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CHEMICAL METHODS FOR THE PURIFICATION
AND ISOLATION OF NEPTUNIUM

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ABSTRACT

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The best methods at the present time for separating neptunium from various types of source material are outlined. For the purpose of analytical classification neptunium may be grouped with uranium and plutonium since all three elements, mixed in an aqueous solution, can be oxidized to a characteristic +6 state. An excellent separation from other metal ions is obtained by extraction of the +6 states into diethyl ether. Methyl isobutyl ketone is also an effective extracting solvent although it is not as specific. All three elements in the +6 state will precipitate with sodium as double acetates of the formula $\text{NaXO}_2(\text{OOCCH}_3)_3$. Neptunium may be separated from uranium and plutonium by solvent extraction or precipitation. Np (IV) forms a benzene soluble, chelate complex with thenoyl trifluoroacetone. Under suitable reducing conditions Np(IV) can be extracted away from Pu(III) and U(VI). A separation method involving the precipitation of fluorides is essentially dependent on the relative rates of oxidation and reduction of uranium, neptunium, and plutonium.

1. Introduction

The isolation of an element by chemical methods in a pure state, or as a compound, or in a solution free from all unwanted elements is dependent on the utilization of whatever unique chemical properties the element possesses. The prime problem in the chemistry of any of the synthetic elements of atomic number greater than 92 was the discovery of enough of these unique properties to permit isolation of significant quantities of the element. The chemical behavior of neptunium has been investigated to the extent that comparatively rapid and reliable isolation methods are now available.

The analytical problem encountered in separating this rare element is simplified by the fact that all the known isotopes of neptunium are radioactive with disintegration half-lives of less than three million years. Detection and assay of exceedingly small amounts of a particular isotope are possible by characterizing the radioactivity and measuring quantitatively the disintegration rate in a suitable aliquot of the gross material. Table 1 gives all the known isotopes of neptunium with brief data on their modes of decay and half-lives. Methods of synthesis of these isotopes are given in the references. With the exception of Np^{237} , the isotopes of neptunium have been studied only at tracer concentrations, that is, less than about one part in 10^6 , because of their short half-lives.

TABLE 1
THE ISOTOPES OF NEPTUNIUM

Isotope	Decay Mode	Energy	Half-Life	Ref.
Np^{233} or 234	Orbital Elec- tron Capture	1.4 Mev	4.5 da.	(1)
Np^{235}	Orbital Elec- tron Capture	no γ > 0.2 Mev	8.0 mo.	(1)
Np^{236}	β^-	?	20 hr.	(1)
Np^{237}	α	4.7 Mev	2.20×10^6 yr.	(2) (3) (4)
Np^{238}	β^-	1.3 Mev	2.0 da.	(5)
Np^{239}	β^-	0.7 Mev	2.33 da.	(6) (7)

The isotope of mass 237 has been the most useful for chemical studies since it has a long half-life and may be produced in macroamounts.⁽³⁾ Recent isolations at the Argonne National Laboratory at Chicago have yielded about one gram. The best source at the present time is neutron bombarded natural uranium from the Hanford piles. Np^{237} may be produced at concentrations of the order of one gram per 10^6 grams of uranium metal and may be concentrated to any desired level by chemical means. The other isotopes may be produced by bombarding various heavy isotopes with accelerated particles.⁽⁴⁾ The isolation from source material in all cases consists of separating neptunium from a mixture of heavy isotopes and fission products of atomic numbers ca. 30-62 (see Vol. 9). Purification methods must be designed to remove all other elements since in actual practice almost any element may be introduced as contamination from apparatus or reagents.

Classification of the elements with atomic numbers greater than 83 on the basis of periodicity of electronic structure and properties is still hypothetical. G. T. Seaborg⁽⁸⁾ has proposed that a new series of elements, in which the additional electrons are in the 5f shell in the ground state, begins with element 90, thorium. Seaborg suggests the term "actinide series" by analogy to the "lanthanide series". One is led to expect a common, very stable oxidation state for the elements of the hypothetical actinide series similar to the dominant plus three state

of the rare earths. A common oxidation state could be utilized in an analytical scheme for separating all the heavy elements as a group. Regardless of the validity of the actinide hypothesis, however, the factors determining oxidation state stabilities in aqueous solution are more complex than in the rare earths and no common oxidation state may be obtained under the same conditions for all the elements. There is a pronounced tendency towards a common plus three state but this state has never been attained for thorium and protactinium. A group separation of the actinide series in a conventional solution analysis is therefore impractical, but on the other hand the greater diversity of stable oxidation states for the elements 89 through 96 facilitates relatively easy separation of the members of the group.

