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GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

PROCESS CHEMISTRY OF NEPTUNIUM
PART - I

by

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BHABHA ATOMIC RESEARCH CENTRE
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ABSTRACT

A brief literature survey on the process chemistry of neptunium has been made. The present work deals with the various methods of estimation of neptunium, effect of nitric acid concentration on the distribution coefficients of neptunium(IV) and neptunium(VI) into 30% TBP in Shell sol-T, the variation of distribution coefficients of neptunium(IV) and neptunium(VI) as a function of TBP saturation by uranium and the analysis of the purex process solutions at different stages for total neptunium content.

From the data, it has been shown that, under the usual uranium loading of 30% TBP in the purex process, both Np(IV) and Np(VI) could be extracted to an appreciable extent, particularly at a nitric acid concentration higher than 2 M, whereas at lower nitric acid concentration very small amounts of Np(IV) may be extracted under the same conditions.

The results of the analyses of the purex process solutions reveal that during the first extraction cycle neptunium is almost quantitatively co-extracted with uranium and plutonium and in the second extraction cycle neptunium is about 50% extracted. In the third extraction cycle, neptunium is almost completely extracted along with uranium.

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1. INTRODUCTION

Neptunium-237 is formed in small but significant amounts during the irradiation of uranium fuel in nuclear reactors. This can be recovered as a by-product during the reprocessing of irradiated fuels. Apart from its use in chemical and nuclear research, this isotope serves as a starting material for the production of plutonium-238, which is one of the most useful isotopic power sources.

2. FORMATION OF NEPTUNIUM-237

During the irradiation of uranium, neptunium-237 is formed by the following nuclear reactions:

$$U^{238}(n, 2n) \xrightarrow{0.013b} U^{237} \xrightarrow[6.7d]{\beta^-} Np^{237} \qquad (1)$$

$$U^{235}(n, \gamma) \xrightarrow{105b} U^{236}(n,\gamma) \xrightarrow{24b} U^{237} \xrightarrow[6.7d]{\beta^-} Np^{237} \qquad (2)$$

At relatively low neutron-fluxes (10^{12} n/cm^2/s) almost all the neptunium-237 is formed by reaction (1). The rate of formation by reaction (1) depends on the ratio of fast to thermal neutron flux. For integrated fluxes of 10^{20} nvt or less the amount of neptunium formed is about 0.3% of the amount of plutonium-239. The contribution from reaction (2) becomes important at high fluxes and especially in enriched uranium fuels. Kilogram quantities of neptunium-237 are produced in power reactors, thus making its recovery a matter of considerable interest. For example, in Tarapore Atomic Power Reactors about 5-8 kilograms of neptunium may be produced annually[1].

3. VARIOUS METHODS USED FOR NEPTUNIUM RECOVERY

3.1 Oxidation-reduction Reactions of Neptunium

Neptunium can exist in solution in three oxidation states as Np^{+4},

NpO_2^+ and NpO_2^{++}. At about 1.0 M acid these three oxidation states are stable with respect to disproportionation in the absence of complexing agents. Under these conditions, Np(III) is also stable provided inert atmosphere is maintained. Since no inert atmosphere is maintained in purex reprocessing conditions, Np(III) need not be considered here. The relative stabilities of Np(IV), Np(V) and Np(VI) depend on the conditions such as presence or absence of complexing agents, oxidising or reducing agents etc. The rate of disproportionation of Np(V) to Np(VI) and Np(IV) increases with increasing acidity and is also favoured by the presence of complexing agents like sulphate and nitrate which complex the Np(IV) strongly.

In the purex process, neptunium will be able to accompany fission products, uranium or plutonium or be divided between these three, depending on the chosen or imposed conditions. After the nitric acid dissolution of the uranium fuels, neptunium should be mostly as NpO_2^+ which is very slightly extracted into TBP. However, it was observed that significant amounts of neptunium are actually extracted into the TBP apparently owing to the oxidation of Np(V) to Np(VI) due to the presence of nitrous acid. The role of nitrous acid in the oxidation of Np(V) to Np(VI) in nitric acid solution may be represented by the equation (3)

$$2NpO_2^+ + NO_3^- + 3H^+ \rightleftharpoons 2NpO_2^{++} + HNO_2 + H_2O \qquad (3)$$

The oxidising system NO_3^-/HNO_2 whose potential may be written as in equation (4)

$$E = 0.93\ V + \frac{RT}{2F} \log \frac{(NO_3^-)\ (H^+)^3}{(HNO_2)} \qquad (4)$$

depends on the acidity (to the third power) on one hand and on the concentration of nitrous acid on the other. It is clear that this system is more oxidising if the acidity is high and nitrous acid concentration low. The oxidation is more favoured by the presence of complexing agent like TBP which complexes and extracts Np(VI). The oxidation of NpO_2^+ by nitrate occurs at a reasonable rate when about 10^{-6}M nitrous acid is present as a catalyst. When the concentration of nitrous acid in the aqueous phase increases, for instance 10^{-2}M, the oxidising power of nitrate decreases sufficiently so that the oxidation of NpO_2^+ to NpO_2^{++} does not take place even in the presence of TBP. Thus, the concentration of nitrous acid as well as that of nitric acid plays an important role in the extraction of neptunium.

3.2 Modified Purex Process at Oak Ridge[2,3]

Neptunium was extracted along with uranium and plutonium into 30% TBP from an aqueous feed solution of composition 1.5 to 2 M HNO_3, 1.0 to 1.5 M uranium and 0.01 M $NaNO_2$. It was found that 90% of the neptunium was co-extracted at this stage along with uranium and plutonium. In the next stage, plutonium was stripped from organic phase using ferrous sulphamate. In the partitioning step, neptunium followed plutonium into aqueous phase as neptunium(IV) when the aqueous plutonium-neptunium stream had a nitric acid concentration of 1.5 M to 2.0 M. In the second cycle, plutonium was re-extracted into TBP from 6 M nitric acid during which about 60-75% of neptunium followed the plutonium into TBP phase. The wastes from both cycles were recycled for recovery of neptunium. The neptunium was separated from plutonium and further purified by ion exchange technique.

3.3 Modified Purex Process used at Hanford[4,5]

The neptunium present in the feed solution was co-extracted as neptunium(VI) along with uranium(VI) and plutonium(IV) into 30% TBP in the first column and scrubbed free from fission products in the second column. Plutonium was stripped into the aqueous phase using ferrous sulphamate. The conditions in this partitioning step were such that neptunium, although reduced to the tetravalent state, remained in the organic phase along with uranium. The neptunium and uranium were back-extracted, concentrated and uranium was re-extracted into TBP for further purification. The neptunium(IV) was left in the aqueous phase during this extraction as a result of high saturation of uranium in the TBP phase. The aqueous raffinate stream containing neptunium was concentrated and back-cycled into the first extraction cycle. About one-third of this back-cycle stream was continuously processed through a set of two solvent extraction columns for separation of neptunium and this accumulated neptunium was removed periodically for final purification by ion exchange. This process permits continuous recovery of neptunium without affecting the schedule of plutonium production in the plant.

3.4 Neptunium Recovery at Savannah River Laboratories from High Active Waste Concentrate Directly by Anion Exchange[6]

In the methods described in 3.2 and 3.3, neptunium(VI) or (IV) was co-extracted with uranium and plutonium in fuel reprocessing plants, partitioned and finally purified by ion exchange. At the Savannah River Laboratory, neptunium was recovered by an alternative method of forcing it into aqueous waste stream in

the first extraction cycle and recovering it from the waste directly by anion exchange technique.

The neptunium in aqueous waste was adjusted to tetravalent state with ferrous sulphamate and hydrazine and 8 M in nitric acid and was fed to an agitated anion exchange column. Neptunium was absorbed on the resin along with significant amounts of plutonium. The column was washed with 8 M nitric acid and the neptunium and plutonium were subsequently eluted with 0.35 M nitric acid. The product from this primary recovery column was further purified by additional anion exchange cycles.

3.5 Neptunium Recovery in the U.K.[7,8]

In the Windscale Reprocessing Plant, the results of the analytical survey showed that about 60% of neptunium enters the aqueous raffinate from the uranium purification cycle. The raffinate provided a more suitable source of neptunium than the highly active fission product solution because of the low level ($\sim$10 mc/l) beta-gamma activity of the former. The neptunium concentration was extremely low ($\sim$80 μg/l). This raffinate was conditioned to 3 M in nitric acid and passed through an anion exchange column during which almost all the neptunium was absorbed on the column. This was eluted with 0.1 M nitric acid. The eluate was conditioned to 7 M in nitric acid and 0.01 M in ferrous sulphamate and was passed through a second anion exchange column. Neptunium absorbed on the second column was eluted with 0.1 M nitric acid. The eluate was adjusted to 1 M in nitric acid and 0.1 M in ferrous sulphamate and the Np(IV) was extracted with TTA. Neptunium was back-washed from TTA by 8 M nitric acid to get the final product.

3.6 Neptunium Recovery Using Trilaurylamine (TLA)

Champion and Chesne[9] used the TLA extraction of neptunium(IV) for its recovery. The starting material was the raffinate from the second plutonium purification cycle at the Marcoule Plutonium Plant. This solution had the composition 1.7 M nitric acid, 19-137 mg/l plutonium, 15-30 mg/l neptunium, and 150-180 mc beta-gamma activity. The feed solution obtained by adjusting the raffinate had the following composition:

Plutonium	15-70 mg/l	Ferrous sulphamate	0.05 M
Neptunium	5-15 mg/l	Sulphamic acid	0.005 M
Nitric acid	1.7 M	Ferric nitrate	0.70 M

The feed solution was contacted with 20% TLA in dodecane in a mixer-settler. Loaded TLA phase was washed with 0.5 M nitric acid and neptunium and plutonium were stripped back with 1.5 M sulphuric acid - 0.07 M nitric acid. Neptunium and plutonium were precipitated with ammonia and the precipitate was dissolved in nitric acid. Two more extraction cycles were carried out for final purification during which neptunium(IV) was selectively extracted into TLA leaving plutonium(III) in the aqueous phase, ferrous sulphamate being used as the reducing agent. The loaded TLA was scrubbed with 0.05 M ferrous sulphamate and neptunium was stripped using sulphuric acid. Though decontamination from plutonium was not very satisfactory, the usefulness of TLA as an extractant for the recovery and purification of neptunium must be considered as established.

4. SCOPE OF THE PRESENT WORK

The present work was undertaken with a view to arrive at suitable conditions like feed adjustment, selective extraction of neptunium etc. for the recovery of neptunium along with plutonium and uranium and the following aspects are relevant.

1. Methods of estimation of neptunium
2. The effect of nitric acid concentration on the distribution coefficients of neptunium(IV) and neptunium(VI) into 30% TBP in kerosene.
3. The variation of distribution coefficients of neptunium(IV) and neptunium(VI) as a function of TBP saturation by uranium.
4. Analysis of the purex process solutions at different stages for total neptunium content.
5. Oxidation states of neptunium in the feed solutions in purex process.
6. The effect of nitrous acid concentration in the feed solution on the distribution of neptunium.
7. Extraction of neptunium by TLA.

5. PRESENT WORK

5.1 Purification of Np^{237} stock

The neptunium stock solution prepared from NpO_2^{237} obtained from Oak Ridge National Laboratory was purified by TTA extraction[10]. Np(IV) in 1 M

nitric acid containing 0.1 M ferrous sulphamate and 0.1 M hydroxylamine hydrochloride was extracted into 0.5 M TTA in xylene. The extracted neptunium was backwashed into 10 M nitric acid and the strip solution was scrubbed with TTA to remove iron. The solution was then fumed with perchloric acid to dryness and dissolved in 1 M nitric acid. Radiochemical purity of Np^{237} was ascertained by alpha spectrum. The chemical purity was checked by spectrographic analysis by the method given by Wheat[11] and the impurities found are shown in Table 1. In this analysis, the impurities present in neptunium were selectively separated by anion exchange and thus further chemical purification of neptunium was achieved. The eluted neptunium was again analysed by the same method and the impurities found are shown in Table 2.

5.2 Estimation of Neptunium

Among the various methods used for the estimation of neptunium in the Process solutions TTA extraction[10] and anion exchange method[12] are most widely used. Experiments were carried out to check the efficiency and reproducibility of these methods.

