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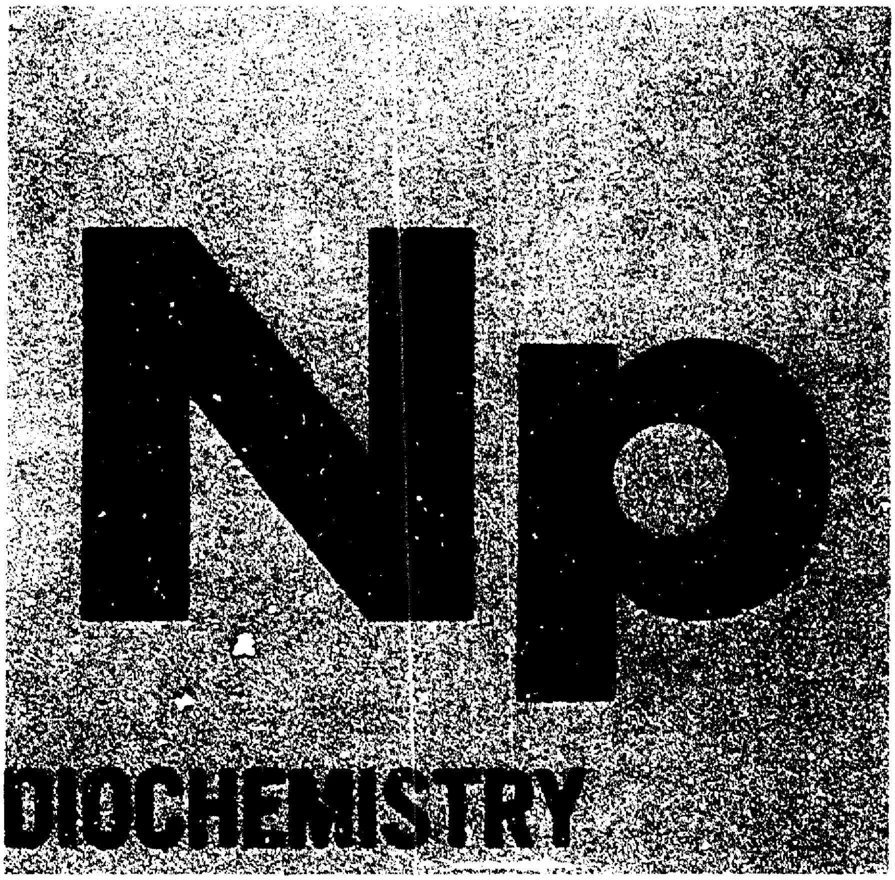

RADIOCHEMISTRY OF NEPTUNIUM

NUCLEAR SCIENCE SERIES

National Academy of Sciences-National Research Council

Published by
Technical Information Center, Office of Information Services
UNITED STATES ATOMIC ENERGY COMMISSION

COMMITTEE ON NUCLEAR SCIENCE

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Subcommittee on Radiochemistry

NAS-NS-3060
AEC Distribution Category UC-4

RADIOCHEMISTRY OF NEPTUNIUM

by

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Prepared for Subcommittee on Radiochemistry
National Academy of Sciences - National Research Council

Issuance Date: December 1974

Published by
Technical Information Center, Office of Information Services
UNITED STATES ATOMIC ENERGY COMMISSION

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National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22161

Printed in the United States of America

USAEC Technical Information Center, Oak Ridge, Tennessee
1974

Foreword

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences—National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the radiochemical purity of reagents, the place of radiochemistry in college and university programs, and radiochemistry in environmental science.

This series of monographs has grown out of the need for compilations of radiochemical information, procedures, and techniques. The Subcommittee has endeavored to present a series that will be of maximum use to the working scientist. Each monograph presents pertinent information required for radiochemical work with an individual element or with a specialized technique.

Experts in the particular radiochemical technique have written the monographs. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to radiochemists but also to research workers in other fields such as physics, biochemistry, or medicine who wish to use radiochemical techniques to solve specific problems.

Gregory R. Choppin, *Chairman*
Subcommittee on Radiochemistry

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I. GENERAL REVIEW OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF NEPTUNIUM

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II. GENERAL REVIEW OF THE RADIOCHEMISTRY OF NEPTUNIUM

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III. DISCOVERY AND OCCURRENCE OF NEPTUNIUM

Neptunium was discovered in 1940 by McMillan and Abelson.[1] They bombarded a thin uranium foil with low-energy neutrons and showed that the 2.3-day activity that was formed was an isotope of element 93 produced by the nuclear reactions:

$$ {}^{238}_{92}\mathrm{U}\ (n,\gamma)\ {}^{239}_{92}\mathrm{U} \xrightarrow[23\ \mathrm{min}]{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow[2.3\ \mathrm{d}]{\beta^-} {}^{239}_{94}\mathrm{Pu} $$

It was shown in 1941 that the decay product of ${}^{239}Np$ was ${}^{239}Pu$.[2]

${}^{239}Np$ is produced in large quantities as the intermediate in the nuclear reactor production of ${}^{239}Pu$, but because of its short half-life it is used only as a tracer.

Wahl and Seaborg[3] discovered the long-lived isotope ${}^{237}Np$ in 1942. It was produced by the nuclear reactions:

$$ {}^{238}_{92}\mathrm{U}\ (n,2n)\ {}^{237}_{92}\mathrm{U} \xrightarrow[6.75\ \mathrm{d}]{\beta^-} {}^{237}_{93}\mathrm{Np} $$

The first weighable quantity of ${}^{237}Np$ (∿45 μg of NpO_2) was isolated by Magnusson and LaChapelle in 1944.[4] These workers were the first to measure the specific activity of ${}^{237}Np$.

As a result of these reactions, Np is produced in relatively large quantities in nuclear reactors fueled with natural U. When fuels enriched in ${}^{235}U$ and ${}^{236}U$ are used in nuclear reactors, the following reactions are increasingly important.

$$ {}^{235}_{92}\mathrm{U}\ (n,\gamma)\ {}^{236}_{92}\mathrm{U}\ (n,\gamma)\ {}^{237}_{92}\mathrm{U} \xrightarrow[6.75\ \mathrm{d}]{\beta^-} {}^{237}_{93}\mathrm{Np} $$

Since about 1957, the U. S. Atomic Energy Commission has recovered and purified byproduct Np in its production facilities. ${}^{237}Np$ is used as target for the production of ${}^{238}Pu$, an isotope in demand for fueling radioisotopic power sources.[5]

$${}^{237}_{93}Np\ (n,\gamma)\ {}^{238}_{93}Np \xrightarrow[2.1\ d]{\beta^-} {}^{238}_{94}Pu$$

The half-life of ${}^{237}Np$ is very short compared to the age of the earth. Therefore, it is found only in trace quantities in U minerals where it is formed continuously by neutron reactions described previously.[6] It was found that the abundance of ${}^{237}Np$ in a sample of Katanga pitchblende was 2.16×10^{-12} atoms per atom of ${}^{238}U$, while that of ${}^{239}Pu$ was 3.10×10^{-12} atoms per atom of ${}^{238}U$.[7]

IV. ISOTOPES AND NUCLEAR PROPERTIES OF NEPTUNIUM

The known isotopes and selected nuclear properties of Np are listed in Table 1. The radioanalytical chemist works mostly with long-lived ${}^{237}Np$ and short-lived ${}^{239}Np$ and ${}^{238}Np$. The decay schemes of these most important isotopes of Np are presented in Figure 1.

Thermal neutron cross sections and resonance integrals for Np isotopes are shown in Table 2.

