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PROCESS CHEMISTRY OF NEPTUNIUM - PART II

by

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**BHABHA ATOMIC RESEARCH CENTRE
BOMBAY, INDIA**

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ABSTRACT

The oxidation state analysis of neptunium in the aqueous feed solution from the Plutonium Plant at Trombay was carried out and it was found that neptunium existed mainly as Np(V) in the feed solution. Batch extraction data for Np(IV) and Np(VI) into 30% TBP/Shell Sol T at different aqueous nitric acid concentration and uranium saturation of the organic phase were obtained at 45°C and 60°C and the results are summarized. The distribution coefficients of Np(IV) and Np(VI) were obtained as a function of TBP concentration and the data are reported. The effect of nitrous acid on the extraction of neptunium, present in the aqueous phase as Np(IV) and Np(V) , by 30% TBP was studied and the data obtained are given. The data on the rate of reduction of Np(VI) and Np(V) to Np(IV) by U(IV) were obtained for different U(IV) and nitric acid concentrations. Some redox reactions involving Np(IV) , Pu(IV) and V(V) were investigated and their possible application in the paxex process for neptunium recovery were explored.

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1. INTRODUCTION

Neptunium-237 is produced in significant amounts in uranium fuelled power reactors and its recovery during the reprocessing of the irradiated fuels has recently become important as it is the starting material for the production of Pu-238 which is used in compact power sources. Kilogram quantities of Np-237 are being produced in power reactors thus making its recovery a matter of considerable interest.

The work on the process chemistry of neptunium was undertaken with a view to arriving at suitable conditions for neptunium recovery, alongwith uranium and plutonium, by the purex process in the PREFRE Plant Tarapur. Batch extraction data at room temperature for Np(IV) and Np(VI) into 30% TB^o at different aqueous nitric acid concentrations and as a function of saturation of the organic phase by uranium were obtained and summarised in the earlier report⁽¹⁾. The path of neptunium in the Plutonium Plant at Trombay was followed by analysing the neptunium content in several process streams and the results obtained were also included in that report. In continuation of that work a few more aspects relevant to the neptunium process chemistry were investigated and the results obtained are summarised here.

From the analyses of the various process streams of the Trombay Plutonium Plant for their neptunium content it was observed⁽¹⁾ that neptunium extraction in the co-decontamination cycle was much higher than that in the

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partitioning cycle through the extraction conditions were identical in both the cycles. In order to understand this extraction behaviour of neptunium in the purex process the oxidation state analysis of neptunium in the feed solution of the Plutonium Plant at Trombay was carried out and the results are described in Section 2.

It is known that the fission product decontamination factors can be improved by operating some sections of the purex process at elevated temperatures⁽²⁾. In order to determine the effect of higher temperatures on neptunium extraction into TBP, batch extraction data for Np(IV) and Np(VI) into 30% TBP at different aqueous nitric acid concentrations and as a function of the organic phase saturation by uranium were obtained at 45° and 60°C and the results are summarised in Section 3.

Batch extraction data for Np(IV) and Np(VI) into TBP as a function of TBP concentration were obtained to determine the dependence of the distribution coefficient on TBP concentration and the results are given in Section 4.

To adjust the oxidation state of plutonium to Pu(IV) nitrous acid is added to the feed solution of the purex process. Hence the effect of nitrous acid on the neptunium extraction by TBP was studied and is reported in Section 5.

For the partitioning of plutonium from uranium in the PUREX plant it is proposed to use U(IV) as a reducing agent. The course of neptunium in the partitioning column, therefore, depends on the rate of reduction of Np(VI) and Np(V) to Np(IV) by U(IV). These reactions were investigated and

the results are given in Section 6.

To divert neptunium to the desired stream in the purex process a close control of its oxidation state is necessary. Some redox reactions that are helpful in achieving this objective were investigated and the results are described in Section 7.

2. OXIDATION STATE ANALYSIS OF NEPTUNIUM IN THE PUREX PROCESS FEED SOLUTION OF THE PLUTONIUM PLANT AT TROMBAY

In the Plutonium Plant at Trombay, the extraction of neptunium was found to be higher in the co-decontamination (first) cycle than that in the partitioning (second) cycle though the conditions of extraction were similar in both the cycles⁽¹⁾. Neptunium can be present as Np(IV) , Np(V) or Np(VI) in the purex process feed solution. Np(IV) and Np(VI) are extractable by TBP whereas Np(V) is not. Since the extraction was higher in the first cycle it was thought that the neptunium might be present in the feed of that cycle mainly as the extractable Np(VI) or Np(IV) . Durham and Baird inferred⁽²⁾ that neptunium is mainly present as Np(VI) in the primary feed solution while Ward and Welch reported⁽⁴⁾ that it exists predominantly as Np(IV) in the Windscale primary feed solution. Finary and Parker, from their analyses found⁽⁵⁾ that about 80% of neptunium existed as Np(V) whereas about 10% as Np(IV) and Np(VI) each. To understand this behaviour of neptunium it was considered necessary to analyse the first cycle feed solution for different oxidation states of neptunium.

2.1. Method of Analysis

Np(IV) is quantitatively extracted from 1M nitric acid into 0.5 M TBA while Np(V) and Np(VI) are not at all extracted under these conditions⁽⁶⁾.

Np(IV) and Np(VI) are extracted by hexone from an aqueous phase which is 1M in nitric acid and saturated with ammonium nitrate⁽⁷⁾. Under these conditions Np(V) is not at all extracted by hexone. Alternatively, coprecipitation of neptunium with LaF_3 is another tool which can distinguish the different oxidation states. Experiments were carried out to find out the coprecipitation behaviour of different oxidation states of neptunium with LaF_3 and the data are presented in Tables 1-4. These data show that Np(IV) and Np(V) are quantitatively carried by LaF_3 while Np(VI) is not at all carried, and that there is little interference due to the presence of uranium upto 100 mg/ml on the coprecipitation behaviour of neptunium in different oxidation states. Hence by a suitable combination of the TTA extraction, hexone extraction and LaF_3 precipitation it was possible to estimate the different oxidation states of neptunium present in a given sample.

2.2 Experimental

Oxidation states of neptunium in the feed solution of the first cycle were analysed before and after conditioning, for the oxidation state adjustment of plutonium, using NaNO_2 . The volume of the sample chosen for analysis depended primarily on the beta-gamma activity level of the sample. A known volume of the sample was taken and its total neptunium content was first estimated by the TTA extraction method^(1,8). In this method the sample was adjusted to 1.0 M in nitric acid and 0.1 M in ferrous sulphamate and equilibrated with 0.5M TTA. Under these conditions neptunium is present as Np(IV) which is extractable by TTA whereas plutonium is present as Pu(III) which is not extractable by TTA. Uranium which is present as U(VI) and a major fraction of fission products are not extractable and hence remain in

the aqueous phase. The extracted neptunium was subsequently stripped into 8M nitric acid. In this stripping process zirconium and protactinium which are extractable by TTA remain in the organic phase. The extraction-stripping process was repeated twice to get good decontamination of the neptunium from plutonium and fission products⁽¹⁾. The percentage yield of neptunium in this process was estimated by tagging neptunium with a known quantity of ^{239}Np .

The Np(IV) present in the sample was estimated by adjusting a known aliquot of the sample to 1M in nitric acid and then extracting the Np(IV) with 0.5M TTA. The extracted neptunium was purified from plutonium and estimated by the TTA extraction method as described above. Lanthanum fluoride precipitation was carried on a known aliquot of the sample and the neptunium carried (Np(IV) and Np(V)) with LaF_3 was purified and estimated by the TTA extraction method. The difference in the values of the neptunium content obtained with direct TTA extraction method, i.e., Np(IV) and that carried by LaF_3 , i.e. $\text{Np(IV)} + \text{Np(V)}$ was taken as the amount of Np(V) present in the sample. The difference between the total neptunium content, i.e. $\text{Np(IV)} + \text{Np(V)} + \text{Np(VI)}$ and that carried by LaF_3 , i.e. $\text{Np(IV)} + \text{Np(V)}$ was taken as the amount of Np(VI) present in the sample. Alternatively Np(V) was estimated, in a couple of samples, by the TTA extraction method starting with a sample from which Np(IV) and Np(VI) together were quantitatively removed by extraction with hexone from the sample which was adjusted to 1M in nitric acid and nearly saturated with NH_4NO_3 .

2.3 Results and Discussion

The data obtained on the oxidation state analysis of neptunium in the feed solution of the first cycle are shown in Table 5. It is seen from these data that neptunium is present mainly as Np(V) in the feed solution.

The presence of about 30-35% Np(IV) in the samples 1-3 may be due to the disproportionation of Np(V) which is enhanced at higher acidity and in the presence of complexing anions such as nitrate⁽⁹⁾. The absence of Np(VI) in these solutions, however, may be due to its reduction to Np(V) by radiolysis or exposure to light which is known to reduce Np(VI) to Np(V) especially in the presence of uranium⁽¹⁰⁾.

Recently Bahr⁽¹⁰⁾ investigated the oxidation states of neptunium by dissolving irradiated neptunium doped- uranium oxide in nitric acid and analysing by extraction with 30% TBP-alkane. Assuming that only Np(IV) and Np(VI) get extracted while Np(V) remains unextracted, Bahr observed that the results were not reproducible as the ratio of the extracted to the unextracted neptunium species varied from 10:1 to 1:10. By adding the neptunium in a known oxidation state, (IV), (V) or (VI) to nitric acid in which irradiated uranium metal or uranium oxide was subsequently dissolved and following the oxidation state of neptunium during and after dissolution by spectrophotometry it was reported that neptunium existed mainly as Np(V) during and after dissolution of uranium. All the neptunium was oxidised to Np(VI) only by boiling the solution in 7M nitric acid for 3 hours. The variation in the results obtained by TBP extraction could be due to different concentrations of nitrous acid present in the solution as its presence is known to affect the oxidation of Np(V) to Np(VI) by nitrate in the presence of TBP^(11,12). The present results on the oxidation state analysis of neptunium are in agreement with those reported by Flanary and Parker⁽⁵⁾ and by Bahr⁽¹⁰⁾.

Assuming that neptunium was present as Np(V) in the second cycle feed also the higher extraction of neptunium in the first cycle compared to that in the second cycle may be explained by the presence of the rate

accelerating material. It was reported⁽¹²⁾ that the products of the reaction of uranium carbide (which is present in the metallic uranium fuel elements) with nitric acid and of the reaction of the plant solvent with nitric acid accelerated the rate of oxidation of Np(V) to Np(VI) by nitrate. Siddall and Dukes reported⁽¹¹⁾ that nitrous acid catalysed the oxidation of Np(V) to Np(VI) by nitrate and that the rate was independent of the concentration of nitrous acid. However, Swanson observed⁽¹²⁾ that the oxidation was dependent on nitrous acid concentration and was enhanced by the presence of TBP probably due to the formation of the rate accelerating materials. Some preliminary work⁽¹³⁾ carried out in this laboratory tends to support the latter view. In the second cycle, the concentration of nitrous acid would be less than that in the first cycle where its radiolytic formation would be more. Thus the absence of the rate accelerating materials and the reduction in the nitrous acid concentration would probably explain the decrease in the extraction of neptunium in the second cycle.

3. THE EFFECT OF NITRIC ACID AND URANIUM CONCENTRATION ON THE EXTRACTION OF Np(IV) AND Np(VI) INTO 30% TBP AT 45°C AND 60°C

The effect of uranium saturation of 30% TBP in Shell sol-T (SST) on the extraction of Np(IV) and Np(VI) at room temperature was reported earlier⁽¹⁾. In the PUREX Plant at Tarapur, under construction, the various extraction columns will be provided with jackets to have the desired temperature as it is known that the decontamination factors can be improved by operating some sections of the purex process at higher temperatures⁽²⁾. It was, therefore, considered necessary to study the extraction behaviour of neptunium at higher temperatures under conditions relevant to the process. In the present work the effect of aqueous nitric acid concentration and

organic phase uranium concentration on the extraction of Np(IV) and Np(VI) into 30% TBP-SST at 45°C and 60°C was studied and is reported here.

3.1 Experimental

The experimental procedure for the extraction of Np(IV) and Np(VI) with varying nitric acid and uranium concentrations into 30% TBP is the same as described earlier⁽¹⁾ except that, prior to use, the TBP was pre-equilibrated with nitric acid of the corresponding concentration. The equilibrations were carried out in a thermostated waterbath the temperature of which was maintained within $\pm 0.1^\circ\text{C}$.

3.2 Results and observations

The data obtained on the equilibrium concentration of uranium and nitric acid in both aqueous and organic phases and the distribution coefficients of Np(IV) and Np(VI) at varying concentrations of uranium and nitric acid at 45°C are given in Tables 6-9 and similar data at 60°C are given in Tables 10-13. The plots of the distribution coefficients of Np(IV) vs organic phase uranium concentration at different nitric acid concentrations at 45°C and 60°C are shown in Figures 1 and 2 respectively. Similar data for Np(VI) at 45°C and 60°C are shown in Figures 3 and 4 respectively.

3.2.1 The effect of temperature on the distribution of various constituents

From the data obtained in the present work, it is seen that the extraction of Np(VI) is higher than that of Np(IV) at all concentrations of uranium and nitric acid at the temperatures studied. Only in the experiments at 4M nitric acid and 60°C, the distribution coefficients of Np(IV) are higher than those of Np(VI) at high uranium concentration in the organic phase.

Except from 1M nitric acid with low uranium concentration, the distribution coefficient of Np(IV) , increased with the increase of temperature from 45° to 60°C and the relative increase in the distribution coefficient was enhanced by the presence of uranium. This effect is similar to that observed in the case of Pu(IV) extraction⁽¹⁴⁾ and is due to the decrease in uranium distribution coefficient with increasing temperature which makes more free TBP available for the extraction of Np(IV) at higher temperature. The distribution coefficients of both U(VI) and Np(VI) decreased with the increase of temperature from 45°C to 60°C and the decrease becomes smaller with increasing concentration of uranium in the organic phase. The behaviour is similar to that observed in the extraction of Pu(VI) ⁽¹⁴⁾ and U(VI) ⁽¹⁵⁾. The distribution coefficient of nitric acid seems to be almost unaffected by increasing the temperature upto 60°C . The present observations on the effect of temperature on the trend of the distribution coefficients are in general agreement with those reported in the literature for HNO_3 ⁽¹⁶⁾, U(VI) ⁽¹⁵⁻²³⁾, Np(IV) ⁽¹⁶⁾ and Np(VI) ^(10,11,16,24).

3.2.2 Uranium to Neptunium Ratios: The ratio of the distribution coefficient of U(VI) to that of Np(VI) for the same concentration of uranium in the organic phase was found to remain approximately constant. At room temperature for 2-4 M nitric acid concentration, and at all uranium concentrations in the organic phase, this ratio was about 2.1⁽¹⁾. This is in good agreement with the value of 2.1 given by Germain et al⁽²⁴⁾. At 45°C and 60°C this ratio was about 2.0 and 1.9 respectively. Thus as suggested by Germain et al⁽²⁴⁾, this ratio can be used to calculate roughly the distribution coefficient of Np(VI) from known distribution coefficient of U(VI) under similar conditions.

3.2.3 Comparison of Np(IV) and Np(VI) extraction data: The comparison of the distribution coefficient data for Np(IV) and Np(VI) shows that the ratio of the distribution coefficient of Np(VI) and Np(IV) at equivalent organic phase uranium loading decreases with increasing acidity at all the temperature studied. This is similar to the observation reported in the extraction of plutonium⁽²⁵⁾.

4. VARIATION OF THE DISTRIBUTION COEFFICIENT OF Np(IV) AND Np(VI) WITH TBP CONCENTRATION

The distribution coefficient of both Np(IV) and Np(VI) vary linearly with the square of the TBP concentration⁽²⁶⁾. However, this relation is true only for very low concentration of TBP. For higher TBP concentrations the distribution coefficient is reported to vary linearly to a degree considerably lower than square of the TBP concentration for U(VI)⁽¹⁵⁾ as well as for Pu(VI)⁽²⁵⁾. It was, therefore, considered interesting to study the dependence of the distribution coefficient of Np(IV) and Np(VI) on the TBP concentration. The data were obtained on the variation of the distribution coefficient of Np(IV) and Np(VI) as a function of the TBP concentration ranging from 5% - 30% and are reported here.

4.1 Experimental

Extraction of Np(IV) and Np(VI) from 2 M nitric acid solution was investigated. The TBP solutions in SST were pre-equilibrated with 2 M nitric acid before use. Approximately 0.01 M ferrous sulphamate was used as the holding reductant for Np(IV) and 0.01 M $K_2Cr_2O_7$ was used as the holding oxidant for Np(VI). Both forward and reverse distribution data were obtained.

4.2 Results and observations

The distribution coefficient data obtained for the extraction of Np(IV) and Np(VI) from 2M nitric acid into different concentrations of TBP are given in Table 14. The forward and reverse distribution data were in good agreement with each other. A log-log plot of the distribution coefficient vs TBP concentration is shown in Figure 5. For Np(IV), the slope obtained is about 1.5 where as for Np(VI) it is 1.2 in the range 10-30% TBP concentration. These slopes are comparable to 1.1 and 1.4 reported for the extraction of U(VI)⁽¹⁵⁾ and Pu(VI)⁽²⁵⁾ respectively.