TTA Extraction

A known aliquot of pure Np^{237} ($\sim 2\,\mu g$) was taken in 1 M nitric acid and extracted into 0.2 M TTA in xylene as Np(IV). The neptunium extracted was back-washed with 10 M nitric acid and the aqueous phase containing neptunium was evaporated to a low volume, planchetted, and the alpha activity was measured. The average recovery in six experiments was 91%.

Bubbling air through the nitric acid to remove the nitrous acid present in it before using it for stripping neptunium from TTA phase, scrubbing the strip solution with TTA to remove iron and evaporating the strip solution to dryness with perchloric acid improved the results. The average recovery in eight experiments was 96%.

Synthetic samples containing Np^{237} ($\sim 2\,\mu g$) and uranium (~ 170 mg) were prepared and Np^{237} was estimated by TTA extraction. The organic phase was scrubbed once with 1 M nitric acid containing 0.1 M ferrous sulphamate and 0.1 M hydroxylamine hydrochloride, before stripping the neptunium. The average recovery in eight experiments was 97%.

Neptunium was estimated in a synthetic mixture containing uranium (~ 200 mg), neptunium (1-2μg) and plutonium ($\sim 160\,\mu g$). Np^{237} was purified

from its daughter Pa^{233} before use and was spiked with a known aliquot of Np^{239} to facilitate the estimation of percentage recovery by beta and gamma counting also. A three cycle TTA extraction was necessary to obtain complete decontamination from plutonium. The average decontamination from plutonium per cycle was about 10^3. The complete decontamination from plutonium was checked by alpha spectrometry using a silicon surface barrier detector and 400-channel analyser. The data are given in Table 3. The average recovery of neptunium in six experiments was 95%.

Lanthanum fluoride precipitation is used in the estimation of neptunium in the process solution as it gives a good separation from uranium and some fission products such as Zr^{95}, Cs^{137} etc. Neptunium was therefore estimated using LaF_3 precipitation followed by TTA extraction. The average recovery of neptunium in six experiments was 96%.

Anion Exchange

The anion exchange method developed by Roberts[12] can be used for the analysis of the purex process solutions having high beta-gamma activity as this method which is easier to use remotely, can remove major fission product activity. Preliminary experiments using a synthetic mixture containing uranium ($\sim$340 mg), neptunium ($\sim 2\,\mu g$) and plutonium ($\sim 160\,\mu g$) showed incomplete decontamination from plutonium. The amount of Np^{237} could not be calculated by alpha spectrometry and hence it was deicded to use TTA extraction for further decontamination from plutonium. The recovery in two experiments was 83%. The lower recovery might be due to incomplete elution of neptunium from anion exchange column.

6. DISTRIBUTION COEFFICIENTS OF Np(VI) AND Np(IV)

6.1 Neptunium(VI)

To oxidise neptunium to Np(VI), several oxidants such as $KMnO_4$, $KBrO_3$, $K_2Cr_2O_7$ and ceric ammonium nitrate were tried. $K_2Cr_2O_7$ and ceric ammonium nitrate were found to be the most suitable taking the agreement between the forward and backward distribution coefficients as the criterion. In the present work, 0.01 M $K_2Cr_2O_7$ containing a trace ($\sim 10^{-6}$M) of Ce(IV) was used as the holding oxidant.

Neptunium-237 was purified from its daughter product Pa^{233} by TTA ex-

traction of the latter from 7 M nitric acid. Np^{239} was added to Np^{237} to enable the estimation of neptunium by gamma counting. The initial concentration of Np^{237} was always about 1-2 μg/ml. When Np^{239} alone was used, the results were sometimes irreproducible[13]. In the present work, as sufficient Np^{237} was used, this difficulty did not arise.

Five ml of aqueous nitric acid solution of varying acidity were equilibrated for 10 minutes with equal volume of 30% TBP pre-equilibrated with the corresponding aqueous solution without neptunium. 2 ml aliquots from both phases were removed for gamma counting after centrifugation.

The data for the distribution coefficient (Kd) of Np(VI) in 30% TBP-Shell sol T at varying nitric acid concentration are given in Table 4. The data from literature are also given for comparison.

These experiments were repeated using another lot of TBP after a few months using both 0.01 M $K_2Cr_2O_7$ as well as 0.01 M ceric ammonium nitrate as holding oxidants and the results are included in Table 4. As seen from the data, these (Kd) values are somewhat higher than the earlier ones. As almost all Ce(IV) used as holding oxidant is extracted into TBP thus decreasing the free TBP concentration, the distribution coefficient values obtained by using 0.01 M Ce(IV) as holding oxidant are slightly lower than the corresponding values obtained with $K_2Cr_2O_7$ as holding oxidant.

6.2 Neptunium(IV)

To check the most suitable reagent for the preparation of Np(IV), $NH_2OH.HCl$, hydrazine hydrate and ferrous sulphamate were tried for reduction of neptunium in HNO_3. Ferrous sulphamate was found to be the most suitable in the concentration range of 1-2 μg/ml Np^{237} taking the agreement between the forward and backward distribution coefficients as the criterion. The experimental procedure was the same as used in the experiments with Np(VI). The initial concentration of ferrous sulphamate was 0.01 M. In experiments with nitric acid concentration more than 7 M, ferrous was oxidised to ferric as apparent from the colour of the ferric ion. However, this did not affect the oxidation state of neptunium. These data are given in Table 5 along with those obtained after a few months using another lot of TBP and are compared with the published ones.

7. EFFECT OF URANIUM SATURATION OF TBP ON THE EXTRACTION OF NEPTUNIUM

It was considered necessary to investigate some factors which affect the extraction of neptunium by TBP under purex process conditions. 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 has been studied.

7.1 Estimation of Uranium

The concentration of uranium in the stock solution was determined volumetrically using Jone's reductor and titration with ceric sulphate using Ferroin indicator[14]. The concentration of uranium in the aqueous and organic phases after equilibration was measured spectrophotometrically using the thiocynate method[15,16].

7.2 Estimation of Free Acid in Presence of Uranium

The concentration of free acid in both aqueous and organic phases after equilibration was determined by pH titration against standard sodium hydroxide using Beckman-G or Beckman Research Model pH meter after complexing uranium by oxalate[17].

7.3 Extraction of Uranium

Five ml of aqueous solution with known nitric acid and uranium concentrations were equilibrated with 5 ml of 30% TBP in Shell sol.T for 10 minutes using a Vortex mixer. The two phases were separated after centrifugation and the concentration of uranium in both phases was estimated spectrophotometrically.

7.4 Extraction of Np(VI) and Np(IV) with Varying Organic Phase Uranium Concentration

An aliquot (50 λ) of Np(VI) (Np^{237} + Np^{239}) was added to 5 ml of aqueous solution of known uranium and nitric acid concentrations. The initial concentration of neptunium was about 1-2 μg/ml. 5 ml of 30% TBP were added and the mixture was equilibrated for 10 minutes. 2 ml aliquots were removed from both phases for gamma counting after centrifugation. Blank experiment without adding neptunium aliquot was also carried out each time and 2 ml aliquots from both aqueous and organic phases of the blank experiments were removed for counting. The neptunium gamma count rate was accordingly corrected for the contribution from uranium and its decay products. Similar experiments were carried out for neptunium(IV) extraction into TBP with varying organic phase uranium concentration.

7.5 Results

The calibration curves for the spectrophotometric estimation of uranium are shown in Figures 1 and 2. The calibration curve was found to vary with the slit width and hence it was necessary to repeat the calibration as the slit width in the earlier calibration could not be adjusted probably due to poor focussing of the tungsten lamp.

The equilibrium concentrations of uranium in both organic and aqueous phases measured at varying concentrations of uranium and nitric acid are shown in Tables 6 - 9. The results are plotted in Figure 3 along with the data previously reported[18,19]. Percent saturation of 30% TBP by uranium was calculated from the equilibrium uranium concentration in TBP phase assuming that 124 g/l of uranium gives 100% saturation of 30% TBP[20]. Organic phase uranium saturation data are plotted in Figure 4.

The variation of the distribution coefficient of uranium with saturation of TBP is shown in Figure 5. For comparison, similar data from literature[18,21] are also included. The distribution coefficient values obtained by us are somewhat lower than the published ones.

The effect of nitric acid concentration on the distribution coefficients of U(VI)[22], Np(VI)[2,23] and Pu(VI)[23] at tracer concentrations is shown in Figure 6. Similar data on the extraction of U(IV)[24], Np(IV)[2,23] and Pu(IV)[25,26] are shown in Figure 7.

The distribution coefficients of Np(VI) and Np(IV) determined at different initial aqueous nitric acid concentrations and saturations of TBP are given in Tables 10-13. Free nitric acid concentration at equilibrium in both aqueous and organic phases are also included in these tables. Some experiments were repeated after about 2 months interval and using a new batch of TBP obtained from the Plutonium Plant. The results of these experiments also are included in these tables. The data are plotted in Figures 8 and 9. Similar data for Pu(IV)[21,27] and U(VI)[27] are also included for comparison.

The variation of extraction of nitric acid with uranium saturation of 30% TBP is shown in Figure 10. Literature data[28] are also shown for comparison.

7.6 Discussion

It has been shown that the tetravalent and hexavalent actinides are

extracted into TBP as represented by equations 3 and 4.

$$M^{+4} + 4\ NO_3^- + 2\ TBP \rightleftharpoons M(NO_3)_4 .2\ TBP \quad (3)$$

$$MO_2^{++} + 2\ NO_3^- + 2\ TBP \rightleftharpoons MO_2(NO_3)_2 .2\ TBP \quad (4)$$

According to equations 3 and 4, increase in nitrate ion concentration will increase the extraction of the actinide elements. Figures 6 and 7 show that as the nitric acid concentration increases there is increase in the extraction of both hexavalent and tetravalent uranium, neptunium and plutonium. However, with increasing aqueous nitric acid concentration, increasing amounts of nitric acid are extracted into TBP, thus reducing the concentration of free TBP available for the extraction of the metal ion. As a result of this, the extraction of the actinide element decreases with increasing nitric acid concentration. The extraction of the tetravalent actinides into TBP follows the order: $Pu^{+4} > Np^{+4} > U^{+4}$ while in the case of hexavalent ones the order is : $UO_2^{++} > NpO_2^{++} > PuO_2^{++}$ at the same nitric acid concentration.

As the aqueous concentration of uranium increases, uranium tends to replace neptunium in the organic phase since the uranium-TBP complex is stronger than that of the neptunium-TBP, thereby reducing the distribution coefficient of neptunium. Similar effect has been observed in the extraction of plutonium also[27]. Thus, Figures 8 and 9 show that distribution coefficients of both Np(IV) and Np(VI) decrease with increasing saturation of the organic phase by uranium. Similar data for the extraction of Pu(IV) and U(VI) are included for comparison. From the plots in Figure 8, it appears that the rate of decrease of the log distribution coefficients of Pu(IV) and Np(IV) with uranium saturation of TBP is approximately the same, though extraction of plutonium is higher than that of neptunium. The same is true for the decrease of the log distribution coefficients of uranium(VI) and neptunium(VI). The decrease in the TBP concentration due to the extraction of uranium will lower the distribution coefficients of these elements relative to their distribution coefficients in the absence of uranium as seen from Figure 8 and 9.

At constant acidity, an increase in the uranium concentration of the organic phase from 25% to 90% saturation range investigated in the present work, causes decrease in the distribution coefficients of nitric acid because of the

reduction in the free TBP concentration. The results of the present work compare fairly well with the literature data.

8. ANALYSIS OF PUREX PROCESS SOLUTIONS

In the purex process, neptunium accompanies fission products, uranium or plutonium or is distributed between the three, depending on the chosen or imposed conditions. It was, therefore, found necessary to analyse the purex process solution at various stages for total neptunium content to know the path of neptunium in the Plutonium Plant.

8.1 The Purex Process

A schematic flow-sheet of the purex process used at the Plutonium Plant is shown in Figure 11. This flow-sheet includes the three cycle solvent extraction process in which the product constituents are decontaminated in the co-decontamination cycle (columns C_1 and C_2) before further decontamination and separation in the partitioning cycle (columns C_3, C_4, C_5). After partitioning, plutonium is further purified by ion exchange and uranium is decontaminated in the third solvent extraction cycle (columns C_6 and C_7).

8.2 Sampling

In the Plutonium Plant, there exists a sampling system to draw samples at various stages for analytical purposes. The same samples which were taken for the routine analysis of plutonium, uranium, acidity etc. were analysed for neptunium-237. Only aqueous samples were taken for this analysis.