TABLE 1

ISOTOPES OF NEPTUNIUM^{a,b}

Mass Number	Half-life	Specific Activity (dpm/μg)	Mode of^a Decay	Decay Energy (MeV)	Methods of Preparation
228^b	60 sec	1.831×10^{15}	sf		^{209}Bi + ^{22}Ne
229	4.0 min	4.55×10^{14}	α(>0.5)	E_α = 6.66	^{233}U(p,5n)
			EC(<0.5)		
230	4.6 min	3.945×10^{14}	EC(0.97)	E_α = 6.89	^{233}U(p,4n)
			α(0.03)		
231	50 min	3.614×10^{13}	EC(~0.99)	E_α = 6.28	^{235}U(d,6n)
			α(~0.01)		^{238}U(d,9n)
232	13 min	1.384×10^{14}	EC		^{235}U(d,5n)
					^{233}U(d,3n)
233	35 min	5.117×10^{13}	EC		^{235}U(d,4n)
			α(7×10^{-6})	E_α = 5.53	^{234}U(d,3n)
234	4.40 day	2.815×10^{11}	EC	E_{β^+} = 0.8	^{235}U(d,3n)
			α($<10^{-3}$)		
235	396.1 day	3.114×10^{9}	EC	E_α = 5.095(4%)	^{235}U(d,2n)
			α($\sim10^{-5}$)	5.015(83%)	
				4.925(12%)	
				4.864(1%)	
236	22 hr	3.397×10^{12}	EC(0.48)	E_{β^-} = 0.518(60%)	^{235}U(d,n)
			β^-(0.52)	0.36(40%)	^{237}U(n,2n)
236^m	>5000 yr		β^-		^{238}U(d,4n)
237	2.14×10^6 yr	1.564×10^{3}	α	E_α = 4.786(42%)	^{238}U(n,2n)
			sf(5×10^{-11})	4.768(28%)	^{235}U(n,γ)^b
				4.764(5%)	^{237}U(β^--decay)
				4.661(5.5%)	
				4.636(6%)	^{241}Am(α-decay)
238	2.12 day	5.744×10^{11}	β^-	E_{β^-} = 1.25(45%)	^{237}Np(n,γ)
				0.26(54%)	^{238}U(d,2n)
				E_γ = 1.027(29%)	^{235}U(α,p)
				0.985(26%)	
239	2.35 day	5.160×10^{11}	β^-q	E_{β^-} = 0.713(7%)	^{238}U(n,γ)
			sf($<8 \times 10^{-12}$)	0.437(48%)	^{239}U(β-decay)
				0.393(13%)	
				0.332(28%)	^{238}(d-n)
				E_γ = 0.278(13%)	^{243}Am(α-decay)
				0.228(12%)	
				0.106(21%)	
240^m	7.5 min	2.319×10^{14}	β^-	E_{β^-} = 2.18(52%)	^{240}U(β-decay)
				1.60(31%)	
240	67 min	2.595×10^{13}	β^-	E_{β^-} = 0.89(100%)	^{238}U(α,pn)
241	16 min	1.082×10^{14}	β^-	E_{β^-} = 1.36	^{238}U(α,p)

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a. sf = spontaneous fission
α = alpha decay
EC = electron capture decay
β^- = negatron decay

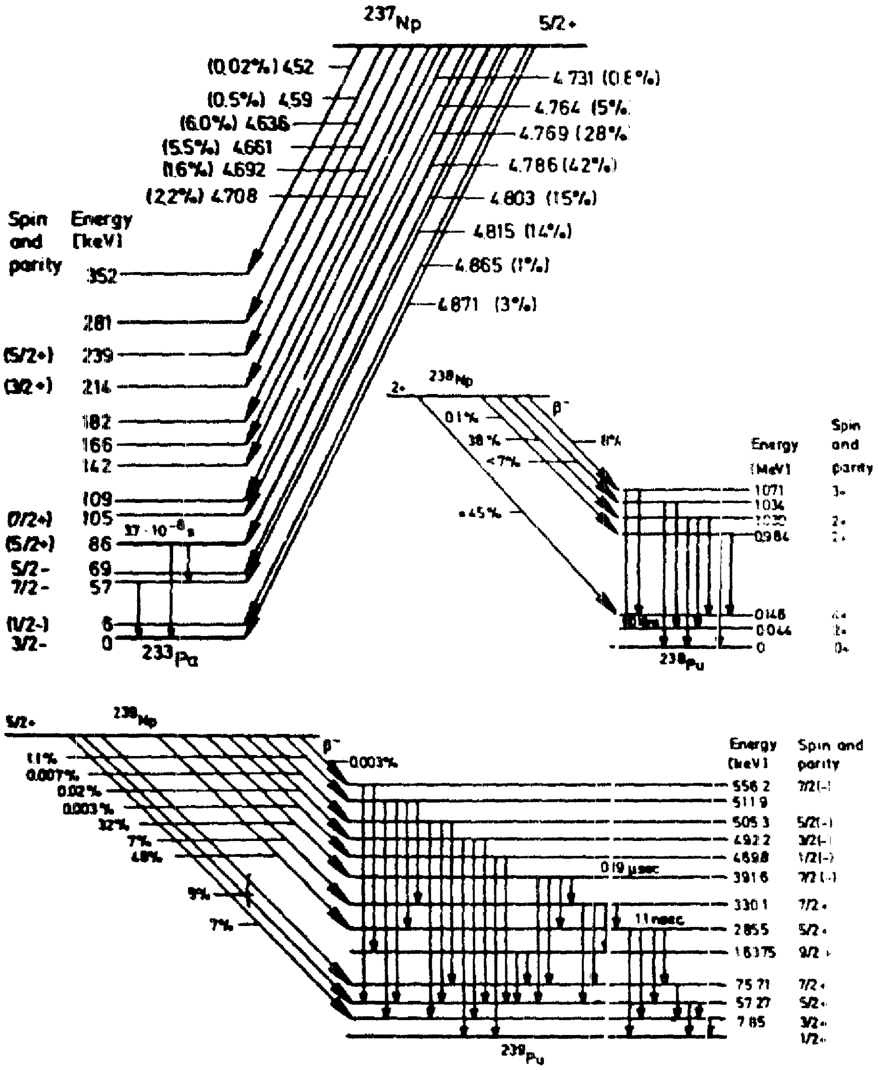

Figure 1. Decay Schemes of the Most Important Neptunium Isotopes, ^{237}Np, ^{238}Np, and ^{239}Np.[8,10]

TABLE 2

CROSS SECTIONS AND RESONANCE INTEGRALS[a] FOR NEPTUNIUM ISOTOPES[*]

	Neutron Capture		Fission		
Mass Number	$\sigma_{(n,\gamma)}$	$I_{(n,\gamma)}$	σ_f	I_f	$\sigma_{(n,2n)}$
234			900		
235	148[b]				
236			2,800		
237	185	600	0.02 1.42[d]	0	0.0013[c]
238	1,600	600	2,070	800	
239	35[e] (to ^{240m}Np) 25[e] (to ^{240}Np)		1		

---

a. Cross-sections expressed in barns, 10^{-24} cm^2.
b. J. H. Landrum, R. J. Nagle, M. Lindner, UCRL-51263 (1972).
c. For neutrons with the fission spectrum.
d. For 3 MeV neutrons.
e. For "reactor neutrons".

V. CHEMISTRY OF NEPTUNIUM

A. METALLIC NEPTUNIUM

A.1 Preparation

Np metal was first prepared by Fried and Davidson in 1948 by the reduction of 50 μg of NpF_3 with Ba vapor at 1200°C.[11] A similar method was used by Westrum and Eyring.[12] Reduction of NpF_4 by excess Ca metal with iodine as a booster[13-15] was used to produce multigram quantities of Np metal.

A.2 Physical Properties

Pure Np is a silvery ductile metal with a melting point of 637°C. The metal undergoes three allotropic modifications below the melting point. The physical properties are summarized in Table 3.

TABLE 3

PHYSICAL PROPERTIES OF NEPTUNIUM METAL[16,17,18]

A. Appearance: Silvery white (slowly coated with oxide in dry air at room temperature)

B. Melting Point: 637°C

C. Boiling Point: 4175°C (extrapolated from vapor pressure measurements of liquid Np[19])

D. Heat of Vaporization: ΔH 1800°K = 94.3 kcal/(g-atom)

E. Properties of Various Allotropic Modifications:

	α	β	γ
Transition temperature to next higher phase, °C	280	577	637
Density, g/cm^3 (at T°C)	20.48	19.40	18.04
Crystal Structure	Orthorhombic	Tetragonal	Cubic

Stephens[20] determined the pressure-temperature relationship for Np. The specific heat (C_p) of Np is high. The Dulong and Petit value of 3R is reached at 140°K and 7.093 cal/(mol-°K) at 27°C.[21] The high specific heat can be entirely accounted for by the very high electronic contributions. No magnetic ordering in α-Np occurs down to 1.7°K.[22]

A.3 Chemical Properties

Np is a reactive metal. The potential for the couple $Np = Np^{3+} + 3e^{-}$ is 1.83 volts. Metallic Np is slowly covered with a thin oxide layer when exposed to dry air at about 20°C, and rapid oxidation to NpO_2 occurs at higher temperatures especially in moist air. Hydrogen, halogens, phosphorus, and sulfur react with Np metal at elevated temperatures. Hydrogen reacts to form the hydride at relatively low temperatures.

Np forms intermetallic compounds of intermediate solid solutions with U, Pu, Be, Al, B, Cd, Ir, Pd, and Rh.

