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Chemistry-Separation Processes
for Plutonium and Uranium

PREPARATION OF HIGH PURITY NEPTUNIUM ON MULTI-GRAM SCALE

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OAK RIDGE NATIONAL LABORATORY
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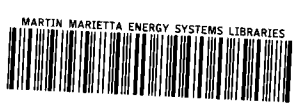

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PREPARATION OF HIGH PURITY NEPTUNIUM ON MULTI-GRAM SCALE.

SUMMARY

This work was undertaken as an extension of this laboratory's effort to prepare and stock-pile multi-gram quantities of high purity Np^{237} for research uses. The preliminary step in the purification of 116 grams was performed by the Metal Recovery Plant[1] of the Oak Ridge National Laboratory by preparing 81 liters of neptunium concentrate from several tons of Paducah Diffusion Plant Ash. The object of this investigation was of a dual nature; first, to develop a process to remove a sixty-fold thorium contamination, traces of uranium, plutonium and the usual plant corrosion products down to less than one part per million by weight; and secondly, to improve the efficiency of the Metal Recovery Plant's neptunium purification. In connection with the second objective several aspects of the neptunium purification process were investigated, such as hydrogen peroxide stabilization of Np(V), NO_2^- - HNO_3 oxidation of Np(V) and a thorium-neptunium separation involving a low percent of tri-n-butyl phosphate.

The Nethix-1 flowsheet was developed and successfully applied to the clean up of the neptunium concentrate, providing a product with less than one part per million of thorium, uranium, or plutonium. It was further determined that hydrogen peroxide is an effective stabilizer for Np(V) in the 1 M HNO_3 solutions and that the decontamination factor for thorium is approximately 20 for each stage height in a 5% TBP-HNO_3 system.

INTRODUCTION

From the stand point of quantity the purification of gram amounts of neptunium no longer represents a unique undertaking, as others[2-12] have purified up to 40 grams. In this case, however, the high ratio of thorium to neptunium (60-1) presented a different problem from that experienced in prior purifications.

Since thorium was the major heavy element contaminant, it was by necessity the first to be removed. In considering the various possible separations methods it was advantageous to review the previous use made of the different behavior of the three oxidation states IV, V, and VI. Separations processes which have been employed in the past can be summarized as cation[9] and anion exchange,[4,6,12] solvent extraction of the chelate complex,[2,5,7,12,13] solvent extraction using an inorganic salting agent[13,5,6,9-12] and precipitation from aqueous solutions.[9] Both anion[14] and cation[15] exchange were eliminated because of the strong absorption of thorium from a nitrate system shown with either exchanger. Extraction of the thenoyltrifluoracetone (TTA) complex of thorium was considered impractical because of the high salt and ferric iron concentration as well as the attendant difficulties invariably encountered in scaling up a low-capacity analytical reagent solvent. Such a step would also require excessive quantities of TTA.

The use of various organic solvents has been demonstrated many times before by others for the extraction of neptunium from heavy metal and fission product aqueous solutions. Some of the reagents used have been diethyl ether,[13,16-21] dibutyl carbitol,[12,16,21] methyl isobutyl ketone,[3,5,22,23]

tributylamine[3,5,22] in methyl isobutyl ketone and tributyl phosphate (TBP)[6, 9-12,24] in an inert solvent. The first three of these showed greater promise as a means of extracting neptunium preferentially from a strong nitric acid solution of neptunium and thorium. Kooi[25] and others[20,26,27] have demonstrated that the distribution coefficients for Np(VI) between nitric acid solutions and the solvents diethyl ether, dibutyl carbitol, and methyl isobutyl ketone are 15 to 110 times those for Th(IV); see Figure 1.

The use of 0.1 M bromate to assure complete oxidation of neptunium to Np(VI) introduced no corrosion difficulties as equipment consisted of glass and plastic tubing. The selection of diethyl ether as the extractant was made on the basis of the most favorable extraction coefficient with a 5 M nitric acid aqueous phase. Extraction with 5% TBP in a Kerosene type diluent as suggested by the work of Hesford, McKay and Scargill[28,29] and Carswell, Fletcher, and Clelland[21] was considered as a means of separating neptunium from thorium; but due to the low extraction coefficients (2 and 0.1, respectively), it was necessary to forego this type of solvent in favor of the ether because only batch extraction facilities were available. The low-percent TBP technique was investigated further and then was successfully demonstrated in plant operation.[1]

Throughout the literature[2,3] there is repeated reference made to the need for a method to stabilize Np(V) in a nitric acid solution. This would facilitate the partition of neptunium from other heavy elements in extractable states. A definite step in this direction has been accomplished by the hydrogen peroxide - 1 M nitric acid reduction of Np(VI) in diluted tributyl phosphate.

THE NETHIX-1 PROCESS FLOWSHEET

The Nethix-1 Process flowsheet (Figure 2) for the purification of neptunium from the primary contaminants thorium, uranium, and plutonium provides for batch solvent extraction and anion exchange spearations. Table I shows the analysis of the neptunium concentrate prepared by the Metal Recovery Plant of the ORNL Chemical Technology Division from several tons of non-volatile Paducah fluorination ash. Feed for the process was prepared by diluting the 81.1 liters of concentrate by addition of the reagents $Al(NO_3)_3$ and $NaBrO_3$ to make a final solution 1.0 M $Al(NO_3)_3$ and 0.1 M $NaBrO_3$, respectively, and approximately 5 M HNO_3. It had been determined that a nitrate salted solution provided 30% better recovery of neptunium than an unsalted one but at the expense of poor thorium decontamination.

TABLE I

ANALYSIS OF PADUCAH ASH NEPTUNIUM CONCENTRATE

COMPONENT	TOTAL, gm.
Al	40.38
Ca	0.97
Cr	83.53
Fe	340.62
F	137.87
Mg	0.48
Mn	7.29
Ni	62.69
Th	6458.96
U	4.21
Np^{237}	113.13
Pu^{239}	0.0003
HNO_3	6 M

I. Ether Extraction Of Np(VI).

Extraction was performed in a cylindrical glass vessel using a propeller type agitator in which 4 volumes of solution was agitated with 1 volume of diethyl ether for 5 minutes. Each aqueous phase was successively extracted three times with ether and the resulting U(VI), Np(VI), and Pu(VI)-bearing solvent was back-extracted for the same number of times with equivalent volumes of water. It was noted (Table II) that the first strip of each series contained 92% of the thorium and 12%[17] of the neptunium which had been extracted by the ether; therefore, the first strip was processed separately from the combined second and third. The nearly complete removal of thorium by the first water strip can be accounted for by the relatively high distribution coefficient (D.C.) of diethyl ether for nitric acid observed by Kooi[25] (D. C. = 0.5 at 5 M HNO_3). The stripping solution acidity was raised to 6 M by contact with the acid bearing solvent so that as the extraction coefficient for Np(VI) remained around 4.0, that for Th dropped to 0.1; see Figure 1. Based on a thorium analysis of three successive water strips of a first diethyl ether re-extraction, 2-5% of the original thorium followed the bulk of the neptunium in the second and third water strips.