8.3 Method of Analysis

The TTA extraction method was used throughout these analyses. 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 to be analysed was spiked with a known sliquot of pure Np^{239} to facilitate the chemical yield determination. The percentage recovery in each analysis was obtained by comparing the areas under photo-peaks of Np^{239} (228 KeV & 278 KeV) obtained by using a 3" x 3" NaI(Tl) detector and a 400-channel analyser. The calculation of efficiency by comparing the areas under photo-peaks with and without subtracting Compton tailing and by beta counting in a few cases was done and the results are given in Table 14. For a particular sample, the efficiencies calculated by all the three methods agreed within a few percent. In the present analysis, however,

the efficiencies obtained by comparing the areas under photo-peaks without correcting for the Compton tail were used. Radiochemical purity of the recovered Np^{237} was ascertained by alpha spectrum. An alpha spectrum of Np^{237} recovered from a typical purex process solution and that of pure Np^{237}, obtained by using a 30 mm^2 silicon barrier detector and a 400-channel analyser, is shown in Figure 12. The gamma spectrum of the neptunium sample recovered from a typical purex process solution initially spiked with Np^{239} and that of pure Np^{239}, obtained by using a 3" x 3" NaI(Tl) detector and a 400-channel analyser, is shown in Figure 13.

8.4 Results and Discussion

The results of analysis of various samples are given in Tables 15-24. As it was rather difficult to follow the same feed in the first cycle through all the three cycles, samples were analysed cycle by cycle. The ratio of neptunium to uranium in the feed for the first, second and third cycles and the final uranium product are compared in Tables 25-28. Neptunium to uranium ratio in the feed of the same cycle was found to be roughly constant and hence it can be taken as an approximate measure of neptunium "moving" from one cycle to the next one. Data in Tables 25 and 26 indicate that neptunium to uranium ratio in the first cycle feed and the second cycle feed are roughly the same for corresponding samples and hence it was inferred that during the first extraction cycle neptunium is almost quantitatively co-extracted with uranium and plutonium. The neptunium to uranium ratio has fallen by a factor of about 2 from the second cycle feed to the third cycle feed (Tables 26,27) which indicates that about 50% of the neptunium was extracted along with uranium and plutonium in the second cycle. During the partitioning step, only a small fraction of the extracted neptunium is lost to the plutonium product (Table 33). The ratio of neptunium to uranium in the feed of the third cycle (Table 27) is comparable to the one in the uranium product (Table 28) which suggests that neptunium is almost completely extracted in the third cycle.

For the corresponding samples of the feed and the raffinate in a particular cycle, the volume ratios were available. Usually the samples for the feed and the raffinate were not simultaneously drawn and hence these volume ratios are approximate. However, these data were used to calculate the percentage extraction of neptunium in each cycle. The results are given in Tables 29-33. The extraction of neptunium-237 in the first cycle was around 80-90% (Table 29) while that

in the second cycle was about 50% (Table 30). The extraction of neptunium in the third cycle was about 60% when the neptunium content of the third cycle feed and that in the product were used for calculation (Table 31) while it was above 90% when the neptunium content in the third cycle feed and the raffinate were used for calculation (Table 32). The difference in the value calculated by these two methods may be due to the uncertainties in the volume ratios. Thus, although these calculations are approximate and not very quantitative, the conclusions drawn from them are comparable with those drawn by comparing neptunium to uranium ratios.

9. CONCLUSIONS

From the data reported here it appears that under the usual uranium loading of 30% TBP in the purex process (viz. about 65% saturation), both Np(IV) and Np(VI) get extracted to an appreciable extent, particularly at a nitric acid concentration higher than 2 M. At lower nitric acid concentrations, however, very small amounts of Np(IV) may be extracted at 65% saturation or more.

Thus a flow-sheet could be designed either to force neptunium as Np(IV) with raffinate at low nitric acid in the feed and high uranium saturation of TBP or to co-extract neptunium with uranium(VI) and plutonium(IV) preferably as Np(VI) at feed acidities greater than 2 M. Mixer-settler experiments using synthetic samples containing neptunium, plutonium and uranium and under controlled conditions are planned. The data obtained from such experiments would help to draw more quantitative conclusions, which would be useful in the design of neptunium recovery facility.

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TABLE - 1

Spectrographic Analysis of Impurities in Neptunium-237

Element	Concentration (ppm)
Fe	200
Al	200
Ca	200
Mg	150
P	4000
Sb	400
Zn	50
Mn	20
Pb	10
Zr	10
Cr	10
Ag	2
Ti	5
Ni	1

In addition to these above Co, Cd, Cu, Bi, Be, As, Hg, Te, B and Si were also looked for but were not detected.

TABLE - 2

Spectrographic Analysis of Impurities in Neptunium-237 after purification

Element	Concentration (ppm)
Fe	67
Si	149
Al	142
Ca	75
Mg	112
Cr	15
B	37
Sb	60

In addition to these above, P, Mn, Pb, Ag, Ti, Ni, Co, Cd, Cu, Bi, Be, As, Hg, Te, Zn and Zr were also looked for but were not detected.

TABLE - 3

Estimation of neptunium-237 after separation from uranium and plutonium

U ~200 mg

Pu ~160 µg

Np ~ 2 µg

Expt. No.	% recovery as estimated by		
	Alpha Counting (Np^{237})	Beta counting (Np^{239})	Gamma counting (Np^{239})
1.	97.9	95.4	97.5
2.	96.3	89.8	94.0
3.	96.5	96.2	97.2
4.	93.8	95.9	95.7
5.	88.6	94.3	91.4
6.	97.0	98.2	97.2

TABLE - 4

Kd of Np(VI) in 30% TBP-Shell sol T at different HNO_3 concentrations

Concn. of HNO_3, M	Kd(A)		Kd(B)	Kd, Literature values (Ref.2)
	1	2		
1.0	4.1	4.4	4.3	4.5
2.0	7.8	9.7	8.7	10.0
3.0	10.9	13.5	13.1	15.0
4.0	13.2	16.6	14.6	19.0
5.0	14.7	16.7	15.7	20.0
6.0	14.1	15.4	14.2	14.0

A - Using 0.01 M $K_2Cr_2O_7$ as the holding oxidant

1 - Earlier values

2 - Repeated values

B - Using 0.01 M Ce(IV) as the holding oxidant

TABLE - 5

Kd of Np (IV) in 30% TBP - Shell sol-T at different HNO_3 concentrations

Concn. of HNO_3, M	Kd		
	1	2	3
1.0	1.1	1.5	0.24
2.0	2.0	2.3	1.1
3.0	3.1	3.5	2.2
4.0	4.7	5.1	3.4
5.0	6.8	7.3	5.5
6.0	9.3	10.0	9.0
7.0	12.6	-	12.0
8.0	14.5	-	15.0
9.0	14.0	-	14.0
10.0	11.0	-	13.0

1 - Earlier values

2 - Repeated values

3 - Literature values (Ref.2)

TABLE - 6

Kd of U (VI) as a function of saturation of 30% TBP with uranium

Initial Aq concn. of HNO_3 - 1 M

Expt. No.	Initial concn. of $U_{(aq)}$, mg/ml	Eq. concn. of $U_{(aq)}$, mg/ml	Eq. concn. of $U_{(org)}$, mg/ml	Kd (U)	% Saturation
1.	41.8	8.5	33	3.88	27
2.	83.3	25.5	58	2.28	47
3.	125.3	47.0	68	1.45	55
4.	167.0	74.0	90	1.22	73
5.	208.9	108.0	101	0.94	82
6.	292.3	180.0	111	0.62	90

TABLE - 7

Kd of U (VI) as a function of saturation of 30% TBP with uranium

Initial Aq. concn. of HNO_3 - 2 M

Expt.No.	Initial concn. of $U_{(aq)}$, mg/ml	Eq. concn. of $U_{(aq)}$, mg/ml	Eq. concn. of $U_{(Org)}$, mg/ml	Kd (U)	% Saturation
1.	21.2	1.9	19.9	10.47	16
2.	42.4	4.4	39.0	8.86	32
3.	63.6	8.4	57.2	6.81	46
4.	84.8	14.5	70.0	4.83	56
5.	101.7	21.5	79.0	3.68	63
6.	110.2	26.0	82.0	3.15	66
7.	118.7	31.0	87.0	2.81	70
8.	127.1	37.0	89.0	2.41	71
9.	135.6	41.0	90.0	2.20	72
10.	152.6	54.0	99.0	1.83	79
11.	169.5	66.3	101.5	1.53	81
12.	203.4	96.0	105.0	1.09	84

TABLE - 8

Kd of U (VI) as a function of saturation of 30% TBP with uranium

Initial Aq. Concn. of HNO_3 - 3 M

Expt. No.	Initial concn. of $U_{(aq)}$, mg/ml	Eq. concn. of $U_{(aq)}$, mg/ml	Eq. concn. of $U_{(org)}$, mg/ml	Kd (U)	% Saturation
1.	41.8	3.4	40.5	11.91	32
2.	83.3	10.0	71.5	7.15	57
3.	125.3	29.2	95.0	3.25	76
4.	142.0	40.5	99.0	2.44	79
5.	167.0	62.0	102.5	1.65	82
6.	208.8	101.2	107.2	1.06	86

TABLE - 9

Kd of U (VI) as a function of saturation of 30% TBP with uranium

Initial Aq. concn. of HNO_3-4.0M

Expt. No.	Initial concn. of $U_{(aq)}$, mg/ml	Eq. concn. of $U_{(aq)}$, mg/ml	Eq. concn. of $U_{(org)}$, mg/ml	Kd (U)	% Saturation
1.	41.8	2.08	40.6	19.52	33
2.	83.3	8.5	73.4	8.64	59
3.	125.3	26.5	96.0	3.62	77
4.	142.0	42.0	100.0	2.38	81
5.	167.0	61.0	104.0	1.71	84
6.	208.8	98.0	106.0	1.08	86

TABLE - 10

Variation of Kd of Np(VI) and Np(IV) with saturation of 30% TBP with uranium

Initial concn. of HNO_3 (aq) - 1.0 M

Expt. No.	Saturation of TBP by U, %	Eq. Acidity (Aq.), M	Eq. Acidity (Org.), M	Kd Np(VI) (1)	Kd Np(VI) (2)	Kd Np(IV) (1)	Kd Np(IV) (2)
1.	26.6	0.90	0.126	2.45	2.41	0.19	0.19
2.	46.8	0.93	0.092	1.60	1.48	0.10	0.094
3.	54.8	0.96	0.076	1.07	1.05	0.058	0.057
4.	72.6	0.97	0.066	0.71	0.71	0.046	0.047
5.	81.5	0.98	0.062	0.51	0.50	0.038	0.038
6.	89.5	-	-	0.27	0.30	0.035	0.032

(1) Earlier values

(2) Repeated values

TABLE - 11

Variation of Kd of Np(VI) and Np(IV) with saturation of 30% TBP with uranium

Initial concn. of HNO_3 (aq) - 2.0 M

Expt. No.	Saturation of TBP by U, %	Eq. Acidity (Aq.), M	Eq. Acidity (Org.), M	Kd Np(VI) (1)	Kd Np(VI) (2)	Kd Np(IV) (1)	Kd Np(IV) (2)
1.	51	1.78	0.279	4.26	3.81	0.56	0.55
2.	57	1.90	0.194	2.49	2.22	0.22	0.22
3.	71	1.96	0.136	1.28	1.20	0.11	0.10
4.	76	1.98	0.121	1.07	0.94	0.088	0.090
5.	80	2.00	0.109	0.83	0.73	0.073	0.076
6.	85	2.02	0.091	0.56	0.49	0.058	0.055

(1) Earlier values

(2) Repeated values

TABLE - 12

Variation of Kd of Np(VI) and Np(IV) with saturation of 30% TBP with uranium

Initial concn. of $HNO_{3(aq)}$ - 3.0 M

Expt. No.	Saturation of TBP by U, %	Eq. Acidity (Aq.), M	Eq. Acidity (Org.), M	Kd Np(VI) (1)	Kd Np(VI) (2)	Kd Np(IV) (1)	Kd Np(IV) (2)
1.	32	2.70	0.415	6.67	7.14	1.05	1.10
2.	57	2.87	0.277	3.39	3.68	0.39	0.44
3.	76	2.98	0.182	1.52	1.32	0.17	0.19
4.	79	3.01	0.160	1.18	1.08	0.13	0.14
5.	82	3.03	0.137	0.83	0.73	0.10	0.10
6.	86	3.05	0.112	0.48	0.42	0.076	0.080

