B.A.R.C.-734

B.A.R.C.-734

सत्यमेव जयते

GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

COUNTER-CURRENT EXTRACTION STUDIES FOR THE RECOVERY OF NEPTUNIUM BY THE PUREX PROCESS (PART I)

by

N. Srinivasan, M. N. Nadkarni, S. V. Kumar, P. K. S. Kartha, R. R. Sonavane
Fuel Reprocessing Division

and

M. V. Ramaniah and S. K. Patil
Radiochemistry Division

BHABHA ATOMIC RESEARCH CENTRE
BOMBAY, INDIA
1974

GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

COUNTER-CURRENT EXTRACTION STUDIES FOR THE RECOVERY OF NEPTUNIUM BY THE PUREX PROCESS (PART-I)

by

N. Srinivasan, M.N. Nadkarni, S.V. Kumar, P.K.S. Kartha, R.R. Sonavane
Fuel Reprocessing Division

and

M.V. Ramaniah and S.K. Patil
Radiochemistry Division

BHABHA ATOMIC RESEARCH CENTRE
BOMBAY, INDIA
1974

INIS subject category: B16; B13

Discriptors :

NEPTUNIUM 237

NEPTUNIUM COMPLEXES

MIXER-SETTLERS

PUREX PROCESS

COUNTER CURRENT

TBP

VANADIUM

URANIUM COMPLEXES

OXIDATION

NITRIC ACID

NITROUS ACID

FLOWSHEETS

ABSTRACT

It is proposed to recover neptunium-237, alongwith uranium and plutonium, during the fuel reprocessing in the PREFRE Plant at Tarapur. Counter-current extraction studies, relevant to the codecontamination (HA) and partitioning (IA) cycles of the purex process, were carried out to arrive at suitable chemical flowsheet conditions which would enable the coextraction of neptunium alongwith uranium and plutonium. The results of the studies carried out using a laboratory mixer-settler unit and synthetic mixtures of neptunium and uranium are reported here. Based on these results, the chemical flowsheet conditions are proposed for the coextraction of neptunium even if it exists as Np(V) in the aqueous feed solution.

COUNTER-CURRENT EXTRACTION STUDIES FOR THE RECOVERY OF NEPTUNIUM BY THE PUREX PROCESS

by

N. Srinivasan, M.N. Nadkarni, S.V. Kumar, P.K.S. Kartha
R.R. Sonavane, M.V. Ramaniah & S.K. Patil

PART - I

1. INTRODUCTION

Neptunium-237 is formed in kilogram quantities in nuclear power reactors with high burn-up, especially with enriched uranium fuels. Although it was discovered nearly 30 years ago(1), this isotope has assumed increasing importance only recently as it is primarily used as the starting material for the production of ^{238}Pu (2). Because of its very desirable nuclear decay properties, ^{238}Pu is one of the most suitable heat sources for fuelling the radioisotopic power sources. Plutonium-238 has a specific power of 0.55 watt per gram and emits little gamma and neutron radiation(2). During fuel reprocessing by the purex process, ^{237}Np can be recovered as a valuable by-product alongwith plutonium and uranium(2-7). In Tarapur Atomic Power Reactors about 5-7 Kg of ^{237}Np is expected to be produced annually assuming a burn-up of 15000 to 20000 MWD/T and 80% load factor(8). From Rajasthan Atomic Power Reactors about 3-4 Kg of ^{237}Np is expected to be produced per year. It is proposed to recover ^{237}Np, along with uranium and plutonium, during the fuel reprocessing of the spent fuels from both these reactors. The present work was undertaken with a view to arrive at optimum conditions for the recovery of ^{237}Np in the fuel reprocessing plant under construction at Tarapur. It is known that in the purex process ^{237}Np could be forced to follow the aqueous raffinate, plutonium or uranium stream by careful choice of acidity, uranium loading of the organic phase and the oxidation state of ^{237}Np. It was, however, felt that it would be most convenient to recover neptunium from the raffinate in the uranium purification cycle (2D cycle).

The distribution coefficient data reported on the extraction of Np(IV) and Np(VI) at varying nitric acid and uranium concentrations obtained at room temperature(9-11) and at 45°C(12) and 60°C(9,12) showed that both Np(IV) and Np(VI) would get extracted appreciably under the

the purex process conditions. It was, however, necessary to carry out counter-current extraction studies relevant to the purex process to establish the same. The results of the studies carried out for the coextraction of neptunium under the conditions relevant to the first (HA) and second (IA) cycles of the purex process carried out using a laboratory mixer-settler and synthetic mixtures of neptunium and uranium are described in this report.

2. THE MIXER-SETTLER UNIT

The usefulness of laboratory mixer-settler studies was summarized by Jamrack et al(13). Such studies furnish valuable data for the chemical flowsheet of a process being investigated for processing of nuclear materials. The stage sample analysis of the various components, in a multicomponent extraction process, at the end of a counter-current extraction experiment gives realistic and convenient equilibrium data for the process. Such data can be compared with theoretical stages data obtained by graphical or by computer calculations for the solvent extraction process. Thus it can provide valuable information which is a sound basis for scaling up.

A 12-stage stainless steel perspex minimixer-settler unit (Fig 1 & 2) of Eurochemic type(14) fabricated in Trombay, was used in the present studies. All the mixing compartments are on one side and the settling compartments are on the opposite side of the central stainless steel rectangular block which is suitably cut and machined. Two perspex sheets (12 mm thick) were fixed on each face of the stainless steel block using teflon gaskets. This made it convenient to observe the mixing and settling as well as interface level during the progress of the experiment. Also it prevented intermixer or intersettler leakages. Each mixer has three holes which connect it to three settlers and each settler also has three holes which in turn connect it to three mixers. The emulsion of the light and heavy phases leaves a mixer from the centre hole to a corresponding settler where the two phases are separated and the light phase moves from the top hole of the settler to the adjacent mixer in one direction and the heavy phase moves from the bottom hole to the adjacent mixer in the opposite direction. Thus the counter-current flow of aqueous and organic phases is achieved in the mixer-settler unit by gravity.

The total hold up volume of each stage is about 40 ml. The unit was operated with a combined flow ranging from about 4 ml to 10 ml/min resulting in an overall residence time of about 10 to 4 minutes per stage. In the earlier experiments the aqueous feed and the scrub were fed to the unit at a constant flow rate using a capillary attached to a constant level overflow system and the flow of the organic solution was controlled using a stopcock attached to a similar overflow system. The rates of the entering and outgoing streams were checked periodically and could be controlled within about ± 10%. In the later experiments microflow metering pumps were used to feed all the inactive streams whereas the active stream was fed to the unit only through the capillary as described earlier. The teflon micro-bellows pump obtained from M/s. Research Appliance Company, U.S.A., was used for TBP stream while for inactive aqueous streams, pumps supplied by M/s. Shapotools India and M/s. CIV mbH, Germany were used.

The mixing was achieved by using two stainless steel tubes (4.5 mm dia) in each mixer to which vacuum was alternately applied. The two stainless steel tubes in each mixer, used for air pulsing to achieve the mixing, were alternately connected to two stainless steel headers using polyethene tubes and vacuum applied to each header was alternated using two three-way solenoid valves (1/4" NPT), obtained from M/s. Automatic Switch co. USA, connected to a vacuum pump. The vacuum pulse frequency could be changed by an electronic timer and the pulse amplitude by changing the vacuum. The pulse frequency was usually maintained at 120 c/min and the vacuum used was about 4-5 cm Hg as was measured with a mercury manometer attached to the vacuum system. The mixer-settler unit was placed in a glove-box whereas the pumps, solenoid valves etc. were outside below the box. The exhaust of the pump was let into a nearby fumehood to ensure radiochemical safety.

The aqueous phase outlet of the mixer-settler unit was through a polythene tube connected to the bottom of the last settler. This tube was attached to an adjustable clamp to enable the control of the interface in the last stage. In all the extraction experiments aqueous nitric acid was the continuous phase while for the partitioning experiments 30% TBP/Shellsol-T was the continuous phase.

The advantages and disadvantages of various types of the laboratory mixer-settler were summarized by Jamrack et al (13). The present mixer-settler has the following limitations:

(a) Tendency of bypassing
(b) Tendency to back-mixing
(c) No interface control for the individual stages.
(d) Difficulty of stage sampling without disturbing the equilibrium conditions as the isolation of each stage is not possible.

However even with these limitations the simplicity and compactness of this unit made it very useful in studying the counter-current extraction behaviour of neptunium under the conditions relevent to the process aimed at in the present investigations.