Np dissolves readily in HCl at room temperature and H_2SO_4 at elevated temperature. The behavior of Np toward various solutions is given in Table 4.

B. ALLOYS AND INTERMETALLIC COMPOUNDS

Complete phase diagrams are reported for Np-Pu and Np-U.[23-26] Complete miscibility has been reported between γ-Np and γ-U and between γ-Np and Σ-Pu. Np is a unique element because of its extremely high solubility in both α-Pu and β-Pu.

The intermetallic compounds of Np with Al and Be ($NpAl_2$, $NpAl_3$, $NpAl_4$, and $NpBe_{13}$) are prepared directly by reducing NpF_3 with an excess of metallic Al or Be. The borides (NpB_2, NpB_4, NpB_6, and NpB_{12}) and the intermetallic compounds $NpCd_6$ and $NpCd_{12}$ are obtained directly from the elements.[27-29] Several

TABLE 4

BEHAVIOR OF Np METAL IN VARIOUS SOLUTIONS[13]

Solution	Concentration (M)	Observations Initial	 After 4 days
H_2O		Very slowly attacked	
HCl^a	1.5	Immediate vigorous reaction	Completely dissolved
	6	"	"
	12	"	"
HNO_3	2	No visible reaction	Some turbidity, hydrated oxide
	8	"	"
	15.7	"	No reaction-clear solvent
$H_2SO_4{}^a$	2.25	Slow reaction	No reaction-clear solvent
	9	"	"
	18	No noticeable reaction	"
CH_3COOH^a	2	Slight initial reaction-ceased	Some turbidity hydrated oxide
	8	"	"
	16	No visible reaction	No reaction-clear solution
$HClO_4$	Conc.	Rapid dissolution when heated	"
H_3PO_4	Conc.	Rapid dissolution when heated	"
HSO_3NH_2		Rapid dissolution when heated	"
Conc. HNO_3 - trace HF		Dissolution when refluxed	"

---

[a] At ambient temperature.

compounds with noble metals, such as $NpPt_3$ and $NpPt_5$, have been prepared by hydrogen reduction of NpO_2 at 1300°C in the presence of platinum.[30] Also, Erdmann[31] used the same method to prepare several other compounds, $NpIr_2$, $NpPd_3$, and $NpRh_3$.

C. COMPOUNDS OF NEPTUNIUM

Compounds of Np for the III, IV, V, VI, and VII oxidation states have been prepared. The solubilities and compositions of some of the compounds have not been verified because they were initially determined with small amounts of Np shortly after discovery and therefore may be semi-quantitative. Where studies have been made with larger amounts of neptunium, i.e., oxalates and peroxides, more quantitive data is available.

Numerous Np compounds, such as nitrates, chlorides, and possibly thiocyanates, are readily soluble in solvating organic solvents such as diethyl ether, hexone, TBP, and other acid-containing solvents saturated with water.

Investigation of compounds containing trivalent neptunium has been limited because of the instability of Np(III) in aqueous solution in the presence of atmospheric oxygen. Np(III) is produced under hydrogen (on a platinum catalyst), by electrochemical reduction and with rongalite, $NaHSO_2 \cdot CH_2O \cdot 2H_2O$. Mefod'eva *et al.*[32] have prepared several Np(III) compounds from solution with protection from oxygen. All the reagent solutions and water were purged with pure argon. The precipitation and subsequent operations (centrifugation and washing) were conducted with a layer of benzene over the solution. The solids were washed with acetone or ether and dried in a stream of argon. Np(III) oxalate was prepared, but it was appreciably oxidized in a few hours. The solid was brown and was in the form of tetragonal prisms. Np(III) phenylarsonate is rose-lilac colored with the composition $Np_2(C_6H_5AsO_3)_3 \cdot nH_2O$ when well dried; the compound is stable for a long period at room temperature. Np(III) salicylate and grayish-lilac Np(III) fluoride were also precipitated under controlled conditions. Two complex double sulfates of Np(III), $K_5Np(SO_4)_4$ and $NaNp(SO_4)_2 \cdot nH_2O$, were precipitated. In the dry form, these salts were stable to oxidation during prolonged storage even at increased temperature.

Only one solid compound of Np(VII), $Co(NH_3)_6NpO_5 \cdot 3H_2O$, has been reported.[33]

Compounds of Np(IV), (V), and (VI) are shown in Tables 5 and 6. Table 5 includes compounds produced in aqueous solution, and Table 6 includes compounds produced by other methods.

TABLE 5

NEPTUNIUM COMPOUNDS PRECIPITATED FROM AQUEOUS SOLUTION

Compound	Color	Composition of Solution	Solubility (mg Np/l)	Reference
$NpO_2(OH)_2 \cdot aq$	Black	$NaOH$ - $NaNO_3$ pH 5 to 9	Dissolves in either acid or base	33
Np(IV) hydroxide	Brown green	1M $NaOH$ - 3M $NaNO_3$	3 to 4	34
Np(V) hydroxide	Green	1M $NaOH$ - dilute ammonia	17 180 180	35
$(NH_4)_2Np_2O_7$	Brown	1M NH_4OH - 0.5M $(NH_4)_2SO_4$	25	35
Np(IV) peroxide	Purple	2.5M HNO_3 - 6.5M H_2O_2	12	36
$NpF_3 \cdot XH_2O$	Grayish lilac	0.3M HCl - 0.3M HF (argon atm)		32
$NpF_4 \cdot XH_2O$	Green	1M HNO_3 - 1M HF		37
NH_4NpF_5	Green	1M HF - 0.01M NH_4F	15	38
KNp_2F_9 $La_2NpF_{10} \cdot XH_2O$	Green	4M HF - 1M KF	11 4	38 39
Np(IV) iodate	Tan brown	1M HCl - 0.1M KIO_3	80	
Np(III) oxalate	Brown			
$Np(C_2O_4)_2 \cdot 6H_2O$	Green	0.1M $H_2C_2O_4$ - 3M HNO_3	6	32 40
$NpO_2C_2O_4H \cdot 2H_2O$	Green			41
$NpO_2C_2O_4 \cdot 3H_2O$	Grey green			42
$KNpO_2CO_3$	Tan	H_2O	10	43
$K_5NpO_2(CO_3)_3$	Greenish blue	H_2O - 0.2M K_2CO_3	23	44
$CsNpO_2(CO_3)_3$	Greenish blue	H_2O	23	44
$KNpO_2(C_2H_3O_2)_3$	Green	0.7M H_2SO_4 - 0.07M $NaNO_2$ - 2M $NaC_2H_3O_2$	100	38
$Np(HPO_4)_2 \cdot XH_2O$	Green	1M HCl - 0.5M H_3PO_4	56	45
$K_4Np(SO_4)_4$	Bluish lilac	0.3M HCl - sat K_2SO_4 - 0.2N H_2SO_4	0	32
$NaNp(SO_4)_2 \cdot mH_2O$	Blue	0.3M HCl - sat K_2SO_4 - 0.2N H_2SO_4	0	32
$Np(C_6H_5AsO_3)_2$	Green	0.1M $C_6H_5AsO_3H_2$ - 0.5M HNO_3	5	46
$NpO_2C_6H_5AsO_3$		0.04M $C_6H_5AsO_3H_2$ - 0.5M HNO_3	140	46
$[(CH_3)_3(C_6H_5CH_2)N]_2 \cdot Np(NO_3)_6$		6 to 8M HNO_3	100	34

TABLE 6

OTHER NEPTUNIUM COMPOUNDS

Compound	Color	Lattice Symmetry	Reference
NpH_2		Cubic	47
NpH_3		Hexagonal	47
NpO_2	Green	Cubic	48,49
Np_2O_5	Dark brown	Monoclinic	49a
Np_3O_8	Dark brown	Orthorhombic	50,51
$NpO_3 \cdot H_2O$	Red brown	Orthorhombic	47

A large number of ternary and polynary oxides of Np(VII), Np(VI), Np(V), and Np(IV) with alkali metals and alkaline earth metals are known. Also, similar compounds are reported with the rare earths, other actinides, and elements in Groups 4 to 7.[52]

NpN	Black	Cubic	53
NpF_3	Purple	LaF_3	54
NpF_4	Green		55
NpF_6	Orange	Orthorhombic	52,56

A large number of fluoro compounds of alkali or alkaline earth metals with Np(IV) and fluoride have been reported; a few such compounds with Np(V) and Np(VI) also are reported.[52]

NpO_2F	Green	Tetragonal	57
$NpOF_3$	Green	Rhombohedral	58
NpO_2F_2	Pink		57
$NpCl_3$	Green		11
$NpCl_4$	Orange brown		11,58
$NpOCl_2$	Orange		59
$NpBr_3$	Green		60
$NpBr_4$	Dark red		61
NpI_3	Brown		62
NpS		Cubic	63,64
Np_2S_3		(4 different structures)	63,64
Np_3S_5		Orthorhombic	63,64
Np_2S_5		Tetragonal	63,64
NpS_3		Monoclinic	63,64

D. NEPTUNIUM IONS IN SOLUTION

D.1. Oxidation States

Neptunium exists in the (III), (IV), (V), (VI), and (VII) oxidation states in aqueous solutions. The heat of formation, the entropy of the individual ionic species, and simple methods of preparation are listed in Table 7. The first four of these oxidation states exist as hydrated ions in the absence of complexing agents. Np(VII) is stable only in alkaline solutions; reduction to Np(VI) occurs in acid solutions.