(1) Earlier values

(2) Repeated values

TABLE - 13

Variation of Kd of Np(VI) and Np(IV) with saturation of 30% TBP with uranium

Initial concn. of $HNO_{3(aq)}$ - 4.0 M

Expt. No.	Saturation of TBP by U, %	Eq. Acidity (Aq.), M	Eq. Acidity (Org.), M	Kd Np(VI)	Kd Np(IV)
1.	33	3.52	0.518	9.47	2.01
2.	46	3.73	0.348	6.63	1.33
3.	59	3.88	0.221	4.24	0.84
4.	71	3.90	0.185	2.42	0.51
5.	77	3.95	0.158	1.48	0.32
6.	83	3.99	0.132	1.01	0.23

TABLE - 14

Efficiency of the method of Separation

Expt.No.	Efficiency by γ-counting (corrected for Compton tail)	Efficiency by γ-counting (uncorrected for Compton tail)	Efficiency by β-counting
1	98.9	99.4	98.3
2	100.9	98.4	93.5
3	98.7	97.7	96.0
4	96.5	97.2	95.9
5	94.8	96.7	93.4
6	74.1	74.3	71.1
7	91.3	92.6	86.6

TABLE - 15

First Cycle Feed (Tank Nos. 181/3)

No. of the sample	Concn. of Np^{237} µg/ml
2076	1.15
2077	1.21
2193	1.0
2194	1.0
2385	1.27
2386	1.29
2794 + 2795	1.56
2828 + 2829	1.30

TABLE - 16

First Cycle Raffinate (Tank No.5)

No. of the sample	Concn. of Np^{237} (µg/ml)
2078	Nil
2086	0.046
2087	0.24
2184	0.064
2192	0.10
2228	0.048
2472	0.39
2484	0.28
1804	0.18
2811	0.14
2843	0.15
2852	0.19

TABLE - 17

Second Cycle Feed (Tank Nos. 15/16)

No. of the sample	Concn. of Np^{237} (µg/ml)
602	2.53
603	2.90
650	1.86
2166	1.48
2167	1.71
1192	2.43
1473	3.23
1646	2.38

TABLE - 18

Second Cycle Raffinate (Tank No.19)

No. of the sample	Concn. of Np^{237} (µg/ml)
640 + 659 + 660	1.28
676 + 683 + 693	0.98
711 + 712 + 743	0.83
1193	1.20
1474	0.99
1543	0.89
1706	0.69
2175	0.51
2181	0.51

TABLE - 19

Third (Uranium) Cycle Feed (Tank No.32)

No. of the sample	Concn. of Np^{237} (µg/ml)
546	0.39
547	0.42
555	0.69
570	0.62
1121	0.38
1260	0.42
1310	0.30
1708	0.38
1743	0.58
1934	0.37
2214	0.39
2266	0.31
2300 + 2302	0.32
2319 + 2320	0.11

TABLE - 20

Third (Uranium) Cycle Raffinate (Tank No.35)

No. of the sample	Concn. of Np^{237} (µg/ml)
2218	0.025
2282	0.004
2289	0.015
2303	0.012
2321	0.010

TABLE - 21

Third Cycle Product (Uranium) - Tank No.37

No. of the sample	Concn. of Np^{237} (µg/ml)
1274	0.029
1278	0.031
1290	0.049
1730	0.060
1936 + 1937	0.069
2219 + 2220	0.045
2322 + 2323	0.009

TABLE - 22

Second Cycle Product (Plutonium) Tank No.21

No. of the sample	Concn. of Np^{237} (µg/ml)
2474	0.11
2797	0.26
2802	0.25
2807	0.27
2830	0.19
2856	0.16

TABLE - 23

Second Cycle Product (Uranium) Tank No.23

No. of the sample	Concn. of Np^{237} (µg/ml)
2475	0.21
2796	0.18
2831	0.31
2857 + 2858	0.22

TABLE - 24

Second Cycle Product (Uranium Concentrate) Tank No.26

No. of the sample	Concn. of Np^{237} (µg/ml)
3090 + 3091	1.06
3108 + 3127	0.87

TABLE - 25

First Cycle Feed (Np : U)

(Tank 181, 3)

No. of the sample	Neptunium-237 µg/ml	Uranium mg/ml	$\left(\frac{Np}{U}\right) \times 10^6$
2076	1.15	300	3.8
2077	1.21	306	4.0
2193	1.00	310	3.2
2194	0.99	310	3.1
2385	1.27	394	3.2
2386	1.29	398	3.2
2794 + 2795	1.56	220	7.1
2828 + 2829	1.30	230	5.7

TABLE - 26

Second Cycle Feed (Np : U)

(Tank 15, 16)

No. of the sample	Neptunium-237 µg/ml	Uranium mg/ml	$\left(\frac{Np}{U}\right) \times 10^6$
602	2.53	71	35.6
603	2.90	177	16.4
650	1.86	310	6.0
1192	2.43	336	7.2
1473	3.23	368	8.8
1646	2.38	332	7.2
2166	1.48	336	4.4
2167	1.71	416	4.1

TABLE - 27

Third Cycle Feed (Np : U)

(Tank 32)

No. of the sample	Neptunium-237 µg/ml	Uranium mg/ml	$(\frac{Np}{U}) \times 10^6$
546	0.39	208	1.9
547	0.42	208	2.0
555	0.69	238	2.9
570	0.62	296	2.1
1121	0.38	284	1.3
1260	0.42	314	1.3
1310	0.30	244	1.2
1708	0.38	270	1.4
1743	0.58	330	1.8
1934	0.37	305	1.2
2214	0.39	380	1.0
2319 + 2320	0.11	271	0.4
2300 + 2302	0.32	297	1.1
2266	0.31	274	1.1

TABLE - 28

Third Cycle Product Uranium (Np:U)
(Tank - 37)

No. of the sample	Neptunium-237 µg/ml	Uranium mg/ml	$(\frac{Np}{U}) \times 10^6$
1274	0.029	36.8	0.8
1278	0.031	30.6	1.0
1290	0.049	32.0	1.5
1730	0.060	43.6	1.4
1936 + 1937	0.069	66.8	1.0
2219 + 2220	0.045	49.2	0.9
2322 + 2323	0.009	11.74	0.8

TABLE - 29

Extraction of Neptunium in First Cycle

No. of the Sample T/181 T/3	Acidity (HNO_3) M	Neptunium-237 µg/ml	No. of the sample T/5	Neptunium-237 µg/ml	Vol. Ratio T/3, T/181 : T/5	Extraction of Np^{237}, %
2193	1.59		2184	0.064	1 : 2	87.2
2194	1.59	1.00	2192	0.10	3 : 5	83.3
			2228	0.048	15 : 23	92.6
2385	2.87		2472	0.39	248 : 371	54.4
2386	2.82	1.28	2484	0.28	174 : 273	65.7
2076	2.71		2078	negligible	164 : 329	100
2077	2.71	1.18	2086	0.046	204 : 329	93.7
			2087	0.24	204 : 313	68.8
2794 + 2795	2.72	1.56	2804	0.18	220 : 408	78.6
			2811	0.14	134 : 212	85.8
2828 + 2829	2.0	1.30	2843	0.15	281 : 387	84.1
			2852	0.19	183 : 323	74.2

TABLE - 30

Extraction of Neptunium in Second Cycle

No. of the sample T/15, T/16	Acidity (HNO_3) M	Neptunium-237 µg/ml	No. of the sample T/19	Neptunium-237 µg/ml	Vol. Ratio T/15, T/16, : T/19	Extraction of Np^{237}, %
1192	1.50	2.43	1193	1.20	9 : 13	28.7
1473	2.49	3.23	1474	0.99	7 : 13	43.1
			1543	0.89	5 : 11	39.4
1646	3.12	2.38	1706	0.69	9 : 13	58.1
2166	5.25	1.48	2175	0.51	2 : 3	52.2
2167	3.44	1.71	2181	0.51	17 : 27	49.4

TABLE - 31

Extraction of Neptunium in Third Cycle

No. of the sample T/32	Acidity (HNO_3) M	Neptunium-237 µg/ml	No. of the sample T/37	Neptunium-237 µg/ml	Vol. Ratio T/32:T/37	Extraction of Np^{237}, %
1260	0.47	0.42	1274	0.029	16 : 97	41.9
			1278	0.031	10 : 81	59.8
			1290	0.049	34 : 173	59.4
1708	1.85	0.38	1730	0.060	16 : 95	93.8
1934	2.82	0.37	1936+1937	0.069	21 : 74	65.7
2214	2.61	0.39	2219+2220	0.045	10 : 43	49.6
2319+2320	2.82	0.11	2322+2323	0.009	102 : 387	31.0

TABLE - 32

Extraction of Neptunium in Third Cycle

No.of the sample T/32	Acidity (HNO_3) M	Neptunium-237 µg/ml	No.of the sample T/35	Neptunium-237 µg/ml	Vol. Ratio T/32:T/35	Extraction of Np^{237}, %
2266	2.45	0.31	2282	0.004	199 : 252	98.4
2300 + 2302	2.74	0.32	2303	0.012	5 : 9	93.3
2214	2.61	0.39	2218	0.025	10 : 12	92.3
2319 + 2320	2.82	0.11	2321	0.010	102 : 165	85.3

TABLE - 33

Distribution of Neptunium during Partitioning

No. of the sample T/21	Neptunium-237 µg/ml	No. of the sample T/23	Neptunium-237 µg/ml	Vol. Ratio T-21:T-23	Neptunium-237 in Pu-Stream, %
2474	0.11	2475	0.21	170 : 1511	5.6
2797	0.26	2796	0.18	106 : 641	19.3
2830	0.19	2831	0.31	58 : 212	14.4
2856	0.17	2857 + 2858	0.22	286 : 965	17.7

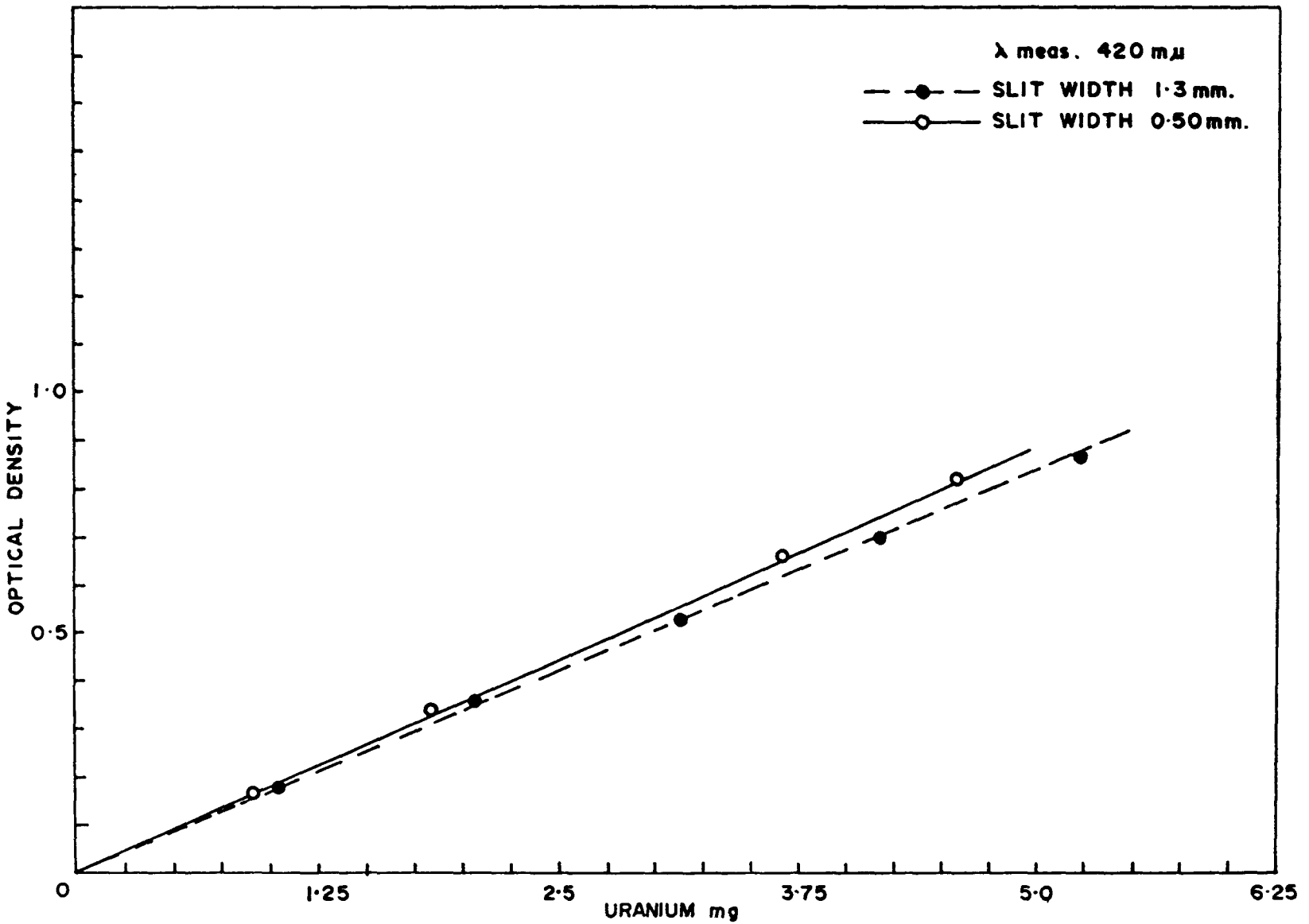

FIGURE-1. ESTIMATION OF URANIUM - CALIBRATION CURVE.