3. EXPERIMENTAL

Neptunium-237 was purified from its daughter ^{233}Pa by extraction of the latter from 7M nitric acid into 0.5 M TTA in xylene. The purified ^{237}Np was spiked with radiochemically pure ^{239}Np or ^{238}Np to enable the estimation of neptunium by gamma counting. Neptunium-239 for this purpose was separated from periodically irradiated natural uranium and ^{238}Np was prepared by irradiating ^{237}Np irradiated in the "Apsara" reactor. The solution of Np(V) was prepared by the following method. Neptunium-237 spiked with ^{239}Np or ^{238}Np in 1M nitric acid solution was reduced to Np(IV) using ferrous sulphamate ($\cong$ 0.1M) and the Np(IV) was extracted into 0.5M TTA in xylene. The extracted Np(IV) was stripped into 8M nitric acid. The strip solution was scrubbed with 0.5M TTA to remove any iron present and was subsequently scrubbed with benezene to remove, dissolved TTA. The strip solution in 8M nitric acid containing Np(IV) was the diluted to 0.5M and was heated on a water-bath for about an hour to oxidize Np(IV) to Np(V). The oxidation of Np(IV) to Np(V) was quantitative as was checked by TTA extraction. The solution of Np(V) thus prepared was added to uranium solution to prepare the feed for the extraction experiment.

Uranyl nitrate solutions were prepared by dissolving U_3O_8 or UO_3 in nitric acid. Uranium was estimated spectrophotometrically using the thiocynate method(15). The concentration of nitric acid in the uranium solution was determined by titration against standard sodium hydroxide solution after complexing uranium by oxalate(16).

Nitrous acid was estimated by using it to diazotise sulphanilamide and coupling the product with N-(1-Naphthyl)-ethylene diamine dihydrochloride and measuring the optical density at 540 mμ spectrophotometrically(17). Nitrous acid in the TBP phase was estimated by directly measuring the absorbance at 377 mμ(18).

Vanadium(V) solution was prepared by dissolving V_2O_5 (L.R. grade) in dilute sodium hydroxide solution and then nitric acid was added to it to give the acidity of about 3M. The concentration of vanadium(V) was estimated by reducing V(V) with excess ferrous to V(IV), oxidizing the excess ferrous by peroxidisulphate and then titrating V(IV) with standard $KMnO_4$ solution(19).

30% TBP in Shellsol-T was used as the solvent in all the experiments. In a few initial experiments, 30% TBP was pre-equilibrated with 2M nitric acid prior to use to avoid the crud formation noticed in uranium extraction experiments(20). This, however, was found unnecessary and was discontinued in most of the experiments.

The initial concentration of ^{237}Np in the aqueous feed was about 1-3 µg/ml. The feed to organic ratio was adjusted to give the desired uranium concentration in the organic phase. The attainment of the equilibrium was checked by periodic analysis of the outgoing streams for neptunium gamma activity using a well-type NaI(Tl) scintillation counter. Usually a continuous operation for 3-4 hours from the start gave a good hydraulic stability as was evident from reasonably constant interfaces in all the settlers. The run was further continued for 3-4 hours (or even longer sometimes) before equilibrium stage samples were drawn for analysis. About 1 ml of both the phases from each settler was withdrawn, with a syringe for analysis at the end of the run. It was assumed that the equilibrium conditions remain almost undisturbed while the stage sampling was carried out.

4. RESULTS AND DISCUSSION

It was reported(6,21) that in the feed solution of the first cycle of the purex process neptunium exists predominantly as Np(V) which is not extractable into TBP. As it was proposed to recover neptunium from the raffinate of the uranium purification cycle, it was necessary to establish the conditions so that neptunium could be coextracted into TBP along with plutonium and uranium in the HA and IA cycles. Several methods were suggested to oxidize Np(V) in the feed solution to Np(VI) which is extractable into TBP, thus enabling the coextraction of neptunium along with uranium and plutonium. Bahr suggested(9) the boiling of the solution in 7M nitric acid while Swanson(22) proposed the addition of the synthetic rate accelerating material which enhance the rate of oxidation of Np(V) to Np(VI) by nitrate. However, the former method does not seem to be feasible on the plant scale while the latter one probably needs further investigations before it could be used on the plant scale. The addition of nitrous acid which helps the oxidation of Np(V) to Np(VI) is commonly used(2,23) in many fuel reprocessing plants. Selective oxidation of Np(V) to Np(VI) by V(V) was reported by Dukes(24) and was successfully used for the coextraction of neptunium by Bahr and Koch(25), even though all the neptunium in the feed solution was present as Np(V). The use of nitrous acid and vanadium (V) to optimize the coextraction of neptunium from the feed solution containing mainly Np(V) was investigated under the conditions relevant to the first (HA) and second (IIA) cycles of the purex process.

4.1 Coextraction of Neptunium using Nitrous Acid

The calibration curve for the estimation of nitrous acid is shown in Fig 3. The spectrum of nitrous acid in TBP is shown in Fig 4 and the calibration curve used for the estimation of nitrous acid in TBP is shown in Fig. 5.

The results of a typical counter-current experiment carried out for the coextraction of neptunium with essentially all the neptunium as Np(V) in the feed are given in Tables 1-4, and the corresponding neptunium extraction profile is shown in Fig 6. The oxidation state of neptunium in the feed solution was always checked at the beginning and at the end of the mixer-settler run. The presence of Np(IV) was checked by its extraction into 0.5M TTA from 1M nitric acid while presence of Np(VI) was checked by hexone extraction from 1M nitric acid saturated with ammonium nitrate. The oxidation state of neptunium as Np(V) was found to remain almost unchanged and hence its coextraction along with uranium was only to the oxidation of Np(V) to Np(VI) by nitrate in the presence of TBP enhanced by nitrous acid either catalytically(23) or due to the formation of the rate accelerating material(22).

The results of all the experiments carried out using nitrous acid in a similar way under various conditions are summarised in Table 5.

In a couple of experiments nitrous acid in the outgoing organic stream was analysed spectrophotometrically(18) and the results are included in Table 5. It was observed that more than 50% of nitrous acid was decomposed. Groh and Schlea reported(2) that 90% of nitrous acid was decomposed in similar mixer-settler experiments. The fraction of the nitrous acid decomposed would depend on the nitric acid concentration, uranium saturation, temperature and also on the residence time in the mixer-settler experiment. The present results cannot be compared with those given by Groh and Schlea for the lack of such data. However such decomposition of nitrous acid is desirable as the nitrous acid addition does not cause excessive consumption of sulphamate (or of hydrazine when U(IV) is used) in the partitioning column where nitrous acid must be destroyed to enable partitioning of plutonium from uranium quantitatively.

Groh and Schlea reported(2) that more than 90% of neptunium was coextracted when 10^{-3}M nitrous acid was used in the entering organic stream when the uranium concentration in the outgoing organic stream was about 70-75 g/l. In the Hanford reprocessing plant 5×10^{-3}M HNO_2 in the solvent was used to coextract neptunium with overall recoveries better than 80%(3). The results obtained in the present work compare well with these data. However, as the experimental details such as acidity and residence time are not reported for the data given by Groh and Schlea(2), an exact comparison of the present results is not possible. Salomon et al reported(26) that the recovery of neptunium was maximum (~70%) when 10^{-3}M nitrous/acid in the solvent was used and the recovery was reduced to about 40% by increasing the nitrous acid to 10^{-2}M. Their results differ from the present results as well as from those given(2) by Groh and Schlea. However the difference in the results could be due to different experimental conditions used.

From the results obtained in the present studies (Table 5) it can be concluded that more than 80% of neptunium could be coextracted along with uranium if (a) the uranium loading of the organic phase is about 70 g/l or less, (b) the feed and the scrub nitric acid concentration are about 3M or more and (c) the nitrous acid concentration in the solvent is about 10^{-3} to 10^{-2}M. In the plutonium plant at Trombay, feed acidity of 2.5 - 3.0M HNO_3 and scrub acidity of 3 - 3.5M HNO_3 and uranium loading of about 70 g/l are used(21). Therefore the above conditions seem quite compatible with the process.

4.2 Coextraction of Neptunium using Vanadium(V)

Dukes(24) reported that Np(V) in HNO_3 is almost quantitatively oxidized by V(V) while a very small fraction of Pu(IV) is oxidized to Pu(VI) by V(V). Experiments were carried out at room temperature (~23°C) to check the oxidation of Pu(IV) over a period of 24 hrs, in the presence and the absence of uranium (100 mg/ml). It was observed that the oxidation of Pu(IV) ($\sim 10^{-4}$M in 2 and 3M HNO_3) by V(V) ($\sim 10^{-2}$M) was only about 5-7%.

