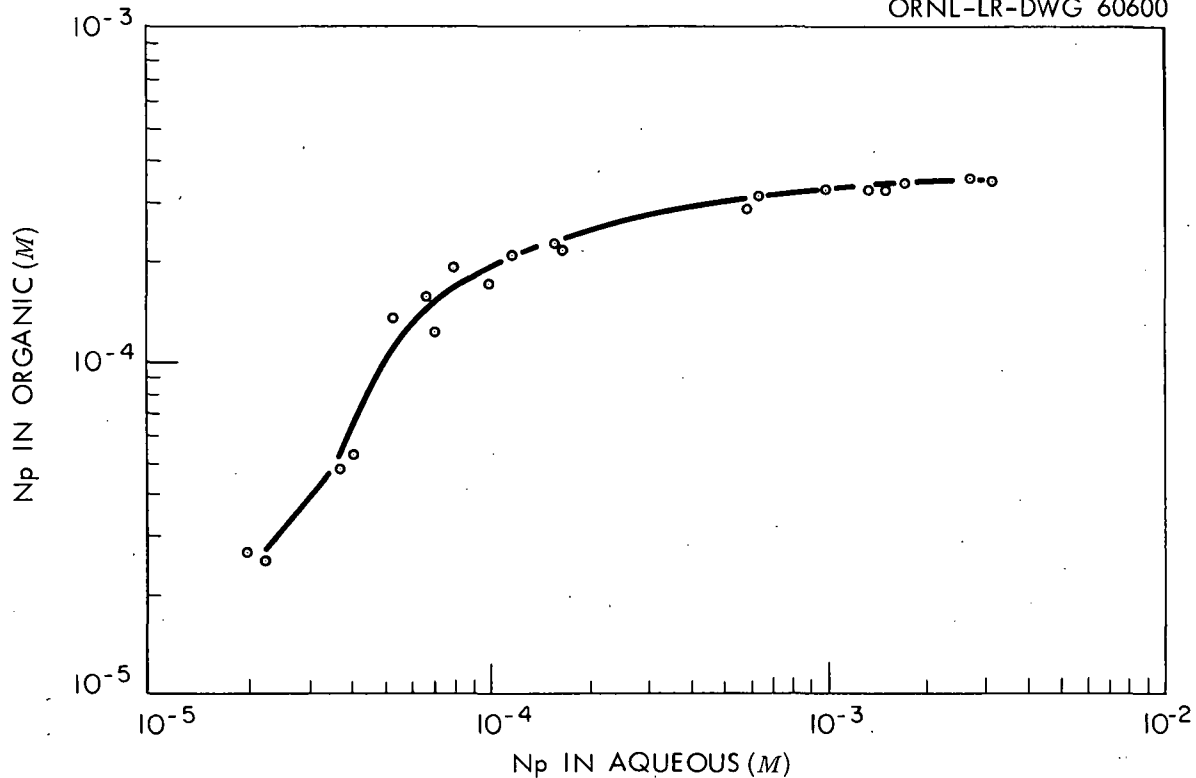Fig. 4. Concentration isotherm for Np (IV) extraction from 2 $N$ HNO$_3$ by 0.001 $M$ di(2-ethylhexyl) phosphoric acid.

The organic was 1 ml of 0.001 $\underline{M}$ D2EHPA in Amsco 125-82. It was loaded by contact with 0.05 $\underline{M}$ Np(IV) nitrate in 2 $\underline{N}$ HNO$_3$, then contacted with several fractional volumes of 2 $\underline{N}$ HNO$_3$. Samples of 10 $\mu$l volume were taken for analysis after each contact. The isotherm was derived from 3 experiments. Evidently 3 moles of reagent was required for each mole of neptunium. This contrasts with the fact that at tracer levels extraction was proportional to the square of the reagent concentration.