TABLE II

ANALYSIS OF WATER STRIPS OF 1st. ETHER EXTRACTION

Concentrate - 79.64 mg/ml Th
1.616 mg/ml Np-237

No. H_2O Strip	Th mg/ml	% of Tot.	Np^{237} mg/ml	% of Tot.
1	17.6	22.1	0.189	11.7
2	1.6	2.0	0.538	33.5
3	0.04	0.05	0.541	33.5
4	-	-	0.025	1.5

II. Metathesis to Chloride Solvent.

A chloride metathesis was performed on the combined second and third strips after evaporation of the dissolved ether on a steam bath. This was accomplished by successive additions of 12 M HCl and evaporation until the resulting solution was 10-12 M HCl. Use was made of the fact that thorium is not complexed in strong hydrochloric acid[17, 30] while uranium, plutonium,[9,17,30] and neptunium[9] are complexed and strongly adsorbed on a strong base anion exchange resin. The batch was divided into 15-20 gram Np^{237} (0.4 M) portions for the sake of safety and ease of handling, and the Np was adsorbed on a HCl-conditioned 500 ml resin column filled with 10% cross-linked Dowex 1. After washing the column with 10-12 M HCl to remove traces of thorium, the complexed ions uranium, neptunium, plutonium, and iron were removed by alternate elution with 3.0 M and 12 M HCl.

III. Removal of Pu(IV).

The volume of the chloride eluate was reduced by evaporation for convenience of handling and the acidity adjusted to 10 M by the addition of 12 M HCl in preparation for Pu decontamination.

As the result of previous experience in purifying 200 grams of neptunium the most effective means of decontaminating macro quantities of traces of plutonium has been shown to involve the reduction of plutonium to Pu(III) with $SnCl_2$ in a strong HCl solution. The Pu(III) does not complex[18] and is readily washed through an anion resin bed. Decontamination factors of as much as 10^5[9] have been attained by this method. Neither ferrous chloride, hydroxylamine hydrochloride, hydrazine hydrochloride or sulfur dioxide have been found as reliable a reducing agent under these conditions as has $SnCl_2$. Generally, the addition of twice the stoichiometric amount of $SnCl_2$ necessary to reduce Np(VI) to Np(IV) was adequate to reduce the plutonium to Pu(III).

The exchange column and solution volume conditions provided for plutonium decontamination were the same as those for thorium decontamination in step 2. The technique employed to determine the extent of Pu removal was to analyze the HCl wash for Pu[13]. If the test was positive, a column volume of $SnCl_2$-12 M HCl was added to the column followed by two column volumes of acid. When negative tests were obtained the column was stripped in the usual manner, alternating with 3 M and 12 M HCl.

IV. Uranium Separation Via H_2O_2 Reduction Of Np(VI).

In preparation for the fourth step, the removal of uranium, the chloride was converted to the nitrate by evaporating to near dryness, adding 16 M HNO_3 and repeating until there was no evidence of chloride. Two hundred ml of either a 2 M HNO_3 - 0.1 M $NaBrO_3$ or a 6-8 M HNO_3 solution was prepared containing the neptunium and the uranium impurity; either of these solutions is capable of producing essentially 100% of the highly extractable Np(VI) and U(VI). Two 200 ml portions of 30% TBP-Amsco were used to extract the 20 grams neptunium from 200 ml nitric acid, the extractions being made in a 1 liter volume cylindrical extractor (Dimensions = .70 cm x 15 cm). The extractor was provided with a glass propeller for stirring, the latter being powered by a small laboratory type motor. To back-extract the Np(VI) from the solvent leaving the U(VI) undisturbed, use was made of the fact that $\frac{1}{2}$% H_2O_2 in 1 M HNO_3 was found to reduce Np(VI) to the essentially unextractable Np(V) (D. C.$\sim$0.06) without causing further reduction to Np(IV). Evidence for this will be presented later in this paper. Because of the extraction of nitric acid by 30% TBP-Amsco from a 2-8 M HNO_3 solution it was necessary to wash the U and Np-bearing solvent with a half volume of 1 M HNO_3 to remove the excess acid, so that when the back-extraction with $\frac{1}{2}$% H_2O_2 - 1 M HNO_3 was accomplished the final acidity would

approach 1 M. Due to the high neptunium concentration (0.2 M) in the solvent and the ensuing rapid reduction it was necessary to stir the H_2O_2-HNO_3 and solvent slowly to prevent excessive foaming. Four back-extractions with 100 ml solutions of a minute or less duration were adequate to remove more than 95% of the neptunium, the remaining having been reduced to Np(IV) and thereby re-extracted. The Np(IV) was recovered along with the uranium when the solvent was completely stripped with an ammonium carbonate solution. The carbonate solution was analyzed for uranium and by applying a predetermined decontamination factor the uranium content of the major portion of the neptunium was known.

Finally the Np(V)-H_2O_2-HNO_3 solution was evaporated to near dryness in a quartz evaporator to complete the destruction of the peroxide and 1 M HNO_3 was added. The resultant material analyzed 0.1 part per million by weight of the heavy elements Th, Am and Pu, and 1 part per million or uranium.

The total purified Np^{237} recovered from the Paducah Ash concentrate was 116.5 grams. Based on the average (112.06 g) of two Np analyses, one furnished by the Metal Recovery Plant (114.27 g) and the other performed in the course of this work (109.85 g), the calculated over all yield was 103.9%.

EXPERIMENTAL WORK.

HYDROGEN PEROXIDE REDUCTION OF NEPTUNIUM TO Np(V)

The stabilization of the unextractable Np(V) in an acid solution has been accomplished with limited success by others by reducing Np(VI) in 0.5 M nitric acid solutions using hydroxylamine hydrochloride, sulfur dioxide, hydrogen peroxide, or sodium nitrite.