The results of the two counter-current experiments carried out by adding V(V) to the aqueous feed containing Np(V) are given in Tables 6 and 7 and the corresponding neptunium extraction profiles are shown in Figs 7 and 8. From the data given in Table 6, it is seen that there was some reflux of neptunium in the scrub region and this was probably due to the reduction of extracted Np(VI) to Np(V) in this region as the holding oxidant V(V) was not present in the scrub section. Bahr(9) has reported that the reduction of Np(VI) to Np(V) by light is favoured by the presence of uranium as well as of the organic phase. Although in all the extraction experiments with Np(V) in the feed, lights were put off, complete protection against light was not possible. However, the mixer-settler unit was protected against light by covering it with a black paper in the following mixer-settler experiments in which neptunium was present as Np(V) in the feed.

Two more experiments were carried out in which V(V) introduced at the 2nd and 4th stage (from the feed stage) mixer in the extraction section. The results of these experiments are given in Tables 8 and 9 and the respective neptunium profiles are shown in the Figs. 9 and 10. The oxidation state of neptunium in the feed was checked as described earlier at the beginning as well as at the end of the experiment.

The results of these experiments show that by using V(V), added either in the feed or in the extraction section, neptunium coextraction acheived could be more than 90%. Although the conditions used by Baehr and Koch for similar experiments are not known$^{(25)}$, the present results are in good agreement with their results.

If V(V) is to be added to the feed in the plutonium plant, prior to its addition it is necessary to destroy all the nitrous acid present in the feed. Nitrous acid, which is usually added to the feed solution to adjust the oxidation state of plutonium to Pu(IV), reduces V(V) instantaneously. Air sparging is normally used to mix the feed solution after adding $NaNO_2$ to it and this causes almost all the nitrous acid to decompose. Air sparging should therefore precede the addition of V(V), thus minimising its reduction by nitrous acid. The oxidation of Np(V) to Np(VI) by V(V) is known to be quite rapid$^{(24)}$ Nitrous acid produced radiolytically subsequently would reduce the remaining V(V). This however, would not affect Np(VI). Thus addition of 10^{-2}M to 10^{-3}M V(V) to the feed after air sparging would ensure the oxidation of Np(V) to Np(VI), without affecting significantly the oxidation state of Pu(IV), enabling its almost quantitative coextraction.

If the addition of V(V) in the feed is not acceptable to the process, it can be introduced in the extraction section, a couple of stages after the feed stage. This alternate method has the advantages that plutonium does not come in contact with V(V) as most of the plutonium gets extracted in the earlier extraction stages and that complete destruction of nitrous acid in the feed is not necessary as any nitrous acid present in the feed gets extracted into the organic stream.

In conclusion it can be said that the use of V(V) for the oxidation of Np(V) to Np(VI) is a very promising method for the coextraction of neptunium although most of itispresent in the feed as Np(V). The recovery of neptunium upto 90% can be achieved by using V(V).

REFERENCES

(1) A.C. Wahl and G.T. Seaborg - Phys. Rev. 73 940 (1948)

(2) H.J. Groh and C.S. Schlea - "Progress in Nucl.Energy Series III Process Chemistry"Vol.4, 507 (1970), Pergamon Press.

(3) R.E. Isaacson and B.F. Judson "Ind. Engg. Chem. Process Design and Development" 3 296 (1964)

(4) J.P. Duckworth and L.R. Michels - Ibid 3 302 (1964)

(5) W.L. Poe, A.W. Joyce and R.I. Martens - Ibid 3 314 (1964)

(6) J.R. Flanary and G.W. Parker - Progress in Nuclear Energy Series III Process chemistry" Vol.2, 501 (1958) Pergamon Press.

(7) A. Chesne - Industries Atomiques 7/8 71 (1966)

(8) D.R. Vondy, J.A. Lane and A.T. Gresky - Ind. Engg. Chem. Process Design and Development 3 293 (1964)

(9) W. Bahr - KFK - 797 (1968)

(10) N. Srinivasan, M.V. Ramaniah, S.K. Patil, V.V. Ramakrishna, R. Swarup and A. Chadha - BARC - 428 (1969)

(11) M. Germain, D. Gourisse and M. Sougen2J.J.Inorg. Nucl. Chem. 32 245 (1970)

(12) N. Srinivasan, M.V. Ramaniah, S.K. Patil, V.V. Ramakrishna, R. Swarup and A. Chadha - Proc. DAE Chemistry Symposium, Madras Vol.II, 367 (1970)

(13) W.D. Jamrack, D.H. Logsdail and G.D.C. Short - Progress in Nucl. Energy Series III Prodess Chemistry Vol.2 332 (1958) Pergamon Press.

(14) E. Lopez-Menchero and J. Cantono - ETR-112 (1962)

(15) ORNL Master Manual - TID-7015 - Method No.1 - 215212

(16) Ibid Method No.9 - 042200

(17) A.I. Vogel "A Text book of Quantitative Inorganic Analysis" Longmans 3rd Ed. P.784 (1961).

(18) P. Morki, L. Humblet, P. Wichmann and H. Eschrich - ETR-220 (1967)

(19) F.P. Treadwell "Analytical Chemistry Vol.II" (English Ed) p.570 (1963) (Enlarged and revised by W.T. Hall) John Wiley & Sons Ltd.

(20) S.V. Kumar - unpublished work

(21) N. Srinivasan, M.V. Ramaniah, S.K. Patil and V.V. Ramakrishna - J. Radioanal.Chem. 8 223 (1971)

(22) S.W. Swanson BNWL - 1017 (1969)

(23) T.H. Siddall and E.K. Dukes - J. Am. Chem.Soc. 81 790 (1959)

(24) E.K. Dukes DP-434 (1959)

(25) W. Behr and G. Koch - unpulished work (Reported by G. Koch in KFK - 976 (1969)).

(26) L. Soloman, E. Lopez - Menchero, J. Lopex de Manterola and G. Leynen - ETR-233 (1968).

Table 1

COEXTRACTION OF NEPTUNIUM BY USING NITROUS ACID
(outgoing streams analysis)

Feed:	(HNO_3)	= 2.9 M
	(U)	= 359 mg/ml
	(^{238}Np)	= 6.6 x 10^5 C/50 Sec/ml
Scrub:	(HNO_3)	= 3 M
Solvent:	30% TBP (HNO_2) Solvent	= 4.7 x 10^{-3} M
Flow rates (ml/min)	Feed	= 1.2
	Scrub	= 1.0
	Solvent	= 6.0

Time hrs.	^{238}Np activity in the outgoing streams C/50 sec/ml x 10^4		Concentration of uranium in the outgoing organic stream (mg/ml)
	Aqueous	Organic	
11.0	2.36	5.25	64
12.0	2.75	7.68	70
13.0	3.26	10.7	67
14.0	2.86	11.7	67
15.0	2.44	11.3	62
16.0	2.52	11.5	63
17.0	2.56	11.1	66
18.0	2.66	10.8	68

Table 2

COEXTRACTION OF NEPTUNIUM BY USING NITROUS ACID
(Stage Samples Analysis)

Stage No.	^{238}Np activity in C/50 sec/ml x 10^{-4}		Concentration of uranium in (mg/ml)	
	Aqueous	Organic	Aqueous	Organic
1 (org.entry)	2.78	2.31	-	-
2 -	4.34	4.63	-	-
3 -	7.22	6.45	-	-
4 -	13.1	10.7	-	-
5 -	26.9	17.8	0.3	13.0
6 -	50.1	22.9	17.4	47.2
7 (Feed entry)	70.3	23.5	164.0	75.8
8 -	58.4	23.2	7.5	72.0
9 -	58.8	18.5	6.3	72.0
10 -	53.1	13.5	6.0	73.2
11 -	33.0	10.1	5.4	69.6
12 (Scrub entry)	29.5	10.9	5.0	69.6

Table 3

TESTING OF OXIDATION STATES OF NEPTUNIUM IN THE FEED

Time	TTA Ext.(a)			Hexone Ext.(b)		
	^{238}Np activity in C/50 sec/ml		Distribution Coefficient Kd	^{238}Np activity in C/50 sec/ml		Distribution Coefficient Kd
	Aq	Org		Aq	Org	
Beginning of the expt.	4.11×10^4	67	0.001	9.65×10^4	3.17×10^3	0.032
End of the expt	2.04×10^5	4.09×10^3	0.021	1.21×10^5	7.0×10^3	0.058

(a) 1.0 ml Feed + 2.0 ml water + 3.0 ml 0.5M TTA equilibrated.

(b) 1.0 ml Feed + 4.0 ml HNO_3 saturated by NH_4NO_3 + 5.0 ml hexone equilibrated.