The singly charged, hydrated neptunyl ion, $[NpO_2(H_2O)_6]^+$, is the most probable oxidation state in solution. Because NpO_2^+ hydrolyzes only at pH >7, disproportionates only at high acid concentrations, and forms no polynuclear complexes, it is stable compared to the other pentavalent actinides. The standard potentials and formal electrode potentials in 1M $HClO_4$ of pairs of neptunium ions are shown in Table 8.

The formal oxidation potentials for Np couples in various 1M solutions are given in Table 9, with the hydrogen electrode in the stated medium as the reference. The change in the potentials in 1.0M H_2SO_4 as compared to 1M solutions of $HClO_4$, HCl, and HNO_3 indicates strong complex formation of Np^{4+} with sulfate ions.

TABLE 7

NEPTUNIUM IONS IN AQUEOUS SOLUTION[a,b,c]

Oxidation State	Ionic Form	Color	Heat of Formation $\Delta H_{298°K}$ (kcal/mol)	Entropy $S_{298°K}$ [cal/(g-atom-°K)]	Simple Methods of Preparation
+3	$Np(H_2O)_n^{3+}$	Blue violet	-127	-43.5[a]	1) Np(>III) + H_2/Pt 2) Electrolytic reduction
+4	$Np(H_2O)_n^{4+}$	Yellow green	-132.5	-78	1) Np^{3+} + O_2 2) Np(V) + SO_2 3) Np(V) + I^-(5M HCl)
+5	$NpO_2(H_2O)_n^{+}$	Green	-231	- 6.2[b]	1) Np^{4+} + HNO_3 (heat) 2) Np(VI) + stoichiometric I^- 3) Np(VI) + NH_2OH
+6	$NpO_2(H_2O)_n^{2+}$	Pink or red	-208	-20[b]	1) Np(<VI) + $HClO_4$ (evaporate) 2) Np(<VI) + Ag(II)O (or BrO_3^-, Ce^{4+})
+7	NpO_5^{3-}	Green[c]			1) Dissolution of thermally prepared Li_5NpO_6 in dilute alkalis 2) Np(VI) + ozone (or XeO_3, $K_2S_2O_8$, periodate) in 0.5 to 3.5M NaOH

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a. J. C. Hinchey, J. W. Cobble. *Inorg. Chem.* *9*, 992 (1970).
b. J. R. Brandt, J. W. Cobble. *Inorg. Chem.* *9*, 912 (1970).
c. C. Brown in $HClO_4$. J. C. Sullivan and A. J. Zielen. *Inorg. Nucl. Chem. Letters* *5*, 927 (1969).

TABLE 8

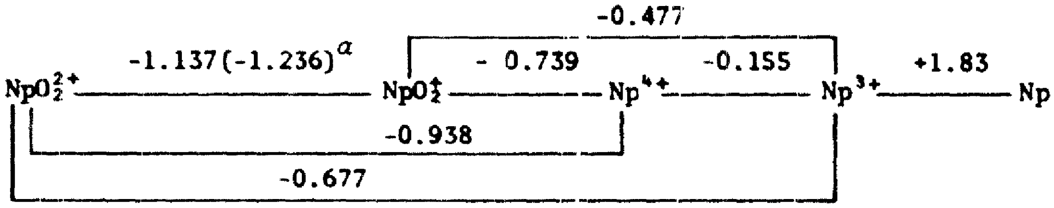
STANDARD AND FORMAL REDOX POTENTIALS OF PAIRS OF NEPTUNIUM IONS[34]

Electrode Process	Standard Potentials (volts)	Formal Potentials in 1M $HClO_4$ (volts)
$Np = Np^{3+} + 3e^-$	-1.856	-1.83
$2Np + 3H_2O = Np_2O_3 + 6H^+ + 6e^-$	-1.420	-
$Np_2O_3 + H_2O = 2NpO_2 + 2H^+ + 2e^-$	-0.962	-
$Np_2O_3 + 5H_2O = 2Np(OH)_4 + 2H^+ \; 2e^-$	-0.928	-
$Np^{3+} = Np^{4+} + e^-$	-0.152	0.155
$Np^{3+} + 2H_2O = NpO_2 + 4H^+ + e^-$	0.337	-
$Np^{3+} + 4H_2O = Np(OH_4) + 4H^+ + e^-$	0.391	-
$Np^{3+} + 2H_2O = NpO_2^+ + 4H^+ + 2e^-$	0.451	0.447
$Np(OH)_4 = NpO_2^+ + 2H_2O + e^-$	0.530	-
$NpO_2 = NpO_2^+ + e^-$	0.564	-
$Np^{4+} + 2H_2O = NpO_2^+ + 4H^+ + e^-$	0.749	0.739
$NpO_2 = NpO_2^{2+} + e^-$	1.149	1.137
$2Np(OH)_4 = Np_2O_5 + 2H_2O + 2H^+ + 2e^-$	1.219	-
$2NpO_2 + H_2O = Np_2O_5 + 2H^+ + 2e^-$	1.253	-
$Np_2O_5 + H_2O = 2NpO_3 + 2H^+ \; 2e^-$	1.310	-
$NpO_2 + H_2O = NpO_3 + 2H^+ + e^-$	1.998	-
$Np^{3+} + 2H_2O = NpO_2^{2+} + 4H^+ + 3e^-$	-	0.677
$Np^{4+} + 2H_2O = NpO_2^{2+} + 4H^+ + 2e^-$	-	0.938

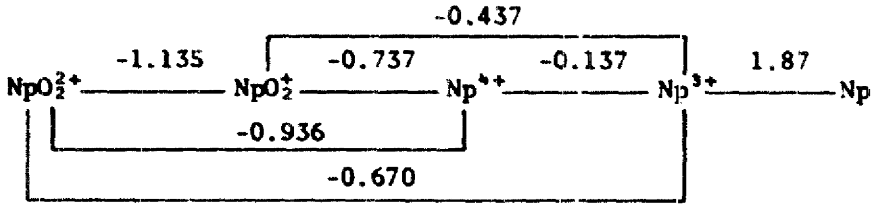
TABLE 9

REDOX POTENTIALS OF NEPTUNIUM (IN VOLTS AT 25°C) [8,66-68]

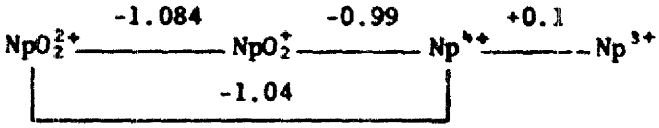
1. 1.0M $HClO_4$



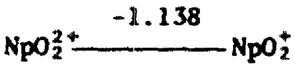
2. 1.0M HCl



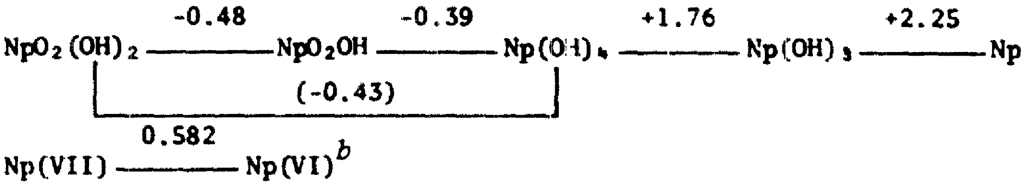
3. 1.0M H_2SO_4



4. 1.02M HNO_3



5. 1.0M NaOH



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a. Standard potential[6]

b. According to the half-reaction $NpO_5^{3-} + e^- + H_2O = NpO_4^{2-} + 2OH^-$;[69] the dependance of E_0 on the OH^- concentration is expressed by[70]:

$$E_0 = 0.600 + 0.059 \cdot \log [OH^-]^{-4}$$

The current-voltage curves for oxidation-reduction reactions of Np in aqueous solutions are shown in Figure 2.