Evans, Seefeldt, and Hyman[3] at Argonne National Laboratories (1950) reported on efforts to separate neptunium from plutonium and thorium in special Hanford wastes using hydrogen peroxide and sodium nitrite as an Np(V) stabilizer.

Their success was limited, as 5% was the lowest amount of neptunium extracted by 0.1 M tri-n-butylamine in hexone. In 1953 J. C. Hindman et al.[5] reported improved stripping of Np(VI) from tributylamine-hexone, probably as Np(V), using nitrite solution rather than H_2O alone.

Investigations of L. B. Magnusson et al.[31] pointed out that reduction of neptunium by hydrogen peroxide is favored by an increase in the hydrogen ion concentration in HCl solutions. This presumably would also be true for nitric acid solutions. Therefore, by selection of the proper acidity it was conceivable that perhaps reduction of Np(VI) could be controlled to proceed only as far as Np(V). Still another requirement for solvent extraction of thorium, uranium, or plutonium from Np(V) was that the selected acidity be adequate to salt their nitrate salts into the solvent.

Figure 3 shows that Np(V) is stable in 1% H_2O_2-1 M HNO_3 at room temperature for periods up to two hours while in 2 M HNO_3, 18% is reduced to Np(IV). The Np(V) was prepared by heating a mixture of the isotopes Np^{237} and Np^{238} in concentrated HNO_3, diluting to 1 M acid and adding H_2O_2. A blank was run on the source solution immediately following the H_2O_2 addition using a 0.5 M thenoyltrifluoroacetone (TTA) - xylene solvent to extract Np(IV). The same method of analysis was used to determine the extent of reduction of Np(V) at the various time intervals. The percentage reduction was determined by dividing the $Np^{238}\gamma$ counts in the solvent by the sum of those in both phases using equivalent volumes.

Having determined that in 1 M HNO_3 solution hydrogen peroxide could be depended upon not to reduce neptunium below Np(V) it was possible to apply this H_2O_2-1 M HNO_3 procedure to a uranium-neptunium separation process. It was a happy coincidence that 1 M HNO_3 would maintain Np in the pentavalent state since that acidity, as shown by K. Alcock et al.,[32] provides a partition coefficient

of 5.3 for $UO_2(NO_3)_2$ with 19% TBP.

The various batches of neptunium concentrate which had been purified except for uranium (1-10 mg U/gm Np^{237}) provided an excellent opportunity to check out the H_2O_2 reduction technique. This was described earlier in the text of this paper. Results on separation of uranium from four batches of neptunium by three successive 30% TBP-Amsco exctractions of U(VI) and Np(VI) followed by back extraction of Np(V) with 1% H_2O_2-1 M HNO_3 are tabulated in Table III. The values are expressed in terms of milligrams U in carbonate strip per gram Np in peroxide strip.

TABLE III

Uranium Decontamination by H_2O_2 Reduction of Neptunium.

Batch No.	1st Extraction mg. U/gm Np	2nd Extraction mg U/gm Np	3rd Extraction mg U/gm Np	Ave. Decont. Factor
1	0.57	0.13	0.0023	30.2
2	0.63	0.075	0.21	4.4
3	9.6	0.96	0.02	29.0
4	5.6	0.83	0.11	7.2

The increase in uranium in the third extraction of batch #2 presumably was due to its inadverdent addition during preparation of peroxide solution for re-extraction. It is evident that by repeated extractions the uranium can be reduced to less than one part per million of neptunium.

SEPARATION OF NEPTUNIUM FROM THORIUM BY 5% TBP

As the result of a material balance survey[33] for neptunium in the Paducah Diffusion Plant it was clearly shown that a continuous supply of neptunium was potentially available in the fluorination ash. However, in addition to the predominate non-volatile uranium tetra-fluoride ash, there existed appreciable quantities of thorium along with other extraneous materials. The difficulty of separating neptunium and thorium in the Metal Recovery Plant using the 30% TBP system was attested to by the high ratios (60:1) of thorium to neptunium in the neptunium concentrate.

Hesford, McKay and Scargill[29] reported distribution coefficients for thorium nitrate of less than 10^{-1} in 5 M HNO_3 and 5% TBP systems. D. J. Carswell, J. M. Fletcher, and D. W. Clelland[21] suggested the use of 4 to 5% TBP to separate uranium from thorium and reported partition coefficients of 5 for uranium and 0.5 for thorium[34] with 5% TBP and an aqueous phase 0.5 M HNO_3 containing 3 - 4 M total nitrate. D. F. Peppard and co-workers[34] reported successful extraction of U(VI), analogous to Np(VI), with undiluted TBP from Th(IV) in 5 M HCl. This approach of course was out of the question with a stainless steel-equipped plant.

The distribution coefficients, organic (cts/min.)/aqueous (cts./min.), for Th^{234} between 5% TBP-95% Amsco (kerosene type diluent) and 0.5-8.0 M HNO_3 were determined in the following manner. Equivalent volumes (10 ml) of acid-equilibrated solvent and unsalted 0.5 - 8.0 M HNO_3 solutions spiked with Th^{234} were shaken in a small separatory funnel at room temperature for three minutes.

The solvents had been initially equilibrated by shaking with two fresh batches of HNO_3. Phases were centrifuged to assure complete separation of components and 1 ml of each was counted with a NaI crystal gamma scintillation counter.

Th^{234} tracer was obtained from natural uranium by adsorbing the chloride complexed uranium on a Dowex 1-W ion exchange column with the uncomplexed thorium passing through. Thorium in the effluent was converted to the nitrate form to free it of fission products by extraction with 30% TBP. Its purity was checked by gamma-ray spectrometer analysis.

Figure 4 indicated that a wide range of acid strengths (3.0 M - 8.0 M) were suited to low thorium extraction (D. C. = 0.1). Our value (0.1) at 5.0 M HNO_3 was in good agreement with that obtained by Hesford et al.[29]

In view of the low neptunium molarity (0.1 - 0.2 M) of the solution concentrate under consideration, the capacity of the 5% TBP was expected to offer no difficulties. With exception of a mention of singular distribution coefficients by Dawson et al.[35] at 5 M HNO_3 no information was available on the distribution coefficients for Np(IV) or Np(VI) in varying HNO_3 strengths with 5% TBP. These data were obtained in a manner comparable to that described previously for thorium. The Np^{238} was prepared by bombarding pure Np^{237} with neutrons to form the high specific activity gamma emitter which was better suited for rapid counting. Np(IV) and Np(VI) acid solutions were prepared by making them 0.02 M in ferrous sulfamate and 0.1 M in sodium bromate, respectively, and allowing adequate time for completion of reaction.