2. Separation of Uranium, Neptunium, and Plutonium

As a Group from Other Metals

Uranium, neptunium, and plutonium have sufficiently similar chemical properties to constitute an analytical group. These elements all show the +3, +4, +5, and +6 oxidation states. The (VI) state is of greatest practical importance for group separation, since all three of the elements go to this state under strong oxidizing conditions. The (VI) state may be easily extracted from aqueous nitrate solutions into diethyl ether.⁽⁹⁻¹¹⁾ Presumably the metal in the (VI) state is in ether solution as a neutral, solvated nitrate molecule. Increasing nitrate

concentration and decreasing water activity favor extraction into the ether. The metals in nitric acid solutions are oxidized to the (VI) states by strong oxidants such as Ce(IV), permanganate, or dichromate. Increasing the nitric acid concentration to 1-3 molar and addition of a nitrate salt to 2-10 molar gives a solution from which the metals may be extracted quantitatively by contact with ether. Ammonium, calcium, and aluminum nitrates have been used as salting agents. The polycharged metal ions are more effective in promoting extraction. A very high degree of separation from all other metals may be obtained by ether extraction. A number of other organic solvents ^(12, 13) will extract the (VI) states of uranium, neptunium and plutonium. Methyl isobutyl ketone has been extensively used, but separation from other elements is not as good as with ether. A large fraction of the nitric acid is also extracted into the organic solvent. The heavy metals and nitric acid are removed from the organic solvent by washing with water. A reducing agent or a complexing anion such as sulfate in the water phase increases the efficiency of extraction.

Uranium, neptunium, and plutonium in the (VI) states form isomorphous double acetates with sodium having the formula $\text{NaXO}_2(\text{OOCCH}_3)_3$ ^(3, 14) In solutions of high sodium ion and acetate ion concentrations the solubility of sodium neptunyl acetate is of the order of 0.1 gm. liter⁻¹. Precipitation of the double acetate gives

very effective purification from most other metals. The appreciable solubility means large losses, however, if large solution volumes are involved. Sodium uranyl acetate has been used as a carrier for trace quantities of Np(VI) and Pu(VI).⁽¹⁵⁾ Solvent extraction is far more satisfactory for most purposes since quantitative recovery of trace quantities is relatively simple.

3. Separation of Neptunium from Uranium and Plutonium

Some type of spectrophotometer is indispensable for the separation of macro amounts of neptunium and in the study of neptunium chemistry. The fact that all the oxidation states have characteristic absorption spectra⁽¹⁶⁾ simplifies the identification and quantitative estimation of each oxidation state. The minimum amount of Np(IV) and Np(V) which may be detected by present spectrophotometric methods is about 10^{-7} mole. Np(VI) has no absorption which is suitable for analytical purposes in the range 500-1000 millimicrons.

Separations of neptunium, uranium, and plutonium may be based upon the relative stabilities of the various oxidation states. Table 2 gives formal potentials for various couples in 1 M HCl. The potential values relative to the standard hydrogen electrode have been calculated or measured for equivalent concentrations of

TABLE 2

FORMAL POTENTIALS OF THE COUPLES OF URANIUM
NEPTUNIUM, AND PLUTONIUM IN 1 M HCl

	III-IV	IV-V	V-VI
Uranium (17) (18) (19)	+0.65	-1.03	-0.05
Neptunium (20)	-0.14	-0.74	-1.13
Plutonium (21)	-0.97	-1.23	-0.92

reduced and oxidized states in 1 M HCl and hence are not true thermodynamic constants for the free energy changes. Nevertheless the potentials serve as useful approximate guides to the relative stabilities. A number of combinations of oxidation states may be produced in a solution of the three elements by proper adjustment of the oxidation potential. In a solution of oxidation potential -0.6 volt, for example, U(VI), Np(IV), and Pu(III) are the dominant stable states. In addition to the wide variation in thermodynamic stabilities, different oxidation states may be maintained for long periods of time in the same solution by virtue of slow reaction rates. Transitions from the +3 or +4 states to the +5 or +6 states are very slow in general compared to the +3 to +4 or +5 to +6 transitions and the rates for the same transitions may vary between the elements. It is possible, for example, with the three elements initially in the (VI) states to reduce neptunium to Np(IV) and plutonium to Pu(III) in certain solutions containing sulfur dioxide with very little reduction of U(VI), although the latter is thermodynamically unstable under such conditions.

The choice of a method for the separation of neptunium from uranium and plutonium is dependent on a number of factors among which are the total and relative amounts of the three elements, equipment limitations, and composition of the source material.

The separation methods which are now available may be roughly divided into precipitation methods and solvent extraction methods.