Table 4

CALCULATION OF % EXTRACTION OF NEPTUNIUM

^{238}Np activity (C/50 sec) in various streams in volume per minute x 10^{-5}				% extraction of neptunium
Entering Feed	Outgoing org.	Outgoing Aq	Total (Aq+Org) outgoing	
7.95	6.88	0.57	7.45	87

Table 5

COEXTRACTION OF NEPTUNIUM BY USING NITROUS ACID
(Summary of the results)

Expt.No.	Nitric acid conc.M		Nitrous acid conc.M x 10^3		Concentration of uranium in the outgoing TBP (mg/ml)	% extraction of neptunium
	Feed	Scrub	TBP-in	TBP-out		
1	3	3	Nil	-	70	11
2	3	3	9.8	-	68-70	100
3	2	3	8.0	-	60-70	70
4	2.5	3	9.0	-	70	86
5	3	3	9.6	-	80-85	29 (a)
6	3	3	9.1	-	65-70	97
7	3	3	9.3	4.4	65-72	88
8	2.9	3	4.7	1.7	62-67	87
9	3.2	3	1.5	0.3	64-67	80

Note: Experiments 1 and 6-9 were done using ^{238}Np activity and TBP without prequilibration.

(a) Neptunium was found to relux in the scrub section due to high uranium saturation.

Table 6

EXTRACTION OF NEPTUNIUM BY USING VANADIUM(V)
(Outgoing streams analysis)

Feed: (HNO_3) = 3M

(U) = 280 mg/ml

$[V(V)]$ = 9.4×10^{-3} M

(^{238}Np) = 8.3×10^{4} C/50 sec/ml

Flow rates(ml/min): Feed = 1.25

Scrub = 0.6

Solvent= 5.4

Time hrs.	^{238}Np activity in outgoing streams C/50 sec/ml $\times 10^{-2}$		Concentration of Uranium in the outgoing organic stream (mg/ml)
	Aqueous	Organic	
14	1.75	3.36	-
15	5.48	35.8	-
16	1.92	149	-
17	2.90	169	-
18	3.25	251	-
19	4.55	225	71
20	-	221	72
20-30	-	201	65
21	-	174	-
21.30	-	171	65

Note: % of neptunium coextracted into TBP (calculated from the last two analysis) = 90.

Table 7

EXTRACTION OF NEPTUNIUM BY USING VANADIUM(V)
(Outgoing streams analysis)

Feed:	(HNO_3)	=	3 M
	(U)	=	328 mg/ml
	$[V(V)]$	=	9.4×10^{-4}
	(^{238}Np)	=	8.48×10^{4} C/50 sec/ml
Scrub :	(HNO_3)	=	3 M
Flow rates (ml/min):	Feed	=	1.25
	Scrub	=	0.6
	Solvent	=	5.4

Time hrs.	^{238}Np activity in the outgoing streams C/50 sec/ml $\times 10^{3}$		Concentration of Uranium in the outgoing organic stream (mg/ml)
	Aqueous	Organic	
14	2.52	12.3	-
15	1.74	16.0	-
16	1.74	16.3	-
17	2.05	15.0	72
18	2.76	16.0	75
19	4.26	15.3	73

Note: % of neptunium coextracted into TBP = 80

Table 6

EXTRACTION OF NEPTUNIUM BY USING VANADIUM(V)

Feed : (HNO_3) = 2 M

(U) = 344 mg/ml

(^{238}Np) = 2.12×10^5 c/50 sec/ml

Scrub: (HNO_3) = 3 M

Vanadium(V) : $[V(V)]$ = 5.4×10^{-2} M

(HNO_3) = 3 M

Flow rates(ml/min): Feed = 1.2

Scrub = 1.1

Solvent = 6.0

V(V) = 0.5

Time hrs.	^{238}Np activity in outgoing streams C/50 sec/ml $\times 10^{-2}$		Concentration of uranium in the outgoing organic stream (mg/ml)
	Aqueous	Organic	
14	0.6	365	–
15	Nil	42[illegible]	–
16	0.3	350	–
17	0.9	383	68
18	0.3	377	69
19	0.5	369	71

Note: % of neptunium coextracted into TBP = 89

Table 9

EXTRACTION OF NEPTUNIUM BY USING VANADIUM(V)

Feed: (HNO_3) = 2 M

(U) = 344 mg/ml

(^{239}Np) = 2.08 x 10^5 C/50 sec/ml

Scrub: (HNO_3) = 3 M

Vanadium(V): (V(V)) = 1.08 x 10^{-2} M

(HNO_3) = 3 M

Flow rates (ml/min): Feed = 1.2

Scrub = 1.1

Solvent = 6.2

V(V) = 0.5

Time hrs.	^{239}Np activity in outgoing streams C/50 sec/ml x 10^{-3}		Concentration of uranium in the outgoing organic stream (mg/ml)
	Aqueous	Organic	
14	1.88	41.1	-
15	0.89	37.3	-
16	1.05	38.0	-
17	1.21	39.2	74
18	1.49	40.7	71
19	1.36	40.1	71