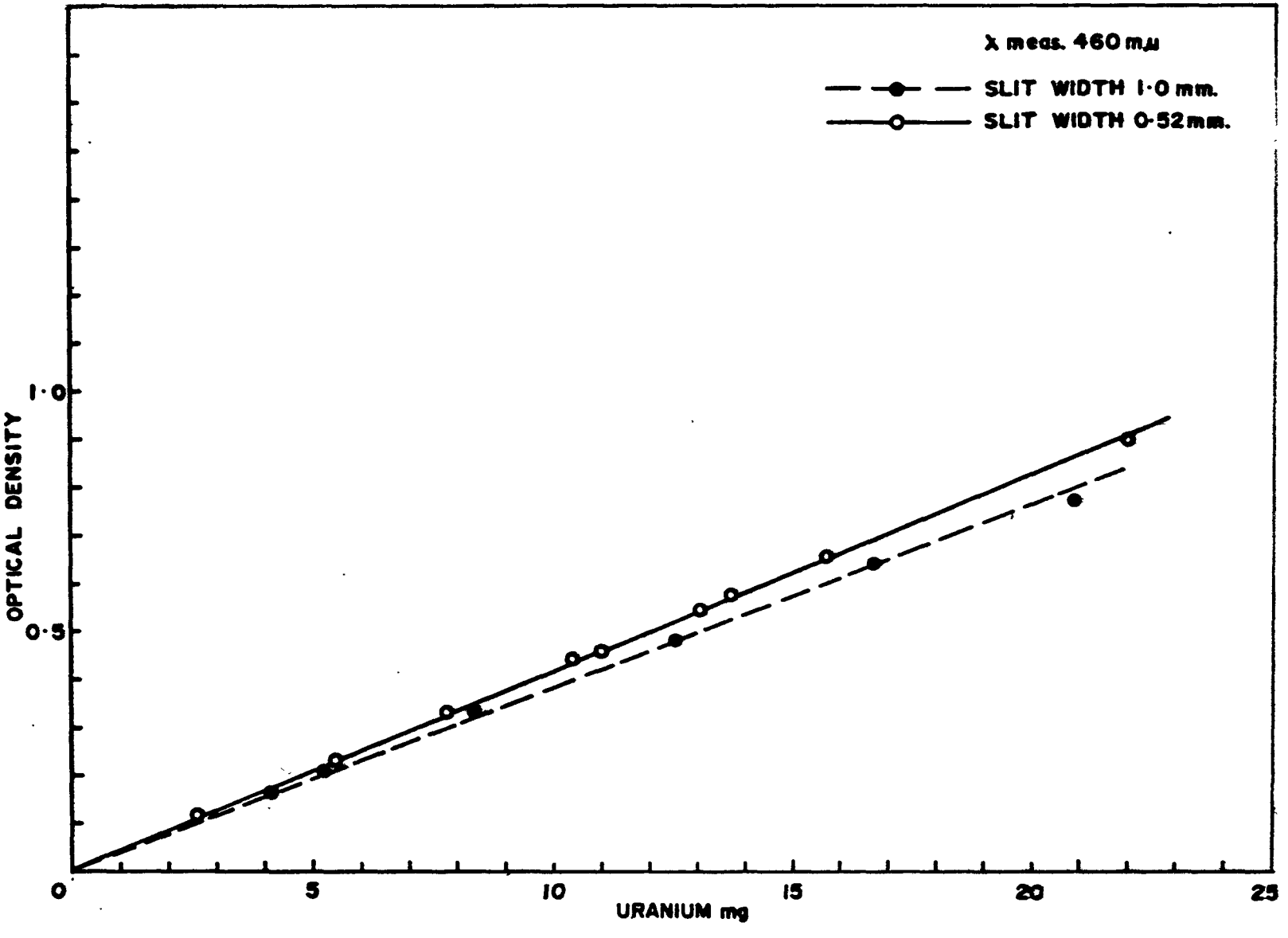

FIGURE - 2. ESTIMATION OF URANIUM CALIBRATION CURVE

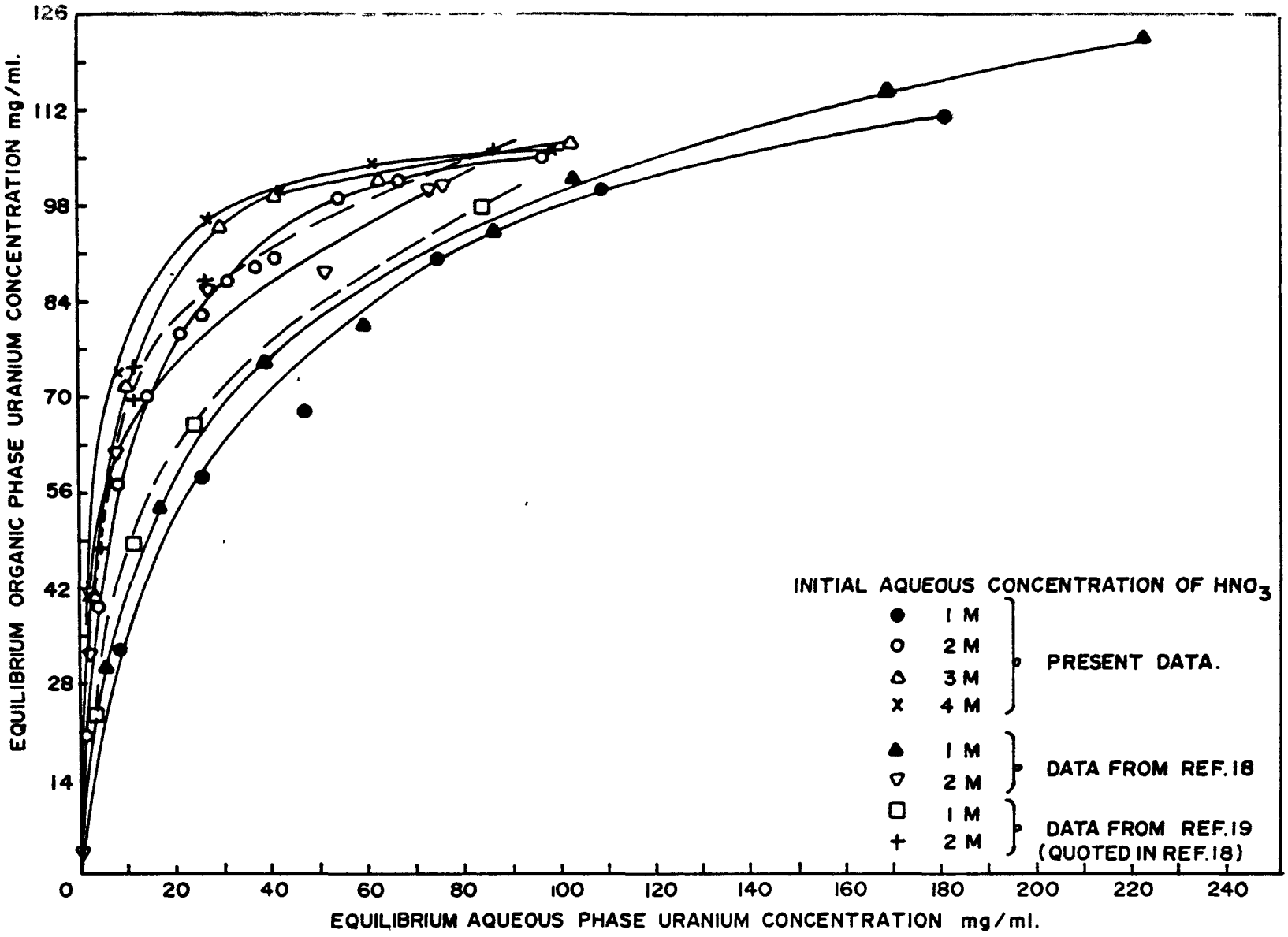

FIGURE-3. EQUILIBRIUM CURVES FOR URANYL NITRATE - HNO_3 - 30 % TBP.

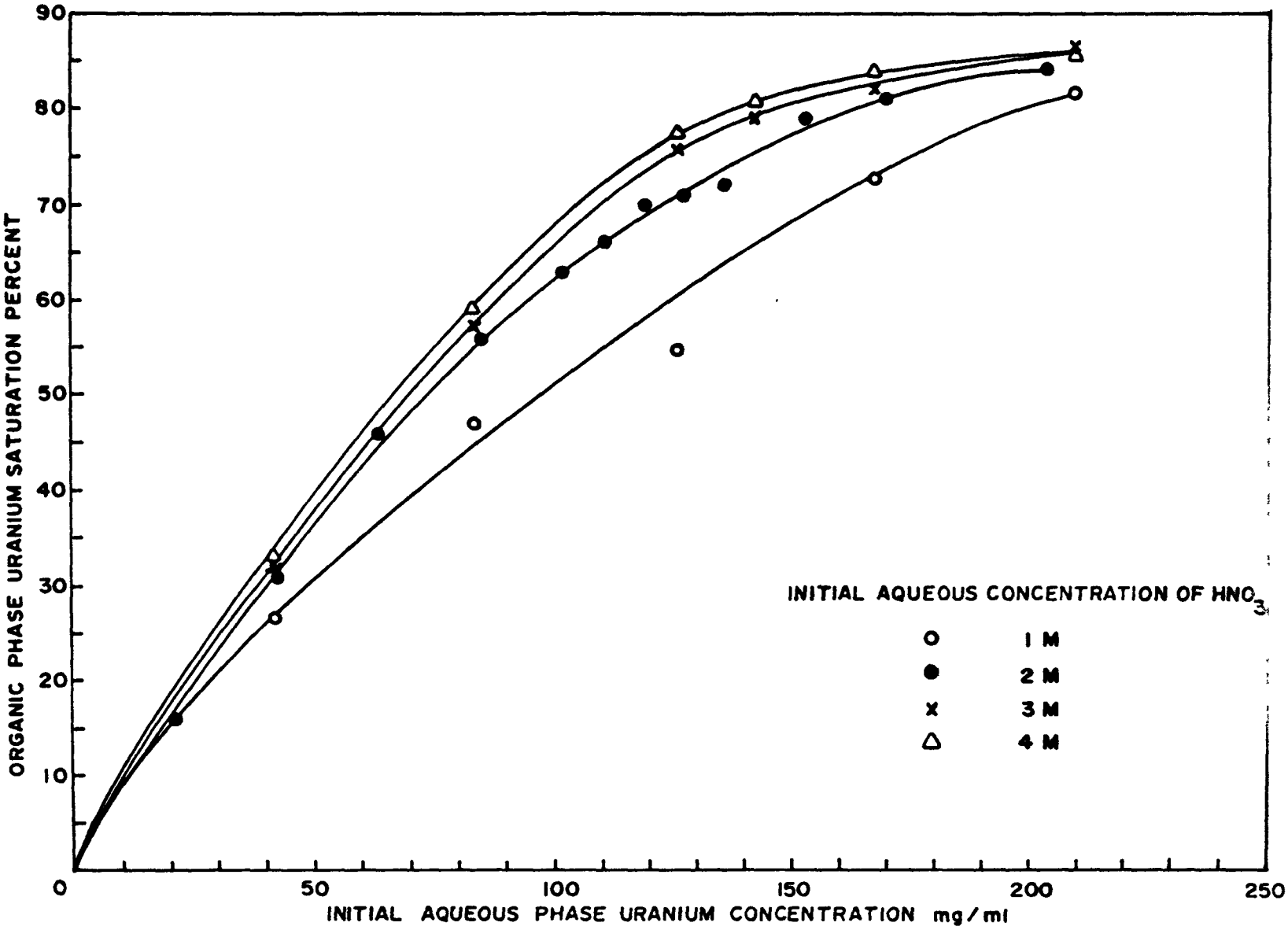

FIGURE - 4. VARIATION OF % SATURATION OF TBP WITH URANIUM CONCENTRATION.