3.1 Precipitation methods. If the neptunium is in a source material such as pile or cyclotron bombarded uranium or one of its compounds, an approach different from a group separation of uranium, neptunium, and plutonium is required. In this case the principal diluent is uranium and obviously little would be gained by a group separation. It has been general practice to dissolve the uranium in nitric acid and to separate the relatively small amounts of neptunium and plutonium from the bulk of the uranium by precipitation of a carrier compound. For laboratory scale operations lanthanum fluoride has long been used, ⁽²²⁾ since it carries nearly quantitatively and is not too inconvenient to process. The uranium is dissolved in hot, concentrated nitric acid and diluted to 20% or less in $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ hydrochloride and about 1 M HNO_3 . A reducing agent such as sulfur dioxide, hydrazine, hydrochloride or hydroxylamine, is then added together with a lanthanum salt to give a concentration of La(III) of 0.1 - 0.2 gm/liter. Addition of hydrofluoric acid to 1-4 M precipitates lanthanum fluoride which carries the neptunium

and plutonium which have been reduced to states other than +6.

The reduction of Pu(VI) is slow so that about thirty minutes reduction time must be allowed if complete carrying of plutonium is desired.

The reduction time for Np(VI) is not critical, however, since complete reduction to Np(V) occurs immediately upon addition of the reducing agent. Recent evidence indicates that Np(V) is carried by lanthanum fluoride.⁽²³⁾ It is also possible that Np(V) reduces very rapidly to Np(IV) in fluoride solution. In any event, essentially complete carrying of the neptunium is obtained. U(VI) reduces only very slowly under these conditions. The (VI) states are not carried by lanthanum fluoride so a good separation from uranium is obtained.

The neptunium may be separated from the plutonium and residual uranium by bromate-lanthanum fluoride cycles which are described in detail in another paper.⁽³⁾

Macro amounts of Np²³⁷ have been separated from pile uranium. The large amounts of uranium involved preclude any laboratory scale operations in the initial stages so that little choice of method has been possible. Increased yields of neptunium have been obtained by modifying the bismuth phosphate method for extracting plutonium.^(24, 25) The plutonium process leaves most of the neptunium in solution with the uranium. If effective reducing conditions are established, the neptunium may be reduced to Np(IV) which is carried by bismuth phosphate. For the express purpose of obtaining macro amounts of neptunium several

special runs have been made in the Hanford plant. The supernatant uranium solution of the approximate composition, 15 per cent uranyl nitrate hexahydrate, 0.1 M HNO_3 , 0.6 M H_2SO_4 , 0.6 M H_3PO_4 , which is waste from the bismuth phosphate extraction of plutonium is reduced by 0.1 M oxalic acid with 0.01 M Mn(II) as catalyst. Ammonium fluosilicate to 0.02 M is also necessary to ensure complete reduction of the neptunium. The resultant solution is extremely complicated and the rates and equilibria involved are not understood, but complete reduction of the neptunium to Np(IV) is obtained by 30-60 minutes heating at 75°C . Precipitation of bismuth phosphate by the ensuing regular plant procedure presumably carries most of the neptunium. Reduction of impurities and carrier bulk is accomplished by the regular method of bismuth phosphate cycles with the exception of modification in the reducing conditions prior to the bismuth phosphate product precipitation step. The neptunium is instantly reduced on addition of 0.2 M $(\text{NH}_4)_2\text{SiF}_6$ and 0.03 M Fe(II) but the prolonged heating involved in the regular plutonium process oxidizes much of the neptunium to Np(V) . For neptunium recovery the heating period is eliminated and bismuth phosphate precipitation is commenced immediately after addition of the reducing agent. Final isolation is accomplished by laboratory scale solvent extraction or precipitation procedures.

3.2 Solvent Extraction. Certain diketones will form chelate complexes with Pu(IV) .^(26, 27) The compound thenoyl trifluoroacetone

has been extensively tested for formation of a benzene soluble, water insoluble chelate complex with Pu(IV).⁽²⁷⁾ Chelation of the +3 and +6 states of plutonium is much weaker than chelation of the +4 state. Presumably four molecules of the enol form of the diketone lose four hydrogen ions and become bonded to each Pu(IV) ion. The resulting chelate complex is preferentially soluble in benzene.

The need for a simpler and more efficient method of separating neptunium from plutonium prompted an investigation of the chelation of neptunium. Two possible types of separation are indicated. Either Np(IV) or Pu(V) may be removed as a diketone complex from an aqueous mixture. The element one desired to retain in the aqueous solution would necessarily be in an oxidation state other than +4. Separation of a Np(IV) complex would require the plutonium to be in the +3 state to satisfy thermodynamic stability in the aqueous solution. Separation of a Pu(IV) complex requires that the neptunium be in the +5 state. The problem of extraction of a Np(IV) diketone complex from a mixture of Np(IV) and Pu(III) has received the most attention to date. The work on the other type of separation is limited to the observation that Np(V) is not extractable from a solution 0.5 M HCl with 0.05 M thenoyl trifluoroacetone in benzene, so that the method will undoubtedly be feasible.