Note: % of neptunium coextracted into TBP = 95

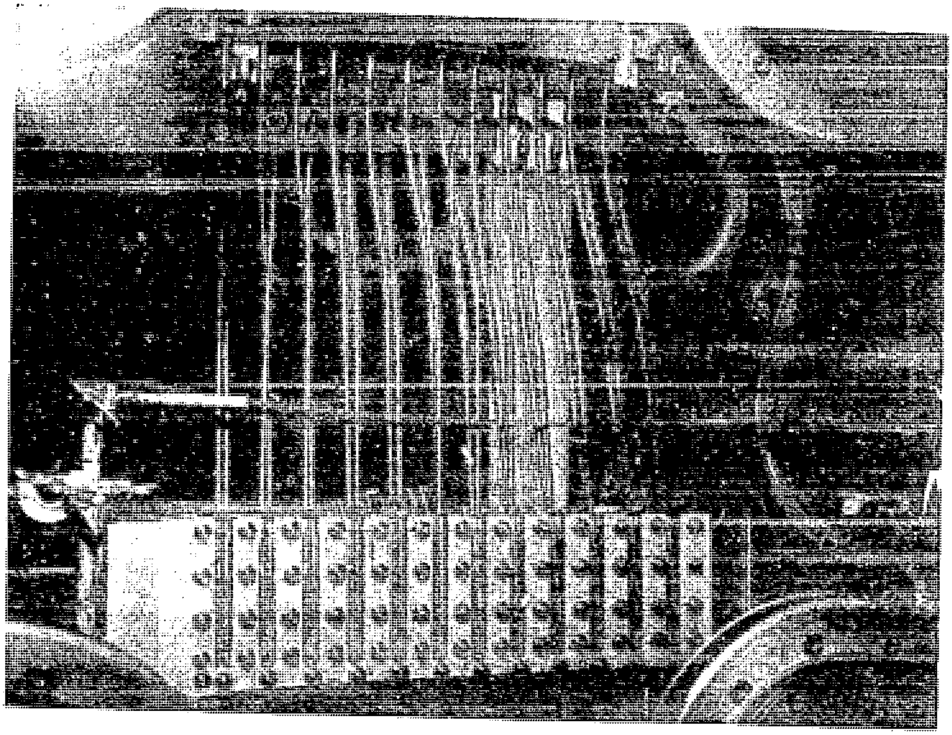


Fig. 1 (a) - A view of the row of Mixers

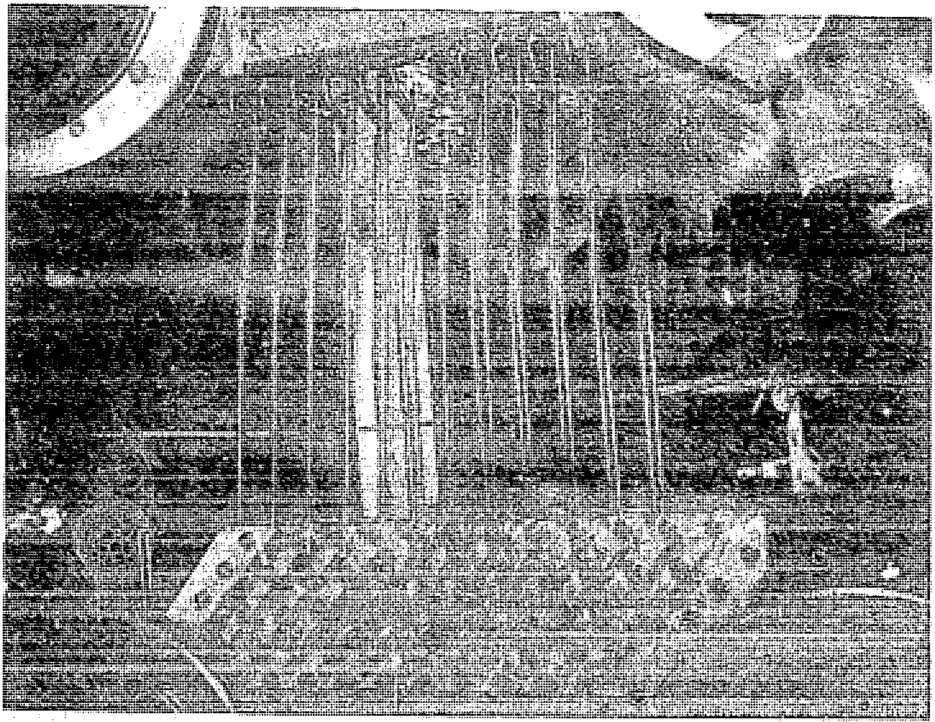


Fig. 1 (b) - A view of the row of settlers

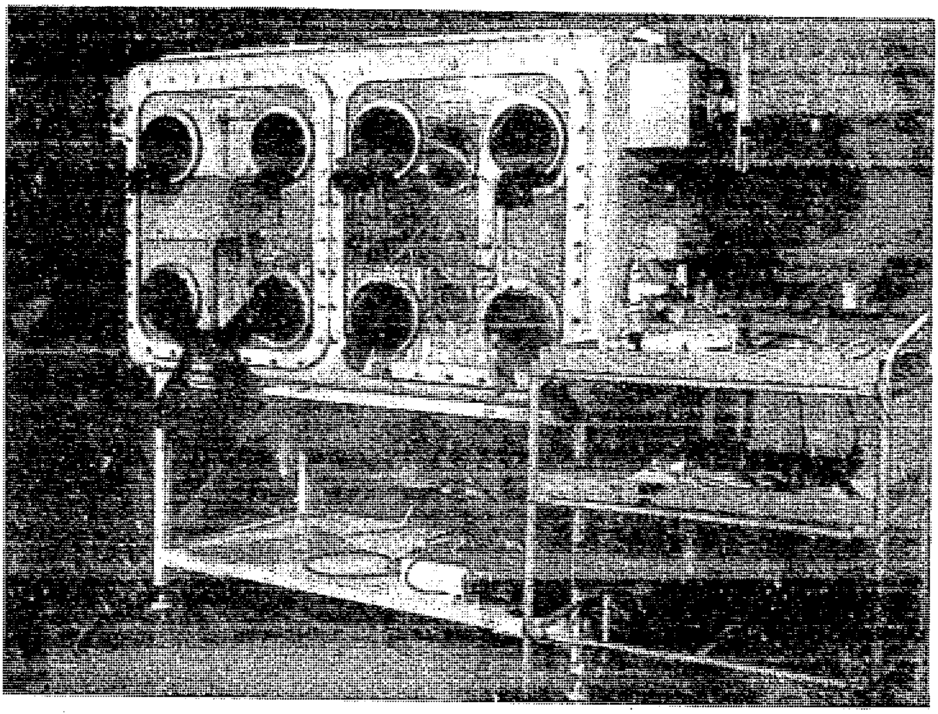


Fig. 2 - A view of the glove box housing the mixer - settler unit and other accessories

FIG. 3.

ESTIMATION OF NITRITE - CALIBRATION CURVE

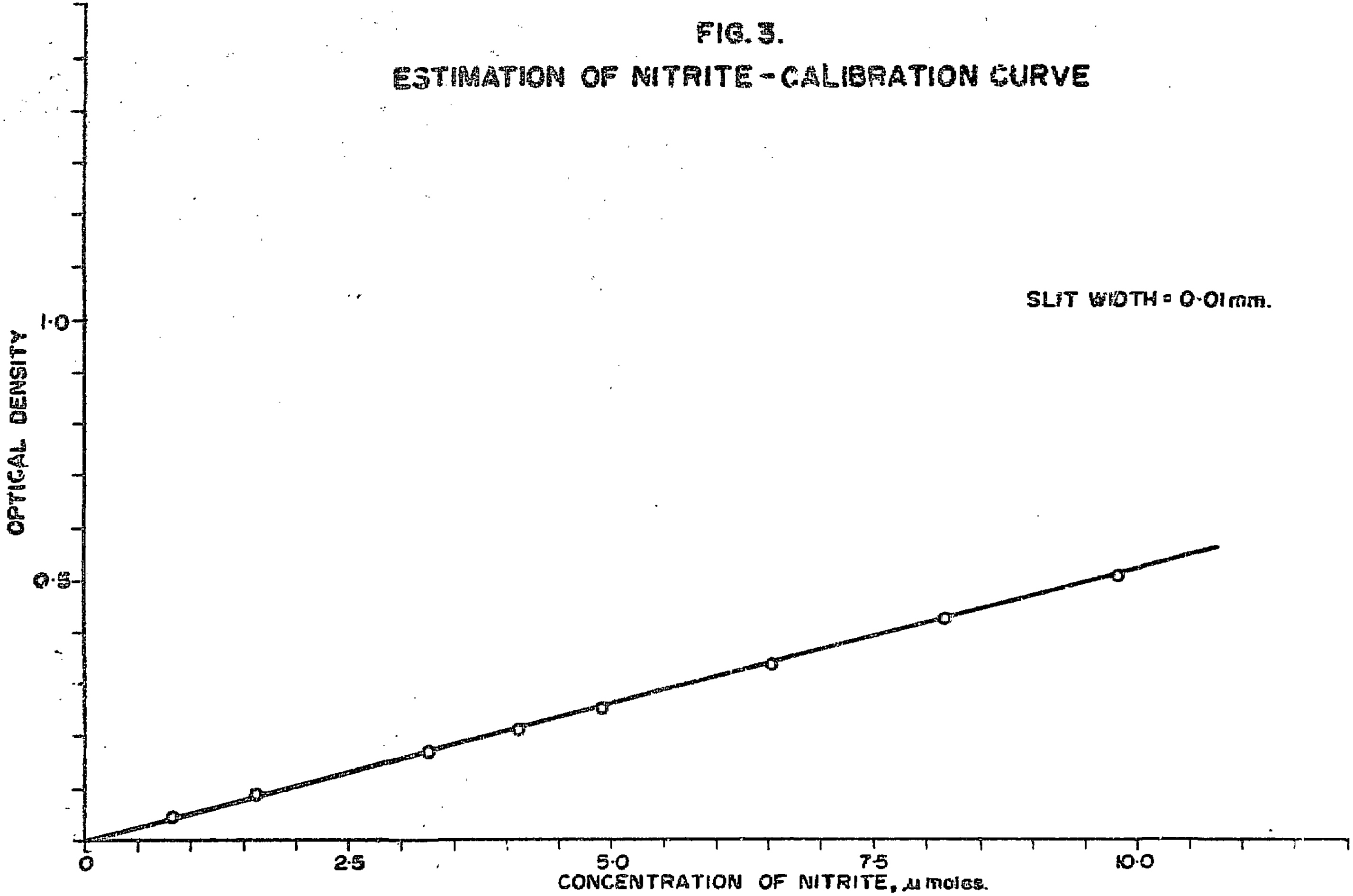
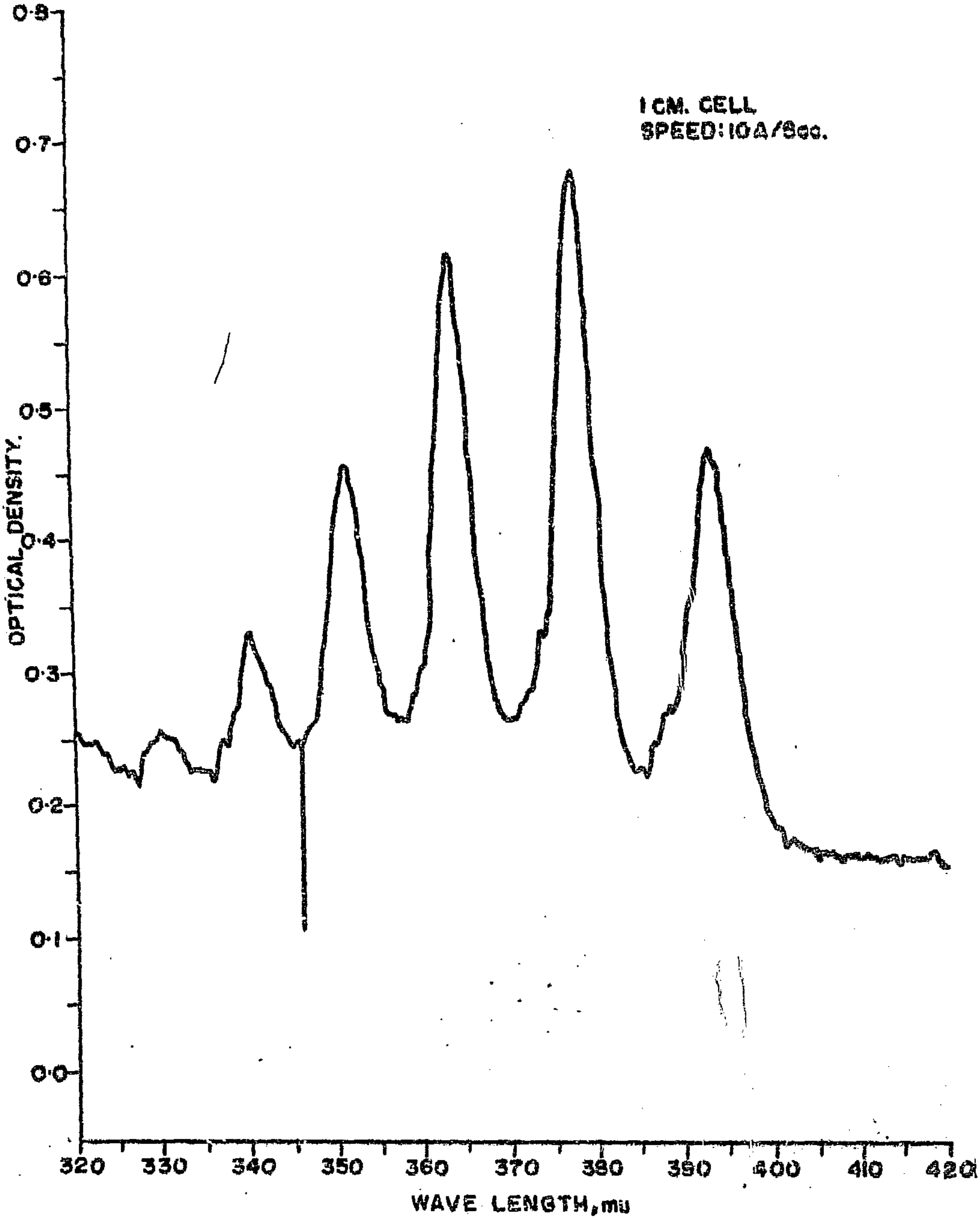