There is no question about Np(VI) (Figure 5) having the more desirable extraction characteristic, with optimum acid conditions being between 3.5 and 5.0 M. A distribution coefficient of 2 is sufficient to provide essentially 100% recovery in a four stage counter current flow extraction system. By increasing the volume ratio of solvent to aqueous it would be possible to

accomplish the desired recovery with even less extraction stages. It should be noted that acid molarities above 4 M have a deleterious effect on Np(VI) distribution coefficients in the same manner as is true in the 30% TBP system, due to the accompanying HNO_3 extraction.

OXIDATION OF NEPTUNIUM BY NITRITE CATALYSIS

The adoption of the 5% TBP-HNO_3 process to separate Np(VI) from Th(IV) on a plant scale made the use of a non-corrosive oxidant mandatory. Sheppard[36] and Siddall[37] have observed that nitrite in nitric acid had a beneficial effect on the TBP extraction of neptunium. Studies by the authors[38] have shown the catalytic effect of the nitrite ion on the oxidation of Np(V) to Np(VI) in 2-4 M HNO_3. Previously Magnusson et al.,[31] demonstrated that Np(VI) is readily reduced by nitrite. Both Np(VI) reduction and reoxidation to Np(VI) in a 0.1 M NH_4NO_2, 2 M HNO_3 and 30% TBP system have been demonstrated by the authors, (Table IV). Portions of 2.6×10^{-5} M Np^{237} in 2 M HNO_3 which were 0.1 M in NH_4NO_2 or 0.04 M in sulphamic acid or which contained neither were shaken with equivalent volumes of acid-equilibrated 30% TBP-Amsco for three minutes. The sulphamic acid was used to destroy any nitrite in the original solution. Phases were separated and extraction of the aqueous phase repeated with four separate batches of solvent with not more than 5 minutes elapsing between extractions. The first extraction with nitrite was performed immediately following its addition. Valence distribution of the neptunium had been determined by spectrophotometric analysis using a Model DU, Beckman Spectrophotometer.

The reduction effect of nitrite on Np(VI) in the first extraction is obvious, particularly in the 51% Np(VI) set. Evidence of reoxidation lies in the increase of the distribution coefficient for the second and third extractions as the result of growth of Np(VI) from the Np(V) which has a D. C. of 0.085. The lower distri-

bution coefficient of the fourth extraction, as will be shown later in this paper, was probably due to a depletion of nitrite below the threshold level (2.5×10^{-5} M)[38] for catalysis, by solvent removal. When sulphamic acid was used to destroy the nitrite in the original neptunium solution the D. C. for the second, third, and fourth extractions were of the order expected for Np(V).

TABLE IV

REDUCTION AND REOXIDATION OF Np(VI) IN HNO_3 - HNO_2 SYSTEM

2 M HNO_3 - 30% TBP - AMSCO

Solution Treatment	Np-237 Valence Dist.	DISTRIBUTION COEFFICIENT = cts. Organic / cts. Aqueous EXTRACTION 1st.	2nd.	3rd.	4th.
None	Np-IV - 16% Np-V - 33% Np-VI - 51%	4.5	0.94	0.16	0.04
0.1 M NH_4NO_2	---	0.16	1.07	1.88	0.16
0.04 M Sulphamic Acid	---	2.52	0.25	0.04	0.02
None	Np-IV - 0 Np-V - 74% Np-VI - 16%	0.50	0.05	0.02	0.003
0.1 M NH_4NO_2	---	0.144	0.83	1.22	0.64
0.04 M Sulphamic Acid	---	0.38	0.04	0.008	0.01

EFFECT OF 200 PPM NO_2^- ON 5% TBP EXTRACTION OF NEPTUNIUM

To demonstrate the feasibility of nitrite catalytic oxidation of neptunium in nitric acid for 5% TBP extraction from thorium the following experiment was conducted.

Nine 10 ml samples of Np^{237} and Np^{238} in 0.5-8.0 M HNO_3 containing 200 ppm $NaNO_2$ were prepared and allowed to sit at room temperature for 60 min. Thirty minutes had been shown to be sufficient to reach maximum extractibility in 6 M HNO_3. Each was shaken with an equivalent volume of acid-equilibrated 5% TBP-Amsco in a 30 ml separatory funnel for three minutes. Phases were separated and equivalent volumes were gamma counted in an NaI crystal well-type scintillation gamma counter.

The aqueous phases were recombined and the extractions repeated with new solvent 5 hours from the inception of the experiment.

This procedure was repeated a total of four times with the third occurring 24 hours and the fourth 28 hours from the start. An additional 200 ppm NO_2^- was added at the start of the fourth, allowing 60 minutes reaction time, to compensate for the apparent nitrite depletion by solvent removal.

Figure 4 indicates the optimum molarity for multi-stage extraction of Np(VI) with 5% TBP from Th(IV) to be in the range of 3.5-6.0 M HNO_3. The low distribution coefficients for the third extraction are due to the presence of Np(V). This assumption is validated by the fact that upon the addition of more nitrite to oxidize the Np(V), the distribution coefficients on the fourth extraction rise sharply.

On the basis of this experiment a decontamination factor for thorium of 10-20 is possible for each extraction stage of a nitrite-nitric acid - 5% TBP system.

A flowsheet embracing the essential features of the above findings was recently used by the Metal Recovery Plant to separate 34 grams Np^{237} from a quantity of fluorination ash[1]. They obtained a thorium decontamination factor of 240.

REFERENCES

(1). R. E. Brooksbank and C. D. Hilton, Recovery of Neptunium-237 from Fluorinator Ash in Metal Recovery Plant, ORNL-2515, (September 15, 1958).

(2). J. C. Magnusson, ANL-WMM-32, (August 2, 1946) and PPR, Vol. 15, (1947).

(3). H. B. Evans, W. B. Seefeldt, and H. H. Hyman, Recovery of Np^{237} from Special Hanford Wastes, ANL-4442, (March 27, 1950).

(4). S. C. Carniglia and B. B. Cunningham, Separation and Purification of Neptunium, U.C.R.L.-2069, p33, (Dec. 31, 1952).