Preliminary work showed that Np(IV) forms a strong complex which is preferentially soluble in benzene and that a good separation from Pu(III) is obtained. The prime difficulty in the procedure, however, is the preparation of pure Np(IV) since the potential of the Np(IV) - Np(V) couple is relatively positive with respect to weak oxidants (-0.74 volt in 1 M HCl) and reduction of Np(V) is, in general, quite slow at room temperature. Nitric acid solution is not suitable for the preparation of Np(IV) since this state is unstable in nitric acid. Hydrochloric acid was chosen as the solvent and found to be satisfactory. Earlier experience with reduction of Np(V) showed the reaction to be extremely slow at room temperature with Sn(II), hydrazine hydrochloride, hydroxylamine hydrochloride and sulfur dioxide in 1 M acid.⁽²⁸⁾ Ferrous ion in 1 M H₂SO₄ or HCl is moderately rapid at room temperature but is not sufficiently strong to give complete reduction in 1 M or less HCl. The preliminary preparations of Np(IV) for diketone complexing were made by reducing in hot 5 M HCl saturated with sulfur dioxide. This reduction was rapid and complete, but the ensuing complex formation with thenoyl trifluoroacetone seemed much weaker than expected. On the premise that sulfite or bisulfite complexing was suppressing diketone complexing, sulfur dioxide was abandoned. Benzene solutions of the thenoyl trifluoroacetone complex of Np(IV) obtained from this preliminary work, however, were used in determining the HCl dependence of the extraction by equilibrating with solutions of various acid concentrations.

Other promising reductants of sufficient power yet which react fairly slowly with air are iodide and hydrazine. These reductants were extensively investigated from a practical point of view. From the potential of the half reaction

it may be calculated that iodide reduction might be incomplete at the low acid concentrations required for good diketone complexing. A potentiometric measurement of a formal potential for the triiodide - iodine couple in 0.5 M HCl gave a value of -0.65 volt. The calculated value of the potential of the Np(IV) - Np(V) couple in 0.5 M HCl is -0.67 volt.

By maintaining a high iodide to iodine ratio in the solution, therefore, essentially complete reduction of Np(V) should be attained in 0.5 M HCl solutions. These predictions were confirmed experimentally. Np(V) in a 0.3 M HCl, 0.05 M KI, and 0.05 M N₂H₄·2HCl solution reacted very slowly to reach an equilibrium at which somewhat better than 50 per cent of the Np was in the +4 state. In 0.5 M HCl the equilibrium was shifted to nearly complete reduction. Pu(IV) in the same solution was reduced rapidly and completely to Pu(III). The rate of reduction of Np(V) increased with acid concentration and temperature. Iodide alone in 0.5 M HCl was very slow but iodide plus hydrazine was moderately rapid at 100°C. In general, iodide alone was considerably faster than hydrazine alone. The hydrazine was added in these experiments primarily to reduce liberated iodine in order to maintain a high iodide-iodine ratio. A very fast reduction rate

was eventually attained with a solution of 0.1 M KI and 0.05 M $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ in 5 M HCl. Two minutes at 100°C was sufficient to obtain a pure Np(IV) solution. A complication arises under these conditions, however, in that air oxidation of the iodide is fairly rapid, and, especially if comparatively large concentrations of plutonium and neptunium are reduced, an appreciable concentration of iodine is formed. The hydrazine-nitrogen potential is shifted to such an extent in 5 M HCl that it is no longer positive enough to reduce the iodine. Upon dilution to 0.5 M HCl preparatory to forming the diketone complex, the rate of reduction of the iodine by hydrazine at room temperature is very slow. The danger exists, therefore, that the free iodine will cause some re-oxidation of the Np(IV). The procedure adopted to circumvent this difficulty was to reheat the solution to 100°C for a minute or two after dilution to 0.5 M HCl, 0.01 M KI, and 0.005 M $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ whereupon the yellow color of the free iodine disappears as it is reduced by hydrazine. A pure Np(IV), Pu(III) solution results.

In order that the reduction may be dependable for any concentration of neptunium, it is essential that the rate depend on the first power of the Np(V) concentration. If the reduction proceeded through disproportionation of Np(V), the rate would have a second power dependence on neptunium concentration. The rate dependence was determined by following spectrophotometrically the reduction at about 25°C of Np(V) at the concentrations of 0.001, 0.002, 0.003 M in 0.05 M KI and 5 M HCl. All three reductions reached the same stage of completion in identical time intervals, essentially

complete reduction requiring about 40 minutes, indicating that the rate is dependent on the first power of the Np(V) concentration.