D.2. Oxidation-Reduction Reactions

Table 10 lists reagents and conditions necessary to change oxidation states for Np ions. For cases where only one electron is transferred, e.g., Np^{3+}/Np^{4+} and NpO_2^{+}/NpO_2^{2+}, the establishment of redox equilibrium is rapid. Redox reactions that involve forming or rupturing of the neptunium-oxygen bond, e.g., Np^{4+}/NpO_2^{+} and Np^{4+}/NpO_2^{2+}, have a slower reaction rate.

Rate constants (k) and half-conversion periods of the redox reactions in 1M acid solutions at 25°C are given in Table 11.

D.3. Disproportionation of Neptunium

Only the Np(V) oxidation state undergoes appreciable disproportionation. The reaction $2NpO_2^{+} + 4H^{+} = Np^{4+} + NpO_2^{2+} + 2H_2O$ shows that disproportionation of Np(V) is favored by high acid concentrations. Because Np^{4+} and NpO_2^{2+} form more stable complexes than the NpO_2^{+} ion, the disproportionation of Np(V) is promoted by the addition of complexing agents. The equilibrium constants, K, for various acid solutions are listed in Table 12 where

$$K = \frac{[Np(IV)][Np(VI)]}{[Np(V)]^2}$$

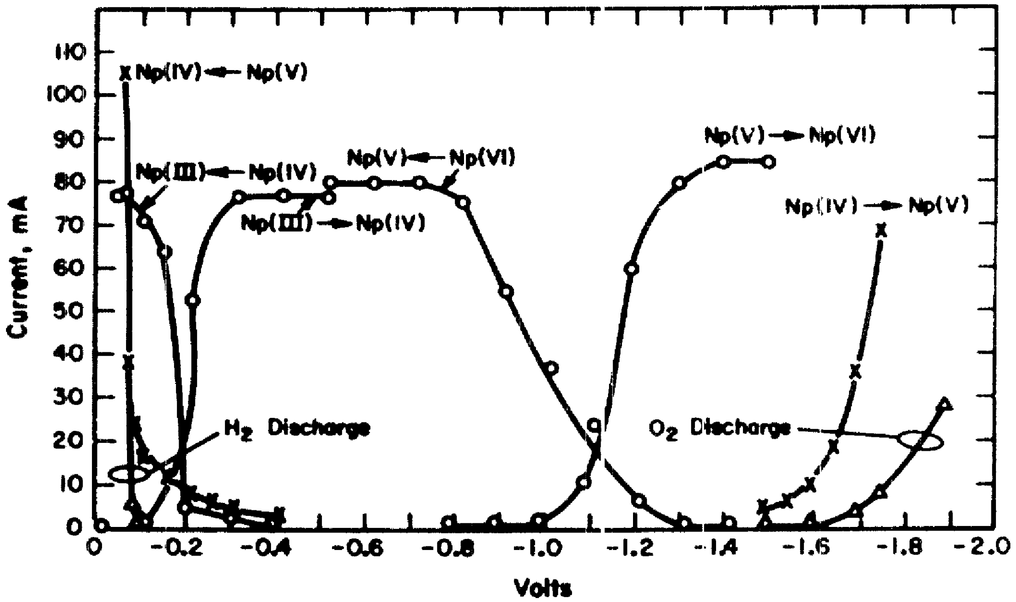

Figure 2. Current-Voltage Curve for Redox Reactions of Neptunium.[71]

TABLE 10

REDOX REACTIONS OF NEPTUNIUM[a,b]

Reaction	Reagent	Medium	Temperature (°C)	Rate
Np(IV) → Np(III)	Electrolysis			Fast
Np(IV) → Np(V)	O_2	1M HCl	75	Fast
	HNO_3	HNO_3	25	Slow
			100	Rapid
	O_2 (air)	1M H_2SO_4	25	Extremely slow
	$HClO_4$		25	Very slow
			100	Fast
Np(IV) → Np(VI)	Ce(IV)	HNO_3, H_2SO_4	25	Very fast
	MnO_4^-,H^+	HNO_3, H_2SO_4	25	Very fast
	Ag(II)	1.0M $HClO_4$	25	Immediate
Np(V) → Np(IV)	Fe^{2+}	H_2SO_4	25	Very fast
	I^-	5M HCl	25	Complete in 40 min
			100	Complete in 1 to 2 min
	H_2O_2	0.5M HNO_3	25	Very slow
	NH_2OH	1M H^+		Very slow
	$NH_2 - NH_2$	1M H^+		Very slow
	SO_2	H_2SO_4	25	Slow
	Sn^{2+}	HCl	25	Very slow
	U(IV)	HCl, $HClO_4$	25	Slow
Np(VI) → Np(IV)	Fe^{2+}	H_2SO_4	25	Very fast
Np(VI) → Np(V)	Cl^-	Pt catalyst	25	Slow
	$NH_2 - NH_2$	1M H^+	25	Very fast
	NH_2OH	1M H^+	25	Very fast
	NO_2^-	1M HNO_3	25	Immediate
	H_2O_2	0.5M HNO_3	15	Immediate
	Sn^{2+}	HCl	25	Rapid
	SO_2	H_2SO_4	25	Fast
Np(VI) → Np(VII)	O_3	2.5×10^{-3}M Np	30	$t_{1/2}$ ~1 min
		2.5×10^{-4}M O_3,	70	$t_{1/2}$ ~0.7 min
		1M NaOH		
		2.5×10^{-3}M Np	50	$t_{1/2}$ ~0.5 min
		2.5×10^{-4}M O_3,		
		0.25 M NaOH		
Np(V) → Np(VI)	Ce(IV)	HNO_3, H_2SO_4	25	Very fast
	BrO_3^-	HNO_3,HCl		Fast
	Cl_2	1M HCl	25	Very slow
			75	Fast
	MnO_4^-	HNO_3,HCl	20	Very fast
	$Cr_2O_7^{2-}$	HNO_3,HCl	20	Fast
	6M HNO_3	5×10^{-3}M HNO_2	20	50% conversion in 50 min
		5×10^{-3}M HNO_2	100	Fast
Np(VI) → Np(VII)	Permanganate	2.5×10^{-3}M Np	70	$t_{1/2}$ <15 min
		1M KOH		
	$S_2O_8^{2-}$	2.5×10^{-3}M Np	55	$t_{1/2}$ ~15 min
		0.1M $K_2S_2O_8$	70	$t_{1/2}$ ~4 min
		0.5M KOH		
	Periodate	2.5×10^{-3}M Np	85	$t_{1/2}$ ~20 min
		0.1M KOH		
		2.5×10^{-3}M Np	85	$t_{1/2}$ ~20 min
		5M KOH		
	HOCl, HOBr	2.5×10^{-3}M Np	55	$t_{1/2}$ ~10 min
		2×10^{-2}M HOX		
		1M KOH		
		2.5×10^{-3}M Np	55	$t_{1/2}$ ~20 min
		2×10^{-2}M HOX		
		0.25M KOH		
Np(VII) → Np(VI)	H_2O_2	0.5 to 5M KOH	20	Fast

TABLE 12

EQUILIBRIUM CONSTANTS FOR DISPROPORTIONATION OF Np(V) IN VARIOUS ACID SOLUTIONS AT 25°C[39]

Solution	K^a
1M $HClO_4$	4×10^{-7}
5.34M $HClO_4$	0.127
8.67M $HClO_4$	200
1M H_2SO_4	2.4×10^{-2}
1.86M H_2SO_4	0.16

---

a. $K = \dfrac{[Np(IV)][Np(VI)]}{[Np(V)]^2}$

The reverse reaction

$$Np^{4+} + NpO_2^{2+} + 2H_2O \rightarrow 2NpO_2^{+} + 4H^{+}$$

takes place rapidly in weakly acid solutions. The rate constant in 1M $HClO_4$ is 2.69 $(M{\cdot}min)^{-1}$.[34]

D.4. Radiolysis of Neptunium Solutions

The radiolysis of Np(VI) by self-radiation of ^{237}Np causes reduction to Np(V) with a rate constant of $(3.1 \pm 0.2) \times 10^{-9}$ sec^{-1} (0.5 to 1.7M $HClO_4$) and a radiolytic reduction yield (G) of 6.4 ions/100 eV.[77-79] Compared to other hexavalent actinides, Np(VI) has a much lower rate of radiolytic reduction.