Extraction of Np(IV) by D2EHPA was very strong from very dilute sulfuric acid solutions but decreased with approximately an inverse 4th power dependence on the acidity as the acidity was increased from 0.5 to 5.0 $\underline{N}$ H$_2$SO$_4$ (Fig. 5). Addition of sodium sulfate decreased extraction somewhat. Extraction of Pu(IV) has been found to differ from that of Np(IV) by increasing as the acidity is increased from 4 to 10 $\underline{N}$ H$_2$SO$_4$ ($\underline{1}$,$\underline{2}$).
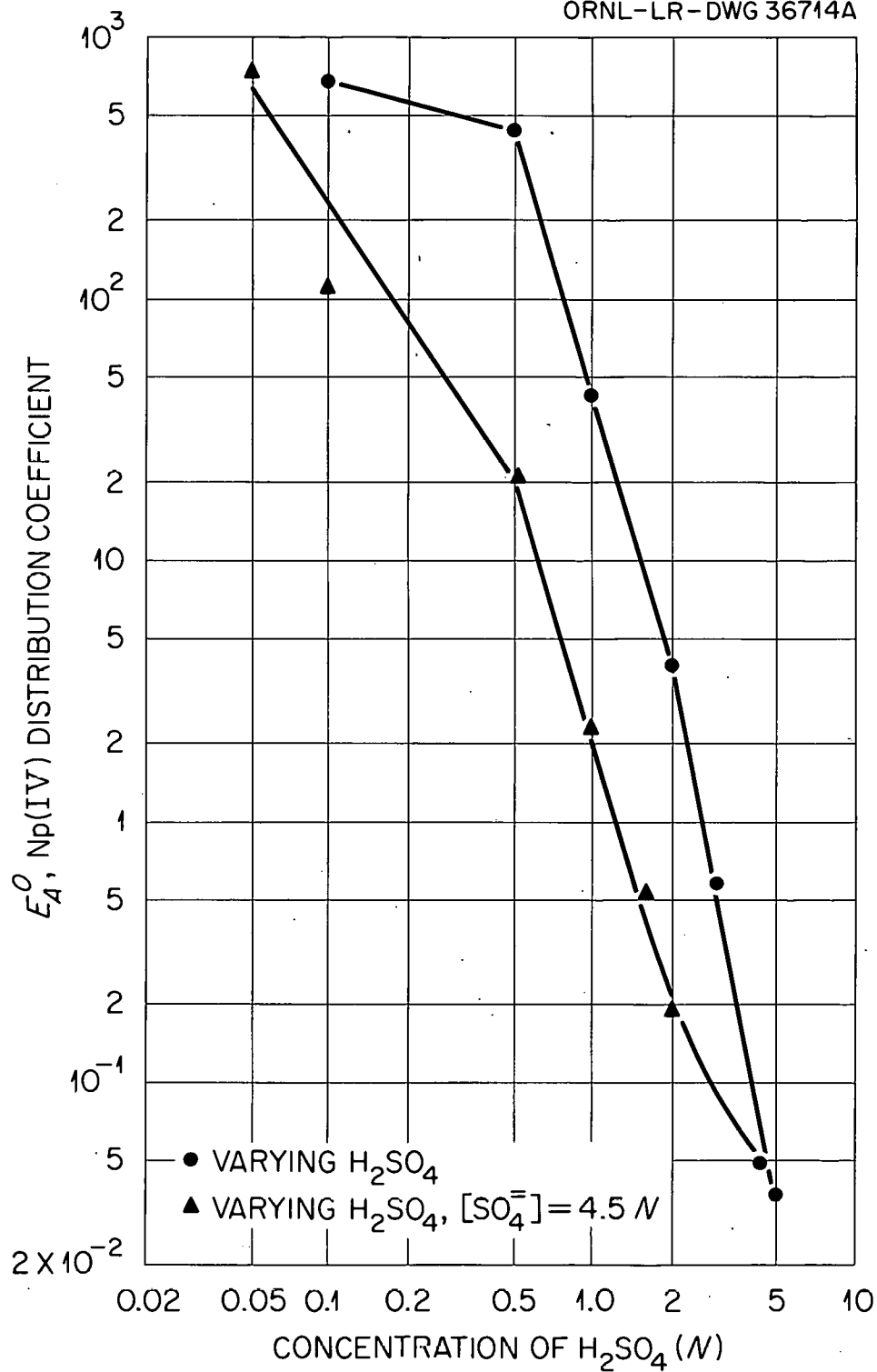
Fig. 5. Neptunium (IV) extraction from sulfate solutions by 0.01 $M$ di-(2-ethyl-hexyl) phosphoric acid.