A basis for separating uranium in the procedure was established by subjecting U(VI) to iodide reduction in 5 M HCl . Five minutes at 100°C and 12 hours at 25°C failed to produce any U(IV) as attested by the non-appearance of absorption in the region of 650 millimicrons wave length. No accurate value for an extraction coefficient of U(VI) into benzene in a 0.1 M thenoyl trifluoroacetone-benzene and 0.5 M HCl system is available, but values from 0.001 to 0.01 have been reported,^(27,29) so that a moderately good separation from U(VI) will be obtained when the neptunium complex is extracted into the benzene.

3.3 Experimental Procedure. A solution of about 0.025 millimoles Np^{237} in 29.4 ml benzene, about 0.15 molar in thenoyl trifluoroacetone, was obtained by extracting Np(IV) from an HCl solution containing sulfur dioxide. This benzene solution was used for measuring the HCl dependence of the distribution of Np(IV) between aqueous and benzene phases. The benzene solution was placed over 2.0 ml of 0.31 M HCl in an open tube and vigorously agitated at room temperature (about 25°C) to mix the two phases thoroughly. Since this particular solution contained a large percentage of alpha activity from Pu^{239} , the neptunium was tagged by the addition of beta active Np^{239} . Measurement of the distribution ratio of neptunium was therefore accomplished by determining the Geiger activity of equal volumes of the benzene and aqueous phases. Agitation was continued with intermittent

assays until equilibrium was attained. Equilibration required somewhat more than twenty minutes. The HCl concentration was increased to 0.59 M by adding standardized 5.0 M HCl and the equilibration and assays repeated. Similarly the distribution ratios were determined at HCl concentrations of 0.84, 1.05, 1.5, 2.0, and 3.0 molar.

A solution for determining distribution dependence on thenoyl trifluoroacetone concentration was prepared by dissolving Np(V) "hydroxide" in a solution of 5 M HCl, 0.1 M KI, and 0.1 M $\text{H}_2\text{H}_4 \cdot 2\text{HCl}$. Reduction to Np(IV) was accelerated by immersion in a boiling water bath for two minutes. The solution was then diluted to 0.5 M HCl and again immersed in boiling water two minutes to promote reduction of free iodine by hydrazine. This treatment has been found to yield complete reduction to Np(IV). The solution [about 0.001 M Np(IV)] was divided into portions which were contacted with benzene phases containing the following concentrations of thenoyl trifluoroacetone: 0.01, 0.02, 0.04, 0.075, 0.2, 0.35 and 0.5 M. The two phases were agitated at room temperature in glass stoppered tubes by turning the tubes end over end on a slowly revolving wheel. The glass stoppers were sealed in with silicone grease to prevent evaporation of benzene. The distribution ratios at equilibrium were determined by alpha assay of the two phases.

Additional equilibrations were performed in a similar manner using the 0.2 M and 0.5 M benzene-thenoyl trifluoroacetone extractions as stock solutions for new dilutions to 0.2, 0.35, 0.9, and 2 M in thenoyl trifluoro-

acetone. These benzene solutions were contacted with fresh aqueous phases, 0.5 M HCl, 0.01 M KI, and 0.01 M $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$.

3.4 Discussion. The experimental distribution ratios, that is, the ratio of Np^{237} alpha activity in the benzene phase to that in the aqueous phase, were very much larger for the 0.2 and 0.35 M thenoyl trifluoroacetone solutions in the second series than in the first. The increase was taken to mean that some Np(V) was present in the aqueous phase in the first series. Since there was actually a lapse of two to three days in the course of the work between the reduction to Np(IV) and the equilibration of the neptunium between the aqueous and benzene phases, a small amount of oxidation to Np(V) is not unreasonable. The experimental observation was that the alpha activity in the water phase approached a minimum with increasing thenoyl trifluoroacetone concentration. This minimum was assumed to be the measure of the concentration of Np(V) in all the aqueous phases and was subtracted from the total alpha activity in the aqueous phases in the systems containing 0.01, 0.02, 0.04 and 0.075 M thenoyl trifluoroacetone to give the Np(IV) alpha activity in the aqueous phase for calculating the distribution coefficient. Distribution coefficients for the systems containing 0.2, 0.35, and 0.5 M thenoyl trifluoroacetone in the first set of equilibrations were not calculated because of the very large corrections necessary for the Np(V) concentration. The second set of equilibrations for systems containing 0.2, 0.35, 0.9, and 2 M thenoyl trifluoroacetone gave much higher distribution coefficients with no evidence for the existence of

any significant concentration of Np(V) . The distribution coefficients for the 0.9 and 1.86 M thenoyl trifluoroacetone systems, were, in fact, so large that it was impossible to get significant assays of the Np^{237} alpha activity in the aqueous phase. Table 3 summarizes the data. Figure 1 is a plot of $\log E$ against $\log C$, where E is the distribution coefficient and C is concentration of thenoyl trifluoroacetone.