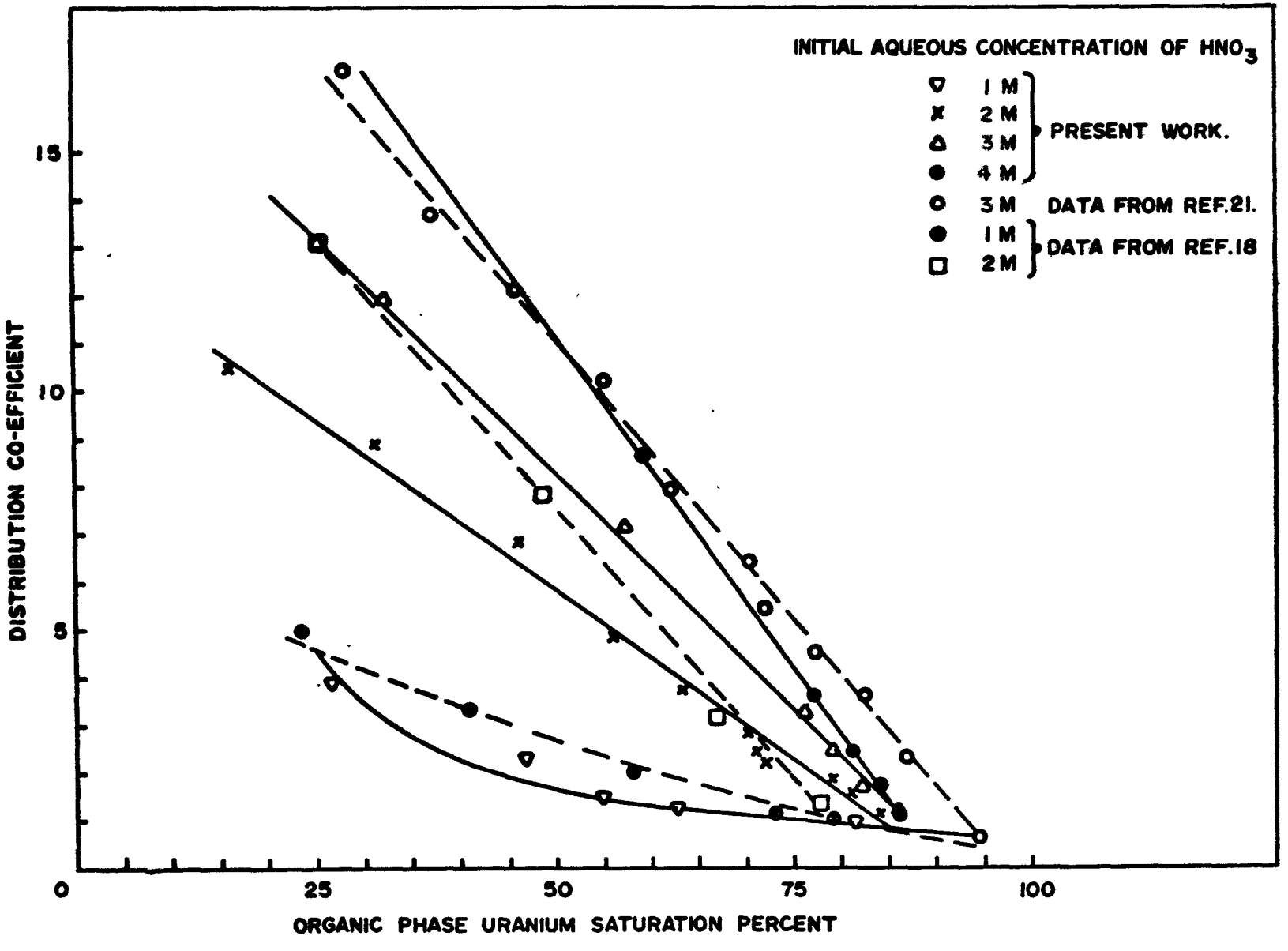

FIGURE-5.VARIATION OF URANIUM DISTRIBUTION CO-EFFICIENT WITH SATURATION OF TBP.

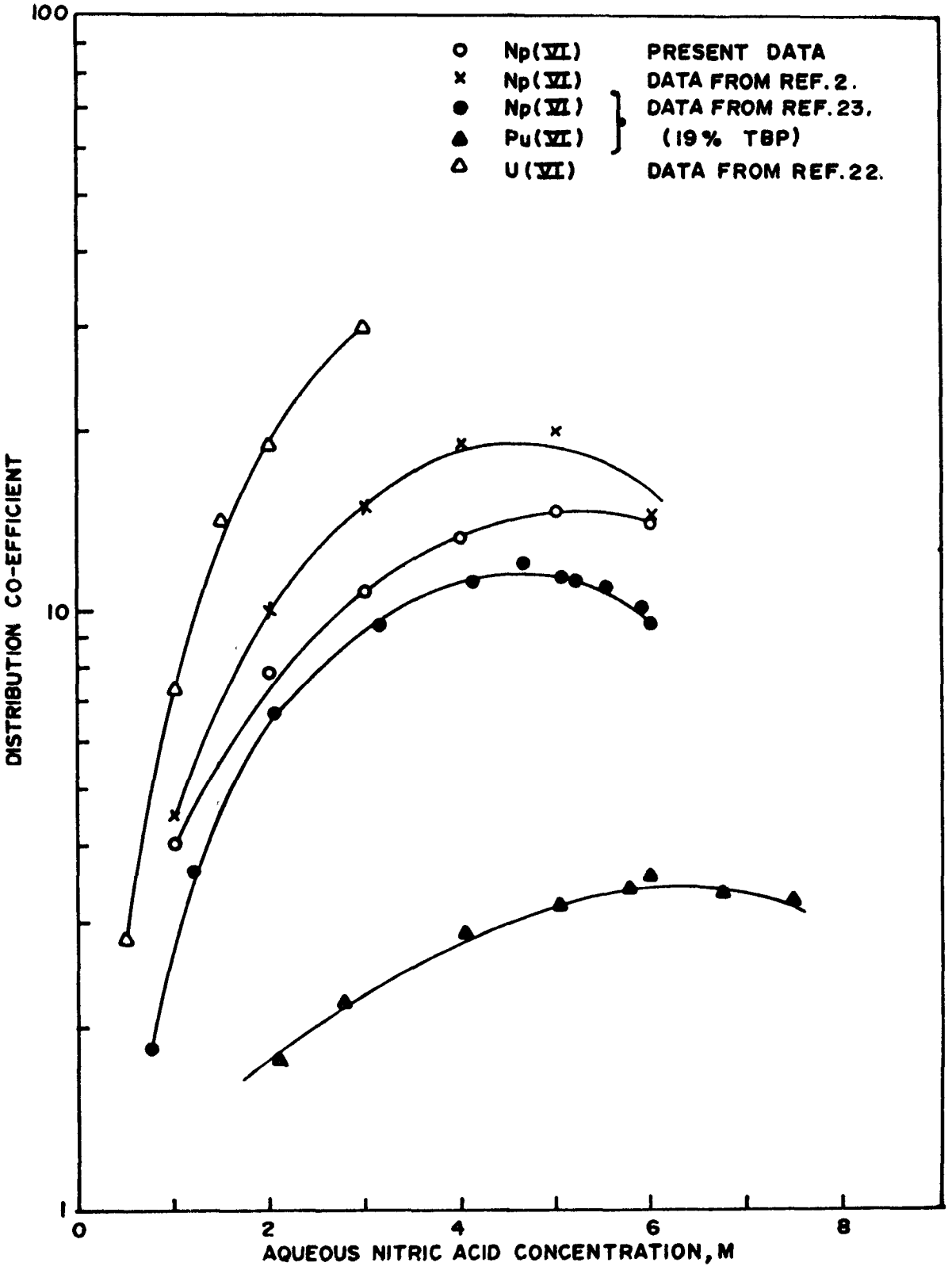

FIGURE-6. VARIATION OF DISTRIBUTION CO-EFFICIENT OF U(VI), Np(VI) AND Pu(VI) WITH NITRIC ACID CONCENTRATION.

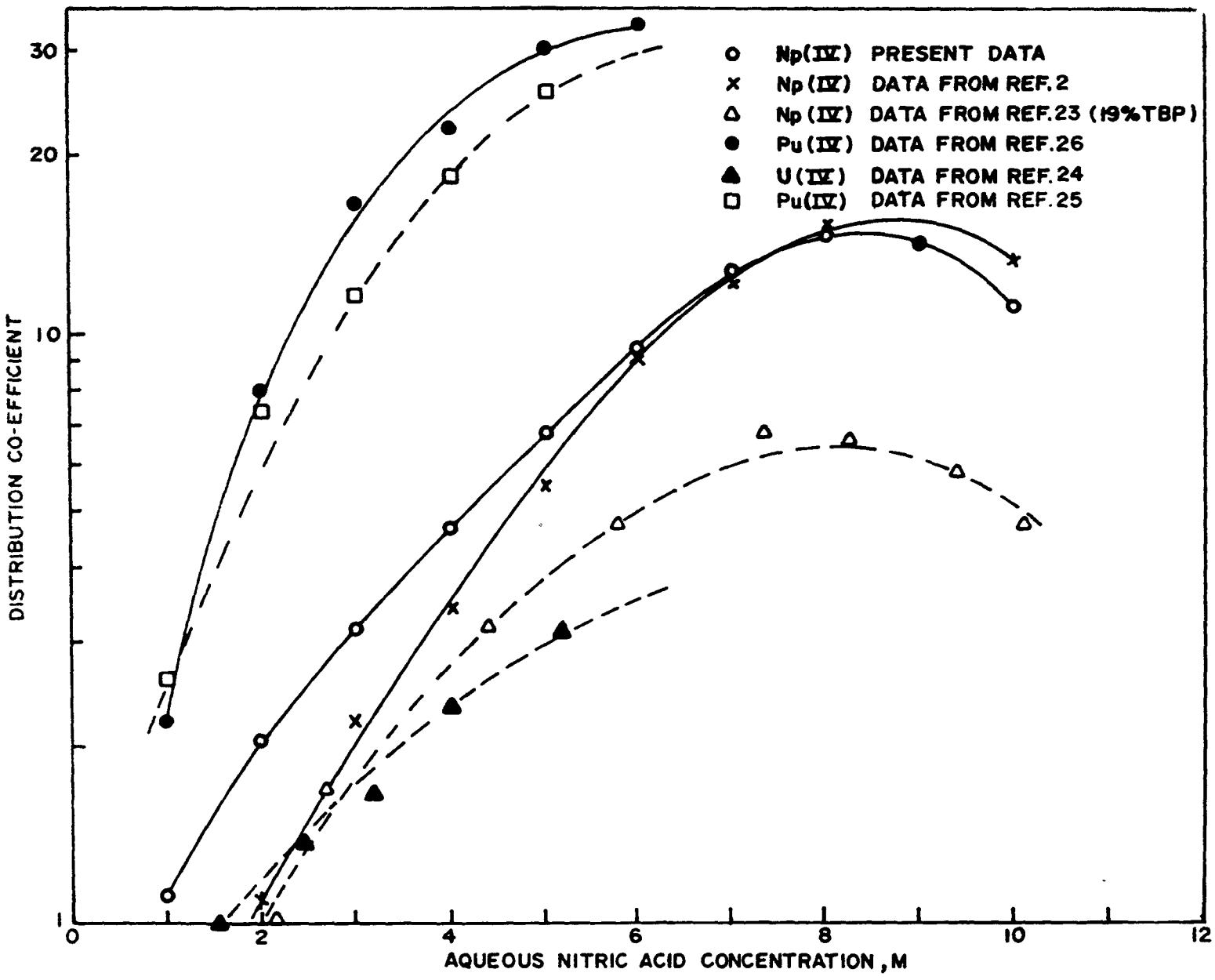

FIGURE-7. VARIATION OF DISTRIBUTION CO-EFFICIENT OF U(IV), Np(IV) AND Pu(IV) WITH NITRIC ACID CONC.