(5). J. C. Hindman, Philip Werner, J. C. Sullivan, and Donald Cohen, Isolation and Purification of Neptunium-237 Obtained from Hanford Wastes, ANL-5037, (May 6, 1953).

(6). R. W. Durham and L. I. Baird, Tributyl Phosphate Process XXIV. Recovery of Neptunium, CRCE-589, p6, (March 6, 1955).

(7). G. W. Parker, W. J. Martin, P. M. Lantz, and G. E. Creek, ORNL Chemistry Division Semi-Annual Progress Report, ORNL-2046, pp. 62-64, (Dec. 20, 1955).

(8). Ibid, ORNL-1940, pp. 57-60, (June 20, 1956).

(9). Ibid, ORNL-2171, pp. 1-6, (June 20, 1956).

(10). J. R. Flanary et al., Chemical Development of the 25-TBP Process, ORNL-1993, (Sept. 24, 1956).

(11). Ibid, Recovery of Np^{237} by the Neptex Solvent Extraction Process, ORNL-2235, (March 11, 1957).

(12). J. S. Nairn and D. A. Collins, U.K., A.E.A. (I. G.), Research and Development Branch, Windscale, The Recovery of Neptunium-237. To be Published in Progress in Nuclear Energy, Paper 6.5, McGraw-Hill Book Co., N. Y., N. Y.

(13). L. B. Magnusson, J. C. Hindman, and T. J. Chappelle, Chemical Methods for the Purification and Isolation of Neptunium, ANL-4066, (Oct. 10, 1947).

(24). A. R. Eberle, M. W. Lerner, Separation of Uranium from Thorium, Bismuth and Ores with Tributyl Phosphate, Analytical Chemistry, 29, pp. 1134-39, August, (1957).

(25). J. Kooi, Tracer Experiments on the Solvent Extraction of Neptunium and Plutonium, Jener Publications, No. 11, (1956).

(26). L. Imre, Z. Anorg. Allgem. Chem. 166, 1 (1927).

(27). Bock, R. and Bock, E., 263, 146, (1950).

(28). H. A. C. McKay, Tri-n-butyl Phosphate as an Extracting Agent for the Nitrates of the Actinide Elements, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 7, pp. 314-317, (1956).

(29). Hesford, E., McKay, H. A. C., and Scargill, D., Tri-n-butyl Phosphate as an Extracting Solvent for Inorganic Nitrates-IV-Thorium Nitrate, Journal of Inorganic and Nuclear Chemistry, Vol. 4, pp. 321-325, (1957), Pergammon Press Ltd., London.

(30). K. A. Kraus and F. Nelson, Anion Exchange Studies of the Fission Products, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 7, pp. 113-125 (1956).

(31). L. B. Magnusson, J. C. Hindman, and T. J. LaChappelle, Paper 15.11 of The Transuranium Elements, Division IV, Volume 14B, National Nuclear Energy Series, McGraw-Hill Book Company, Inc., New York, N. Y., (1949).

(32). K. Alcock, G. F. Best, E. Hesford, and H. A. C. McKay, Tri-n-butyl Phosphate as an Extracting Solvent for Inorganic Nitrates-V, to be published in Journal of Inorganic and Nuclear Chemistry, Pergammon Press Ltd., London (1958).

(33). P. M. Lantz, G. W. Parker, Investigation of Paducah Fluorination Ash and Metal Recovery Wastes as a Large Scale Source of Neptunium-237, ORNL-CF-57-8-34, (1957).

(14). D. J. Carswell, Separation of Thorium and Uranium Nitrates By Anion Exchange, Journal of Inorganic and Nuclear Chemistry, Vol. 5, pp. 384-387, (1957), Pergammon Press Ltd., London.

(15). W. K. Eister, G. P. Monet, and F. L. Steahly, Report Mon-N-139, (Aug. 9, 1946).

(16). E. K. Hyde, Chapter 15 of The Actinide Elements, National Nuclear Energy Series, Division IV, Volume 14-B, McGraw-Hill Book Co., Inc., New York, (1954).

(17). E. K. Hyde, Radiochemical Separation Methods for the Actinide Elements, Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Vol. 7, pp. 281-303, (1956).

(18). I. K. Shvetsov and A. M. Vorobyev, On Methods of Separation of Neptunium and Plutonium, Ibid, p. 304.

(19). E. K. Hyde and Martin H. Studier, The Formation and Properties of U^{240} and Np^{240}, ANL-4182, August 4, 1948.

(20). P. Misciatelli, The Separation of Thorium and Uranium by Means of Ether, Phil. Mag. (7), 7:670, (1929).

(21). D. J. Carswell, J. M. Fltecher and D. W. Clelland, The Recovery of Thorium 230 from Uranium Wastes, Journal of Inorganic and Nuclear Chemistry, Volume 5, pp. 147-152, (1957), Pergammon Press Ltd., London.

(22). H. R. Baxman, G. R. B. Elliott, Jr., J. P. McBride, F. T. Miles, J. M. Roth, The Recovery of Uranium from Enriched Piles, ORNL, Chemistry Division Report for Months March, April and May 1948.

(23). Paul Fields, Paper 15.10 of The Transuranium Elements, National Nuclear Energy Series, Division IV, Volume 14-B, McGraw-Hill Book Company, Inc., New York, (1949).

(34). D. F. Peppard, G. W. Mason and M. V. Gergel, The Mutual Separation of Thorium, Protactinium and Uranium by Tributyl Phosphate Extraction from Hydrochloric Acid, Journal of Inorganic and Nuclear Chemistry, Volume 3, pp. 370-378, Pergammon Press Ltd., London, (1957).

(35). J. K. Dawson, R. Elliott, H. A. C. McKay, The Extraction of Neptunium by Tributyl Phosphate, A.E.R.E. C/R-1117 (2-15-53).

(36). J. C. Sheppard, Path of Neptunium in the Hanford Process, Neptunium Information Meeting Proccedings, ORNL, March 7-8, 1957, TID-7542.

(37). T. H. Siddall, III, and E. K. Dukes, Kinetics of Oxidation of Neptunium V, by Nitrous Acid in Aqueous Solutions of Nitric Acid, Nuclear Technology Symposium, ACS Meeting, San Francisco, April 13-18, 1958.

(38). G. W. Parker, P. M. Lantz, and W. J. Martin, ORNL Chemistry Division Annual Progress Report Ending June 20, 1957, ORNL-2386, pp. 22-25.