For the ^{60}Co irradiation of 0.1M Np(VI) in 1.1M $HClO_4$, G = 3.4. The radiolytic yields for radiolysis of Np solutions (saturated with atmospheric oxygen) exposed to a ∿ 1 MeV electron beam[80,81] are shown in Table 13. Np(V) has a comparatively high stability to radiolysis. Np(IV) is oxidized to Np(V).

When ^{239}Np is prepared by neutron irradiation of uranyl salts, 80 to 90% of Np is in the tetravalent state.[82]

TABLE 13

RADIOLYSIS OF NEPTUNIUM SOLUTIONS IN AN ACCELERATED 1-MeV ELECTRON BEAM[6]

Ion	Acid	Acid Concentration (M)	Radiolytic Yield G (number of ions per 100 eV)
$NpO_2^{2+} \rightarrow NpO_2^+$	$HClO_4$	0.018	4.45
		0.80	5.76
		0.126	6.7
		0.7	6.7
		1.5	4.7
		3.4	1.9
	HNO_3	0.05	8.2
	H_2SO_4	0.86	3.0
$Np^{4+} \rightarrow NpO_2^+$	H_2SO_4	0.8	2.1

D.5. Hydrolysis of Neptunium

The hydrolysis of a metal ion is a special case of complex formation with OH^- ion. Hydrolysis consists of the transfer of a proton from a coordinated water molecule to a water molecule in the outer sphere, e.g.,

$$Np(H_2O)_8{}^{4+} + H_2O = [Np(OH)(H_2O)_7]^{3+} + H_3O^+$$

with $$K_H = \frac{[Np(OH)(H_2O)_7]^{3+}\ [H_3O]^+}{[Np(H_2O)_8]^{4+}}$$

The most recent and extensive hydrolytic studies of Np were made by A. I. Moskvin.[83] Hydrolysis constants, K_H, are listed in Table 14 for Np(IV), (V), and (VI).* The tendency for Np ions in dilute acid solutions to undergo hydrolysis increases with increasing ionic potential (d) where $d = Z/r$, Z is the ionic charge, and r is the ionic radius. Thus, the tendency to undergo hydrolysis increases in the order:

$$NpO_2{}^+ < NpO_2{}^{2+} < NpO_2{}^{3+} < Np^{3+} < Np^{4+}.$$

Successive hydrolysis reactions in Pu(IV) solutions result in the formation of colloidal aggregates. The polymer presumably forms irreversibly with oxygen or hydroxyl bridges.[86]

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*The stability constant K_1 of the Np hydroxo complexes may be calculated from $K_1 = \frac{K_H}{K_W}$ where K_W is the ionic product of water, 10^{-14}.

TABLE 14

FIRST HYDROLYSIS CONSTANTS AND SOLUBILITY PRODUCTS FOR NEPTUNIUM IONS

Ion	Hydroxide	K_{sp}	Hydrolysis Product	K_H	Reference
Np^{4+}	$Np(OH)_4$	6×10^{-56}			83
			$(NpOH)^{3+}$	5×10^{-3}	84
				9×10^{-3}	34
$NpO_2{}^+$	$NpO_2(OH)$	9.5×10^{-10}	NpO_2OH	8.3×10^{-11}	86
				1.3×10^{-9}	85
		8×10^{-10}		10^{-10}	34
NpO_2^{2+}	$NpO_2(OH)_2$	2×10^{-23}	$[NpO_2(OH)]^+$	4.3×10^{-6}	83

Moskvin[43] reports evidence for formation of polymer forms of Np(IV) in aqueous solution at $[H^+] < 0.3M$.

D.6. Complex Ion Formation

The formation of complex species by the actinides in different oxidation states with a variety of ligands offers potential for separating the actinides from each other and from other cations. Complex formation and hydrolysis are competing reactions. The mechanism of complex ion formation can be represented as successive reactions between water molecules from the inner sphere of the hydrated cation and anions, A, e.g.,

$$Np(H_2O)_8^{4+} + A^- = NpA(H_2O)_7^{3+} + H_2O$$

The ability of an ion to form complexes is dependent on the magnitude of the ionic potential. The relative tendency of Np ions to form complexes is usually:

$$Np^{4+} > Np^{3+} > NpO_2^{3+} > NpO_2^{2+} > NpO_2^{+}$$

Neptunium (III)

Np(III) exists in aqueous solutions as $Np(H_2O)_8^{3+}$. The chloride and bromide complexes of Np(III) have been studied spectroscopically in concentrated LiCl and LiBr solutions (see Table 15).

TABLE 15

COMPLEXES OF NEPTUNIUM IN AQUEOUS SOLUTION[100]

Cation	Ligand	Method[a]	Temperature (°C)	Medium	Species	Log of Equilibrium Constant[b]	Reference
Np^{3+}	Chloride	spec	25	Conc LiCl	$NpCl^{2+}$	β_1 - 2.42	88
					$NpCl_2^+$	β_2 - 4.96	
	Bromide	spec	25	Conc LiBr	$NpBr^{2+}$	β_1 - 3.45	88
					$NpBr_2^+$	β_2 - 6.54	
Np^{4+}	Chloride	distn	20	1.0M $HClO_4$	$NpCl^{3+}$	β_1 - 0.04	89
					$NpCl_2^{2+}$	β_2 - 0.24	
					$NpCl_3^+$	β_3 - 0.48	
		emf	25	1.0M $HClO_4$		β_1 - 0.31	90
		distn	20	2.0M $HClO_4$		β_1 + 0.04	89
						β_2 - 0.16	
		distn	25	4.0M $HClO_4$		β_1 - 0.10	91
						β_2 - 0.10	
	Fluoride	iex	20	4.0M $HClO_4$	NpF^{3+}	β_1 + 4.82	92
					NpF_2^{2+}	β_2 + 7.57	
					NpF_3^+	β_3 + 9.91	
					NpF_4	β_4 ~11	
	Nitrate	distn	20	1.0M $HClO_4$	$Np(NO_3)^{3+}$	β_1 + 0.34	89
					$Np(NO_3)_2^{2+}$	β_2 + 0.08	
					$Np(NO_3)_3^+$	β_3 - 0.26	
		emf	25	1.0M $HClO_4$		β_1 + 0.38	90
		distn	20	2.0M $HClO_4$		β_1 + 0.34	89
		distn	25	4.0M $HClO_4$		β_1 - 0.15	91
						β_2 - 0.75	
	Hydroxide	spec		0.2 to 2M $HClO_4$	$NpOH^{3+}$	β_1 +11.7	86
Np^{4+}	Sulfate	distn	25	2.0M $HClO_4$	$[Np(SO_4)]^{2+}$	β_1 + 2.43	93
					$Np(SO_4)_2$	β_2 + 3.47	
		emf	25	3.0M $NaClO_4$		β_1 + 2.49	94
						β_2 + 3.57	
		iex	20	4.0M $HClO_4$		β_1 + 2.70	92
						β_2 + 4.26	
	Oxalate	sol	25	-	$[Np(C_2O_4)]^{2+}$	β_1 + 8.53	95
					$Np(C_2O_4)_2$	β_2 +17.53	
					$[Np(C_2O_4)_3]^{2-}$	β_3 +23.96	
					$[Np(C_2O_4)_4]^{4-}$	β_4 +27.40	
		sol	26	1.0M $HClO_4$		β_1 + 7.40	96
						β_2 +13.62	
						β_3 +19.46	
		distn	26	1.0M $HClO_4$		β_1 + 8.19	
						β_2 +16.42	
	Formate	spec	-	0.1 to 0.3M NaOOCH	$[Np(HCOO)_3]^+$	β_3 + 2.7	34
	Acetate (AC^-)	iex, emf	-	0.8M NH_4Cl	$[Np(AC)]^{3+}$	β_1 + 2.68	97
					$[Np(AC)_2]^{2+}$	β_2 + 4.76	
					$[Np(AC)_3]^+$	β_3 + 7.49	
					$Np(AC)_4$	β_4 + 9.67	
					$[Np(AC)_5]^-$	β_5 +12.0	
					$[Np(AC)_6]^{2-}$	β_6 +14.7	
					$[Np(AC)_7]^{3-}$	β_7 +17.4	
					$[Np(AC)_8]^{4-}$	β_8 +20.2	

a. distn, distribution measurements; iex, ion exchange; spec, spectrophotometry; emf, electromotive force; redox, emf with redox electrode; pH, pH method.

b. Stability constants are given as logarithm to base 10 of the equilibrium constants.