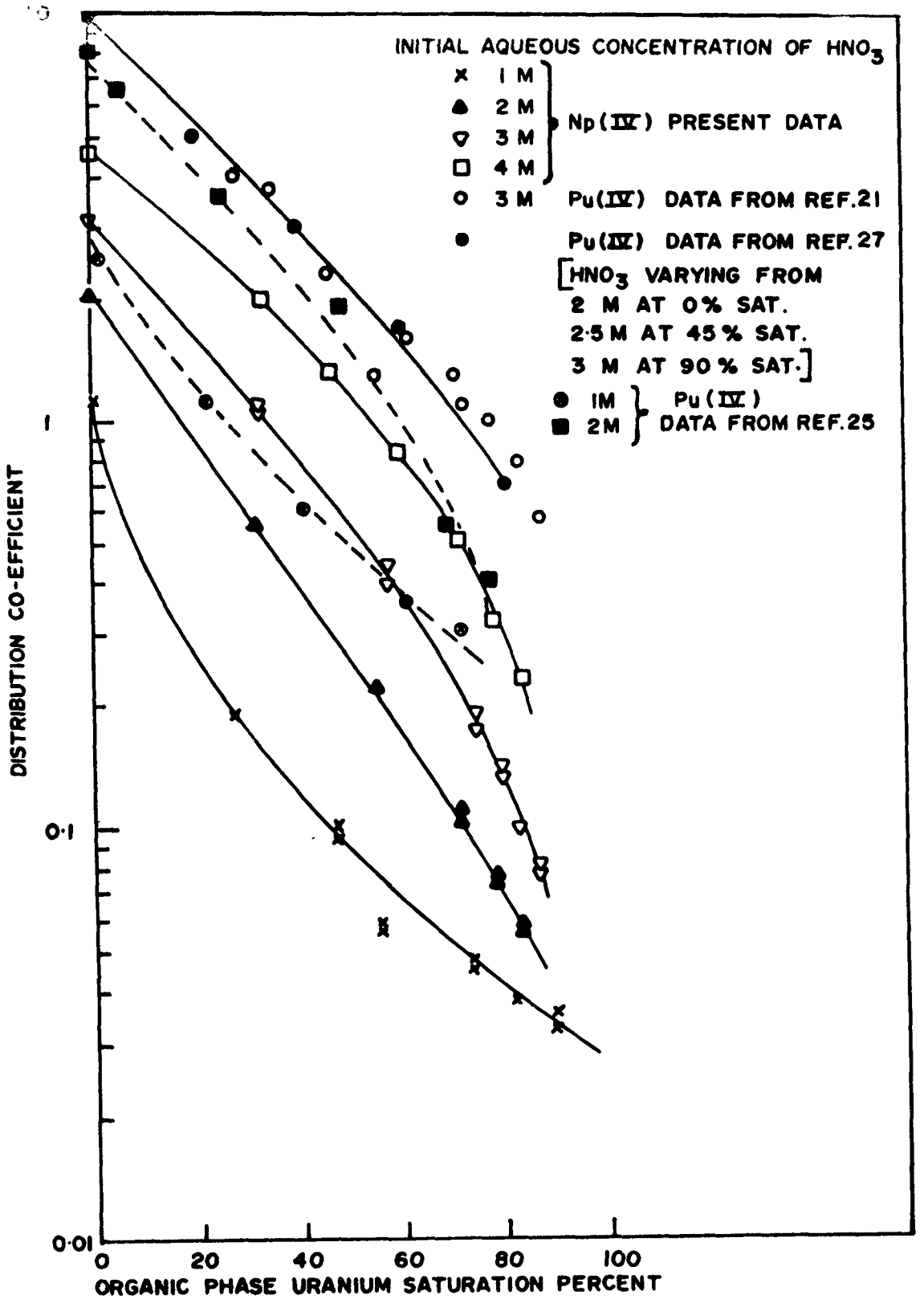

FIGURE-8. VARIATION OF DISTRIBUTION CO-EFFICIENT OF Np(IV) AND Pu(IV) WITH TBP SATURATION.

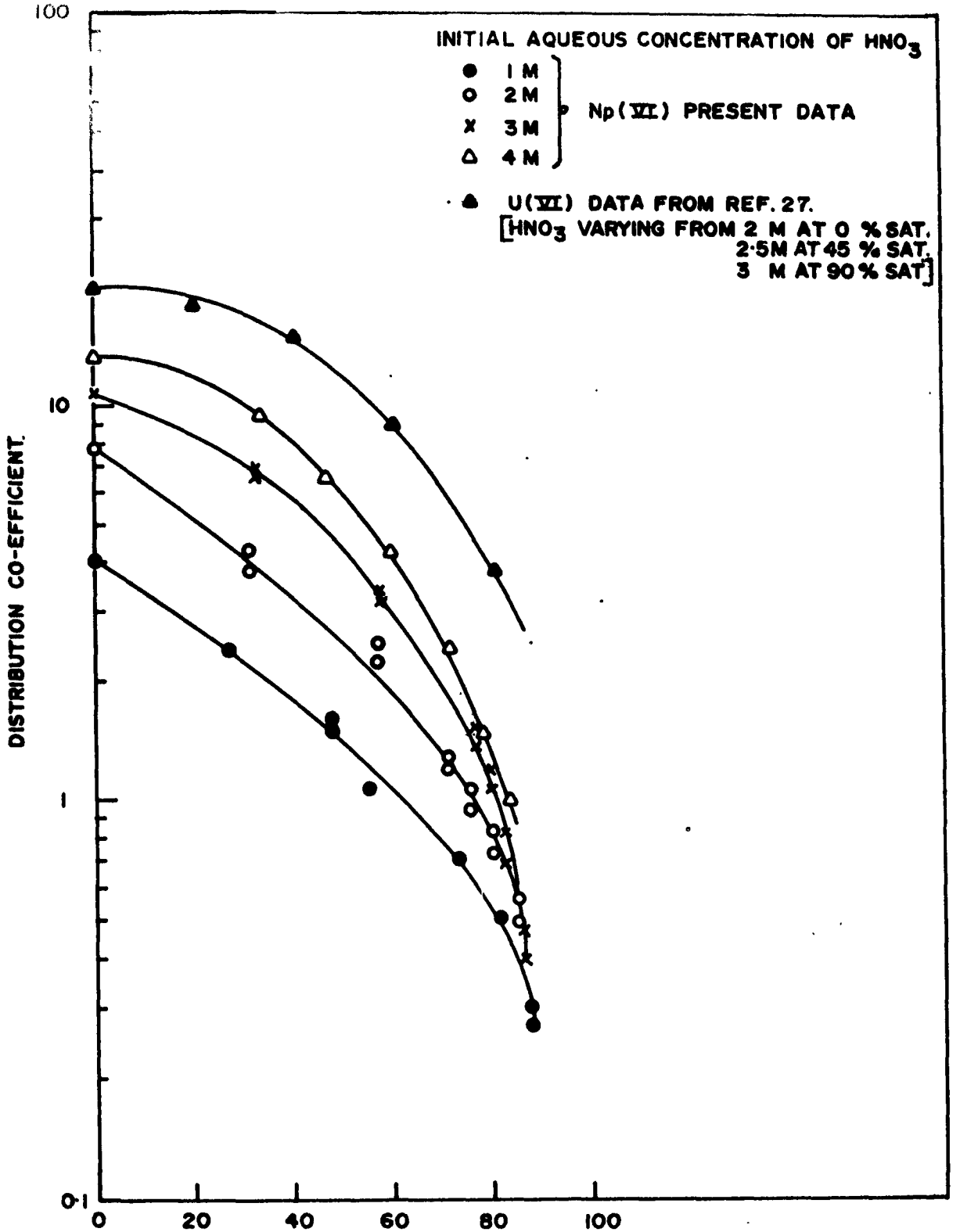

FIGURE-9. VARIATION OF DISTRIBUTION CO-EFFICIENT OF U(VI) AND Np(VI) WITH TBP SATURATION.

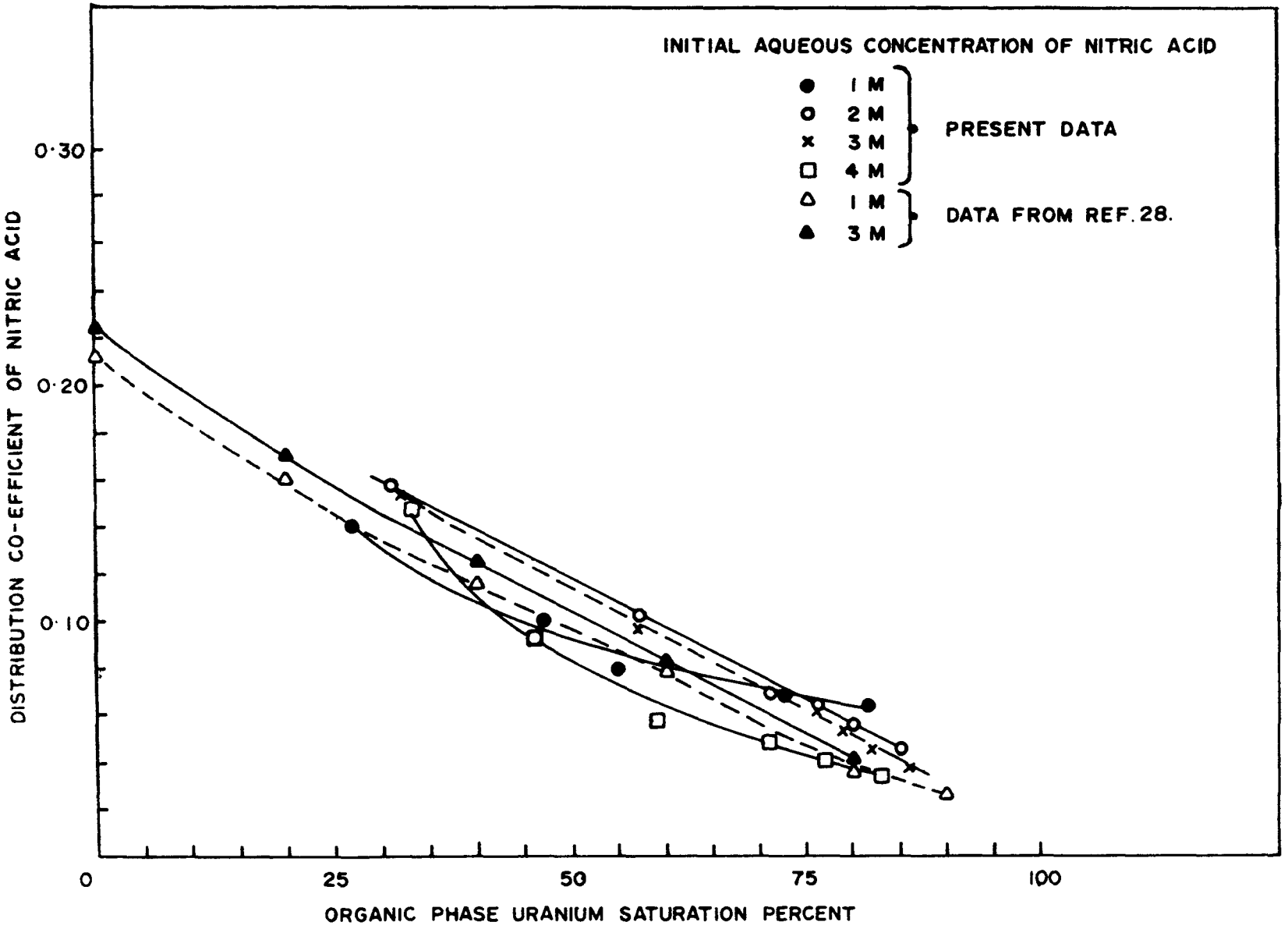

FIGURE - 10. VARIATION OF DISTRIBUTION CO-EFFICIENT OF NITRIC ACID WITH TBP SATURATION.