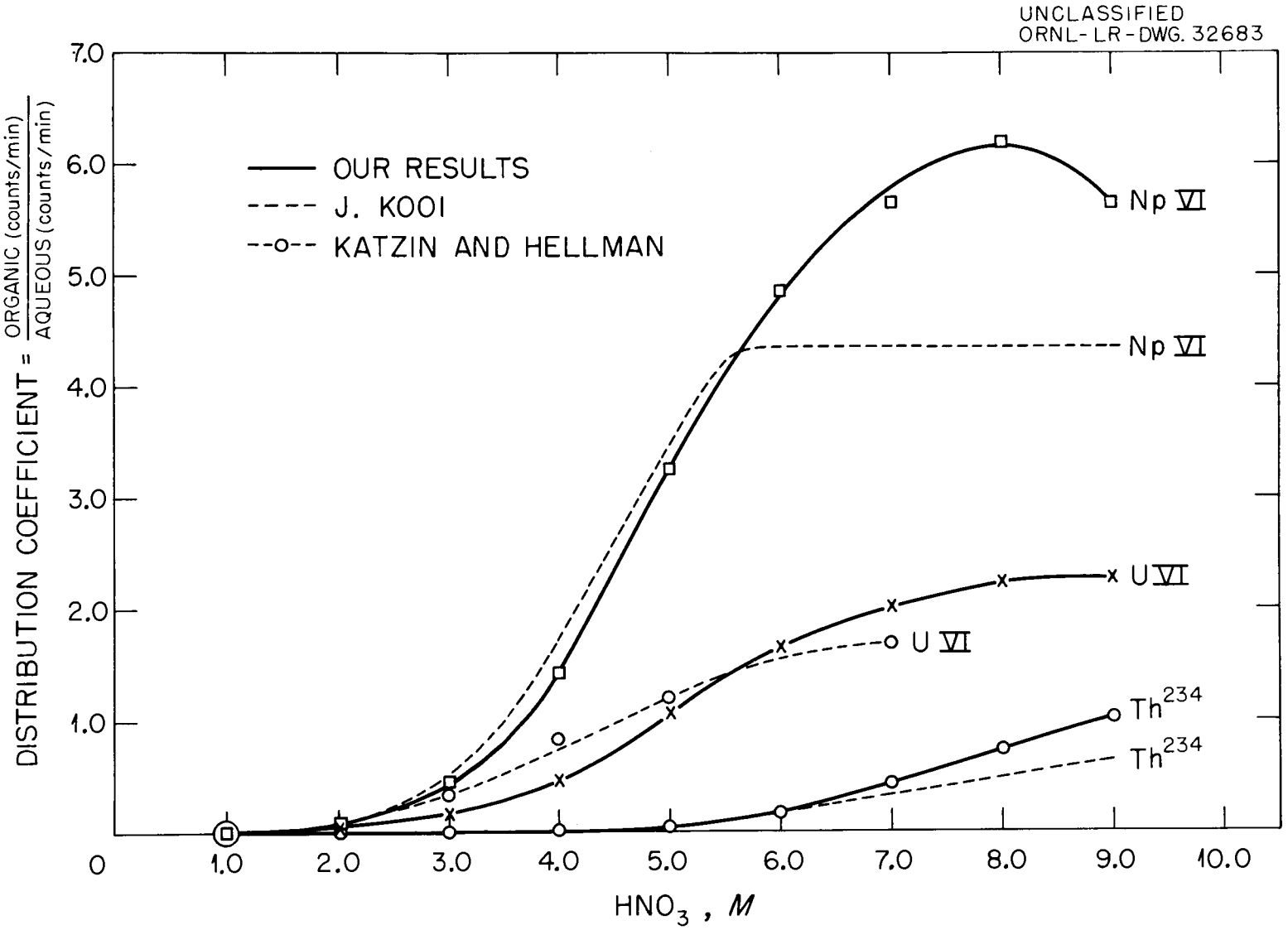

Figure 1

THE PARTITION OF THORIUM, URANIUM AND NEPTUNIUM BETWEEN NITRIC ACID AND DIETHYL ETHER

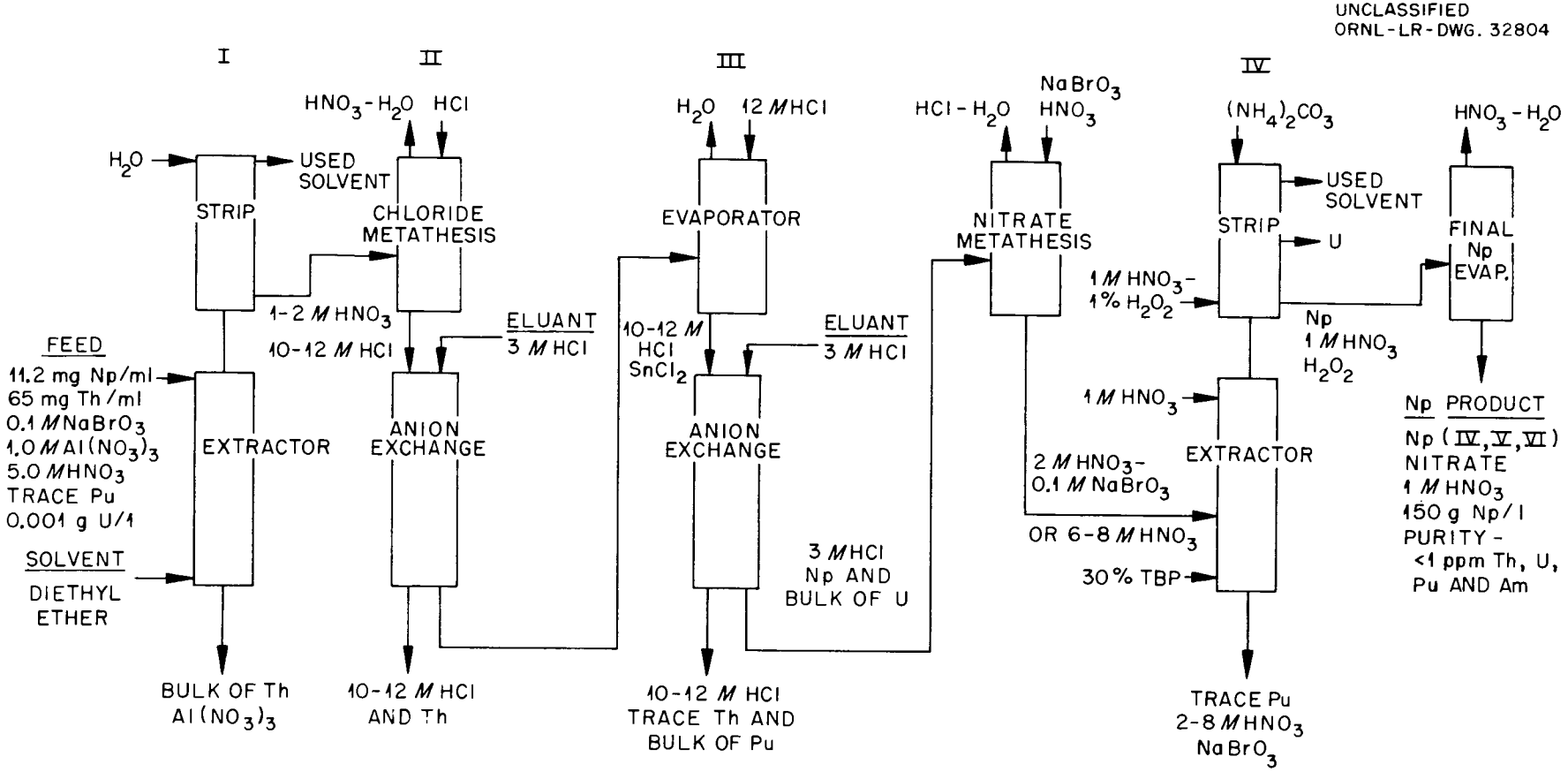