3.2.2 <u>Extraction by Trialkyl Phosphates</u>.  Tributyl phosphate (TBP) is a much weaker extractant for Np(IV) than are dialkylphosphoric acids, but it may be used in sufficiently high concentration to give useful extractions (Fig. 6).  Extraction increased approximately proportionally to the square of the acidity below ~1 $\underline{N}$ HNO$_3$, somewhat less up to 8 $\underline{N}$ HNO$_3$, and finally decreased sharply.  With a constant high nitrate concentration from nitric acid and sodium nitrate, extraction increased as the acidity decreased. Practical stripping of Np(IV) from 1 $\underline{M}$ TBP by nitric acid somewhat more dilute than 1 $\underline{N}$ is indicated.

3.2.3 <u>Extraction by Phosphonates</u>.  Some dialkyl alkylphosphonates and dialkyl arylphosphonates were tested for extraction of Np(IV) from nitrate solutions.  Consistent data were difficult to obtain with these compounds because of an apparently very slow separation of the last traces of organic from aqueous phases.  Extraction of nitric acid by the organic also resulted in equilibrium conditions significantly different from those of the original aqueous solutions.  In some cases repetitive back extractions were made to improve the reliability of the data.

The alkylphosphonates tested were considerably stronger extractants than the arylphosphonates, which were about equal to TBP (Fig. 7).  Diamyl amylphosphonate (DAAP), 1 $\underline{M}$ in 80% Amsco 125-82-20% xylene, which had been purified by washing with a slurry of aluminum oxide in 2% Na$_2$CO$_3$ solution before equilibration with nitric acid, gave extractions proportional to the square of the acidity over at least part of the range below 1 $\underline{N}$ HNO$_3$.  Extractions at higher acidity were less dependent on acidity.  Extractions by unpurified DAAP and dibutyl butylphosphonate (DBBP) in Amsco 125-82 were considerably higher at low acidity than by purified DAAP, indicating the presence of an impurity with very strong extractive powers from very dilute acid.

Extractions by di-n-butyl phenylphosphonate (DnBPP) and di-sec-butyl phenylphosphonate (DsBPP) in Amsco 125-82 were about 100 times lower than by the alkyl compounds and were roughly proportional to the 1.5 power of the acidity up to ~6 $\underline{N}$ HNO$_3$.  Higher acidity decreased extraction by all reagents.  Treatment of DnBPP for removal of impurities had no apparent effect on the extraction.

Stripping of Np(IV) by dilute nitric acid was impractical from 1 $\underline{M}$ alkylphosphonates and marginal from 1 $\underline{M}$ arylphosphonates, as shown by the high distribution coefficients.

3.2.4 <u>Extraction by Alkyl Phosphine Oxides</u>.  Tri-n-octyl phosphine oxide (TOPO) was a very strong extractant of Np(IV) from nitrate solutions (Fig. 8) with distribution coefficients by 0.01 $\underline{M}$ TOPO from 1 $\underline{N}$ HNO$_3$ approaching 50.  Below 1 $\underline{N}$ HNO$_3$ coefficients were approximately proportional to the cube of the acidity.  Extraction was less at higher acidities but had another maximum at ~8 $\underline{N}$ HNO$_3$.  Adding sodium nitrate to 1 $\underline{N}$ HNO$_3$ steadily increased the extraction, as did replacement of the acid with sodium nitrate while maintaining the total nitrate constant at 6 $\underline{N}$.

Fig. 6. Neptunium (IV) extraction from nitrate solutions by 1 $M$ TBP.