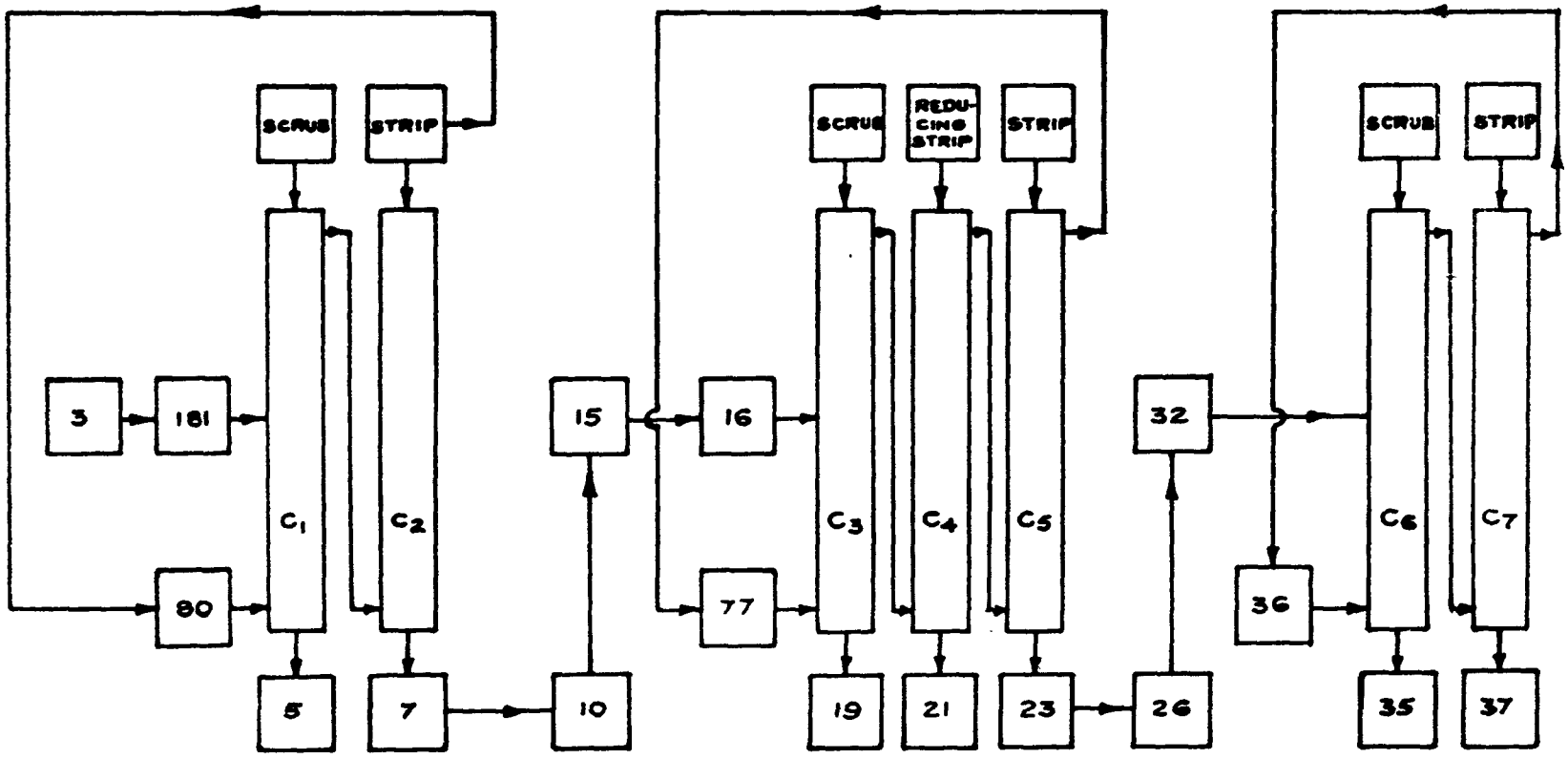

FIGURE-11. SCHEMATIC FLOWSHEET OF THE PUREX PROCESS.

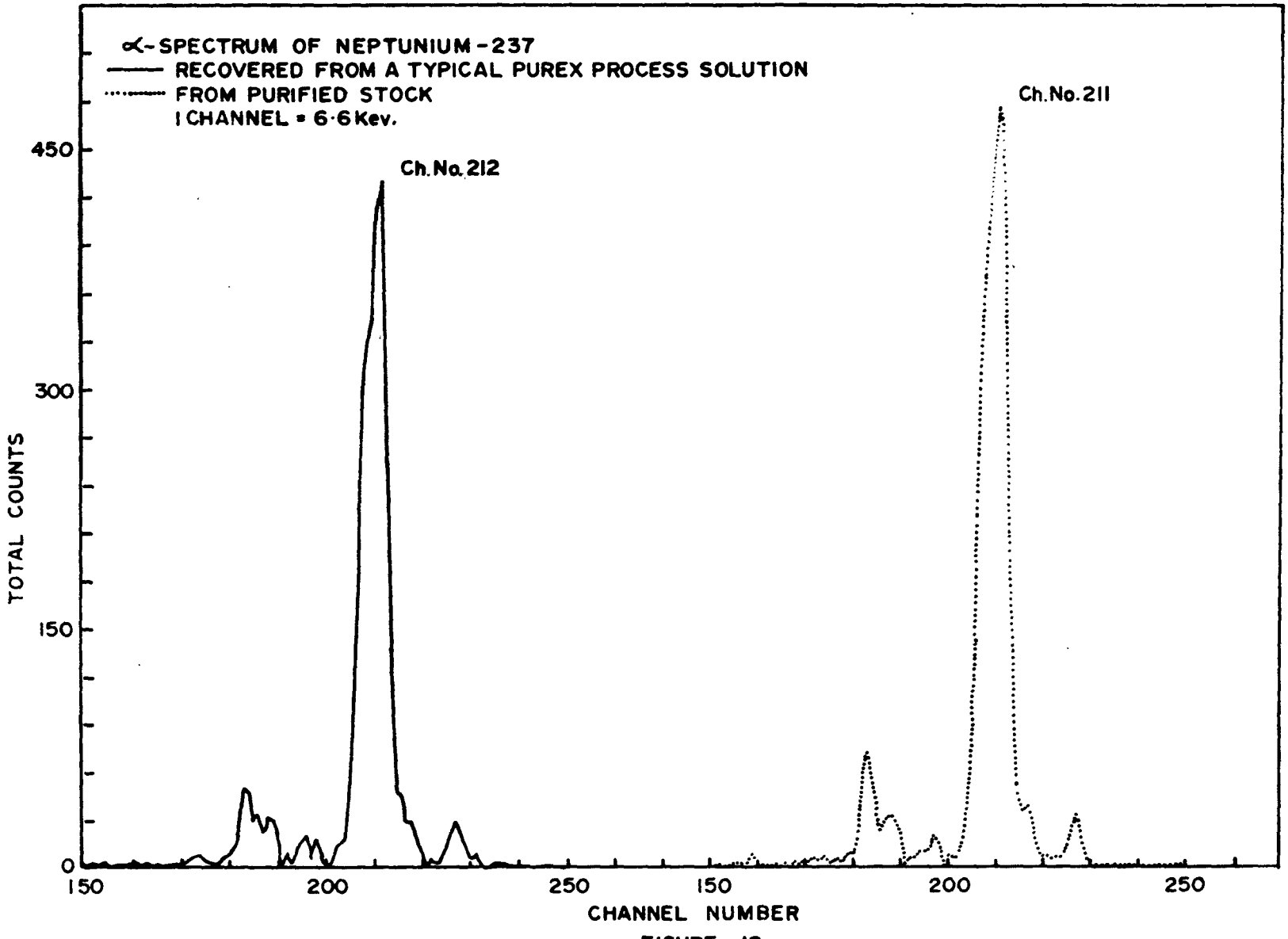
∝-SPECTRUM OF NEPTUNIUM-237
—— RECOVERED FROM A TYPICAL PUREX PROCESS SOLUTION
····· FROM PURIFIED STOCK
1 CHANNEL = 6·6 Kev.
Ch.No.212
Ch.No.211
TOTAL COUNTS
0
150
300
450
150
200
250
150
200
250
CHANNEL NUMBER

FIGURE - 12.

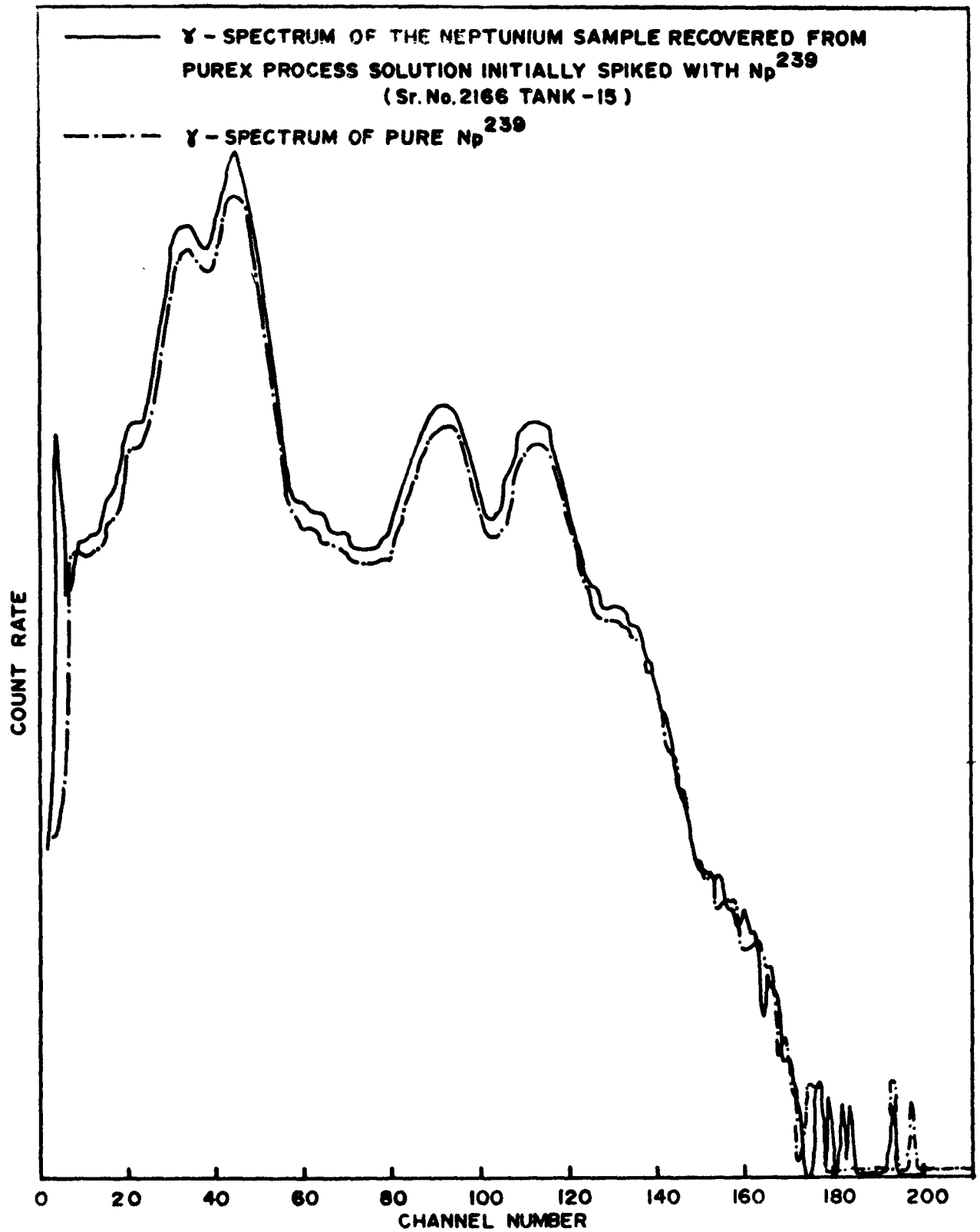
γ - SPECTRUM OF THE NEPTUNIUM SAMPLE RECOVERED FROM PUREX PROCESS SOLUTION INITIALLY SPIKED WITH Np^{239}
(Sr. No. 2166 TANK - 15)
γ - SPECTRUM OF PURE Np^{239}
COUNT RATE
0
20
40
60
80
100
120
140
160
180
200
CHANNEL NUMBER

FIGURE-13.