5. THE EFFECT OF NITROUS ACID ON THE EXTRACTION OF NEPTUNIUM BY TBP

It is known that nitrous acid can act both as an oxidizing agent and a reducing agent and depending on the experimental conditions, can oxidise Np(IV) to Np(V)⁽²⁷⁾ and Np(V) to Np(VI)⁽¹¹⁾ and as well reduce Np(VI) to Np(V)⁽²⁸⁾ and Np(V) to Np(IV)⁽²⁹⁾. In the purex process nitrous acid is added to the feed solution, to adjust the oxidation state of plutonium to Pu(IV) which is extractable by TBP. The beneficial effect of nitrous acid on neptunium extraction by TBP was observed in various separation plants^(30,31). As Np(VI) is the most extractable oxidation state of neptunium by TBP, conversion of the neptunium to Np(VI) would result in the maximum coextraction of neptunium by TBP in the purex process. The effect of nitrous acid on the extraction of Np(IV) and Np(V) by TBP, under the purex process conditions, was studied.

5.1 Experimental

5.1.1. Preparation of nitrite: A stock solution of NaNO_2 in water was made and the nitrite concentration was estimated volumetrically⁽³²⁾ by adding a known aliquot of the nitrite solution to an excess of the standard ceric

sulphate solution and then titrating the excess Ce(IV) with standard ferrous ammonium sulphate using ferroin as the indicator.

5.1.2 Preparation of Np(IV): About 100 μ g of Np-237 was mixed with a suitable amount of Np-239 and the mixture was reduced to Np(IV) by ferrous sulphamate ($\sim 0.01M$) in 1M nitric acid. The Np(IV) was then extracted into 0.5 M TTA and subsequently stripped from the organic phase into 8M nitric acid. This was the stock solution of Np(IV). Prior to use, the oxidation state of neptunium in the stock solution was checked by TTA extraction.

5.1.3 Preparation of Np(V): A stock solution of Np(V) was prepared by heating a Np(IV) solution, prepared as described above, in a dilute nitric acid solution ($\sim 0.5M$) for about an hour on a waterbath. This time was sufficient for the quantitative oxidation of Np(IV) to Np(V) as seen from the data presented in Table 15. The absence of Np(IV) in this solution was checked by the TTA extraction method and that of Np(VI) by the hexone extraction method.

5.1.4 Procedure: Aliquot of Np(IV) or Np(V) was pipetted into 1-4M nitric acid solutions in the absence as well as in the presence of a known amount of uranium followed by the addition of $NaNO_2$ to give an initial nitrite concentration of $2.9 \times 10^{-2} M$. The neptunium concentration was kept at 1-2 μ g/ml. After allowing a definite period for the reaction to proceed at the required temperature, these solutions were equilibrated with equal volumes of 30% TRP-SST. The experiments using Np(V) were done in the presence as well as in the absence of light. In a few experiments, after adding Np(V) and $NaNO_2$ into the nitric acid solutions containing uranium, air was bubbled through the solution for 15 minutes and then the solutions were kept for 2 hours before equilibrating with 30% TRP. At the end of the equilibration suitable

aliquots from both phases were removed and their gamma activity was counted using a NaI(Tl) scintillation counter.

5.2 Results and observations

The distribution coefficient of Np(IV) obtained as a function of nitric acid concentration and temperature under the conditions mentioned, are given in Table 16. Similar data in the presence of uranium are given in Table 17. The distribution coefficients of Np(IV) , using $\sim 0.01\text{M}$ ferrous sulphamate as the holding reductant and with no NaNO_2 addition, under identical conditions, at room temperature were obtained and included in these Tables for comparison. It is seen from the data in these two Tables as well as those presented in Table 18 that in the presence and the absence of uranium, Np(IV) was practically not affected by an initial nitrite concentration of $2.9 \times 10^{-2}\text{M}$. The data obtained on the distribution coefficient of neptunium, initially present in the aqueous phase as Np(V) are given in Table 19. It is seen from these data that the distribution coefficient of neptunium increases with increasing nitric acid concentration showing thereby that Np(V) is getting oxidised to Np(VI) by increasing the nitric acid concentration in the presence of $2.9 \times 10^{-2}\text{M}$ initial nitrous acid.

It was reported by Bahr⁽¹⁰⁾ that in the presence of light, particularly when TBP and uranium are present, Np(VI) is slowly reduced to Np(V) . To eliminate this possibility experiments were also done in the absence of light by covering the equilibration tubes with black paper and the data obtained are presented in Table 20. It is seen from these data that the extraction of neptunium increases with increasing nitric acid concentration and temperature but decreasing slightly with increasing nitrous acid concentration in the range of 2-4 M nitric acid.

After the addition of NaNO_2 the purex process feed solutions are usually mixed by air sparging. It is, therefore, considered desirable to study the effect of bubbling air after NaNO_2 addition to Np(V) before equilibrating the same with TBP. Table 21 gives the data on neptunium extraction into TBP in the presence of uranium after bubbling air for 15 minutes to the solution of Np(V) in nitric and nitrous acids and then leaving for 2 hours before equilibrating with TBP. From a comparison of the data presented in Tables 20 and 21, it can be said that air-sparging has little effect on the extraction of neptunium.

The role of nitrous acid in the oxidation of Np(V) to Np(VI) in nitric acid solutions may be represented by the equation (1)



The oxidising system $\text{NO}_3^-/\text{HNO}_2$ whose potential may be written as in equation (2) depends on the acidity (to the third power) on one hand,

$$E = 0.93 + \frac{RT}{2F} \log \frac{[\text{NO}_3^-] [\text{H}^+]^3}{[\text{HNO}_2]} \quad (2)$$

and on the concentration of HNO_2 on the other. It is clear that this system is more oxidising if the acidity is high and HNO_2 concentration low. The oxidation is more favoured in the presence of complexing agents like TBP which complexes and extracts Np(VI) . The role of nitrous acid in the oxidation of Np(V) to Np(VI) in the presence of TBP and uranium has already been discussed in the section 2.3.

6. REDUCTION OF Np(VI) AND Np(V) TO Np(IV) BY U(IV)

The separation of plutonium from uranium by reducing plutonium to Pu(III) is a familiar feature of the purex process. Most of the reducing agents

described^(33,34) for the purpose of separating plutonium from uranium in a solvent extraction process introduce "foreign" substances in the system e.g., cations like Fe^{+2} and Fe^{+3} and anions like SO_4^{-2} which disturb or complicate the subsequent purification steps and also add to the problems of corrosion and waste management. Since the conditions can easily be chosen so that the tetra and hexavalent actinides prefer the organic phase while the trivalent actinides remain in the aqueous phase^(35,36) the use of U(IV) as an alternative to ferrous sulphamate was studied by several workers⁽³⁷⁻⁴⁰⁾. As it is proposed to use U(IV) as a reducing agent in the partitioning cycle of the purex process in the PREFRE Plant at Tarapur it was considered interesting to study the effect of U(IV) on the reduction of Np(VI) and Np(V) to Np(IV) under the purex process conditions.

6.1 Experimental

6.1.1 Preparation of U(IV): Uranium (IV) was prepared by electrolytic reduction of 0.1 M uranyl nitrate solution in 2M nitric acid using mercury cathode⁽⁴⁰⁾ and was estimated spectrophotometrically by adding an excess of ferric chloride and o-phenanthroline to a known aliquot of U(IV) and measuring the ferrous phenanthroline at 506 m μ ⁽³⁶⁾. The reduction of Fe(III) to Fe(II) by U(IV) is rapid and complete⁽⁴¹⁾. As U(IV) is rapidly oxidised to U(VI)⁽⁴²⁾ in the presence of nitrite ions this was stabilized by killing HNO_2 with hydrazine. The amount of hydrazine in U(IV) was also estimated spectrophotometrically by complexing it with p-dimethylemine benzaldehyde⁽⁴³⁾.

6.1.2 Preparation of Np(V) and Np(VI): Neptunium (V) was prepared in the same way as described earlier in section 5.1.3. Neptunium(VI) was prepared by oxidising the neptunium with AgO . The excess of Ag(II) was destroyed by heating.

6.1.3 Procedure: An aliquot of Np(V) or Np(VI) was added to a solution having known uranium and nitric acid concentrations and an aliquot of U(IV) was then added to it to give the desired concentration of U(IV) . After allowing the reaction to proceed for a desired length of time, either in presence or in absence of light, the amount of Np(IV) formed was estimated by removing an aliquot from the reaction mixture, adjusting it to 1M in nitric acid and extracting the Np(IV) formed by 0.5 M TTA. Hydrazine concentration of 0.02 M and neptunium concentration of 1-10 $\mu\text{g/ml}$ were kept in all the experiments as it was observed that the rate of reduction to Np(IV) by U(IV) was not affected by varying the amounts of hydrazine in the range 0.01 - 0.1 M and neptunium concentration in the range 1 - 10 $\mu\text{g/ml}$. In some experiments with Np(VI) , Np(VI) was extracted into 30% TBP-SST along with U(VI) (to give $\sim 80 \text{ mg/ml}$ uranium in the organic phase) and this was equilibrated for a desired length of time with an aqueous phase of the desired concentration of U(IV) and nitric acid. At the end of the equilibration suitable aliquots from both phases were removed for gamma counting.

6.2 Results and observations

The rate of reduction of Np(V) by U(IV) in nitric acid is accelerated by the presence of uranyl nitrate as seen from the data presented in Figure 6. Figure 7 shows the effect of U(IV) concentration on the reduction of Np(V) to Np(IV) in the presence of uranium in 1M nitric acid and in the absence of light. Similar data in the presence of light at room temperature ($\sim 25^\circ\text{C}$), 45° and 60°C are respectively shown in Figures 8-10. Figure 11 shows the effect of U(IV) concentration on the reduction of Np(V) in the presence of uranium in 2M nitric acid at room temperature and in the absence of light. Similar data at 2 M nitric acid in the presence of light at room temperature, 45°C and 60°C are respectively shown in Figures 12-14. Figures 15 and 16 show the results on the reduction of Np(VI) by U(IV) in the absence of light

at 1M and 2M nitric acid concentrations respectively. Figure 17 shows the results on the reduction of Np(V) as well as Np(VI) at a neptunium concentration of $40\text{ }\mu\text{g/ml}$ in 1M nitric acid by 0.2 mg/ml U(IV) in the presence of 140 mg/ml uranyl nitrate both in the presence and the absence of light.

In the purex process U(IV) will be introduced in the partitioning cycle where plutonium, uranium and neptunium are present in the organic phase. Hence it was of interest to study the reduction of Np(VI) in the organic phase with U(IV) in the aqueous phase. Figures 18 and 19 show the results of equilibrating Np(VI) present in 30% TBP along with $\sim 60\text{ mg/ml}$ of uranyl nitrate with U(IV) present in the aqueous phase at 1M and 2M nitric acid respectively.

6.2.1 Effect of light: The data presented in Figure 17 and a comparison of the data presented in Figure 7 with Figure 8 and that in Figure 11 with Figure 12 reveal that the presence of light accelerates the rate of reduction of either Np(VI) or Np(V) to Np(IV) by U(IV) .

6.2.2. Effect of temperature: The data presented in Figures 8-10 and those in Figures 12-14 reveal that an increase in temperature favours the formation of Np(IV) appreciably.

6.2.3 Effect of nitric acid concentration: The data presented in Figures 7-10 and those in Figures 11-14 show that higher the nitric acid concentration faster the reduction of Np(V) to Np(IV) .

6.2.4 Effect of U(IV) concentration: The data presented in Figures 7-14 show that higher U(IV) concentration causes faster reduction of Np(V) to Np(IV) .

6.2.5 Comparison of the reduction of Np(VI) and Np(V) by U(IV) : It is seen from the data presented in Figures 7 and 11 and those in Figures 15 and 16 that the reduction of Np(VI) or Np(V) by U(IV) under identical conditions resulted in the same amount of Np(IV) in a definite period. This observation is contradictory to that reported by Solomon et al.⁽⁴⁴⁾ who observed that the reduction of Np(VI) to Np(IV) by U(IV) was faster than that of Np(V) to Np(IV) . To resolve this discrepancy the experiments of Solomon et al.⁽⁴⁴⁾ were repeated and the results are included in Figure 17. The data in this figure indicate that the reduction rates of Np(VI) and Np(V) are close to each other, the reduction of Np(V) being slightly faster than that of Np(VI) . It may be inferred that the reduction of Np(VI) to Np(IV) by U(IV) is a two-step process, i.e., almost instantaneous reduction to Np(V) and then slow reduction to Np(IV) .

6.2.6 Reduction of Np(VI) in TBP by aqueous U(IV) : From the data presented in Figure 19, it is seen that about 25% of the neptunium activity still remained in the organic phase when 1 mg/ml of U(IV) in 2M nitric acid was equilibrated with 30% TBP containing Np(VI) and U(VI) . It is likely that Np(VI) , which might have almost instantaneously reduced to Np(V) , might have further reduced to Np(IV) (especially in the presence of U(VI) which accelerates this reduction) which is extractable into 30% TBP. In order to confirm this an experiment was carried out wherein Np(VI) in the TBP phase, in the absence of U(VI) was equilibrated with 1 mg/ml of U(IV) in 2M nitric acid. It was found that after 20 minutes of equilibration only 6% of neptunium activity remained in the organic phase concluding thereby that the absence of U(VI) retarded the further reduction of Np(V) to Np(IV) .

7. REDOX REACTIONS OF INTEREST TO THE PUREX PROCESS

7.1 Oxidation of Pu(IV) by V(V): It is known that ~~maximum~~ coextraction of neptunium in the purex process, is possible when it is present as Np(VI) in the feed solution. Selective oxidation of Np(V) to Np(VI) by V(V) was reported by Dukes⁽⁴⁵⁾ and was successfully used for the coextraction of neptunium by Bahr and Koch⁽⁴⁶⁾. To achieve this it was proposed⁽⁴⁷⁾ to add V(V) to the feeds of the first and second cycles of the purex process to cause selective oxidation of neptunium species to Np(VI). Under these conditions, it is necessary that plutonium should remain as Pu(IV). Hence it was considered relevant to study the effect of V(V) on the oxidation state of Pu(IV), under the purex process conditions.

7.1.1 Experimental: A stock solution of Pu(IV) was prepared by adding a little H_2O_2 to a plutonium solution in 8M nitric acid and then destroying the excess H_2O_2 by heating. Vanadium(V) solution was prepared by dissolving L.R. grade V_2O_5 in dilute sodium hydroxide solution and then nitric acid was added to it to give the acidity of about 3M. The concentration of V(V) was estimated by reducing V(V) with excess Fe(II) to V(IV), oxidising the excess Fe(II) by peroxy disulphate and then titrating V(IV) with standard $KMnO_4$ solution⁽⁴⁸⁾. Suitable aliquots of Pu(IV), V(V) and nitric acid are mixed together to give the desired concentrations. The experiments were carried out in the absence of light and in a few cases in the presence of uranium. Suitable aliquots from the reaction mixture were withdrawn at various time intervals, and after adjusting the acidity to 1M in nitric acid the Pu(IV) was extracted into 0.5 M TTA. The plutonium which was not extracted by TTA was taken as the amount of Pu(VI) formed by oxidation due to V(V).

7.1.2 Results and Discussion: The results of the experiments carried out to study the effect of V(V) on Pu(IV) are given in Table 22. From these data it is seen that less than 10% of Pu(IV) was oxidized by V(V) and that the presence of uranium has little influence on this oxidation. In the purex process feed solution, however, even this small amount of Pu(VI) thus formed will be reduced to Pu(IV) by nitrous acid produced radiolytically which will also reduce most of V(V) thus preventing the oxidation of Pu(IV). It is anticipated that the addition of V(V) to the feed solution (first cycle or second cycle) will not have any adverse effect on the recoveries of plutonium.

7.2 The co-stability of Np(IV) and Pu(IV): When U(IV) is used as the partitioning agent, a major fraction of neptunium accompanies the aqueous stream as Np(V) assuming neptunium to be present as Np(VI) in the loaded organic stream entering the partitioning column^(49,50). However, if neptunium is present in the loaded organic stream entering the partitioning column as Np(IV), it can be made to follow uranium in the organic stream by a careful choice of nitric acid concentration^(30,49) irrespective of the reducing agent used for partitioning. To achieve this condition, it is necessary that the feed to the second cycle should contain neptunium as Np(IV) and plutonium should remain as Pu(IV). Champion and Chesne have established⁽⁵¹⁾ the conditions for stabilizing Np(IV) and Pu(IV) together by controlling the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio in the solution. However, this would require excess of Fe(III) added to the solution and this would add a large amount to the active wastes. It may be convenient to prepare Np(IV) and Pu(IV) together by first reducing the mixture of neptunium and plutonium to Np(IV) and Pu(III) by ferrous sulphate or U(IV) and then selectively oxidising Pu(III) to Pu(IV) by nitrous acid.

As seen from the data presented in section 5.2 Np(IV) is not affected by nitrous acid under these conditions. The stability of the Np(IV) and Pu(IV) mixture against oxidation-reduction needed investigation. The redox potential of the Pu(III)/Pu(IV) couple in 1M acid solution is - 0.92 V⁽⁵²⁾ and that of the Np(IV)/Np(V) couple is - 0.74 V⁽⁵³⁾. From these potential values, it is seen that the oxidation of Np(IV) to Np(V) by Pu(IV) is thermodynamically possible. The rate of this oxidation, under the purex process conditions at room temperature was studied.