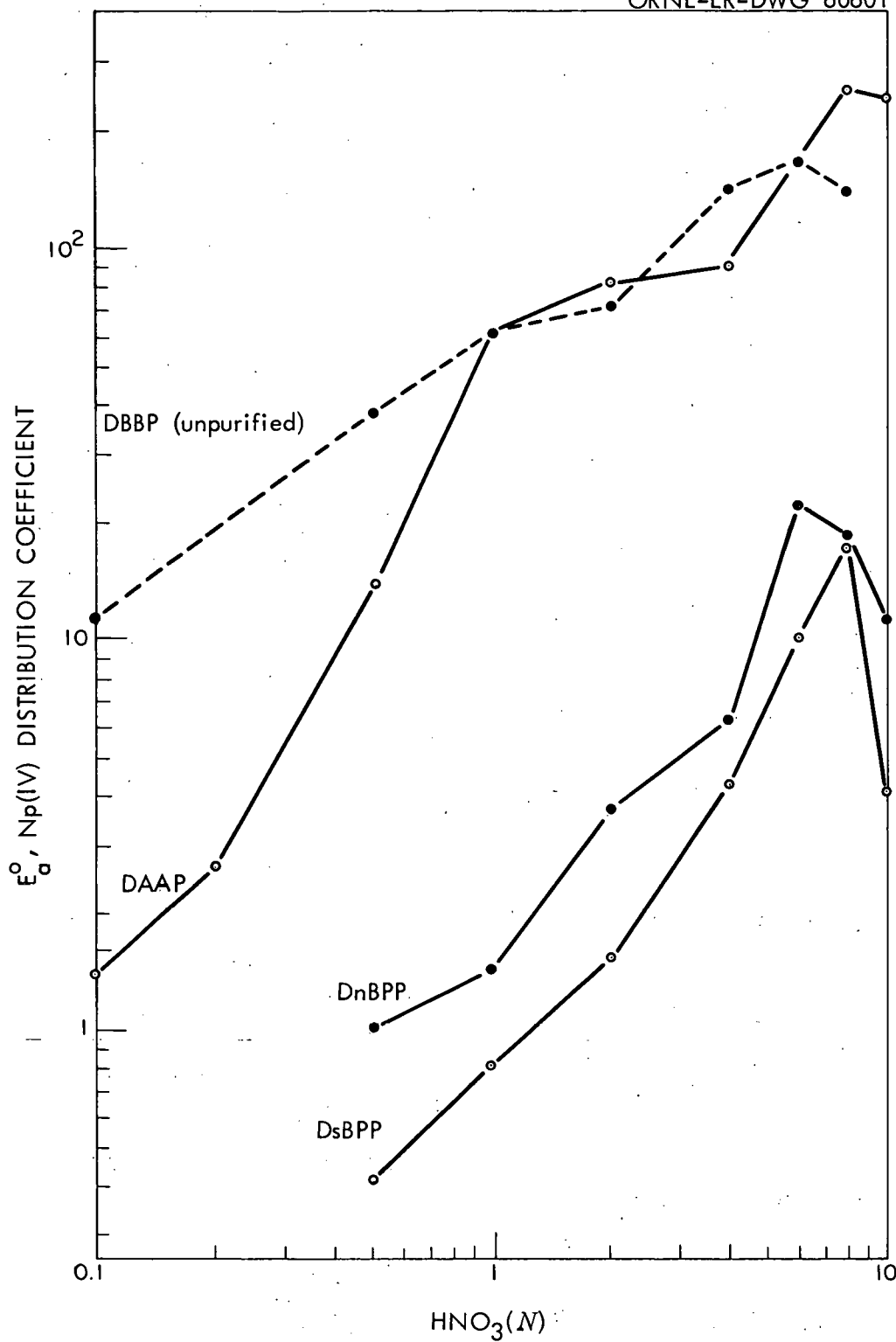
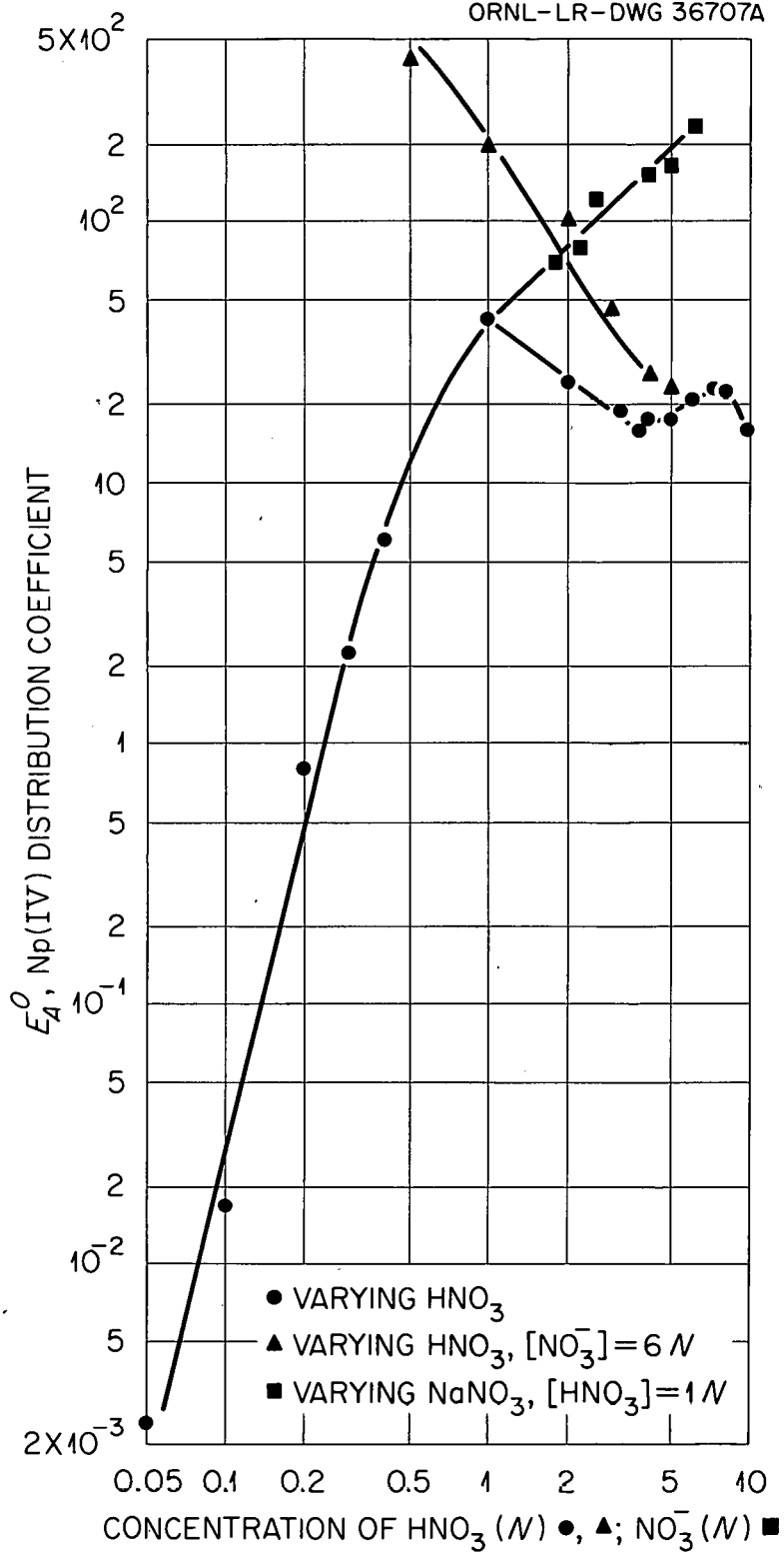