For the reaction of a cation M with ligands L, the constant K and β are defined as:

$$K_1 = \beta_1 = \frac{[ML]}{[M][L]},\ K_2 = \frac{[ML_2]}{[ML][L]},\ K_3 = \frac{[ML_3]}{[ML_2][L]},\ \text{etc.}$$

$$\beta_2 = \frac{[ML_2]}{[M][L]^2},\ \beta_3 = \frac{[ML_3]}{[M][L]^3},\ \text{etc.}$$

Therefore $\beta_2 = K_1K_2$, $\beta_3 = K_1K_2K_3$, etc.

Table 15. Continued

Cation	Ligand	Method[a]	Temperature (°C)	Medium	Species	Log of Equilibrium Constant[b]	Reference
Np^{4+}	8-hydroxy-quinolinate (OX^-)	distn	25	0.1M NH_4ClO_4	$Np(OX)_4$	β_4 +45.28	98
	5,7-Dichloro-8-hydroxy-quinolinate (DCO^-)	distn	25	0.1M NH_4ClO_4	$Np(DCO)_4$	β_4 +46.05	98
	Ethylene-diamine-tetraacetate $(EDTA)^{4-}$	distn	25	0.5M (HCl)	Np(EDTA)	β_1 +26.3	99
	Thenoyl-trifluoro acetonate $(DTPA)^{4-}$	distn	25	0.1M HNO_3	$Np(TTA)_4$	β_4' + 5.15[c]	100
	Diethylene-triamine-pentaacetate $(DTPA)^{5-}$	iex	-	1M $HClO_4$	$Np(DTPA)^-$	β_1 + 29.79	101
NpO_2^+	Chloride	iex	25	2.0M HCl	NpO_2Cl	β_1 - 0.30	102
		distn	25	4.0M $HClO_4$		β_1 - 2.52	91
					$[NpO_2Cl_2]^-$	β_2 - 1.55	
	Nitrate	iex		2.0M $HClO_4$	NpO_2NO_3	β_1 - 0.25	102
		distn	25	4.0M $HClO_4$		β_1 - 1.6	91
					$[NpO_2(NO_3)_2]^-$	β_2 - 1.4	
	Hydroxide	emf		10^{-}[illegible]M HNO_3	NpO_2OH	β_1 ~ 5.1	74
		spec				β_1 ~ 4	66
	Sulfite	iex			$[NpO_2(SO_3)]^-$	β_1 + 2.15	103
					$[NpO_2(SO_3)_2]^{3-}$	β_2 + 3.00	
	Bicarbonate	iex			$NpO_2(HCO_3)$	β_1 + 2.43	103
	Oxalate	iex		0.05M NH_4ClO_4	$[NpO_2(C_2O_4)]^-$	β_1 + 4.0	104
						β_2 + 7.3	
	Acetate $(AC)^-$	spec			$NpO_2(AC)$	β_1 + 1.33	105
					$[NpO_2(AC)_2]^-$	β_2 + 1.80	
		spec		1.5M NH_4ClO_4		β_1 + 1.08	
						β_2 + 1.55	
	8-hydroxy-quinolinate $(OX)^-$	spec	25	0.1M NH_4ClO_4	$NpO_2(OX)$	β_1 + 6.32	106
					$[NpO_2(OX)_2aq]^-$	β_2 +11.50	
	Glycolate $(GLYC)^-$	spec	25	0.1M NH_4ClO_4	$NpO_2(GLYC)$	β_1 + 1.51	107
	Lactate $(LACT)^-$	spec iex	25	0.1M NH_4ClO_4	$NpO_2(LACT)$	β_1 + 1.75	107
				0.2M NH_4ClO_4	$[NpO_2(LACT)_2]^-$	β_2 + 2.20	107

a. distn, distribution measurements; iex, ion exchange; spec, spectrophotometry; emf, electromotive force; redox, emf with redox electrode; pH, pH method.

b. Stability constants are given as logarithm to base 10 of the equilibrium constants.

For the reaction of a cation M with ligands L, the constant K and β are defined as:

$$K_1 = \beta_1 = \frac{[ML]}{[M][L]},\ K_2 = \frac{[ML_2]}{[ML][L]},\ K_3 = \frac{[ML_3]}{[ML_2][L]},\ \text{etc.}$$

$$\beta_2 = \frac{[ML_2]}{[M][L]^2},\ \beta_3 = \frac{[ML_3]}{[M][L]^3},\ \text{etc.}$$

Therefore $\beta_2 = K_1K_2$, $\beta_3 = K_1K_2K_3$, etc.

c. $\beta_4' = \frac{[Np(TTA)_4][H^+]^4}{[Np^{4+}][HTTA]^4}$

Table 15. Continued

Cation	Ligand	Method[a]	Temperature (°C)	Medium	Species	Log of Equilibrium Constant[b]	Reference
NpO_2^+	α-hydroxy-isobutyrate $(HIBA)^-$	spec	25	0.2 M NH_4ClO_4	$NpO_2(HIBA)$	$\beta_1 = 2.17$	109
					$[NpO_2(HIBA)_2]^-$	$\beta_2 = 3.07$	
					$[NpO_2(HIBA)_3]^{2-}$	$\beta_3 = 3.53$	
	Tartrate $(TART)^{2-}$	ion	20	0.65M NH_4ClO_4 pH 3.2 to 6.2	$NpO_2(HTART)$	$\beta_H = 2.36$	110
					$[NpO_2(TART)]^-$	$\beta_1 = 2.32$	
					$[NpO_2(TART)_2]^{3-}$	$\beta_2 = 4.30$	
					$[NpO_2(TART)_3]^{5-}$	$\beta_3 = 6.18$	
	Citrate $(CITR)^{3-}$	ion	20	0.05M NH_4ClO_4 pH 4.5 to 5.4	$[NpO_2(HCITR)]^-$	$\beta_H = 2.60$	110
					$[NpO_2(CITR)]^{2-}$	$\beta_1 = 3.67$	
	Acetyl acetonate (AA)	spec	25	0.1 M NH_4ClO_4	$NpO_2(AA)$	$\beta_1 = 4.08$	111
					$[NpO_2(AA)_2]^-$	$\beta_2 = 7.00$	
	Thenoyltri-fluoroacetonate $(TTA)^-$	spec	25	0.1 M NH_4ClO_4	$NpO_2(TTA)$	$\beta_1 = 2.00$	111
					$[NpO_2(TTA)_2]^-$	$\beta_2 = 5.40$	
	Diethylene-triamine-pentaacetate $(DTPA)^{5-}$	spec	25	0.1 M NH_4ClO_4	$[NpO_2(DTPA)]^{4-}$	$\beta_1 = 5.83$	112
	Nitrilo-triacetate $(NTA)^{3-}$	spec	25	0.1 M NH_4ClO_4	$[NpO_2(HNTA)]^-$	$\beta_H = 1.77$	113
					$[NpO_2(NTA)]^{2-}$	$\beta_1 = 6.85$	
	Ethylene-diamine-tetraacetate $(EDTA)^{4-}$	spec	25	0.1 M NH_4ClO_4	$[NpO_2(HEDTA)]^{2-}$	$\beta_1^H = 4.08$	113
					$[NpO_2(EDTA)]^{3-}$	$\beta_1 = 7.33$	
NpO_2^{2+}	Chloride		25	0.4M $NaClO_4$	$[NpO_2Cl]^+$	$\beta_1 = -0.32$	114
		distn	25	4M $HClO_4$	$[NpO_2Cl]^+$	$\beta_1 = -0.15$	91
	Nitrate		25	0.4M $HClO_4$	$[NpO_2(NO_3)]^+$	$\beta_1 = -0.08$	114
		distn	25	4M $HClO_4$		$\beta_1 = -0.60$	91
	Fluoride	emf	21	1.0M $HClO_4$	$[NpO_2F]^+$	$\beta_1 = 3.86$	115
					NpO_2F_2	$\beta_2 = 6.27$	
	Sulfate	emf	25	1.0M $HClO_4$	NpO_2SO_4	$\beta_1 = 1.90$	116
					$[NpO_2(SO_4)_2]^{2-}$	$\beta_2 = 2.77$	
	Oxalate		20	1.0M $HClO_4$	$NpO_2C_2O_4$	$\beta_1 = 6.0$	42
			15	1.0M HNO_3	$[NpO_2(C_2O_4)_2]^{2-}$	$\beta_2 = 4.08$	
	Acetate	pH	-	-	$[NpO_2(AC)]^+$	$\beta_1 = 2.38$	97
					$NpO_2(AC)_2$	$\beta_2 = 4.60$	
					$[NpO_2(AC)_3]^-$	$\beta_3 = 6.40$	
		pH	20	1.0M $NaNO_3$		$\beta_1 = 2.32$	117
						$\beta_2 = 4.23$	
						$\beta_3 = 6.0$	
NpO_2^{3+}	Sulfate	spec	6	1.0 $HClO_4$	$[NpO_2SO_4]^+$	$\beta_1 = 2.20$	118
					$[NpO_2(SO_4)_2]^-$	$\beta_2 = 6.24$	

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[a] distn, distribution measurements; ion, ion exchange; spec, spectrophotometry; emf, electromotive force, redox, emf with redox electrode; pH, pH method

[b] Stability constants are given as logarithm to base 10 of the equilibrium constants.