7.2.1 Experimental: A stock solution of Np(IV) was prepared as described in section 5.1.2 and a stock solution of Pu(IV) was prepared as described in section 7.1.1. Suitable aliquots of Np(IV) and Pu(IV) were pipetted into a solution containing known concentrations of uranium and nitric acid. The experiments were carried out in the absence of light. Aliquots of this mixture were withdrawn, at different time intervals, into 1M nitric acid and the oxidation state of neptunium was determined by extraction with 0.5 M TTA. The neptunium which was not extracted by TTA was taken as the amount of Np(V) formed by oxidation due to Pu(IV) .

7.2.2 Results: The co-stability of Np(IV) and Pu(IV) in a synthetic solution similar to the expected feed solution in the Tarapur ^PPREFME plant was studied and the results are given in Tables 23 and 24. From these data, it is seen that more than 80% of Np(IV) remains unoxidised in the presence of Pu(IV) upto 8 hours. Thus it is possible to keep Np(IV) and Pu(IV) together to cause their co-extraction without the need to add any external reagent for this purpose.

7.3 Oxidation of Np(IV) by Pu(IV) at Higher temperatures.

To recover any neptunium which follows plutonium during the partitioning step, which can happen when neptunium is present as Np(VI) in the loaded organic stream and U(IV) is used as the partitioning agent, it is necessary to force it to the raffinate of the plutonium purification cycle. This can be achieved by adjusting the oxidation state of neptunium in the feed of this cycle to Np(V). The plutonium product stream from the partitioning column will contain neptunium mainly as Np(V) which will be reduced to Np(IV) by U(IV) during the hold-up period. When this solution containing Pu(III) and Np(IV) is conditioned with nitrite, to oxidise Pu(III) to Pu(IV) for plutonium purification cycle, the oxidation state of Np(IV) will remain unchanged. The feed thus conditioned for the plutonium purification cycle will contain neptunium as Np(IV) which will be coextracted with Pu(IV) in this cycle. To prevent this coextraction of neptunium it is necessary to oxidise Np(IV) in this feed to the nonextractable Np(V). As the oxidation of Np(IV) to Np(V) by Pu(IV) at room temperature, was found to be very slow as seen from the data presented in section 7.2.2. the same was attempted at higher temperatures and the results are reported here.

7.3.1 Experimental: The experimental procedure for these experiments is the same as that described in section 7.2.1 except that uranium is absent in the present experiments.

7.3.2 Results and discussion: The data obtained on the oxidation of Np(IV) by Pu(IV) at higher temperatures are given in Table 25. It is seen from these data that Np(IV) can be oxidised almost quantitatively, in 2M nitric acid, by Pu(IV) at higher temperatures. The composition of the solution used for these studies is similar to the anticipated feed solution composition of the plutonium

purification cycle in the Tarapur Plant assuming 50% and 100% of the total neptunium follows the plutonium stream during the partitioning step. The feed tanks of the plutonium purification cycle in the Tarapur Plant are provided with heating jackets and the hold-up time in these tanks is expected to be 35-40 minutes. It is, therefore, possible to oxidize Np(IV) in this feed to Np(V) in this period of time. All the neptunium present as Np(V) will then follow the aqueous raffinate from which neptunium can be recovered either by combining it with the raffinate from uranium purification cycle and using anion exchange process or by backcycling it to the process for the accumulation of neptunium.

3. CONCLUSIONS

It is seen from the data presented in this report that:

- i) neptunium exists mainly as Np(V) in the feed of the co-decontamination cycle of the purex process. As Np(VI) is the most extractable oxidation state of neptunium use of nitrous acid or vanadium(V) to cause the oxidation of neptunium to Np(VI) would be necessary to achieve the maximum co-extraction of neptunium in the purex process.
- ii) even at higher temperatures upto 60°C it is possible to co-extract neptunium which was present in the feed either as Np(VI) or Np(IV) by a suitable choice of the nitric acid and uranium concentrations.
- iii) nitrous acid helps in the extraction of neptunium, especially at high nitric acid concentration, by TBP even if it was originally present as Np(V) . Also it is seen that nitrous acid has no effect on the oxidation state of Np(IV) under the purex process conditions.

iv) Uranium(IV) reduced Np(VI) almost instantaneously to Np(V) and that further reduction to Np(IV) is slow. Thus the use of U(IV) as the partitioning agent would cause diversion of a major fraction of neptunium to the plutonium stream if the neptunium in the loaded organic stream entering the partitioning column was present as Np(VI) .

v) the use of redox reactions involving V(V) , Np(IV) and Pu(IV) and temperature gives various alternatives to force neptunium to the desired stream.

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Table 1

COPRECIPITATION OF Np(IV) ON LaF_3

$[\text{Np}] = 1-2 \text{ } \mu\text{g/ml}$; $[\text{HNO}_3] = 1 \text{ M}$; $[\text{U}] = 100 \text{ mg/ml}$; $[\text{F}^{+2}] = 0.01 \text{ M}$

Total La = 10 mg; Volume of conc. HF added = 1 ml; Total volume = 9 ml

Ex. No.	Initial total ^{239}Np activity, cpm	Final ^{239}Np activity left in the supernate, cpm	% Np(IV) carried on LaF_3
1	52267	990	98.1
2	52510	676	98.7

Table 2

COPRECIPITATION OF Np(V) ON LaF_3

$[\text{Np}] = 1-2 \mu\text{g/ml}$; $[\text{HNO}_3] = 1 \text{ M}$; Total La = 10 mg

Ex. No.	Volume of conc. HF added, ml	Total volume, ml	Initial total ^{239}Np activity opm	Final ^{239}Np activity left in the supernate opm	% Np(V) carried on LaF_3
1	1	9	71184	4059	94.3
2	1	9	72912	3150	95.7
3	1	9	75208	2866	96.2
4	2	5	207695	588	99.7
5	2	5	207695	735	99.7
6	2	3	207695	492	99.8
7	2	3	207695	573	99.7

Note: Np(V) used in experiments no.1-3 was prepared by oxidising Np in 1M HNO_3 with $0.01\text{N K}_2\text{Cr}_2\text{O}_7$ and then reducing it to Np(V) with 4-5 mg/ml of NaNO_2 . Np(V) used in experiments no.4-7 was prepared by oxidation of Np(IV) from $\sim 0.05\text{M HNO}_3$ by keeping it in a hot water bath for about 2 hours.

Table 3

COPRECIPITATION OF Np(V) ON LaF_3 IN PRESENCE OF URANIUM

[Np] = 1-2 $\mu\text{g/ml}$; $[\text{HNO}_3]$ = 1 M; [U] = 100 mg/ml

Total volume = 5 ml; Initial total ^{239}Np activity = 518305 cpm

Ex. No.	Amount of La , mg	Volume of conc. HF added, ml	Final ^{239}Np activity left in the supernate, cpm	% Np (V) carried on LaF_3
1	10	1	0	100
2	10	1	300	99.91
3	10	2	100	99.97
4	10	2	65	99.98
5	5	1	410	99.98
6	5	1	295	99.91
7	5	2	430	99.87
8	5	2	235	99.93

Note: Np(V) was prepared by oxidizing Np in 1 M HNO_3 with 0.01 M ceric ammonium nitrate and then reducing it to Np(V) with NaNO_2 .

Table 4

COPRECIPITATION OF Hf(VI) ON LaF_3

$[\text{Hf}] = 1\text{--}2 \mu\text{g/ml}$; $[\text{HNO}_3] = 1\text{M}$; $[\text{Ce(IV)}] = 0.01 \text{ M}$

Amount of $\text{La} = 10 \text{ mg}$; Volume of conc. HF added $\approx 1 \text{ ml}$; Total volume $\approx 9 \text{ ml}$

Ex. No.	Initial total ^{239}Hf activity, cpm	Final ^{239}Hf activity left in the supernate, cpm	% Hf(VI) carried on LaF_3
1	193092	193540	H11
2	201816	204660	H11
3	91068	91255	H11
4	90540	91705	H11
5	91744	91912	H11
6	93392	94090	H11
7	131772	132971	H11
8	142060	146632	H11
9*	131404	132361	H11
10*	129104	132525	H11

* About 100 $\mu\text{g/ml}$ uranium was present in these experiments

Table 5

OXIDATION STATE ANALYSIS OF NEPTUNIUM IN
THE FIRST CYCLE FEED

Sample No.	[HNO ₃] M	** [Total Np] µg/ml	[Np(IV)] µg/ml	[Np(V)] µg/ml	[Np(VI)] µg/ml	Time elapsed between sampling and analysis
1	5.3	1.09	0.35	0.69	0.05	3 weeks
2	4.8	0.98	0.35	0.66	N11	2 days
3	4.8	0.98	0.35	0.65*	N11	2 days
4	2.2	1.83	0.07	1.75	N11	3 weeks
5	1.9	1.48	0.01	1.49	N11	2 days
6	3.5	0.96	0.07	0.94	N11	2 days
7	3.5	0.96	0.07	0.92*	N11	2 days
8	1.9	1.74	0.02	1.66	0.06	4 days
9	3.6	1.00	0.09	0.89	N11	2 days
10	3.6	1.00	0.09	0.91*	N11	2 days

No.1-7 feed conditioned with NaNO₂

No.8-10 feed not conditioned.

* Np(V) assay by using hexone to remove Np(IV) and Np(VI)

** Acidity analysis data obtained from the control laboratory,
Plutonium Plant.

Table 6

EQUILIBRIUM DATA AND VARIATION OF THE DISTRIBUTION COEFFICIENT OF NITRIC ACID,
U(VI), Np(VI) AND Np(IV) WITH ORGANIC PHASE URANIUM CONCENTRATION

Initial concentration of HNO_3 in Aq. Phase = 1 M

Temperature = 45°C

Expt. No.	Initial concn. of U in Aq. phase mg/ml	Equilibrium concn. of U, mg/ml		Equilibrium Acidity M		Distribution coefficient (K_d)				$\frac{K_d \text{ U(VI)}}{K_d \text{ Np(VI)}}$	$\frac{K_d \text{ Np(VI)}}{K_d \text{ Np(IV)}}$
		Aq.	Org.	Aq.	Org.	HNO ₃	U(VI)	Np(VI)	Np(IV)		
1	0	0	0	1.02	0.19	0.19	—	3.60	0.80	—	4.5
2	27.1	4.4	22.8	1.05	0.16	0.15	5.17	2.81	0.54	1.84	5.2
3	54.2	10.6	40.5	1.08	0.13	0.12	3.84	2.10	0.36	1.85	5.8
4	103.4	32.9	66.3	1.13	0.10	0.09	2.08	1.20	0.19	1.73	6.3
5	162.6	66.1	83.8	1.14	0.087	0.076	1.27	0.76	0.12	1.67	6.0
6	216.8	104.0	98.5	1.17	0.077	0.066	0.95	0.52	0.087	1.63	6.0
7	271.0	162.0	101.0	1.18	0.068	0.058	0.62	0.38	0.071	1.63	5.4

Table 7

EQUILIBRIUM DATA AND VARIATION OF THE DISTRIBUTION COEFFICIENT OF NITRIC ACID,
U(VI), Np(VI) AND Np(IV) WITH ORGANIC PHASE URANIUM CONCENTRATION

Initial concn. of HNO_3 in Aq. phase = 2 M

Temperature = 45°C

Expt. No.	Initial concn. of U in Aq. phase mg/ml	Equilibrium concn. of U, mg/ml		Equilibrium Acidity M		Distribution coefficient (K_d)				$\frac{K_d \text{U(VI)}}{K_d \text{Np(VI)}}$	$\frac{K_d \text{Np(VI)}}{K_d \text{Np(IV)}}$
		Aq.	Org.	Aq.	Org.	HNO ₃	U(VI)	Np(VI)	Np(IV)		
1	0	0	0	1.95	0.474	0.24	—	7.91	2.34	—	3.4
2	30	2.64	28.0	2.08	0.373	0.18	10.6	5.64	1.52	1.68	3.7
3	60	7.65	51.3	2.16	0.283	0.13	6.7	3.64	0.89	1.84	4.1
4	120	32.0	84.8	2.27	0.183	0.081	2.65	1.42	0.34	1.87	4.2
5	180	77.9	94.0	2.34	0.139	0.059	1.21	0.70	0.17	1.73	4.1
6	240	130.0	105.6	2.35	0.102	0.043	0.81	0.45	0.13	1.80	3.5
7	300	184.5	111.0	2.39	0.093	0.039	0.60	0.33	0.11	1.82	3.0

Table 6

EQUILIBRIUM DATA AND VARIATION OF THE DISTRIBUTION COEFFICIENT OF NITRIC ACID,
U(VI), Np(VI) AND Np(IV) WITH ORGANIC PHASE URANIUM CONCENTRATION

Initial concentration of HNO_3 in Aq. phase = 3M

Temperature = 45°C.

Expt. No.	Initial concn. of U in Aq. phase mg/ml	Equilibrium concn. of U, mg/ml		Equilibrium Acidity M		Distribution coefficient (K_d)				$\frac{\Sigma_d \text{ U(VI)}}{K_d \text{ Np(VI)}}$	$\frac{K_d \text{ Np(VI)}}{K_d \text{ Np(IV)}}$
		Aq.	Org.	Aq.	Org.	HNO ₃	U(VI)	Np(VI)	Np(IV)		
1	0	0	0	2.98	0.68	0.23	—	10.79	4.05	—	2.7
2	30	1.83	27.7	3.13	0.56	0.18	15.10	7.52	2.65	2.00	2.8
3	60	6.08	51.3	3.27	0.44	0.13	8.43	4.64	1.61	1.82	2.9
4	120	27.5	86.6	3.48	0.26	0.075	3.15	1.51	0.55	2.10	2.7
5	180	73.4	98.0	3.54	0.18	0.051	1.34	0.67	0.25	2.00	2.7
6	240	128.0	102.0	3.59	0.15	0.042	0.80	0.43	0.19	1.86	2.3
7	300	185.0	116.0	3.60	0.13	0.036	0.63	0.30	0.16	2.10	1.9

Table 2

EQUILIBRIUM DATA AND VARIATION OF THE DISTRIBUTION COEFFICIENT OF NITRIC ACID,
U(VI), Np(VI) AND Np(IV) WITH ORGANIC PHASE URANIUM CONCENTRATION

Initial concentration of HNO_3 in Aq. phase = 4M

Temperature = 45°C

Expt. No.	Initial concn. of U in Aq. phase mg/ml	Equilibrium concn. of U, mg/ml		Equilibrium Acidity M		Distribution coefficient (K_d)				$\frac{K_d \text{ U(VI)}}{K_d \text{ Np(VI)}}$	$\frac{K_d \text{ Np(VI)}}{K_d \text{ Np(IV)}}$
		Aq.	Org.	Aq.	Org.	HNO ₃	U(VI)	Np(VI)	Np(IV)		
1	0	0	0	4.00	0.83	0.21	—	12.53	6.20	—	2.0
2	30	1.64	27.4	4.09	0.65	0.16	16.71	8.38	4.12	1.99	2.0
3	60	5.21	51.4	4.26	0.50	0.12	9.87	4.99	2.48	1.96	2.0
4	120	30.6	85.2	4.53	0.27	0.06	2.78	1.36	0.79	2.04	1.7
5	180	78.6	100.5	4.70	0.20	0.042	1.28	0.64	0.40	2.00	1.6
6	240	129.0	100.5	4.73	0.17	0.036	0.78	0.40	0.29	1.93	1.4
7	300	193.0	107.5	4.74	0.15	0.032	0.56	0.29	0.26	1.93	1.1

TABLE 10

EQUILIBRIUM DATA AND VARIATION OF THE DISTRIBUTION COEFFICIENT OF NITRIC ACID,
U(VI), Np(VI) AND Np(IV) WITH ORGANIC PHASE URANIUM CONCENTRATION

Initial concentration of HNO_3 in Aq. phase = 1M

Temperature = 60°C

Expt. No.	Initial concn. of U in Aq. phase mg/ml	Equilibrium concn. of U, mg/ml		Org. M	Distribution coefficient (K_d)		$\frac{K_d \text{ U(VI)}}{K_d \text{ Np(VI)}}$	$\frac{K_d \text{ Np(VI)}}{K_d \text{ Np(IV)}}$
		Aq.	Org.	Aq.	HNO_3	U(VI)	Np(VI)	Np(IV)
1	0	0	0	1.03	0.18	0.17	2.73	0.61
2	27.1	6.0	21.5	1.04	0.152	0.15	3.58	0.51
3	54.2	14.0	39.0	1.07	0.132	0.12	2.79	0.40
4	108.4	37.8	67.7	1.11	0.105	0.095	1.79	0.26
5	162.6	73.5	61.0	1.14	0.090	0.080	1.10	0.19
6	216.8	113.0	95.0	1.16	0.082	0.070	0.84	0.16
7	271.0	160.5	102.0	1.16	0.076	0.066	0.64	0.15

3.37

4.27

4.20

4.04

3.63

3.13

2.60

Table 11

EQUILIBRIUM DATA AND VARIATION OF THE DISTRIBUTION COEFFICIENT OF NITRIC ACID,
U(VI), Np(VI) AND Np(IV) WITH ORGANIC PHASE URANIUM CONCENTRATION

Initial concentration of HNO_3 in Aq. phase = 2M

Temperature = 60°C

Expt. No.	Initial concn. of U in Aq. phase mg/l	Equilibrium concn. of U, mg/ml		Equilibrium Acidity M		Distribution coefficient (K_d)				$\frac{K_d \text{ U(VI)}}{K_d \text{ Np(VI)}}$	$\frac{K_d \text{ Np(VI)}}{K_d \text{ Np(IV)}}$
		Aq.	Org.	Aq.	Org.	HNO ₃	U(VI)	Np(VI)	Np(IV)		
1	0	0	0	2.00	0.445	0.220	—	5.97	2.76	—	2.16
2	30	3.6	25.5	2.05	0.359	0.175	7.08	4.41	1.87	1.61	2.36
3	60	9.6	51.5	2.13	0.288	0.135	5.36	2.89	1.18	1.85	2.45
4	120	36.3	83.5	2.24	0.188	0.084	2.30	1.24	0.52	1.85	2.38
5	180	80.8	94.5	2.29	0.142	0.062	1.17	0.68	0.29	1.72	2.34
6	240	134.5	108.0	2.30	0.115	0.050	0.80	0.45	0.22	1.78	2.05
7	300	186.0	107.0	2.33	0.103	0.044	0.58	0.33	0.20	1.76	1.65

Table 12

EQUILIBRIUM DATA AND VARIATION OF THE DISTRIBUTION COEFFICIENT OF NITRIC ACID, U(VI), Np(VI) AND Np(IV) WITH ORGANIC PHASE URANIUM CONCENTRATION

Initial concentration of HNO_3 in Aq. phase = 3M

Temperature = 60°C.