Figure 2
NETHIX-1 PROCESS

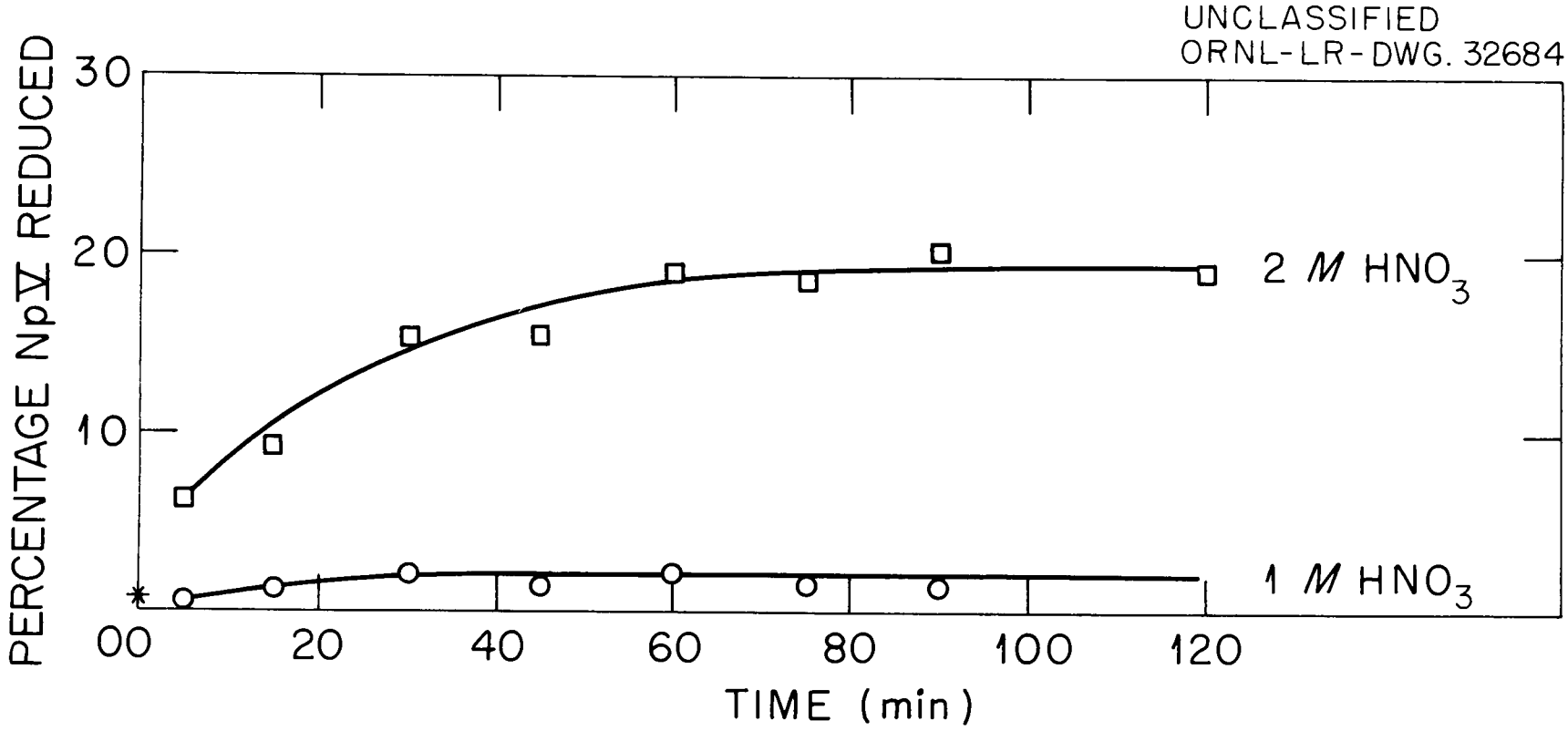

Figure 3
HYDROGEN PEROXIDE (1%) REDUCTION OF NpV IN 1-2 *M* HNO_3
(* % NpIV in Tracer)