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$E_a^o$, Np(IV) DISTRIBUTION COEFFICIENT
$10^2$
10
1
0.1
1
10
$HNO_3(N)$
DBBP (unpurified)
DAAP
DnBPP
DsBPP

Fig. 7. Neptunium (IV) extraction from nitric acid by 1 *M* phosphonates.

Fig. 8.   Neptunium (IV) extraction from nitrates by tri-n-octyl phosphine oxide.

Extraction of Np(IV) by TOPO from sulfate solutions was relatively low (Table 3). Distribution coefficients increased with acidity in the range 1 $\underline{N}$ to 4.5 $\underline{N}$ $H_2SO_4$ and decreased on addition or substitution of sodium sulfate. Neptunium(IV) extracted by <0.1 $\underline{M}$ TOPO from nitrate solutions was stripped by very dilute sulfuric acid.

Table 3. Extraction of Np(IV) by Trioctyl Phosphine Oxide from Sulfate Solutions. 0.1 M TOPO in Amsco 125-82

| Concentration ($\underline{N}$) | | $E_a^o$, Np(IV) |
|---|---|---|
| $H_2SO_4$ | $Na_2SO_4$ | |
| 4.5 | | 1.1 |
| 2.0 | 2.5 | 0.06 |
| 0.10 | 4.4 | 0.004 |
| 1.0 | | 0.34 |
| 1.0 | 1.0 | 0.13 |
| 1.0 | 3.5 | 0.013 |
| 2.0 | | 0.46 |

Tris-(2-ethylhexyl)phosphine oxide is a considerably weaker extractant for Np(IV) than is TOPO. A 0.1 $\underline{M}$ solution gave about the same coefficients as 0.01 $\underline{M}$ TOPO in extractions from nitric acid. Neptunium(V) was poorly extracted by dilute solutions of TOPO, but 0.3 $\underline{M}$ TOPO gave coefficients of 1.5 and 1.0 from 2 $\underline{N}$ and 8 $\underline{N}$ $HNO_3$. Part of this may have been Np(IV).