Expt. No.	Initial concn. of U in Aq. phase mg/ml	Equilibrium concn. of U, mg/ml		Equilibrium Acidity M		Distribution coefficient (K_d)				$\frac{K_d \text{ U(VI)}}{K_d \text{ Np(VI)}}$	$\frac{K_d \text{ Np(VI)}}{K_d \text{ Np(IV)}}$
		Aq.	Org.	Aq.	Org.	HNO ₃	U(VI)	Np(VI)	Np(IV)		
1	0	0	0	2.92	0.638	0.22	---	8.11	4.84	---	1.68
2	30	2.50	26.9	3.09	0.529	0.17	10.76	5.62	3.27	1.91	1.72
3	60	7.42	57.5	3.22	0.420	0.13	7.75	3.49	2.04	2.22	1.71
4	120	32.9	75.5	3.42	0.265	0.077	2.29	1.27	0.81	1.60	1.57
5	180	61.0	94.0	3.51	0.194	0.055	1.16	0.65	0.42	1.78	1.55
6	240	139.7	102.3	3.54	0.168	0.047	0.73	0.41	0.31	1.78	1.32
7	300	183.5	102.3	3.56	0.151	0.042	0.56	0.31	0.28	1.81	1.11

Table 13

EQUILIBRIUM DATA AND VARIATION OF THE DISTRIBUTION COEFFICIENT OF NITRIC ACID,
U(VI), Np(VI) AND Np(IV) WITH ORGANIC PHASE URANIUM CONCENTRATION

Initial concentration of HNO_3 in Aq. phase = 4M

Temperature = 60°C

Expt. No.	Initial concn. of U in Aq phase mg/ml	Equilibrium concn. of U, mg/ml		Equilibrium Acidity, Distribution coefficient (K_d) M		Equilibrium Acidity, Distribution coefficient (K_d)				$\frac{K_d \text{ U(VI)}}{K_d \text{ Np(VI)}}$	$\frac{K_d \text{ Np(VI)}}{K_d \text{ Np(IV)}}$
		Aq.	Org.	Aq.	Org.	HNO ₃	U(VI)	Np(VI)	Np(IV)		
1	0	0	0	4.03	0.828	0.21	—	0.70	7.01	—	1.24
2	30	2.49	27.3	4.15	0.665	0.16	10.96	5.87	4.71	1.87	1.25
3	60	7.35	51.2	4.22	0.519	0.12	6.97	3.34	2.96	2.09	1.13
4	120	35.2	80.0	4.51	0.319	0.071	2.27	1.16	1.12	1.96	1.04
5	180	82.0	94.5	4.59	0.242	0.053	1.15	0.58	0.62	1.98	0.94
6	240	135.5	107.5	4.63	0.206	0.044	0.79	0.38	0.48	2.08	0.79
7	300	192.0	105.0	4.65	0.190	0.041	0.55	0.30	0.41	1.83	0.73

Table 14

VARIATION OF THE DISTRIBUTION COEFFICIENT OF Np(IV) AND Np(VI) WITH TRP CONCENTRATION

Aqueous phase = 2M HNO₃

Diluent = Shell sol-T

Exp. No.	[TBP] Vol%	[TBP] M	[TBP. HNO ₃] M	[TBP] _{Free} M	Distribution coefficient of			
					Np(IV)		Np(VI)	
					Forward	Reverse	Forward	Reverse
1	5	0.183	0.066	0.117	0.100	0.099	1.05	1.02
2	10	0.365	0.138	0.227	0.395	0.375	2.96	2.94
3	15	0.548	0.215	0.333	0.798	0.775	4.77	4.86
4	20	0.731	0.294	0.437	1.25	1.23	6.75	6.80
5	25	0.913	0.358	0.555	1.78	1.79	8.97	8.85
6	30	1.096	0.451	0.645	2.25	2.27	10.10	10.30

Table 15

OXIDATION OF Np(IV) IN NITRIC ACID

[Np] = 1-2 $\mu\text{g/ml}$; [HNO₃] = 0.28 M; Temperature = 70°C

Time of reaction, min	% Np(IV) remained
0	100
5	81
10	69
15	63
25	45
35	19
45	7
60	0.5
120	0

Note: Np(IV) determined by extraction with 0.5M TPA
from 1.0 M nitric acid medium.

Table 16

EFFECT OF NITROUS ACID ON THE DISTRIBUTION OF
Np(IV) IN NITRIC ACID - 30% TBP

[Np] = 1-2 $\mu\text{g/ml}$; Initial aqueous $[\text{HNO}_2]$ = 0.029 M

Reaction time = 2 hours; Time of equilibration = 5 min.

$[\text{HNO}_3]$ M	Distribution coefficient (K_d) obtained after allowing the reaction to proceed at			K_d of Np(IV) using 0.01 M Fe^{+2} as holding reductant
	Room temp	45°C	60°C	
1	1.26	1.28	1.07	1.40
2	1.90	1.90	1.79	2.64
3	2.87	2.92	2.87	2.95
4	4.14	4.14	4.21	4.20

Table 17

EFFECT OF NITROUS ACID ON THE DISTRIBUTION OF Np(IV)
IN NITRIC ACID - 30% TBP IN PRESENCE OF URANIUM

[Np] = 1-2 $\mu\text{g/ml}$; Initial aqueous $[\text{HNO}_2]$ = 0.029 M

Saturation of 30% TBP by uranium $\approx$ 65%

Reaction time = 24 hours; Time of equilibration = 5 min.

[HNO ₃] M	Distribution coefficient (K_d) obtained after allowing the reaction to proceed at			K_d of Np(IV) using 0.01 M Fe ⁺² as holding reductant
	Room temp.	45°C	60°C	
1	0.091	0.079	0.076	0.097
2	0.25	0.22	0.22	0.23
3	0.45	0.45	0.45	0.43
4	0.72	0.76	0.76	0.74

Table 10

EFFECT OF NITRIC ACID ON Np(IV) OXIDATION

$[\text{Np}] = 4.5 \text{ } \mu\text{g/ml}$; Initial aqueous $[\text{HNO}_3] = 0.029 \text{ M}$

Reaction time = 24 hours

$[\text{HNO}_3]$ M	% Np(IV) remaining	
	In absence of uranium	In presence of uranium
1	99.4	99.2
2	97.4	97.6
3	96.9	97.6
4	95.6	97.3

Note: Np(IV) determined by TTA extract. on.

* Initial Aq U conc. of 140 $\mu\text{g/ml}$ for 1M and about 100 $\mu\text{g/ml}$ for 2-4M nitric acid.

Table 19

EFFECT OF NITROUS ACID ON THE DISTRIBUTION OF Np PRESENT
AS $Np(V)$ IN NITRIC ACID - 30% TBP

$[Np]$ = 2-3 $\mu g/ml$; Initial aqueous $[HNO_2]$ = 0.029 M

Time of equilibration = 5 min.

$[HNO_3]$, M	Reaction time, hours	K_d
1	3	0.05
2	2	0.13
3	2	0.35
4	2	0.64

Table 20

EFFECT OF NITROUS ACID ON THE DISTRIBUTION OF Np PRESENT AS Np(V)
IN NITRIC ACID - 30% TBP IN PRESENCE OF URANIUM

$[Np] = 5-10 \mu g/ml$; $[U] = 100 \text{ mg/ml}$ (initial Aq conc.)

Reaction time = 2 hours; Time of equilibration = 20 min.

$[HNO_3]$ M	Initial aqueous $[HNO_2]$, M	Distribution coefficient (K_d) obtained after allowing the reaction to proceed at		
		Room temp.	45°C	60°C
2	0.029	0.097	0.12	0.17
3	0.029	0.30	0.38	0.55
4	0.029	0.51	0.53	0.90
2	0.072	0.069	0.10	0.13
3	0.072	0.23	0.32	0.43
4	0.072	0.51	0.59	0.70

Notes: Experiments were done in the absence of light.

Table 21

EFFECT OF AIR-SPARGING ON THE DISTRIBUTION OF Np PRESENT
AS Np(V) IN NITRIC ACID - 30% TBP

$[\text{Np}] = 4-5 \mu\text{g/ml}; [\text{U}] = 100 \text{ mg/ml};$

Initial aqueous $[\text{HNO}_2] = 0.029 \text{ M}$

$[\text{HNO}_3], \text{ M}$	K_d
2	0.105
3	0.31
4	0.47

Table 22

OXIDATION OF Pu(IV) BY V(V)

Initial [Pu(IV)] = 2 mg/ml; Initial [V(V)] = 0.01 M

Time of reaction, hours	% Pu(IV) remained at	
	1M HNO ₃	3M HNO ₃
0.33	98.9	99.2
1.33	98.1	98.9
3	96.9	99.0
4	95.8	98.7
5	95.5	98.1
22*	91.4	98.4
25	91.4	98.3
28	90.6	98.2

* After assaying for the Pu(IV) valence after 22 hours,

uranium was added to give a concentration of 100 ng/ml

and the reaction was further followed.

Table 23

CO-STABILITY OF Np(IV) AND Pu(IV)

[U] = 50 mg/ml; [Pu(IV)] = 116 µg/ml;

Initial [Np(IV)] = 12 µg/ml

Time of reaction hours	% Np(IV) remained at	
	2M HNO ₃	3 M HNO ₃
2	99	99
4	98	98
6	98	97
22	96	98
46	92	97

Note: Initially Np(V) was added to a mixture of U and Pu and subsequently Np(V) was reduced to Np(IV) by adding 0.5 mg/ml of U(IV) and keeping it for 2 hours. The Pu(III) formed was then oxidised to Pu(IV) by adding NaNO₂. The reaction kinetics were followed after the addition of NaNO₂.

Table 24

CO-STABILITY OF Np(IV) AND Pu(IV)

Ex. No.	Initial composition	Time of reaction, hrs	% Np(IV) remained
1	[U] = 33 mg/ml; [Pu(IV)] = 60 µg/ml; [Np(IV)] = 2-3 µg/ml; [HNO ₃] = 2M.	2	99.0
		5	98.6
		6	98.5
		48	93.3
2	[U] = 50 mg/ml; [Pu(IV)] = 116 µg/ml; [Np(IV)] = 5 µg/ml; [HNO ₃] = 3M.	2	96.9
		4	96.9
		24	96.8
		54	96.6
3	[U] = 352 mg/ml; [Pu(IV)] = 2 mg/ml; [Np(IV)] = 135 µg/ml; [HNO ₃] = 2.4M.	2	96.4
		4	92.6
		8	85.9
		24	57.7
4	[U] = 294 mg/ml; [Pu(IV)] = 1 mg/ml; [Np(IV)] = 67 µg/ml; [HNO ₃] = 2.1M.	0	99.4
		2	95.3
		4	90.4
		6	85.8
		20	54.8

Table 25

OXIDATION OF Np(IV) BY Pu(IV)

[Pu(IV)] = 2.26 mg/ml

Ex. No.	Initial [Np(IV)] µg/ml	Temperature °C	Time of reaction min.	% Np(IV) oxidised in	
				2M HNO ₃	3M HNO ₃
1	113	50	15	67	14.2
			30	93	29.2
2	57	50	15	65	14.6
			30	87	29.0
3	113	60	15	97.6	45.0
			30	99.5	74.5
4*	113	60	15	1.1	---
			30	2.4	---

* Ex. No. 4, Pu was absent.

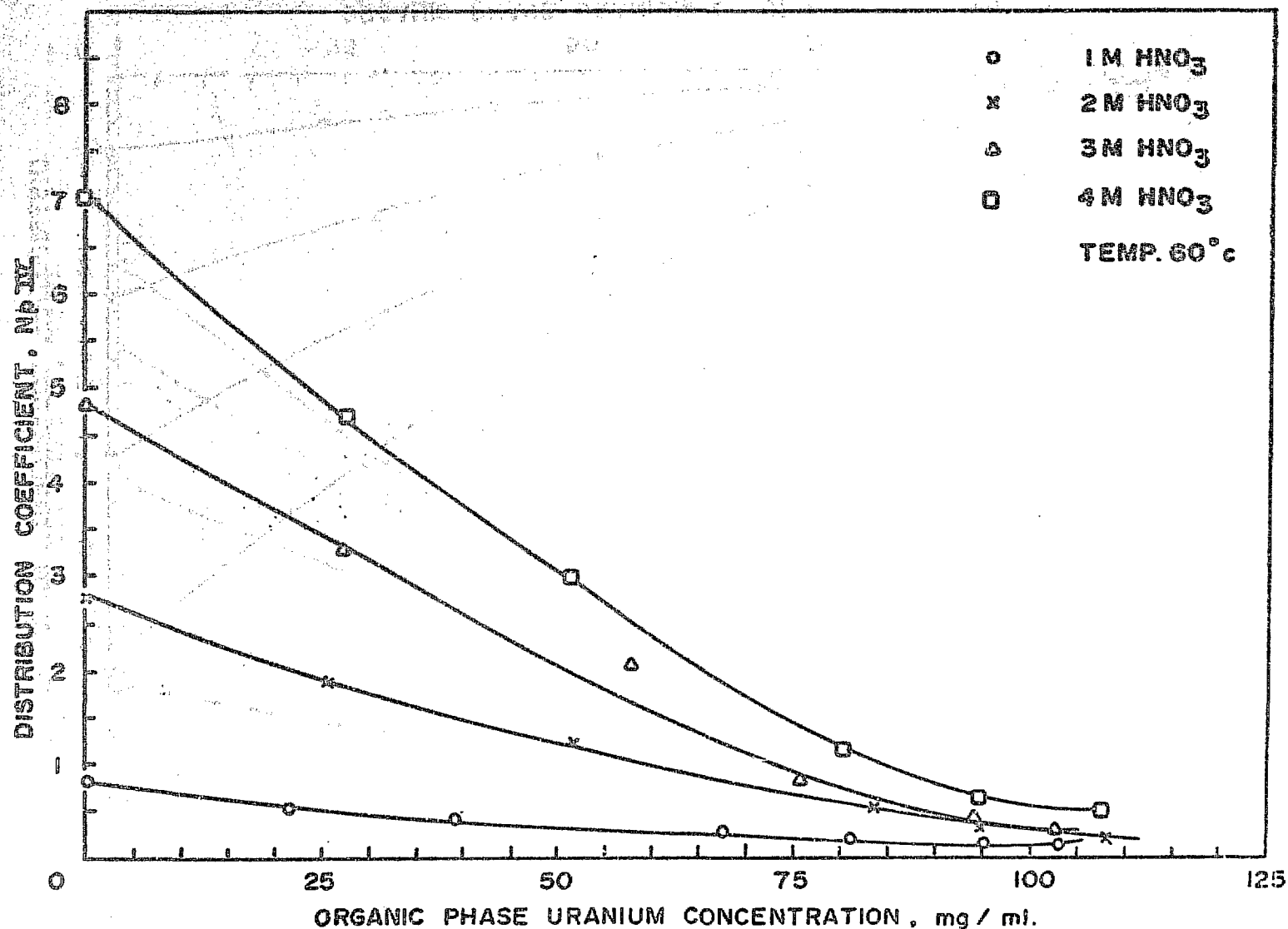


FIGURE-2. VARIATION OF THE DISTRIBUTION COEFFICIENT OF Np(IV) WITH ORGANIC PHASE URANIUM CONCENTRATION.