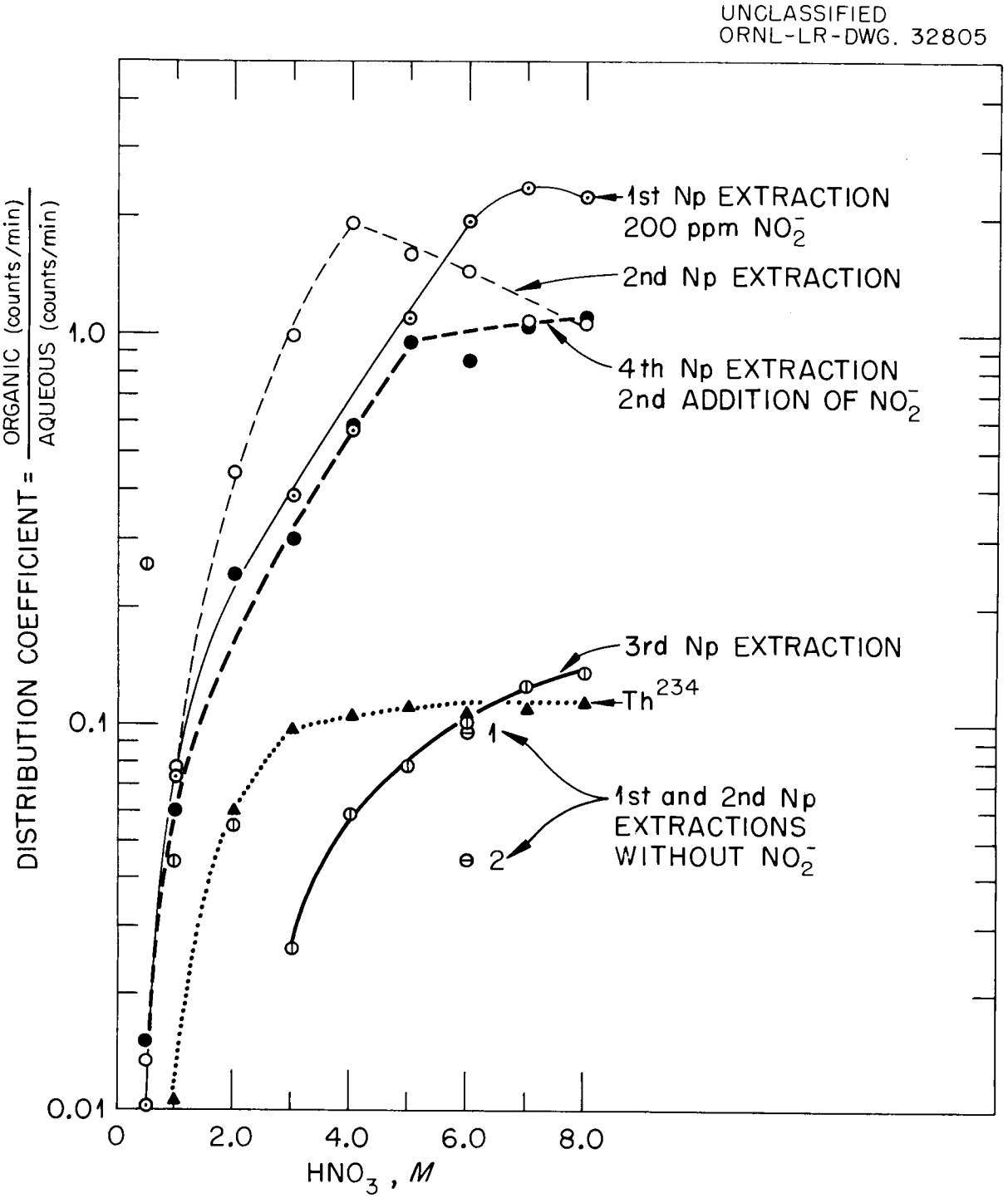

Figure 4

THE PARTITION OF NEPTUNIUM AND THORIUM BETWEEN NITRIC ACID AND 5% TBP-95% AMSCO

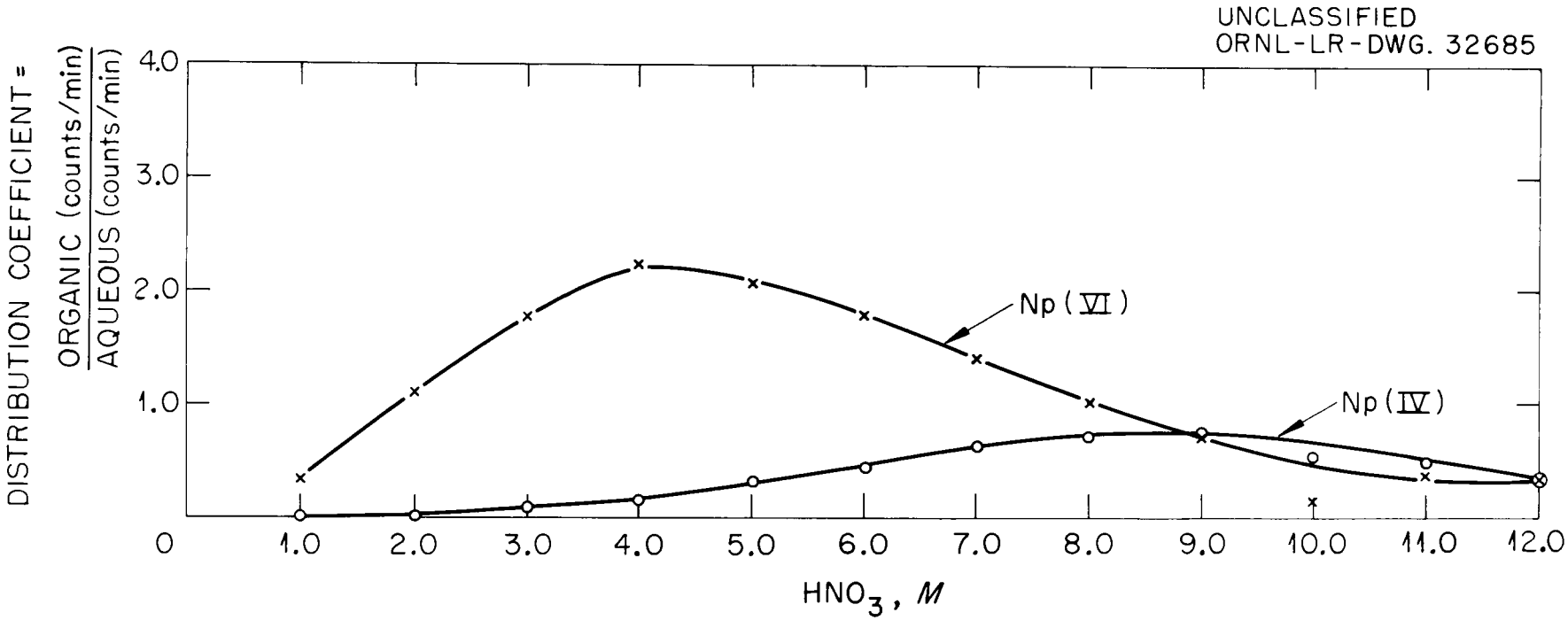

Figure 5

THE PARTITION OF NEPTUNIUM IV AND VI
BETWEEN NITRIC ACID AND 5% TBP - 95% AMSCO

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