TABLE 3

DISTRIBUTION COEFFICIENTS OF Np(IV) IN BENZENE-AQUEOUS SYSTEMS CONTAINING THENOYL TRIFLUOROACETONE

(Aqueous phase: 0.5 M HCl , 0.01 M KI , 0.01 M $\text{N}_2\text{H}_4 \cdot \text{HCl}$)

C	a	b	E
0.01	1922 $\left(\begin{smallmatrix} \pm 18 \\ -11 \end{smallmatrix}\right)$	4 $\left(\begin{smallmatrix} \pm 2 \\ -10 \end{smallmatrix}\right)$	.0385
0.02	1395 $\left(\begin{smallmatrix} \pm 11 \\ -6 \end{smallmatrix}\right)$	596 $\left(\begin{smallmatrix} \pm 10 \\ -23 \end{smallmatrix}\right)$	.427
0.04	465 $\left(\begin{smallmatrix} \pm 6 \\ -2 \end{smallmatrix}\right)$	1513 $\left(\begin{smallmatrix} \pm 23 \\ -16 \end{smallmatrix}\right)$	3.25
0.075	153 $\left(\begin{smallmatrix} \pm 2 \\ -0.9 \end{smallmatrix}\right)$	1825 $\left(\begin{smallmatrix} \pm 16 \\ -7 \end{smallmatrix}\right)$	11.9
0.2	6 $\left(\begin{smallmatrix} \pm 0.9 \\ -0.04 \end{smallmatrix}\right)$	2187 $\left(\begin{smallmatrix} \pm 7 \\ -7 \end{smallmatrix}\right)$	365
0.35	0.73 $\left(\begin{smallmatrix} \pm 0.04 \end{smallmatrix}\right)$	1351 $\left(\begin{smallmatrix} \pm 7 \end{smallmatrix}\right)$	1851

C = molar concentration thenoyl trifluoroacetone in benzene.

a = alpha counts minute $^{-1}$ per 10 microliters aqueous phase $\pm$ nine-tenths counting error.

b = alpha counts minute $^{-1}$ per 10 microliters benzene phase $\pm$ nine-tenths counting error.

$E = \frac{b}{a}$

The straight lines included in Figure 1 show the slopes 3 and 4. The points for the systems containing 0.02, 0.04, 0.2, and 0.35 M thenoyl trifluoroacetone

lie in a straight line of slope very near 3. The point at 0.075 M appears to be low which might be explained by the fact that the correction applied for Np(V) was too small. The conclusion from these data is that the distribution coefficient is dependent on the third power of the thenoyl trifluoroacetone concentration in the range 0.02 - 0.35 M. The lone point at lower concentration, that at 0.01 M, indicates an approach to fourth power dependence.

Although the data are insufficient to establish the actual equilibria involved in these systems, the third power dependence of the distribution coefficient on the thenoyl trifluoroacetone concentration indicates that the distribution coefficient is not a direct measure of the equilibrium involving four molecules of thenoyl trifluoroacetone per Np(IV) ion. Other equilibria are evidently involved, but the complexity of the system makes analysis impossible on the basis of these data alone. Two alternate or combined processes may be postulated. The Np (IV) may exist in the benzene phase as a molecule containing only three thenoyl trifluoroacetone groups, or appreciable concentrations of complex ions containing less than four thenoyl trifluoroacetone groups may exist in the aqueous phase.

Table 4 gives the distribution coefficients in the systems containing variable concentrations of HCl. Figure 2 is a plot of log E against log HCl. Slopes of 3 and 4 are included in the figure. It may be seen that the HCl concentration dependence of the distribution coefficient is between third

and fourth power. The thenoyl trifluoroacetone concentration was not precisely constant in all runs since some benzene evaporated from the open equilibration tube, resulting in increased thenoyl trifluoroacetone concentration. Small numerical corrections based on the known benzene volumes were applied to the measured distribution coefficients, E' , on the assumption that the distribution coefficient is proportional to the cube of the thenoyl trifluoroacetone concentration. The column under E gives the corrected distribution coefficients. The corrections made very little change in the log-log plot.