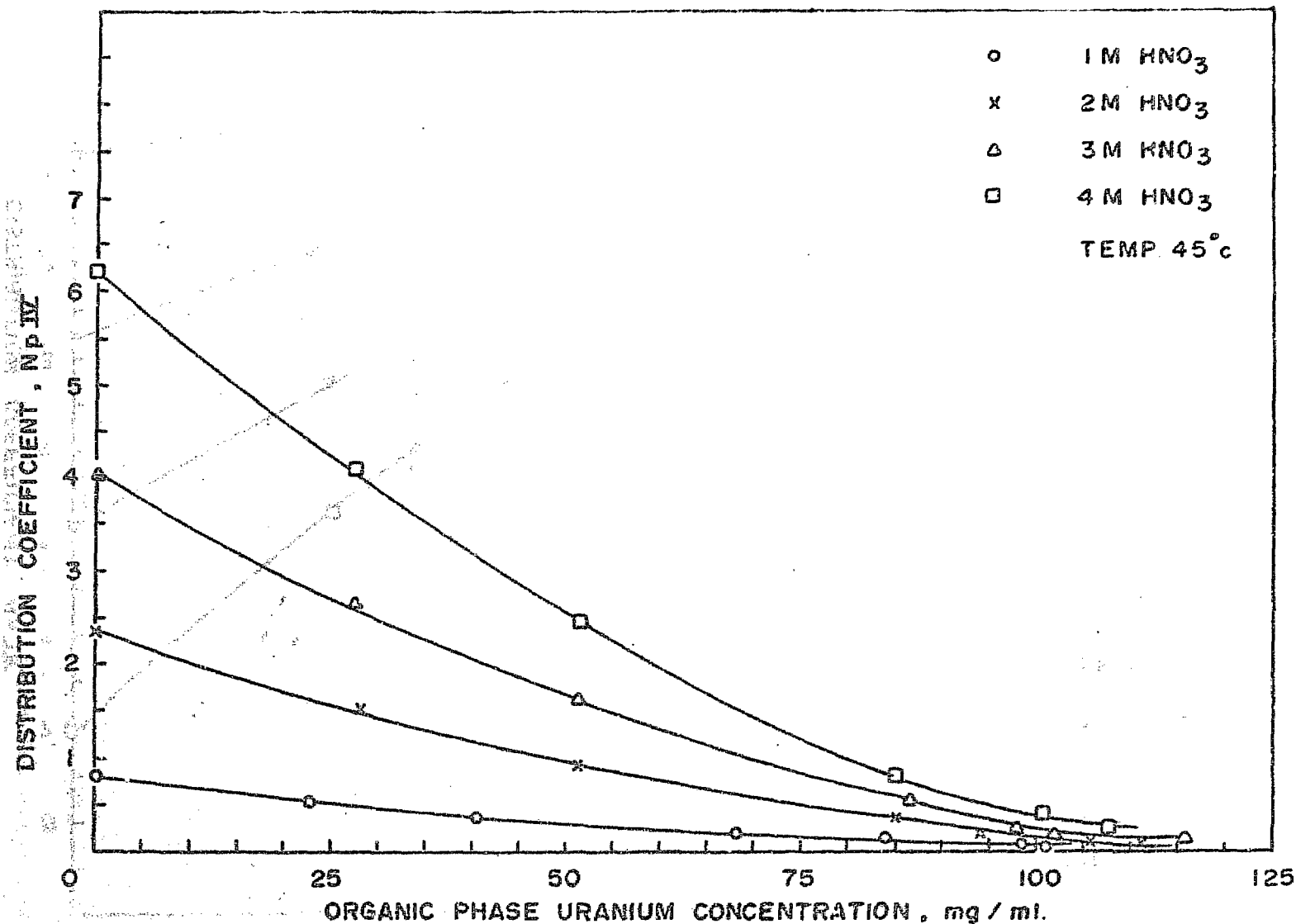


FIGURE - I. VARIATION OF THE DISTRIBUTION COEFFICIENT OF Np (IV) WITH ORGANIC PHASE URANIUM CONCENTRATION.

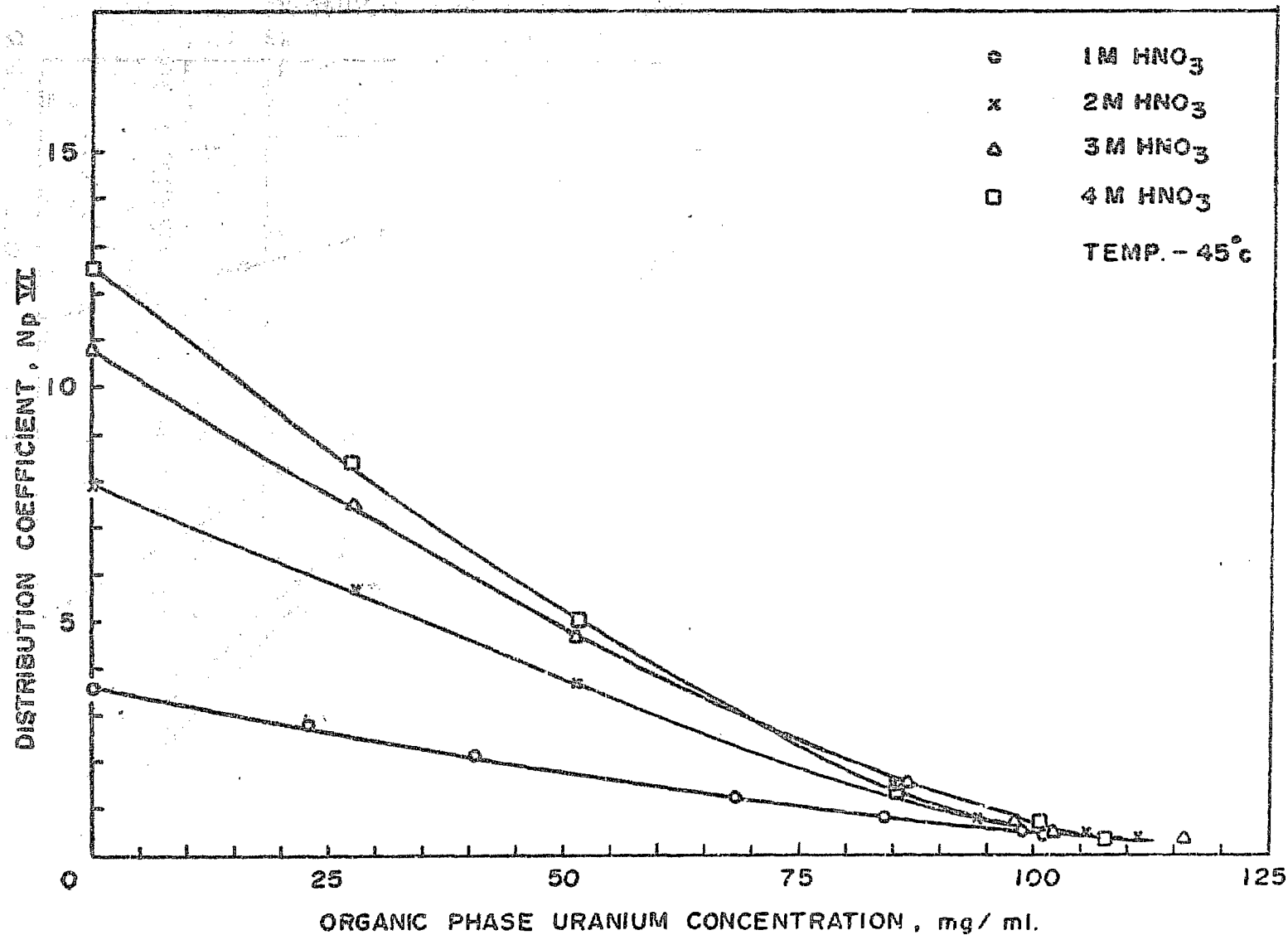


FIGURE-3. VARIATION OF THE DISTRIBUTION COEFFICIENT OF Np(VI) WITH ORGANIC PHASE URANIUM CONCENTRATION.

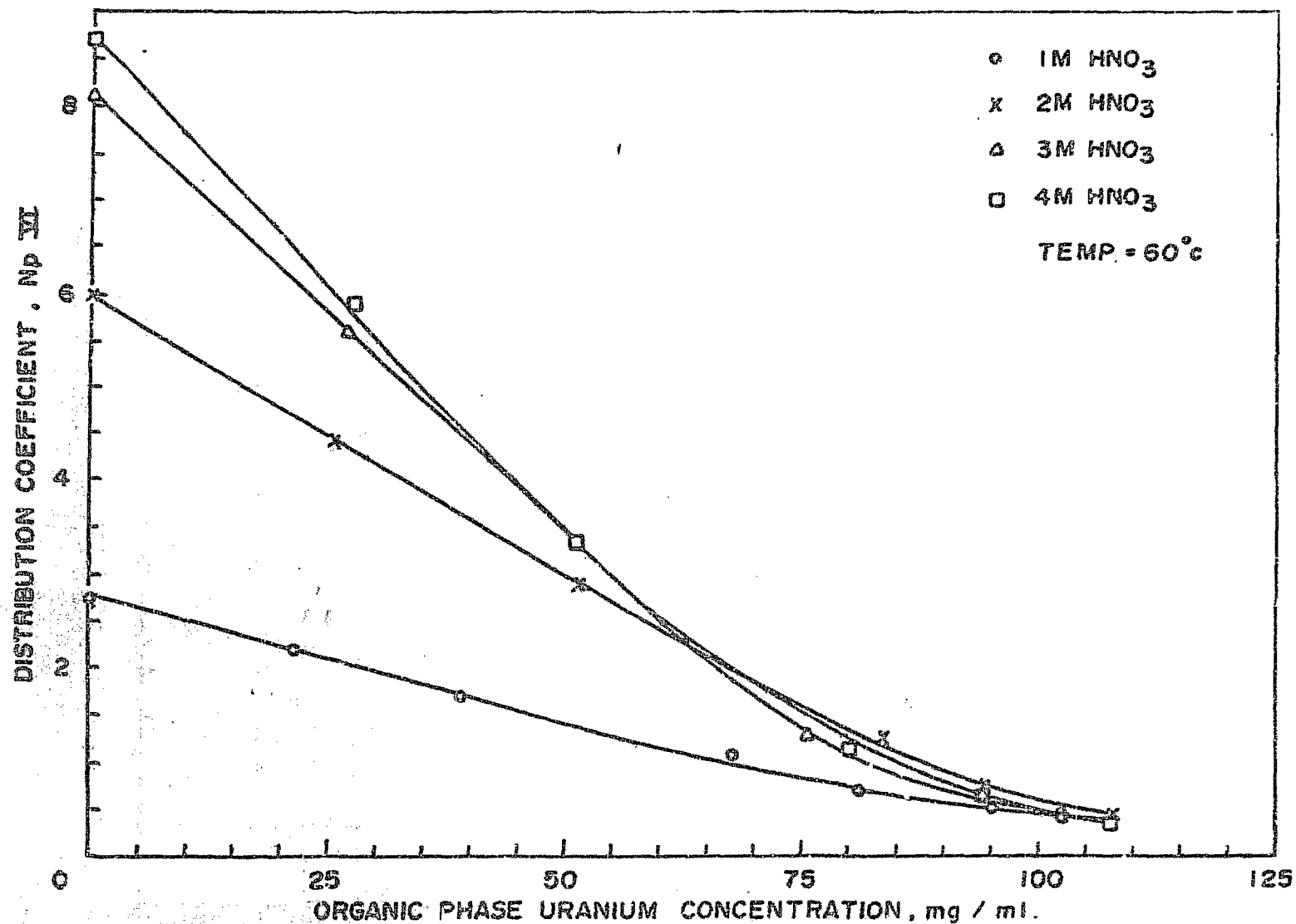


FIGURE-4. VARIATION OF THE DISTRIBUTION COEFFICIENT OF Np(VI) WITH ORGANIC PHASE URANIUM CONCENTRATION.

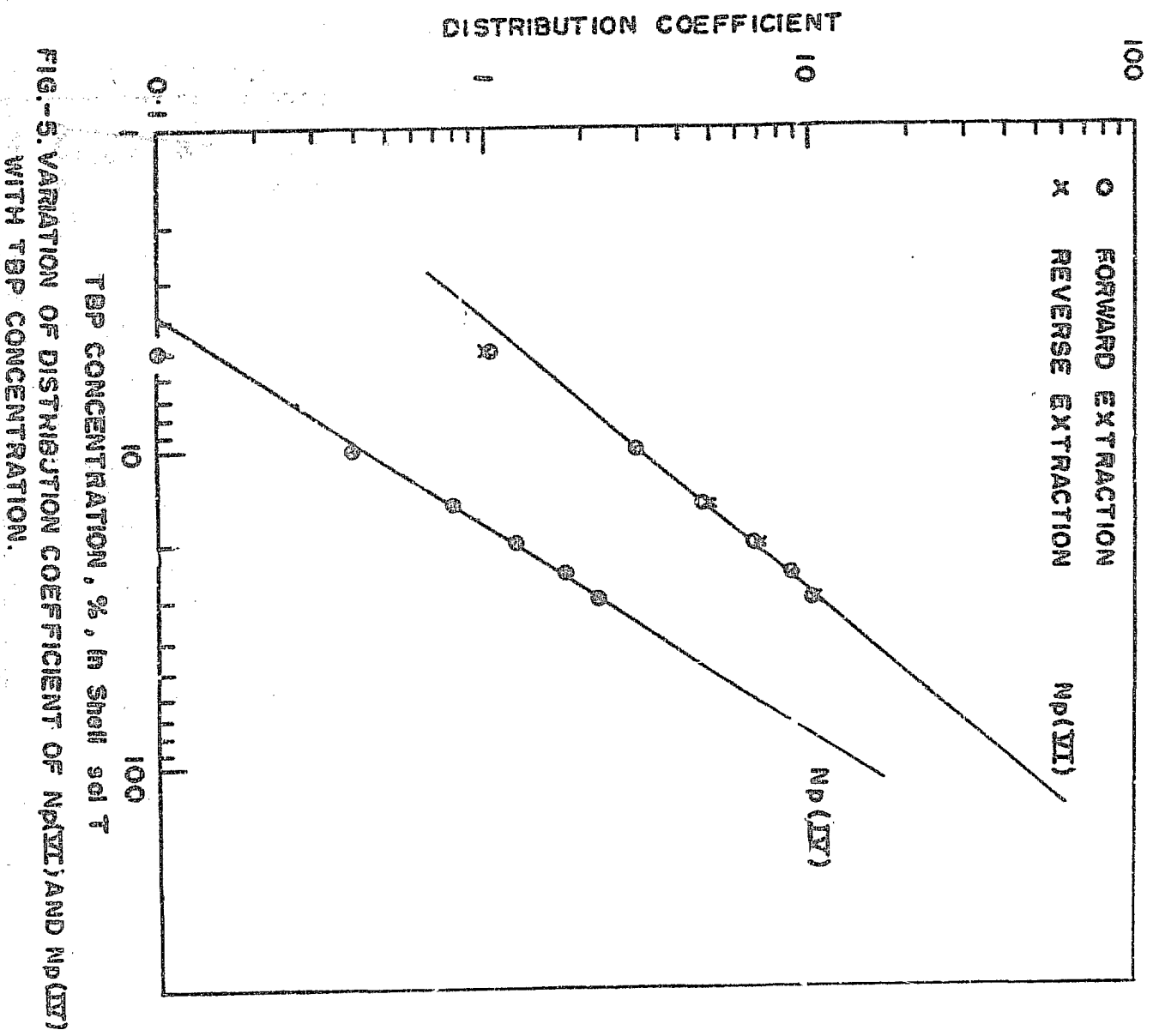


FIG.-5. VARIATION OF DISTRIBUTION COEFFICIENT OF $Np(VI)$ AND $Np(IV)$ WITH TBP CONCENTRATION.