FIG. 4.

SPECTRUM OF TBP HNO_2 (BLANK TBP 30% IN SST.)



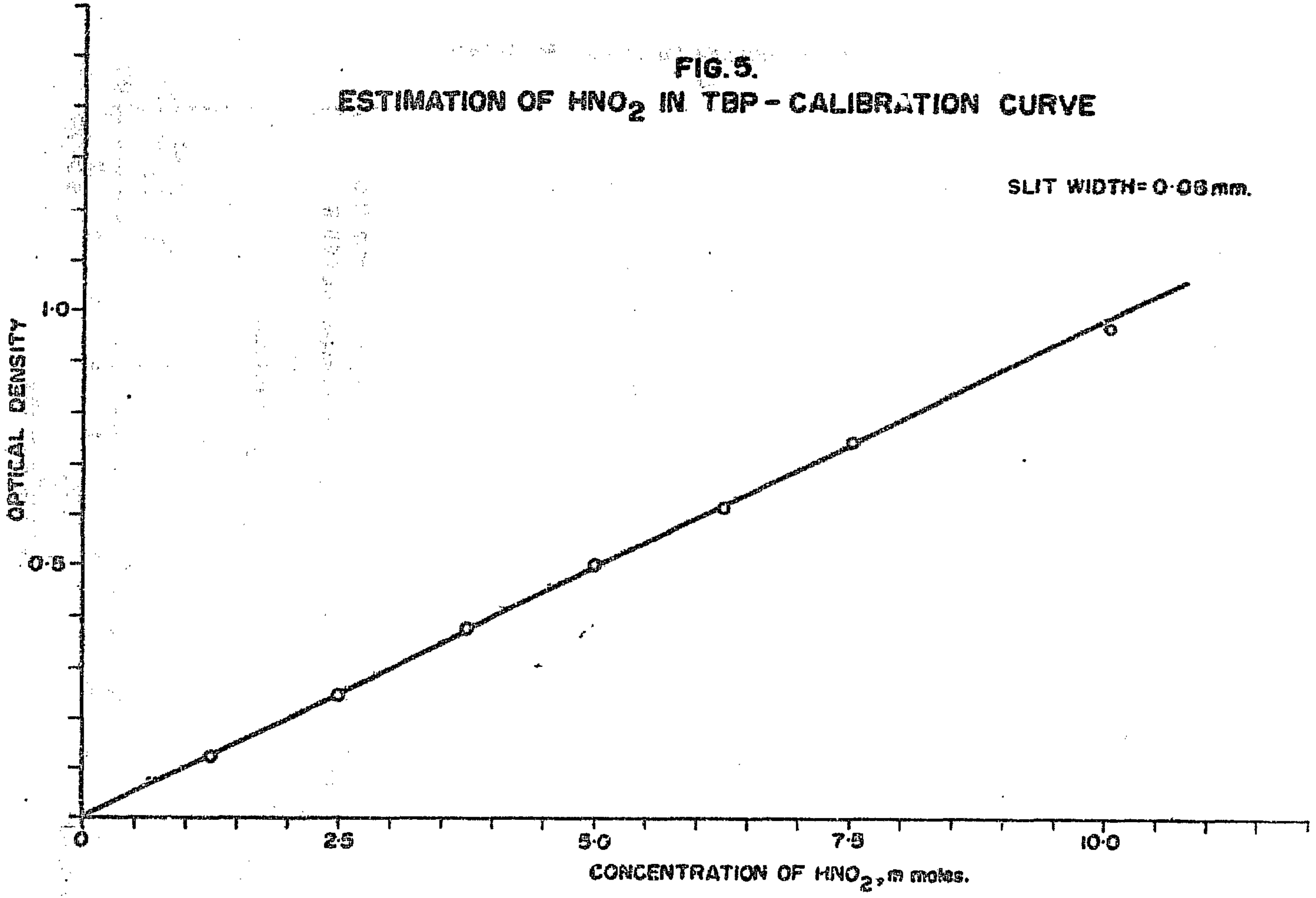


FIG. 5.

ESTIMATION OF HNO_2 IN TBP - CALIBRATION CURVE

FIG.6.

EXTRACTION PROFILE OF NEPTUNIUM AND URANIUM IN THE PRESENCE OF NITROUS ACID.

(FOR EXPERIMENTAL CONDITIONS REF. TABLE.1.)

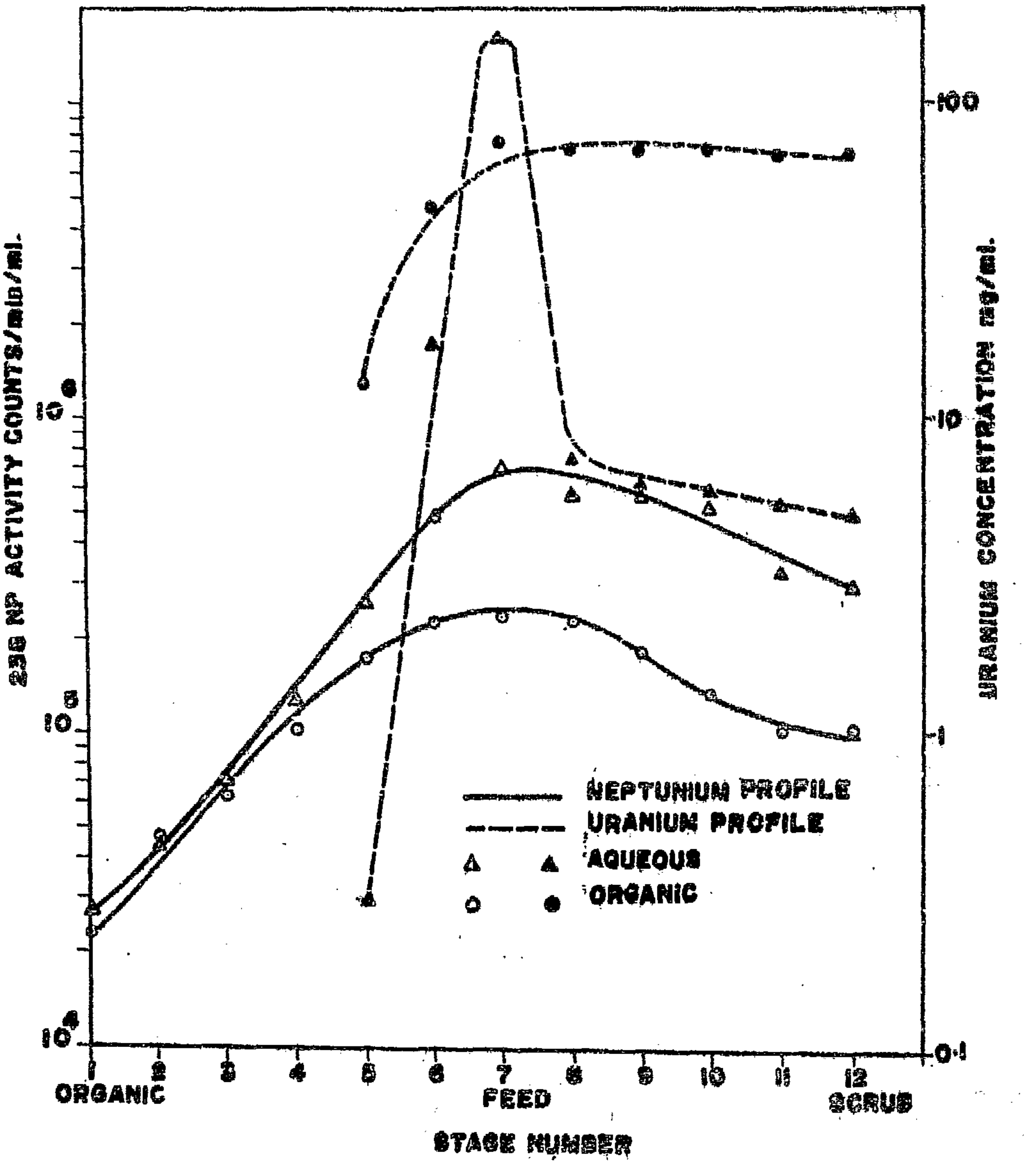


FIG.7.