TABLE 4

DISTRIBUTION COEFFICIENTS OF Np(IV) AT VARIOUS HYDRO-
CHLORIC ACID CONCENTRATIONS

M HCl	a	b	E'	E
0.31	7.9	4656	589	589
0.59	71.5	4697	65.7	63.1
0.84	225	4836	21.5	19.0
1.05	478	4938	10.3	8.38
1.5	1490	4940	3.32	2.52
2.0	3270	4817	1.47	1.05
3.0	11500	3172	0.276	.194

The equilibrium data obtained in this work are regarded as preliminary since the primary aim was to secure approximate guides for a practical separation of plutonium and neptunium by solvent extraction. The

data obtained are sufficient for establishing favorable concentrations for separation of neptunium and plutonium. The HCl concentration for the extraction is fixed approximately at 0.5 M to maintain the complete reduction to Np(IV) by iodide. The thenoyl trifluoroacetone concentration depends on considerations of the desired efficiency of recovery, mechanical convenience, and required final volumes. Minimum amounts of thenoyl trifluoroacetone for given conditions may be calculated to give any desired recovery from the following equation:

$$\frac{(C_w)_n}{S} = \frac{(V_w)^{n-1}}{(V_b E - V_w)^n}$$

where n = number of equilibrations

$(C_w)_n$ = a measure of the Np concentration in aqueous phase after n equilibrations with a benzene-thenoyl trifluoroacetone phase giving a distribution coefficient, E

S = a measure of the total neptunium (as moles or total disintegration rate).

V_w = constant volume of aqueous phase

V_b = constant volume of benzene phase.

In laboratory separations S and V_w are usually fixed by prevailing conditions, and C_w , the measure of the neptunium not removed from the aqueous phase, n , and V_b are arbitrarily set at convenient values. The equation may then be solved for E , the desired distribution coefficient. Reference to Figure 1 will give the required concentration of thenoyl trifluoroacetone.

A number of other factors may influence the extraction efficiency. The aqueous phase should contain no anions other than chloride which may complex the Np(IV) and thereby reduce the distribution coefficient. The preliminary equilibrations, in which sulfur dioxide was present, yielded distribution coefficients 100 to 200 times lower than those in which iodide was the reducing agent, so that sulfite or bisulfite complexing is evident. Large salt concentrations will also reduce the distribution coefficient. An aqueous phase containing 1.0 M HCl and 1.0 M KCl gave a distribution coefficient of 0.3 whereas the aqueous phase containing 1.0 M HCl gave a coefficient of 10 with the same benzene phase. There is also a limit to the solubility of the chelate complex in the system. It was found that contacting an aqueous phase, initially 0.1 M Np(IV) , with benzene containing 0.1 M thenoyl trifluoroacetone produced a gray precipitate containing neptunium. The precipitate contributes to the formation of a foam in the system which makes clean separation of the phases very difficult and the distribution coefficients are low. A benzene solution containing 0.008 M Np(IV) chelate has been obtained, however, in the presence of 0.06 M thenoyl trifluoroacetone, which fact may be used as a safe solubility limit until more accurate values are determined. The time required to equilibrate the Np(IV) between the two phases is about 30 minutes. The lengthy equilibration time is the principal disadvantage of the method.

The Np(IV) is recovered from the benzene phase by extracting with 5 - 10 M HCl. The distribution coefficient to be expected may be extrapolated roughly from Figure 2. Extraction with strong acid is not desirable from a purification standpoint since chelated metals other than Np(IV) are probably also extracted into the acid. The method would be greatly improved if the Np(IV) were extracted from the benzene by oxidizing to Np(V) or Np(VI) at low acid concentration.

In actual practice, the solvent extraction method is highly satisfactory. One separation cycle for which complete data is available gave a plutonium decontamination factor of 300 with essentially complete recovery of the Np. This amount of decontamination is as good as the average bromate cycle. The method has the great advantage of minimizing mechanical losses which are the main difficulty encountered with the bromate method of purification. The plutonium content can apparently be lowered to any desired level by repeated cycling. A number of milligrams of neptunium have been purified by this method to the extent that no Pu²³⁹ alpha activity is detectable by the best method of alpha pulse analysis available. The pulse analysis in this case will detect about 0.1% Pu²³⁹ activity which is equivalent to 0.001% Pu²³⁹ by weight. A more sensitive analysis for Pu²³⁹ is slow neutron fission rate determination. This method is not, however, an absolute determination for the Pu²³⁹ content of Np²³⁷ since the slow neutron fission cross-section of Np²³⁷ apparently is not insignificant. That is, a supposedly pure sample of Np²³⁷ gives a fission rate corres-

ponding to a Pu^{239} content of ca. 0.1% by alpha activity. Repeated solvent purification of the Np^{237} does not lower the fission rate, but it is practically certain that repeated cycling continues to remove plutonium. A method for extracting Pu(IV) away from Np(V) should be very valuable for removing traces of plutonium from macro amounts of neptunium, thereby avoiding the unnecessary transfer of large amounts of neptunium between the phases. This type of method may also circumvent the neptunium solubility limitation encountered in the Np(IV) extraction and will be well worth developing.