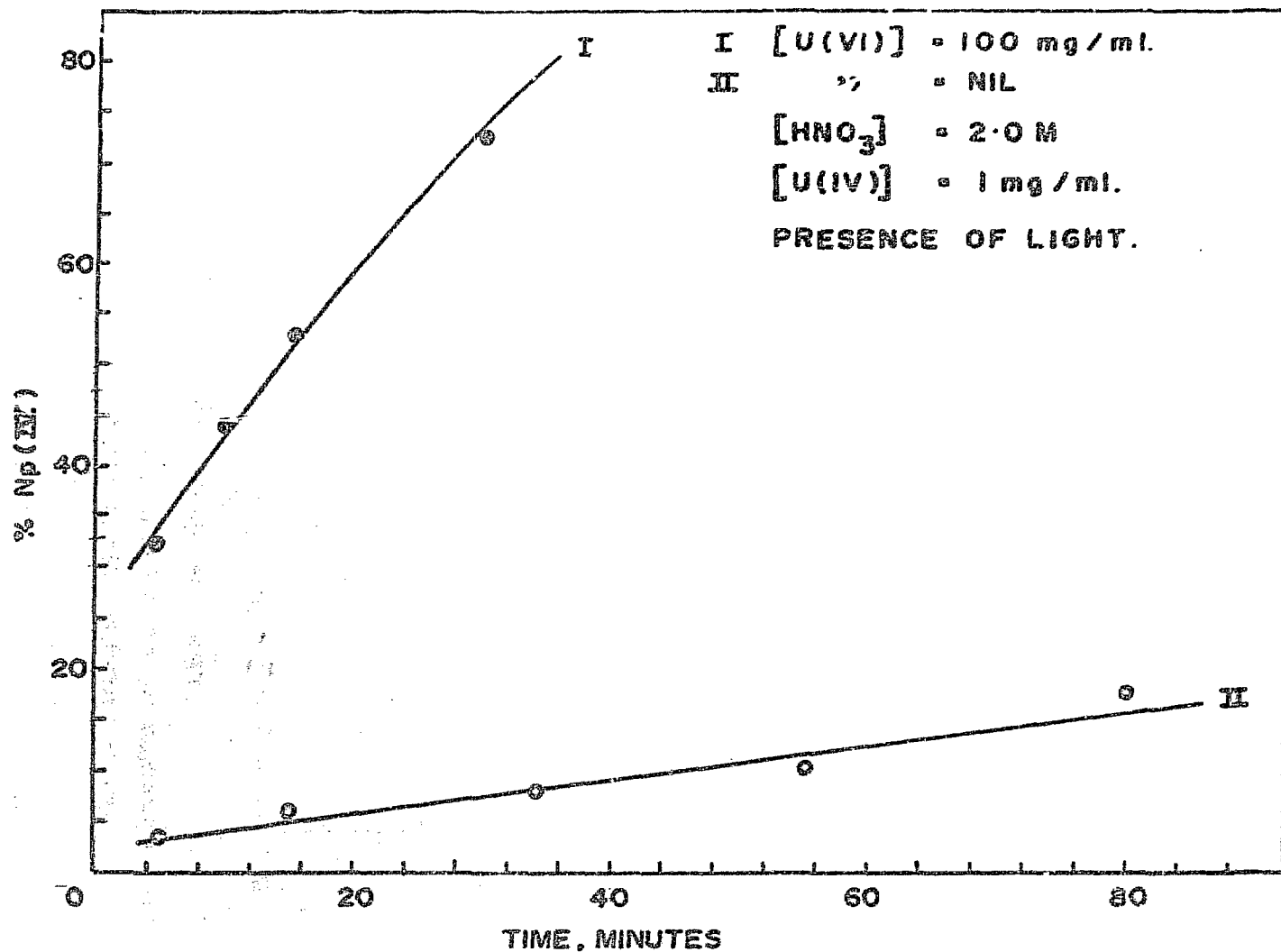


FIGURE - 6. RATE OF REDUCTION OF Np(V) BY U(IV)

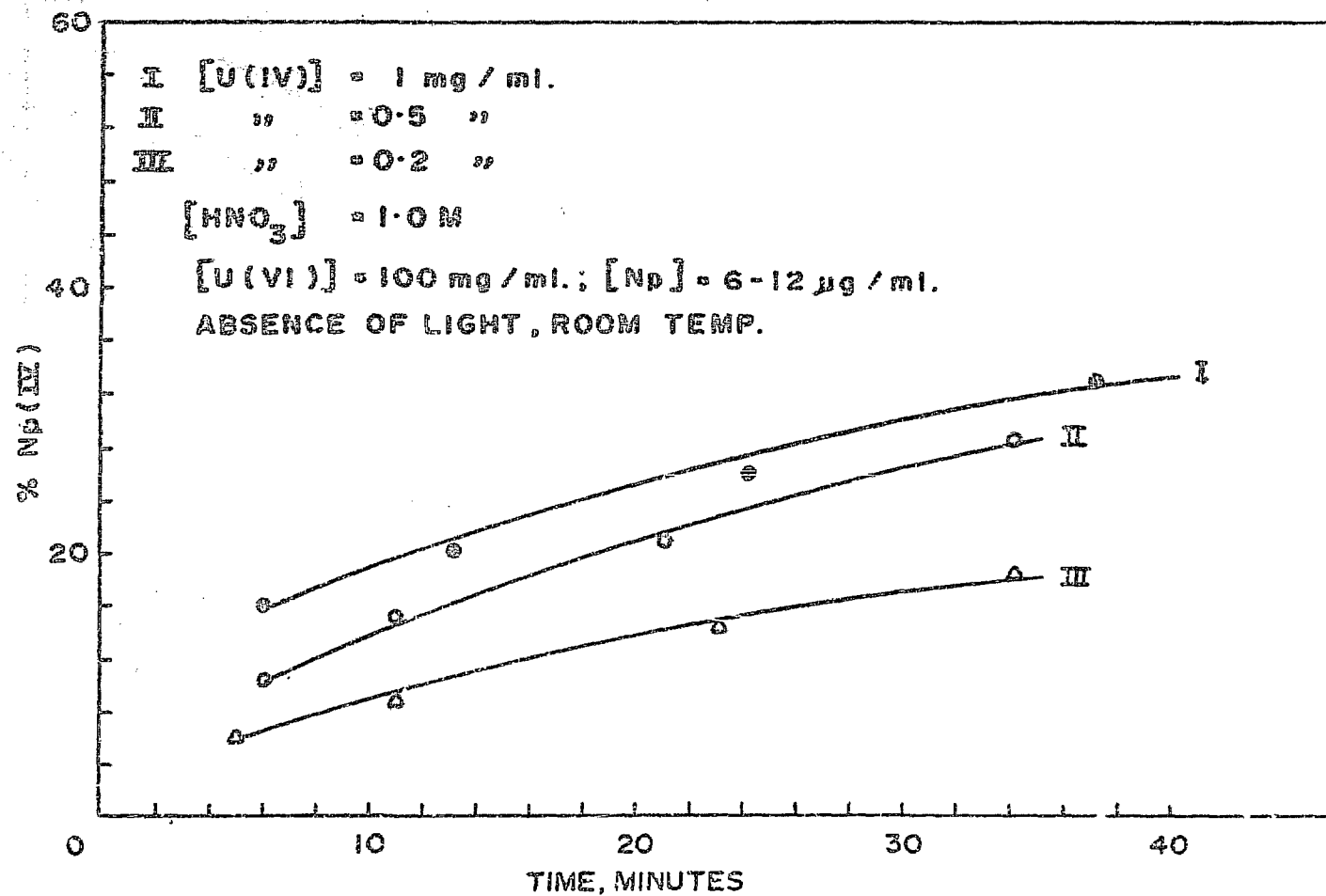


FIGURE-7. RATE OF REDUCTION OF Np(V) BY U(IV)

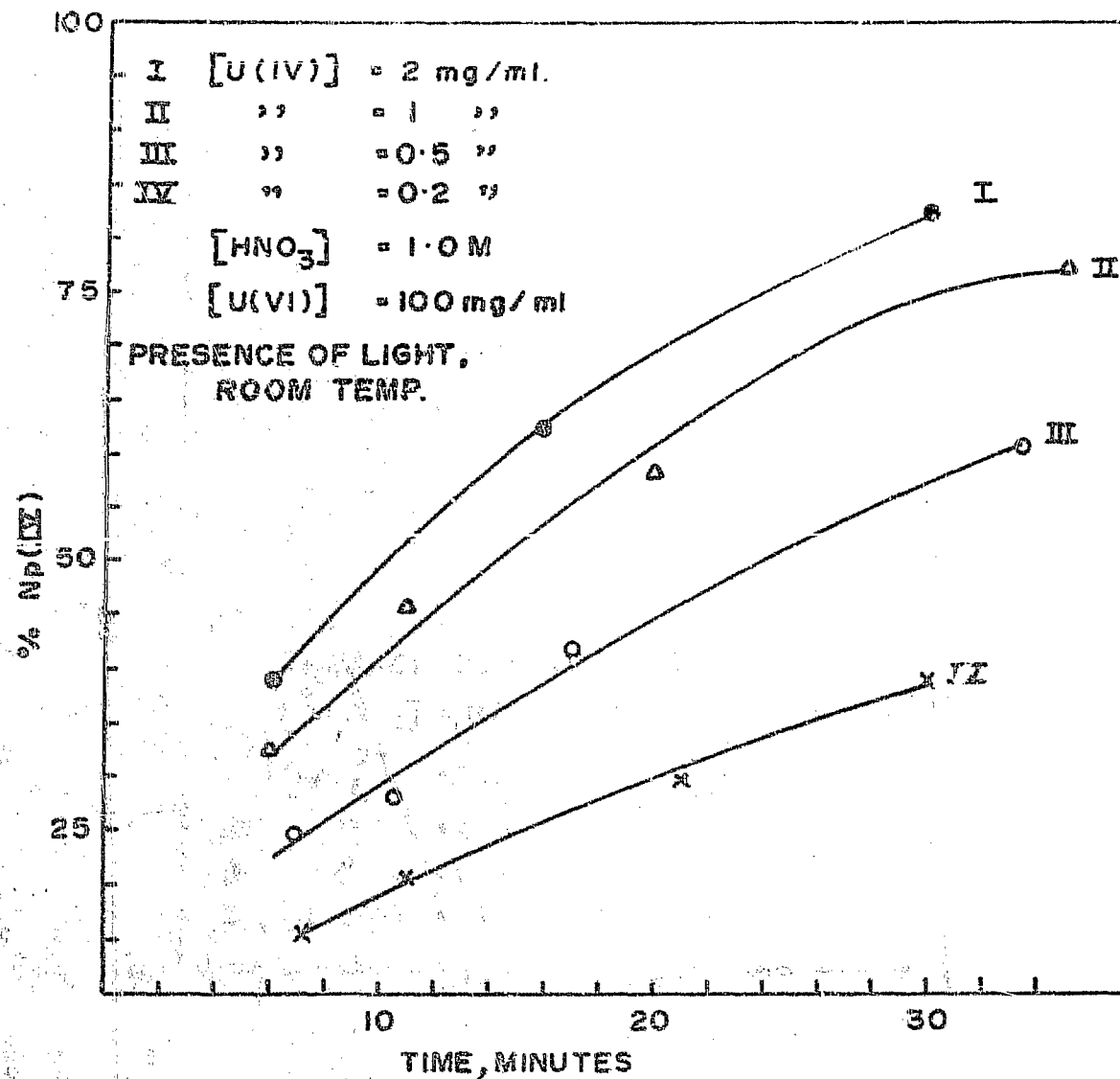


FIGURE-8. RATE OF REDUCTION OF Np(V) BY U(IV).

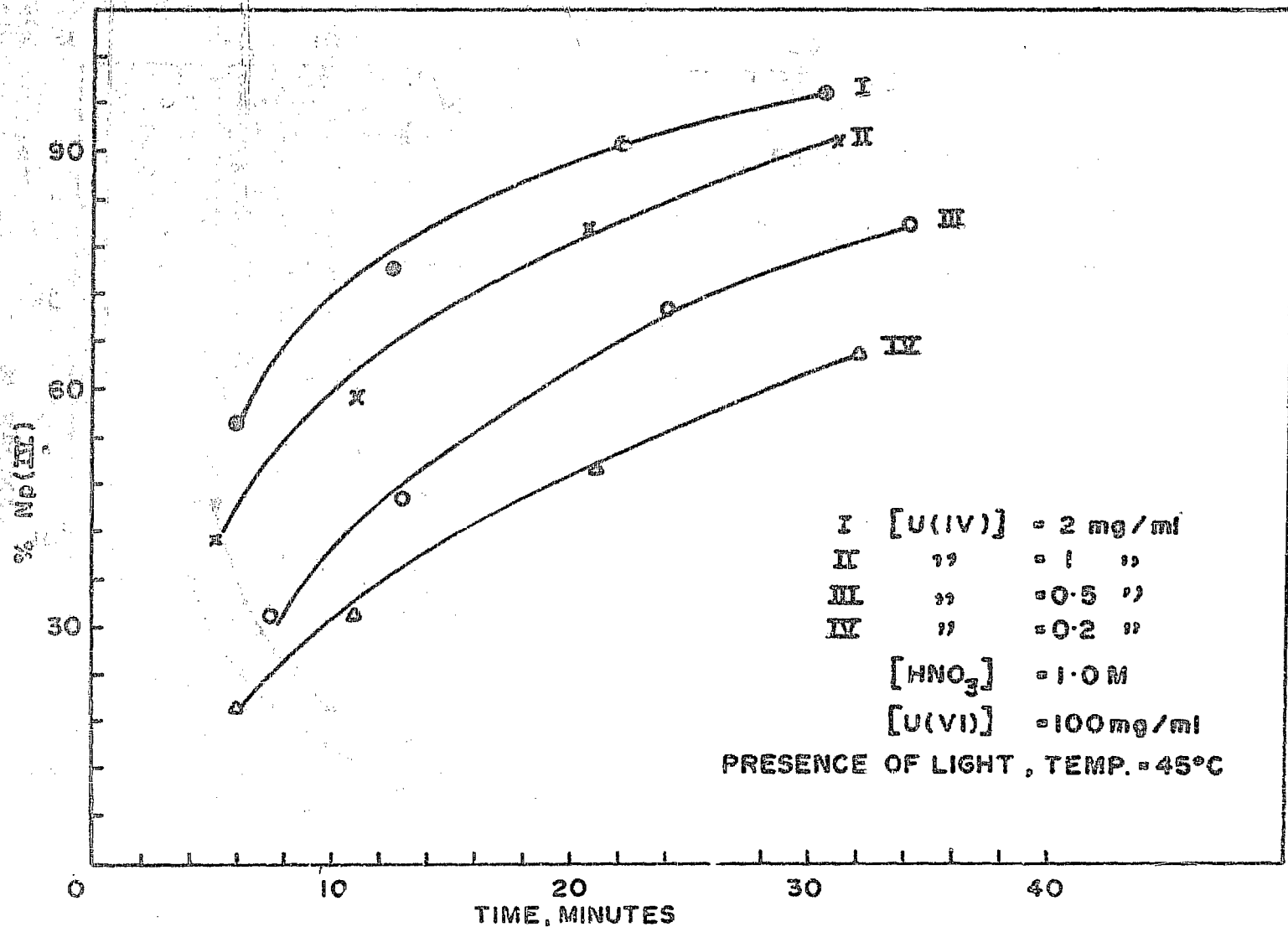


FIGURE-9. RATE OF REDUCTION OF Np(V) BY U(IV).

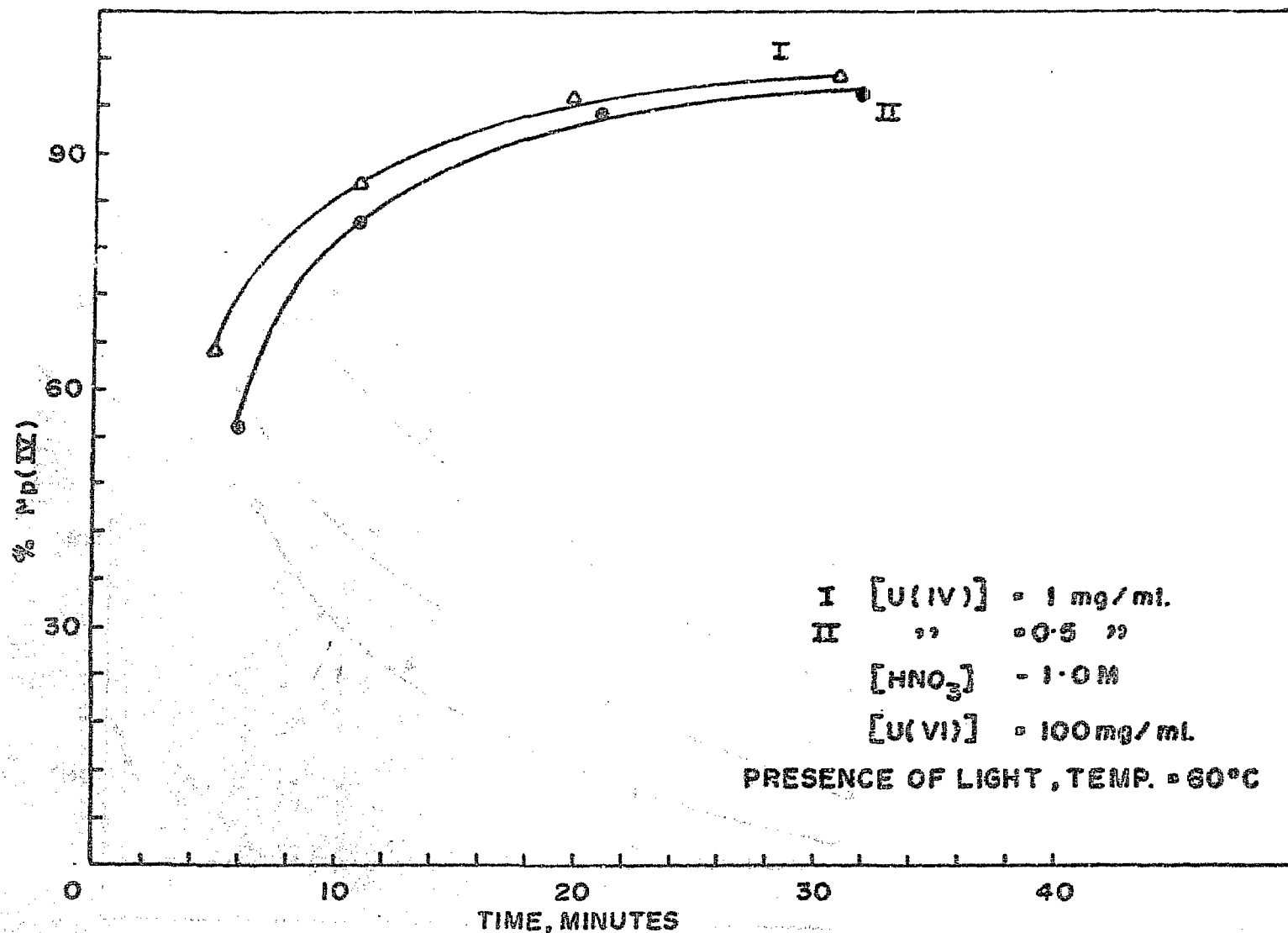


FIGURE-10. RATE OF REDUCTION OF Np(V) BY U(IV).