EXTRACTION PROFILE OF NEPTUNIUM USING $\simeq 10^{-2}$ M VANADIUM (V) IN THE FEED.

(FOR EXPERIMENTAL CONDITIONS REF. TABLE.6.)

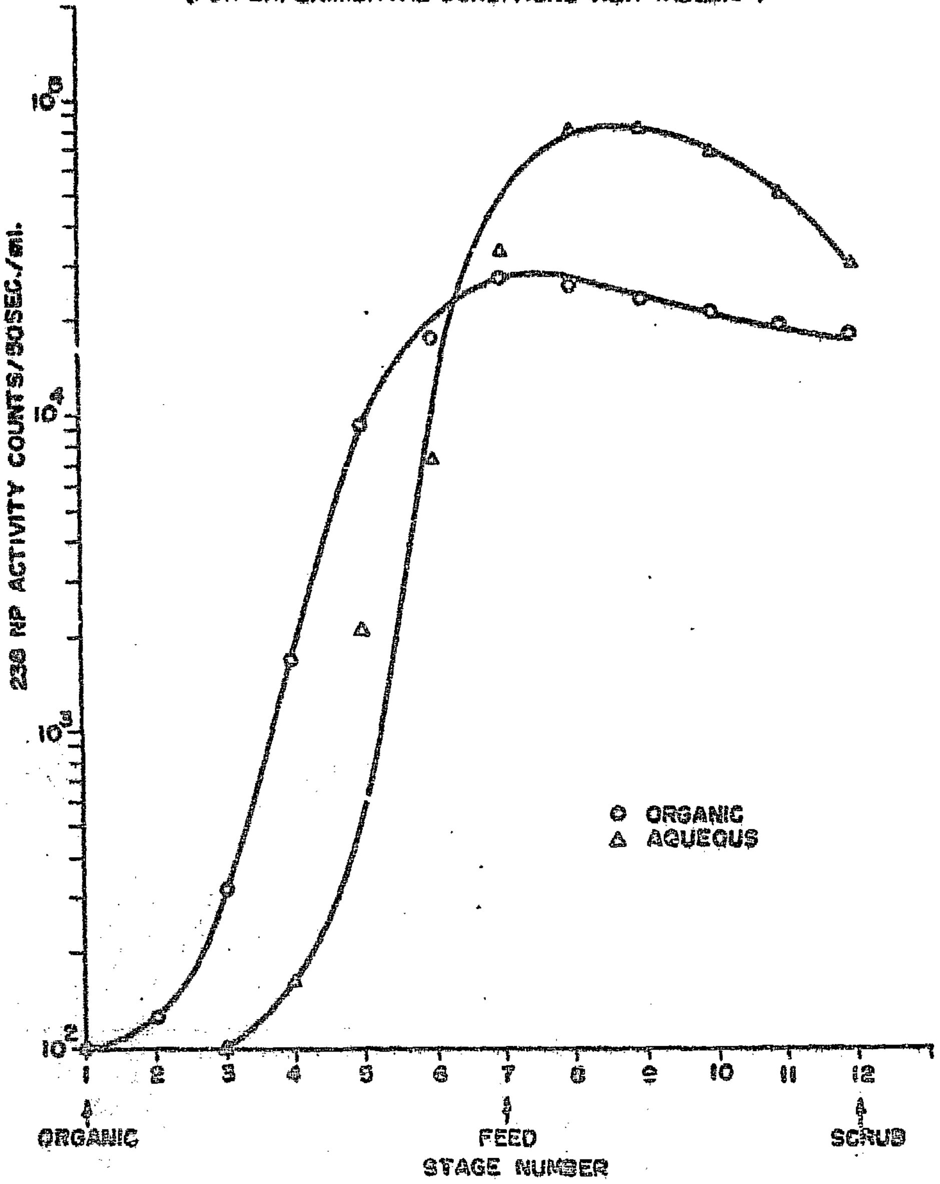


FIG. 8.

EXTRACTION PROFILE OF NEPTUNIUM USING $\simeq 10^{-3}$ M VANADIUM (V) IN THE FEED.

(FOR EXPERIMENTAL CONDITIONS REF. TABLE 7.)

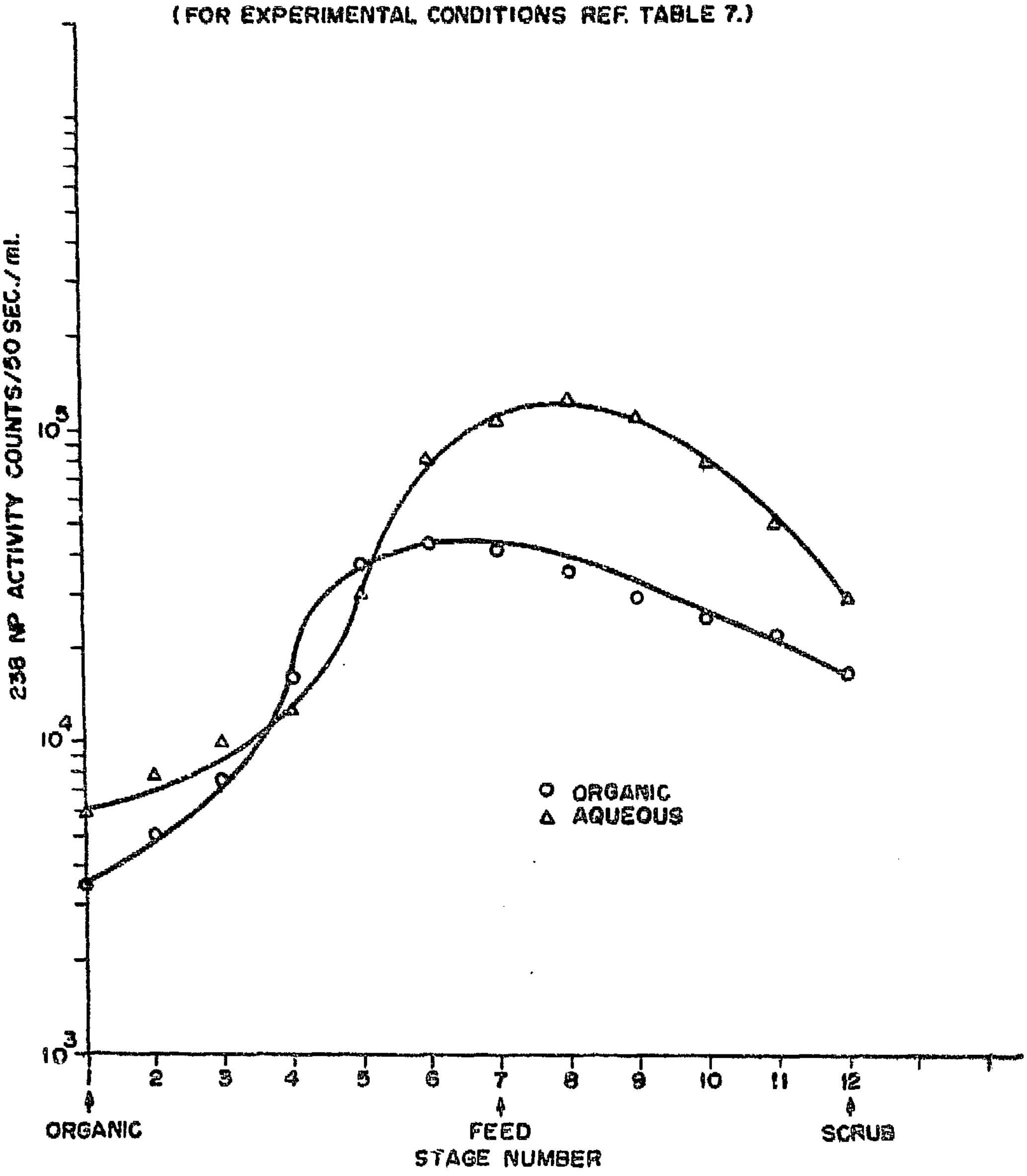


FIG. 9.
EXTRACTION PROFILE OF NEPTUNIUM WHEN VANADIUM (V) WAS ADDED TO THE 4TH STAGE BEFORE THE FEED STAGE.
(FOR EXPERIMENTAL CONDITIONS REF. TABLE 9.)