4. Separation of Neptunium from Alkali, Alkaline Earths,
Other Metals, and Various Cations

There has been to date practically no systematic analytical work on neptunium so that it is impossible to state with absolute certainty that a given separation method will remove a particular impurity. There is, however, considerable evidence from qualitative observations and from assuming an analogy with compounds of the corresponding oxidation states of plutonium and uranium to support the belief that the methods described herein are effective. All of the methods described above are very specific in their purpose, separating neptunium, plutonium, and uranium, as the case may be, from all other cations and most anions. The ether extraction, for example, yields a uranyl nitrate nitric acid solution of very high purity and unquestionably will purify neptunium just as effectively. Benzene extraction from 0.5 M HCl solution is efficient in separating most metals not in the

+4 oxidation state, and all anions. Some metals, such as Zr(IV), are undoubtedly not efficiently separated. (27)

The operation which has occurred most frequently in neptunium research is the transfer of the neptunium from one aqueous medium to another, that is, substitution and adjustment of hydrogen ion and anion concentrations. The transfer is accomplished easily since Np(IV), Np(V), and Np(VI) precipitate in moderately alkaline solutions, in all cases with the formation of hydroxyl compounds which probably contain no other anions. The alkaline precipitants used have been NaOH, KOH, and NH_4OH . The solubilities of the Np(IV) hydroxide are quite low, of the order of 0.001 g/l. while the solubilities of the Np(V) and Np(VI) hydroxyl compounds are of the order of 0.1 g/l. in 0.1 - 1.0 M hydroxyl ion concentration. Np(IV) hydroxide is believed to be hydrated $\text{Np}(\text{OH})_4$. The compositions of the Np(V) and Np(VI) compounds are not known. The alkaline precipitations are also useful for removing the neptunium from solutions containing alkalis, alkaline earths, and all ions which are soluble in alkaline solutions. Excess base is removed from the precipitated neptunium compound by repeated water washing and centrifugation. These compounds either have low water solubilities or reach equilibrium solubility slowly since very little neptunium is lost in the water wash. The compounds are soluble in the required acid solution. To achieve rapid dissolution, the acid should be more concentrated than 2 M and after solution is complete the acid may be diluted to the desired concentration. In dissolving the

Np(V) hydroxyl compound, it should be kept in mind that Np(V) disproportionates to Np(IV) and Np(VI) with a probable dependence on the hydrogen ion concentration of fourth power.⁽²⁶⁾ The rate constant is rather small at room temperature.⁽²⁸⁾

For some purposes it may be convenient to remove anions by vaporization methods. Sulfate solutions may be prepared, for example, by adding sulfuric acid and heating the solution to the appearance of sulfur trioxide fumes.

Np(IV) will precipitate as a white peroxide compound from 1 M acid solutions containing 5-10 per cent H_2O_2 .⁽³⁰⁾ It has not been necessary to resort to precipitation of this compound for purification although conceivably it might be of some use for separating neptunium from metals which do not form insoluble peroxides. Pu(IV) peroxide precipitations are not particularly effective as a means of separating plutonium from anions since anions other than peroxide are incorporated into the compound.

A noteworthy purification for a special purpose is a cathodic deposition.⁽³¹⁾ Np(VI) in solutions of low acid concentration (ca. 0.1 M) with ca. 0.01 M oxalate concentration may be electrolyzed at a high current density to deposit a neptunium compound, probably NpO_2 hydrate, on the cathode. The NpO_2 hydrate is deposited as a very thin uniform film. This property is useful for preparing plates for measuring alpha radiation since the films may be made so thin that emerging alpha particles lose no energy in traversing the film.

An illustration of the efficacy of some of these purification methods is the preparation of pure NpO_2 and the determination of the specific activity of Np^{237} .⁽³⁾ The accuracy of the determination is dependent on the purity of the weighed neptunium compound, which was assumed to be NpO_2 . An independent check on the determination has been made by an oxidation titration.⁽³²⁾ The values agreed to 1 per cent which was the approximate precision of the check method.

The preparation of neptunium metal is described in another paper of this volume.⁽³³⁾

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FIGURE I--THE DISTRIBUTION COEFFICIENT OF Np(IV) AS A FUNCTION OF THENOYLTRIFLUOROACETONE CONCENTRATION

FIGURE 2--THE DISTRIBUTION COEFFICIENT OF Np(IV) AS A FUNCTION OF HCl CONCENTRATION

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