## 3.3  Extraction of Other Elements

Experiments were performed with several of the reagents to determine the extractability of some potentially competing or desirable elements likely to occur along with neptunium (Table 4). Since zirconium, niobium, and ruthenium may occur in various forms with different extractabilities, these data from single first-stage extractions may not present a complete picture of behavior throughout a multistage process. The data for zirconium alone were obtained from experiments at macro concentrations; others are all from tracer experiments. Europium was used as an example of the fission-product lanthanides, americium an example of the transplutonium elements.

The data indicate only low extraction by amines of any of the elements tested, but rare earths were highly extracted by 0.3 $\underline{M}$ tertiary amines from 6 $\underline{N}$ $LiNO_3$ or $Al(NO_3)_3$ with less than 0.1 $\underline{N}$ $HNO_3$ in the aqueous. This extraction is very sensitive to acidity. Concentrated TOPO extracted lanthanides and americium well from dilute nitric acid with maximum extraction at about 0.4 $\underline{N}$ $HNO_3$. Rare-earth extraction by D2EHPA from dilute acids varied widely, being directly proportional to the cube of the reagent concentration and inversely proportional to the cube of the acidity. Qualitative experiments also showed that D2EHPA extracts zirconium highly under some conditions. Tracer zirconium-niobium was also extracted well by concentrated TOPO.

Table 4.  Extraction of Reactor Products by Various Reagents

| Reagent | $HNO_3$ ($\underline{N}$) | Element | $E_a^o$ |
|---|---|---|---|
| 0.3 $\underline{M}$ TIOA | 2 | Zr | < 0.01 |
| | 8 | Zr | < 0.02 |
| | 1 + 5 $\underline{N}$ $NH_4NO_3$ | Zr | < 0.01 |
| | 2 | Ru | 0.027 |
| | 8 | Ru | 0.006 |
| 0.5 $\underline{M}$ Amberlite LA-1 | 8 | Zr | < 0.01 |
| | 1 + 5 $\underline{N}$ $NH_4NO_3$ | Zr | < 0.01 |
| 0.3 $\underline{M}$ TOPO | 0.1 | Zr-Nb | 11 |
| | 2 | Zr-Nb | 11 |
| | 8 | Zr-Nb | 1.2 |
| | 2 | Ru | < 0.001 |
| | 8 | Ru | < 0.001 |
| 0.3 $\underline{M}$ N-benzyl-heptadecylamine | 8 | Eu | < 0.001 |
| 0.3 $\underline{M}$ TIOA | 2-8 | Eu | < 0.001 |
| 0.3 $\underline{M}$ TLA | 2 | Am | 0.2 |
| 0.1 $\underline{M}$ D2EHPA | 8 | Eu | < 0.01 |
| 0.4 $\underline{M}$ D2EHPA | 2 | Am | < 0.01 |
| 0.3 $\underline{M}$ TOPO | 0.02 | Eu | 0.2 |
| | 0.1 | Eu | 5 |
| | 0.5 | Eu | 10 |
| | 1 | Eu | 5 |
| | 2 | Eu | 1.5 |
| | 8 | Eu | 0.02 |
| | 0.2 | Am | 17 |
| | 2.0 | Am | ~1.0 |
| 0.1 $\underline{M}$ Primene JM-T | a | Am | 0.04 |

[a]Extracted from 3 $\underline{N}$ $H_2SO_4$.

Plutonium(IV), with the exceptions noted in the cases of extraction by primary amines and D2EHPA from sulfuric acid, was extracted about 10 times as well as Np(IV) and behaved like Np(IV) in response to various changes in conditions. However the aqueous conditions which produce Np(IV) are in general suitable only for the existence of Pu(III) rather than Pu(IV). Therefore Np(IV) and Pu(IV) are not likely to be present together. Advantage can usually be taken of the relatively poor extractability of Pu(III) for separation of the two elements. However, high plutonium extraction has been found ($\underline{1},\underline{2}$) when tertiary amines are contacted with 6 $\underline{N}$ Al(NO$_3$)$_3$ containing plutonium which had been reduced to Pu(III) before addition of the salt. The fact that nearly all the plutonium was retained in the amine on subsequent scrubbing with 2 $\underline{N}$ HNO$_3$ indicates that oxidation to Pu(IV) had occurred in either the original salt solution or in the organic. This behavior indicates the feasibility of coextracting neptunium and plutonium by tertiary amines from concentrated salt solutions and separating the two elements by stripping the plutonium with a reducing solution, such as ferrous sulfamate.

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