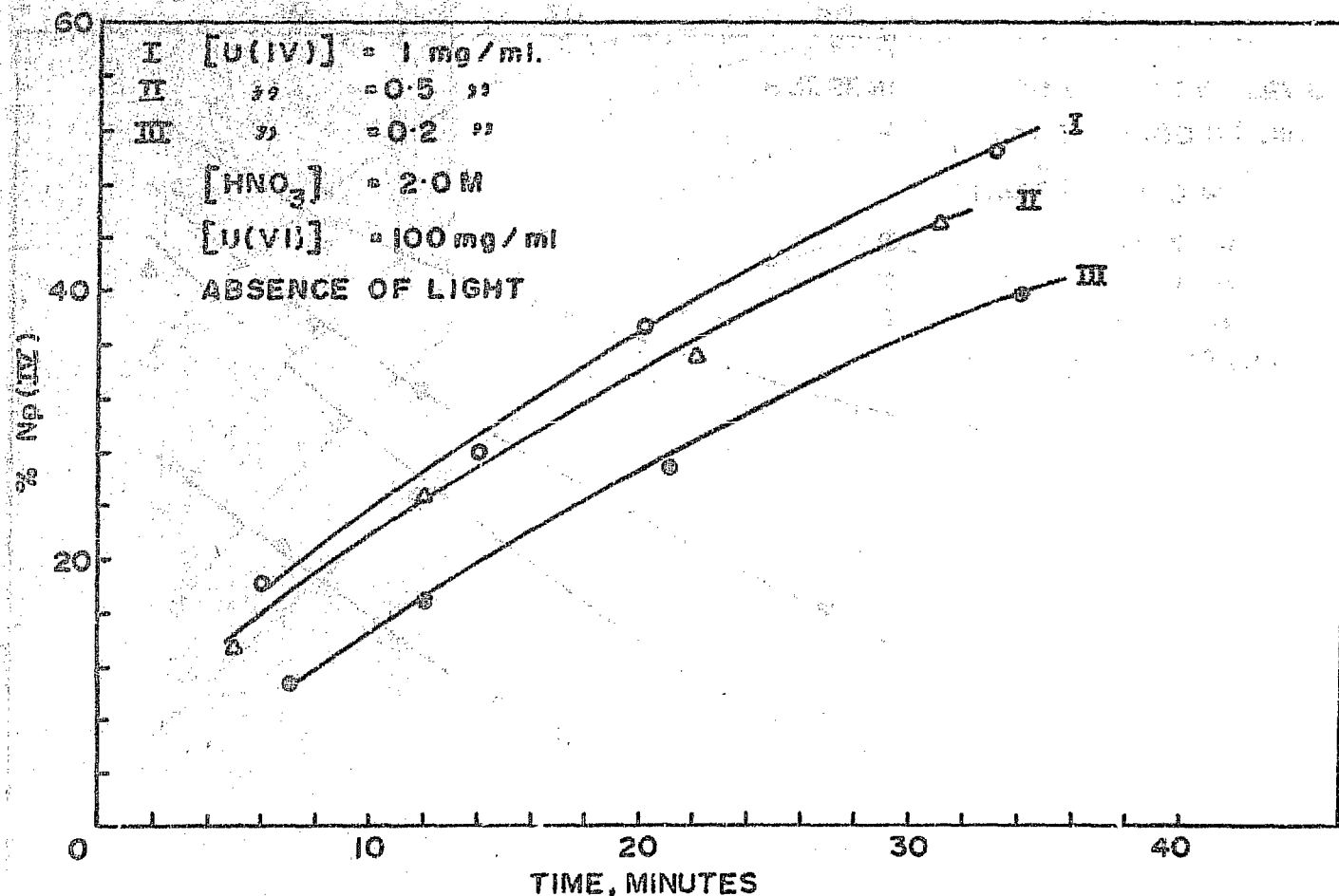


FIGURE-II. RATE OF REDUCTION OF $Np(V)$ BY $U(IV)$.

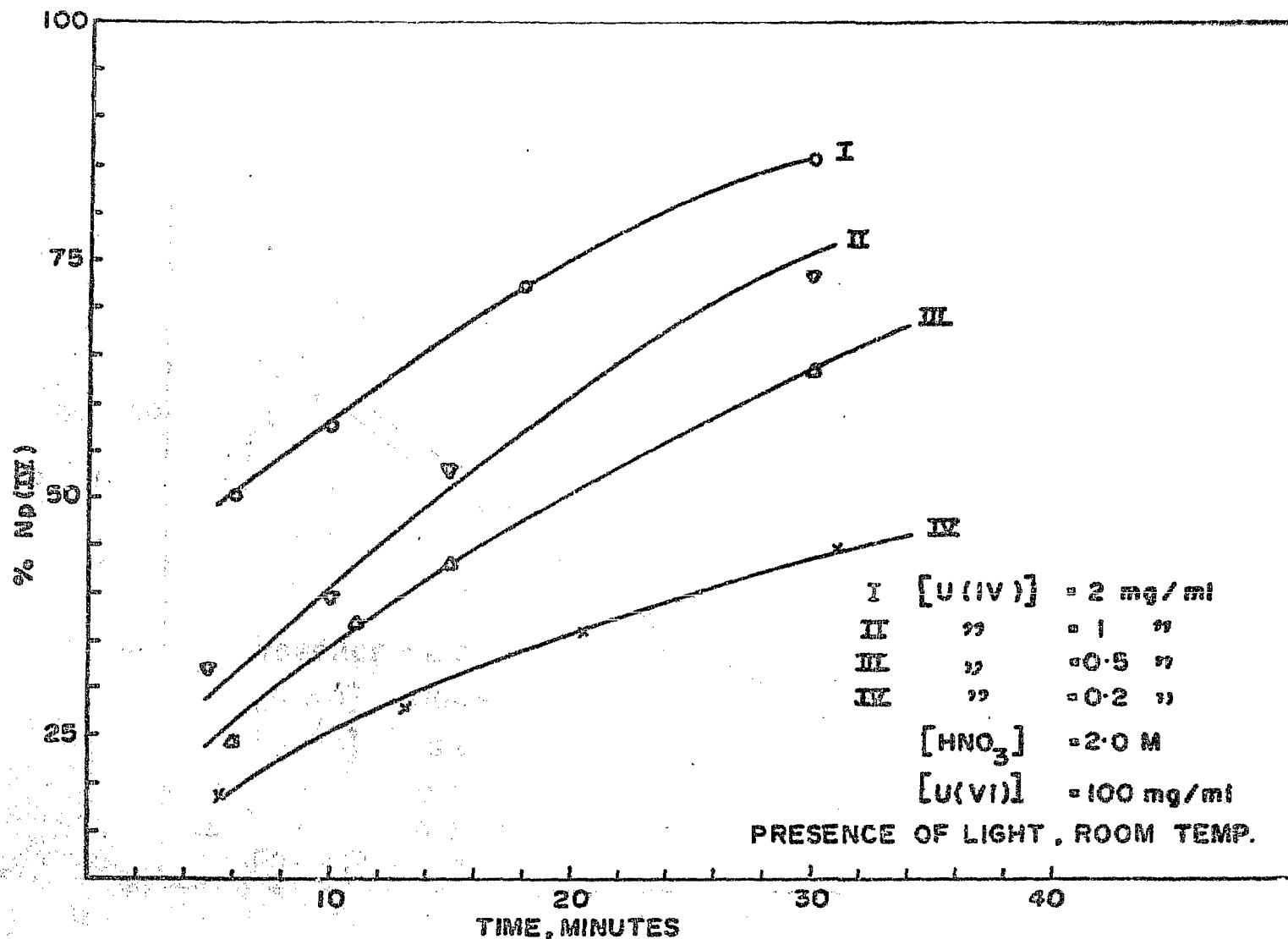


FIGURE-12. RATE OF REDUCTION OF Np(V) BY U(IV)

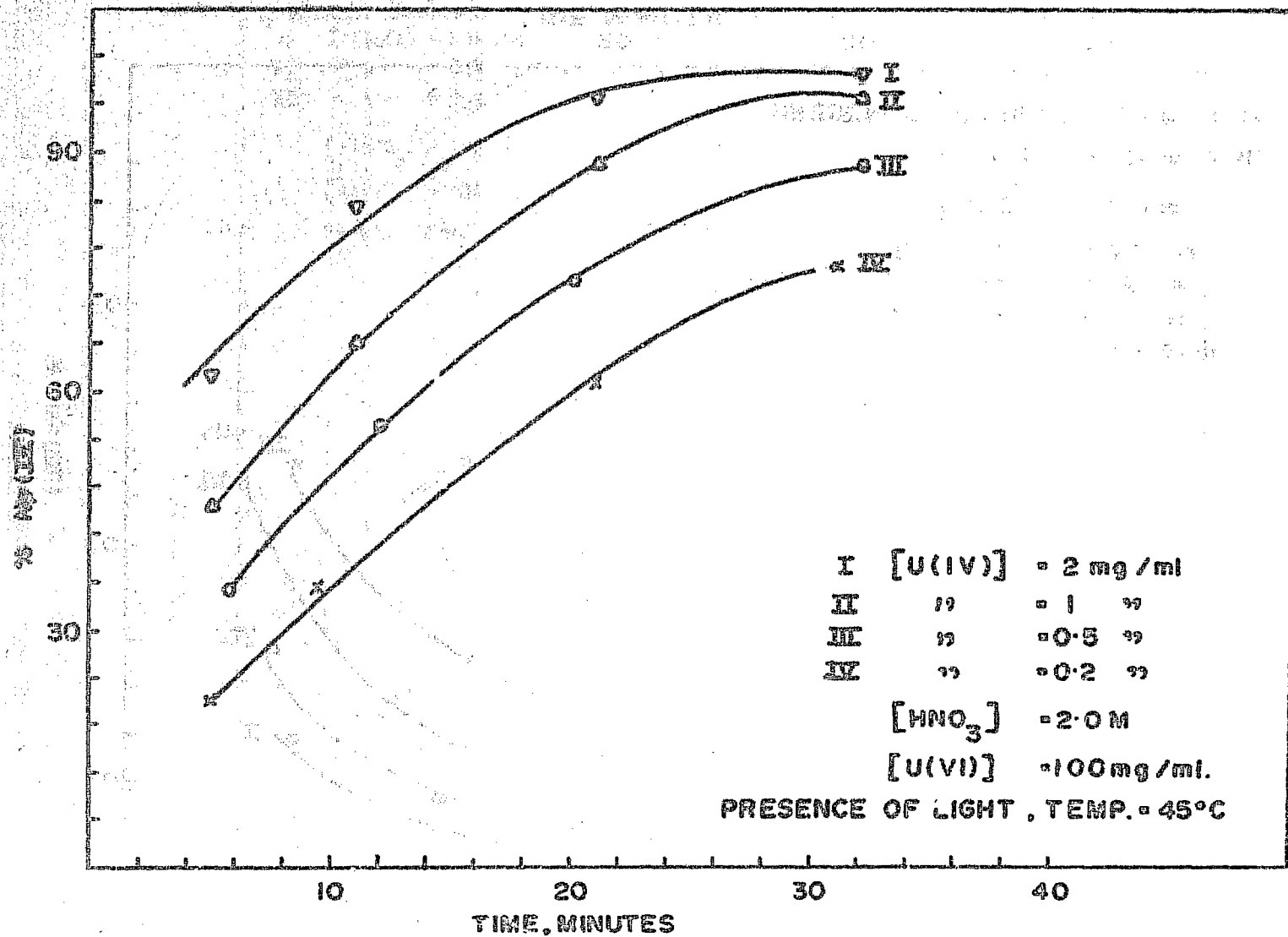


FIGURE-13. RATE OF REDUCTION OF Np(V) BY U(IV)

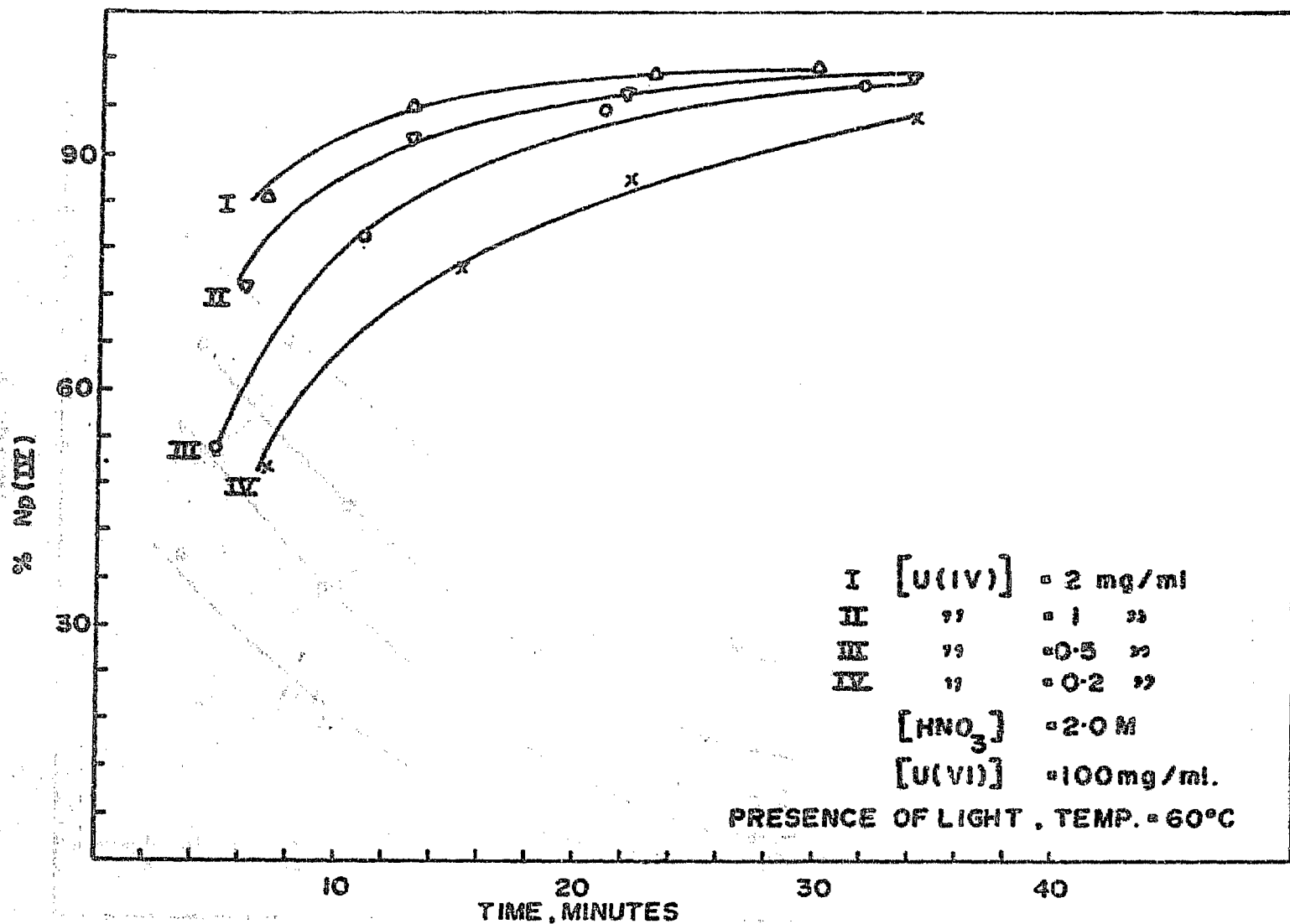


FIGURE-14. RATE OF REDUCTION OF Np(V) BY U(IV)

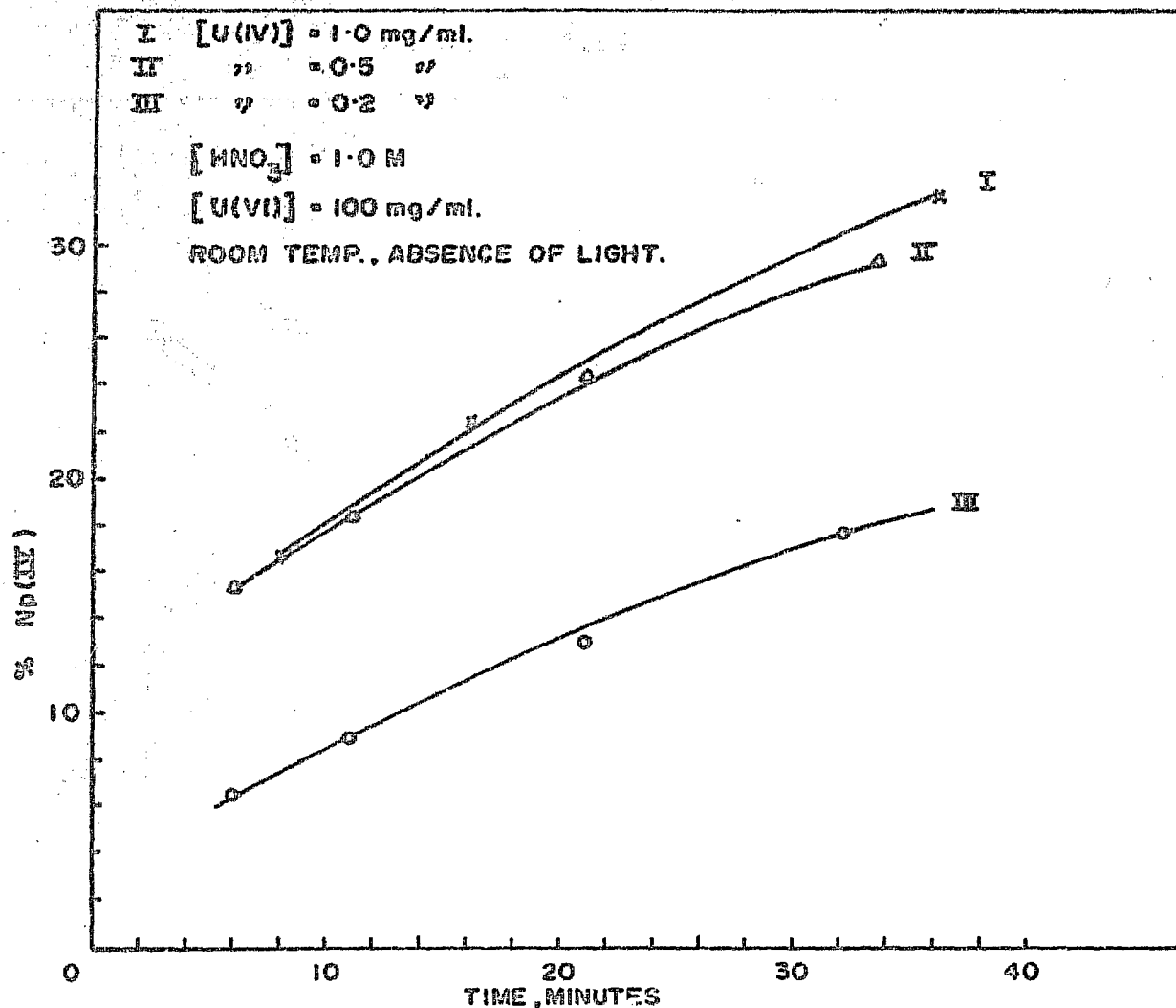


FIGURE-15. RATE OF REDUCTION OF Nd(VI) BY U(IV)