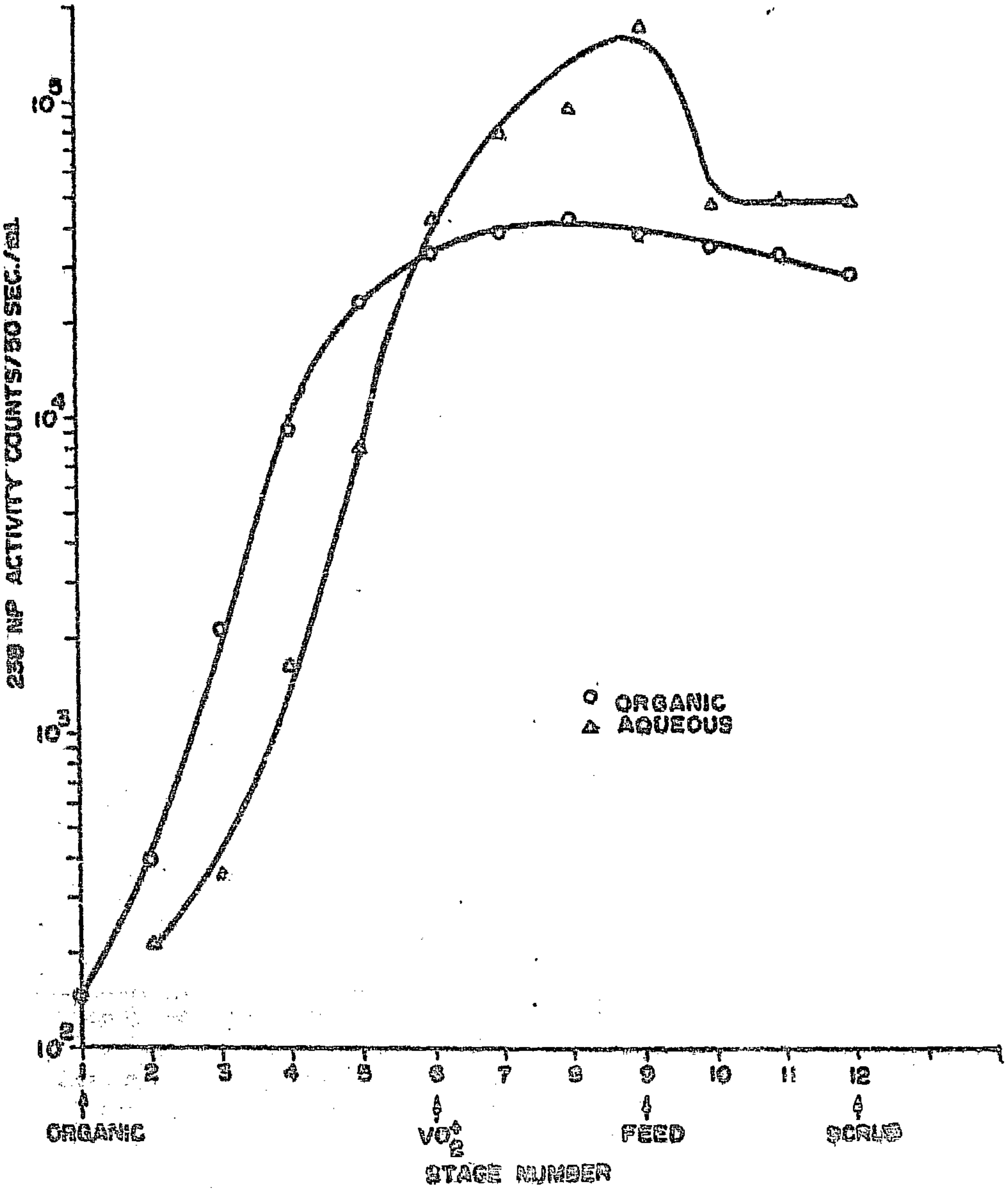


FIG.10.
EXTRACTION PROFILE OF NEPTUNIUM WHEN VANADIUM (V) WAS ADDED TO THE 2ND STAGE BEFORE THE FEED STAGE.
(FOR EXPERIMENTAL CONDITIONS REF. TABLE 9.)

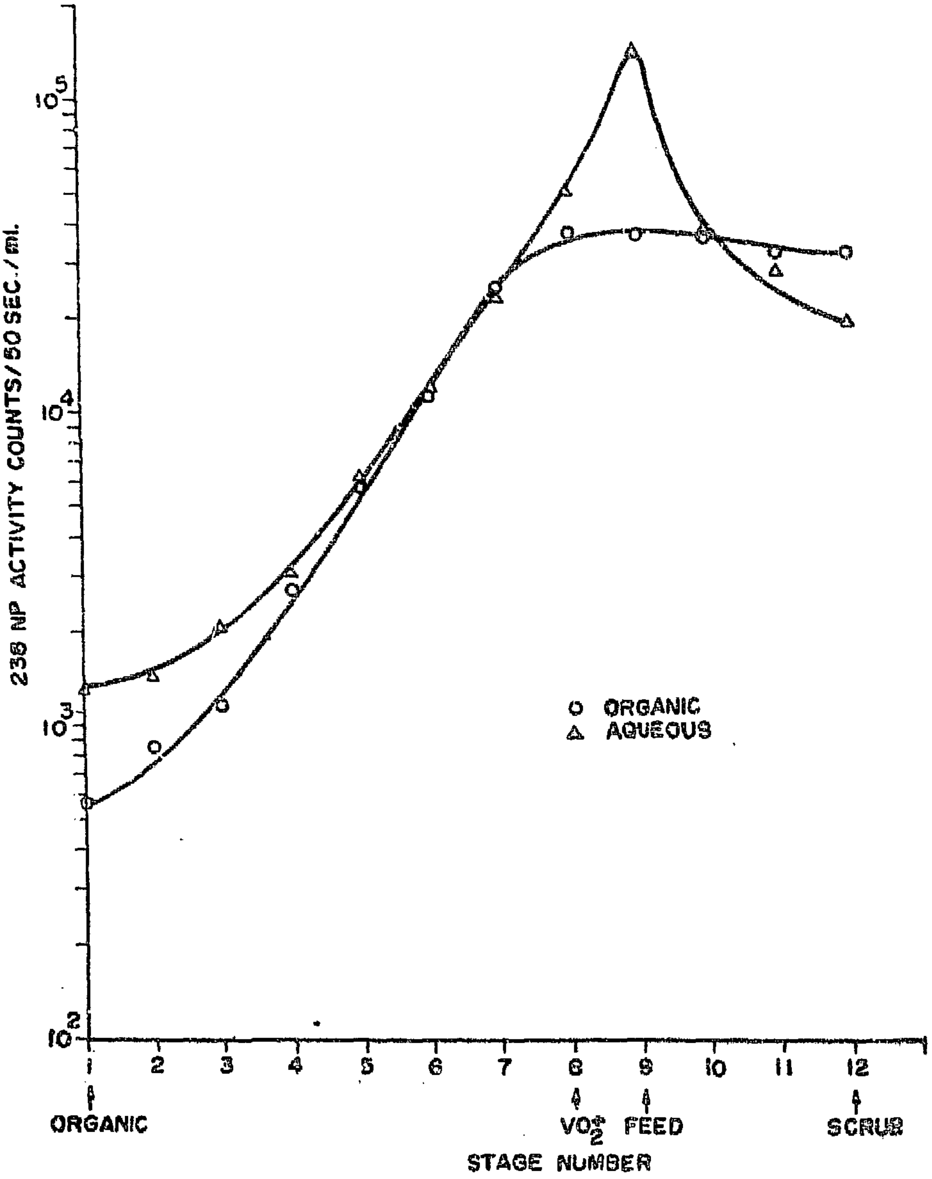


FIG.11.
PROFILE OF NEPTUNIUM (IV), URANIUM (VI) AND HNO_3 IN THE EXTRACTION
(FOR EXPERIMENTAL CONDITIONS REF. TABLE II.)