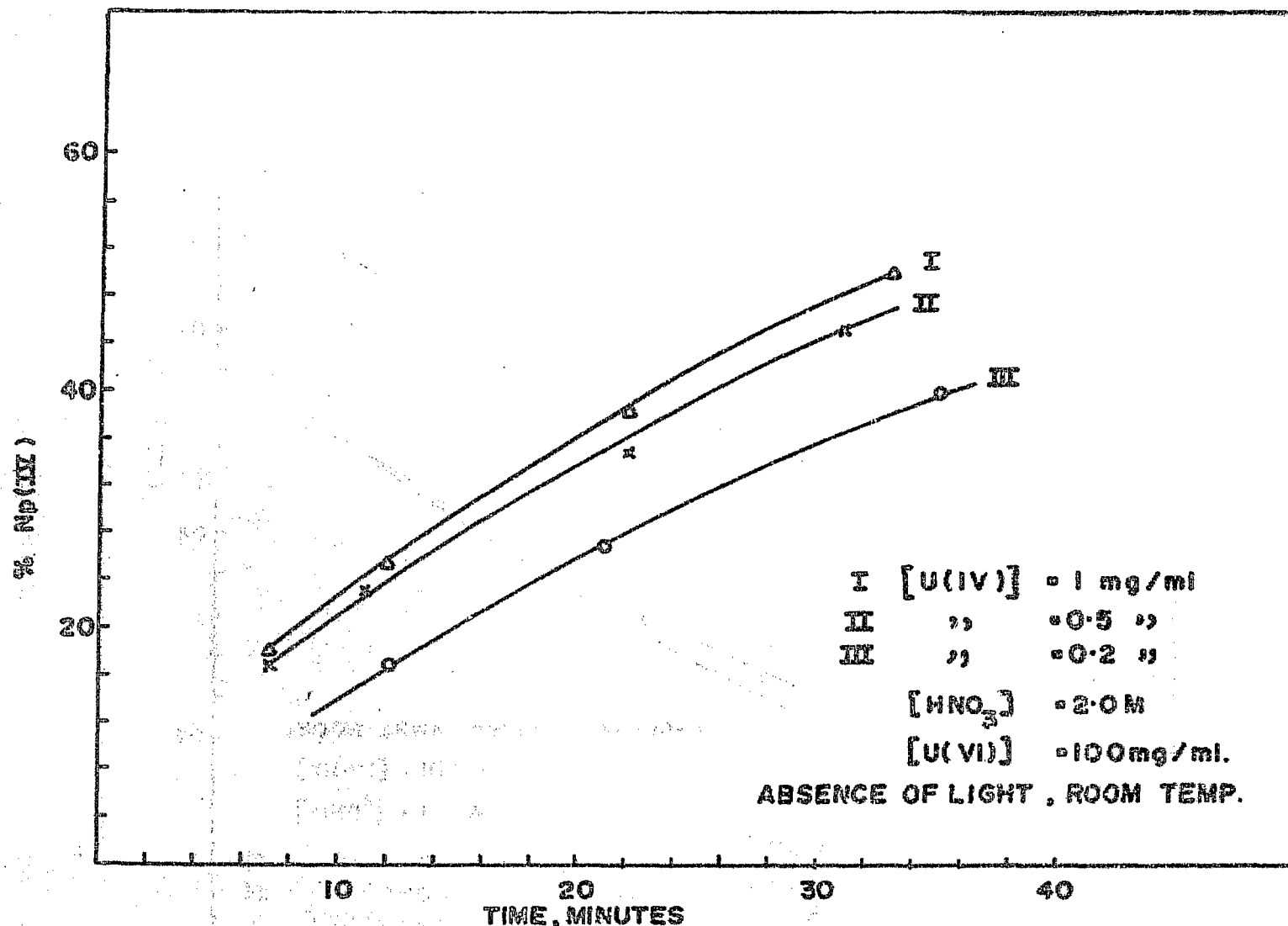


FIGURE-16. RATE OF REDUCTION OF Np(VI) BY U(IV)

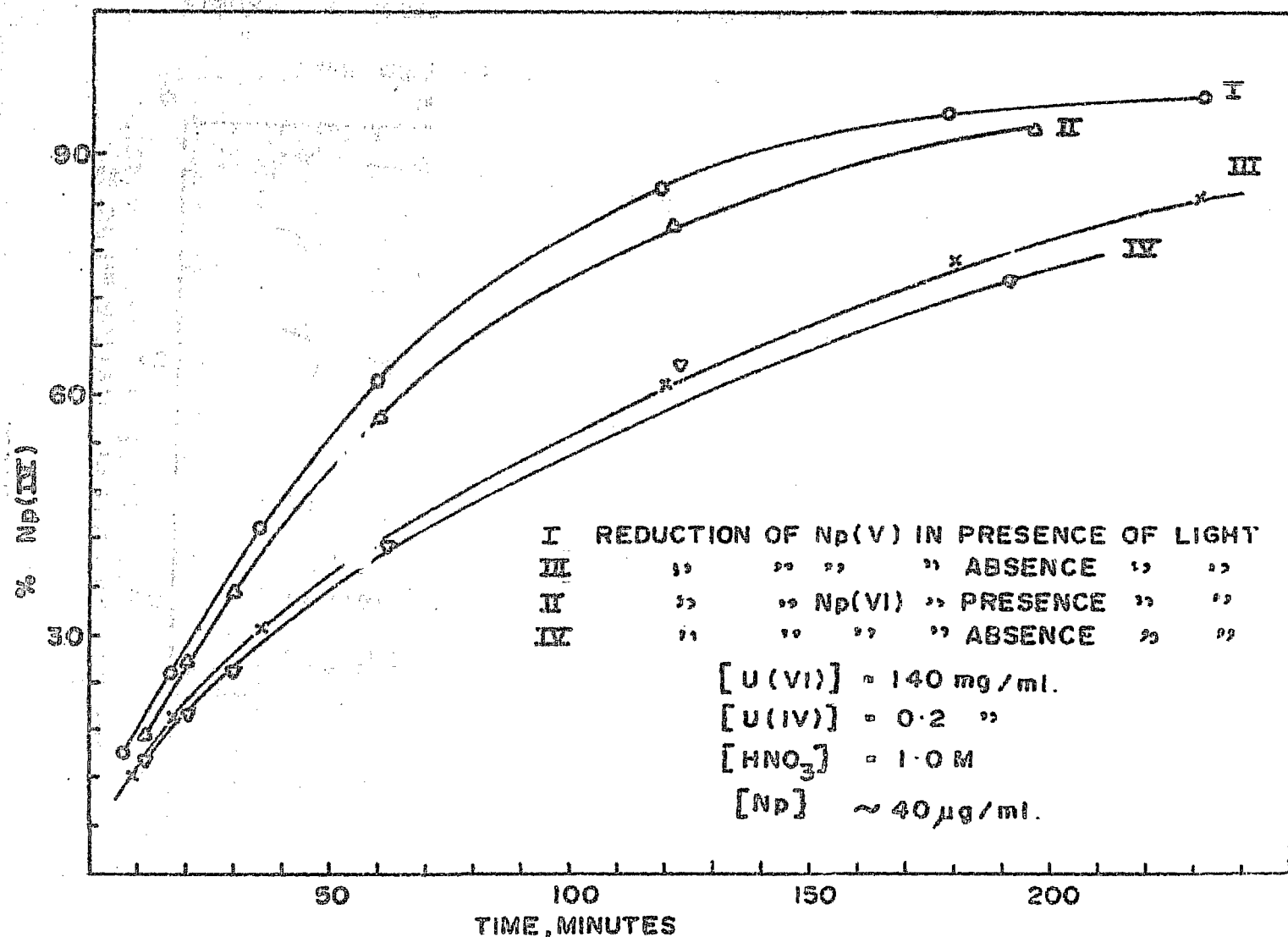


FIGURE-17. RATE OF REDUCTION OF Np(VI) AND Np(V) TO Np(IV) BY U(IV) .

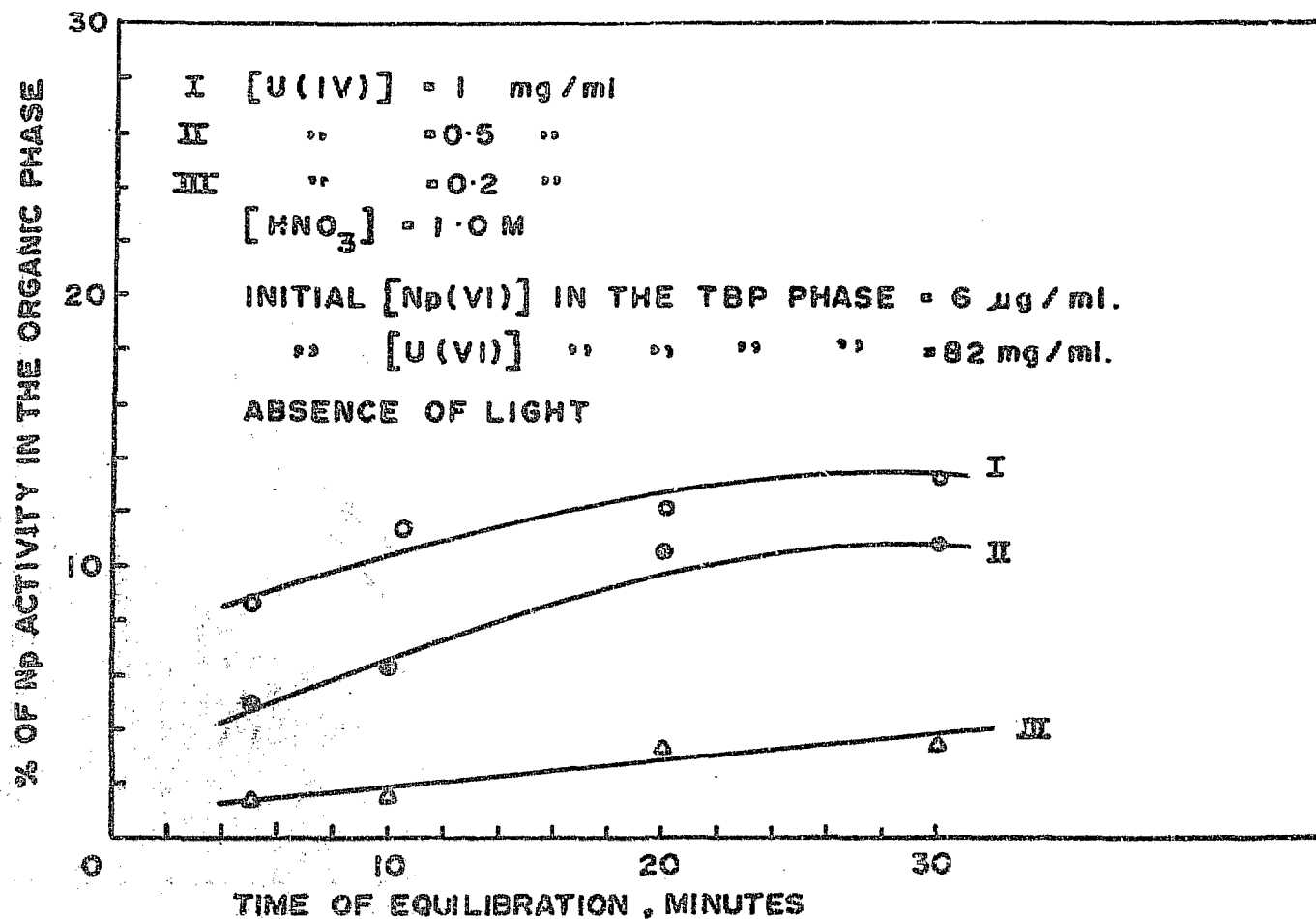


FIGURE-18. STRIPPING OF Np (VI) FROM TBP USING U(IV)

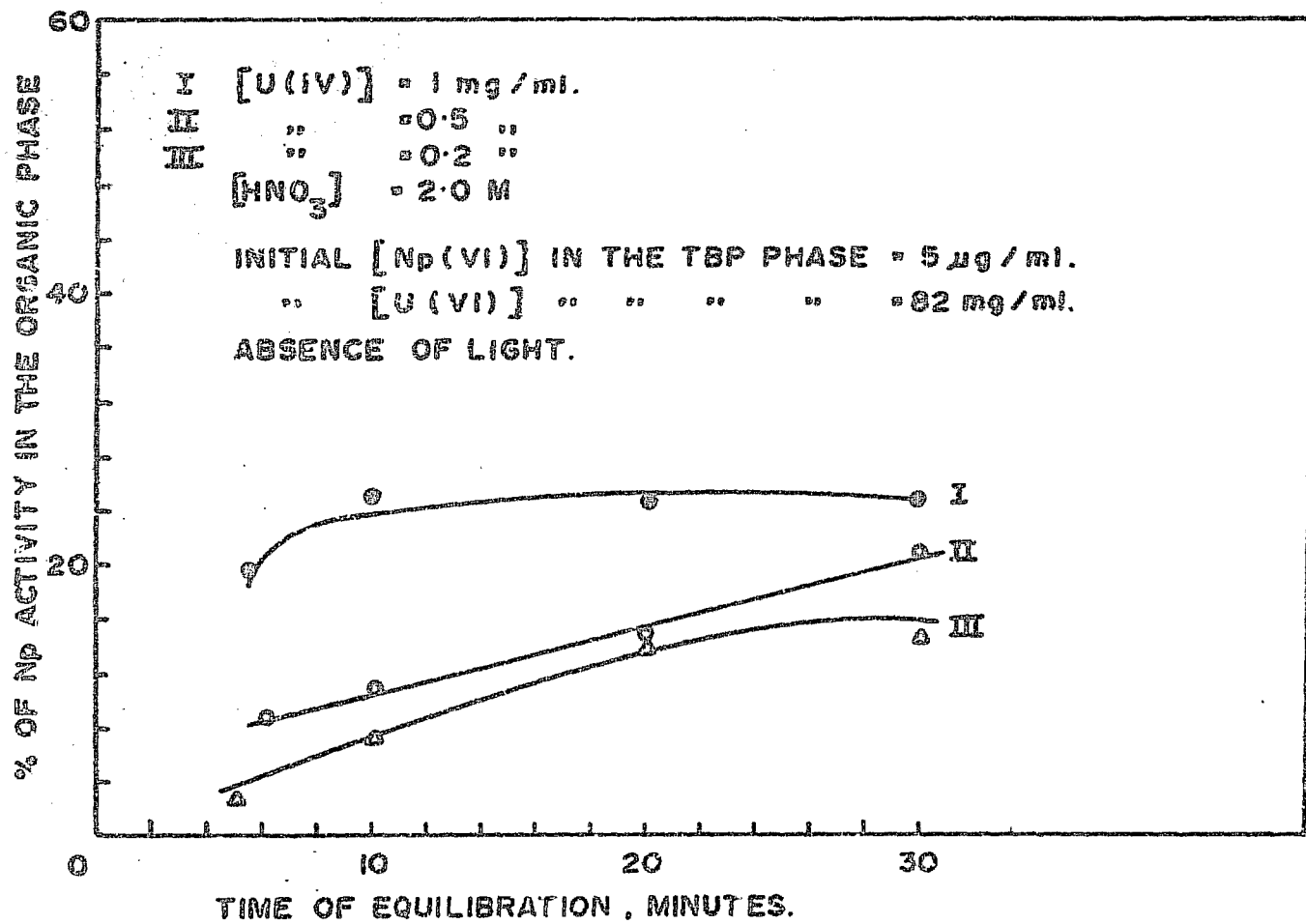


FIGURE-19. STRIPPING OF $Nd(VI)$ FROM TBP USING $U(IV)$