For the reaction of a cation M with ligands L, the constant K and β are defined as:

$$K_1 = \beta_1 = \frac{[ML]}{[M][L]},\ K_2 = \frac{[ML_2]}{[ML][L]},\ K_3 = \frac{[ML_3]}{[ML_2][L]},\ \text{etc.}$$

$$\beta_2 = \frac{[ML_2]}{[M][L]^2},\ \beta_3 = \frac{[ML_3]}{[M][L]^3},\ \text{etc.}$$

Therefore $\beta_2 = K_1K_2$, $\beta_3 = K_1K_2K_3$, etc.

Neptunium (IV)

Np(IV), which exists as $Np(H_2O)_8^{4+}$ in aqueous solution, forms strong complexes with most anions. Analogous to U and Pu, Np(IV) forms negatively charged chloro and nitrate complexes in concentrated HCl and HNO_3; these complexes are sorbed on anion exchangers. $Np(C_2O_4)_2$ is soluble in dilute $(NH_4)_2CO_3$ solution indicating that the carbonate complexes, which have not been studied in detail, are more stable than the oxalate complexes.[8] Definitive studies of the nature and composition of peroxide complexes in solution have not been made. A purple-gray Np(IV) peroxide precipitate is formed by addition of H_2O_2 to a solution of Np(IV) in nitric acid.

From the stability constants listed in Table 15, the following series of ligands were arranged according to increasing strength of the complexes formed by addition of the first ligand to Np^{4+}:

$$ClO_4^- < Cl^- < NO_3^- < SO_4^{2-} < CH_3COO^-$$

$$< F^- < C_2O_4^{2-} < OH^- < EDTA^{4-} < DTPA^{5-} < OX^-$$

Neptunium (V)

Np(V), present in aqueous solution as singly charged neptunyl ion, $NpO_2(H_2O)_6^+$, is a poor complexing agent because of its large size and low charge. The neptunyl complexes, which are comparable in stability to Mg^{2+}, Ca^{2+}, and Zn^{2+}

complexes,[87] are much more stable than pentavalent uranium, plutonium, and americium complexes.

Studies of cationic complexes of Np(V) with UO_2^{2+}, Cr^{3+}, Fe^{3+}, Th^{4+}, and other cations in $HClO_4$ solutions have been made.[5]

From the stability constants listed in Table 15, the following series of ligands were arranged according to increasing strength of the complexes formed by the addition of the first ligand to NpO_2^+:

$ClO_4^- < Cl^- < NO_3^- < AC^- < NTA < SO_3^{2} \sim HIBA^-$

$\sim TART^{2-} \quad HCO_3^- < TTA^- < CITR^{3-} \quad C_2O_4^{2-} \sim HAA^-$

$< OH^- < DTPA^{5-} < EDTA^{4-}$

Neptunium (VI)

Np(VI) exists in aqueous solution as $NpO_2(H_2O)_6^{2+}$. From the stability constants listed in Table 15, the following series of ligands were arranged according to increasing strength of the complexes formed by the addition of the first ligand to NpO_2^{2+}:

$ClO_4^- < NO_3^- < Cl^- < SO_4^= < CH_3COO^- < F^- < C_2O_4^=$

Neptunium(VII)

Very few studies of Np(VII) complexes have been made. Sulfate complexes of the NpO_2^{3+} ion in acid solution show that NpO_2^{3+} has a higher tendency towards complex formation with sulfate ions than the neptunyl NpO_2^{2+} ion. This is reasonable because the charge of the NpO_2^{n+} group increases from hexavalent to heptavalent neptunium.

VI. PREPARATION OF NEPTUNIUM SAMPLES FOR ANALYSIS

A. NEPTUNIUM METAL AND ALLOYS

Neptunium metal dissolves in HCl, other halogen acids, and sulfamic acid but not in HNO_3 or concentrated H_2SO_4. Hot dilute H_2SO_4 attacks Np slowly. Np is dissolved slowly in hot concentrated nitric acid containing fluoride.

Np-Al alloys are soluble in 6 to 10M HNO_3 containing ∿0.05M $Hg(NO_3)_2$ and ∿0.02M KF; they are also soluble in HCl and $HClO_4$. An alternative method is to selectively dissolve the Al in a solution of $NaOH$-$NaNO_3$; the Np and other actinide elements are separated by filtration or centrifugation and are soluble in boiling HNO_3-HF or HCl.

B. NEPTUNIUM COMPOUNDS

NpO_2 prepared by ignition of the oxalate at 400 to 600°C is soluble in hot 10M HNO_3. When ignition is done at higher temperatures, refluxing in strong nitric acid for a long period, even with the addition of HF, is required. Fusion with potassium bisulfate and dissolution of the melt in dilute acid is useful for dissolving NpO_2 fired at very high temperatures. Np fluorides are readily soluble in nitric acid solutions containing aluminum or borate ions.

NpO_2-Al targets are soluble in hot strong nitric acid solutions containing mercuric and fluoride ions.

C. BIOLOGICAL AND ENVIRONMENTAL SAMPLES

Np in these samples ranges from readily soluble metabolized neptunium in excreted samples to extremely refractory fallout samples. Most procedures for dissolving fallout or other environmental samples involve treatment with HF or a basic fusion step which renders Np soluble in acids. There has been little investigation of Np in these types of samples; however, numerous determinations of plutonium in tissue, bone, feces, urine, vegetation, soil, and water have been reported and the same methods of dissolution would probably be applicable for Np; Nielsen and Beasley[119] have summarized many of these methods. Dissolution of biological samples and vegetation is generally accomplished by multiple wet ashing or a combination of wet and dry ashing. In wet ashing, strong oxidizing agents such as perchloric acid and nitric acid are used (individually or in combination), or sulfuric acid and hydrogen peroxide. In some cases the sample is fused with sodium or potassium carbonate, and the melt is dissolved in water or dilute acid.[120]

VII. SEPARATION METHODS

A. COPRECIPITATION AND PRECIPITATION

Coprecipitation is the "classic" method for separating tracer quantities in radiochemical analyses. Because Np in aqueous solution is easily converted to different oxidation states that exhibit markedly different behavior in coprecipitation, separation from other elements can be attained. However, ion exchange, extraction chromatography, and solvent extraction separation are used almost exclusively because more complete separation is attained more rapidly.

Precipitation of neptunium oxalate is regularly used in large-scale processing of neptunium as an intermediate to neptunium oxide. Precipitation of other Np compounds is very limited.

The coprecipitation behavior of the different oxidation states of Np is shown in Table 16.

Lanthanum Fluoride. The first separation of a pure Np compound described by Magnusson and LaChapelle[4] used LaF_3 coprecipitation. Np(IV), Pu(III), and Pu(IV) are carried almost quantitatively by lanthanum fluoride from mineral acids. U decontamination is best from H_2SO_4 because of the strong uranyl sulfate complexes. Np is reduced to the tetravalent state and precipitated by adding fluoride and lanthanum ions. Insoluble fluorides

TABLE 16
COPRECIPITATION BEHAVIOR OF TRACE AMOUNTS OF NEPTUNIUM

Carrier Compound	Np(IV)	Np(V)	Np(VI)
Lanthanum Fluoride	C[a]	C	NC
Zirconium Phosphate	C	NC	NC
Thorium Oxalate	C		
Lanthanum Oxalate	NC[b]		
Thorium Iodate	C		NC
Zirconium Phenylarsonate	C	Poor	NC
Zirconium Benzenesulfinate	C	NC	NC
Sodium Uranyl Acetate	NC	Poor	C
Thorium Peroxide	C		
Bismuth Phosphate	C	NC	NC
Barium Sulfate	C	NC	NC
Potassium Lanthanum Sulfate	C	NC	NC
Potassium Uranyl Carbonate	NC	C	C
Hydroxides	C	C	C

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a. C indicates co-precipitation nearly complete under proper condition.

b. NC indicates co-precipitation less than a few percent under proper conditions.

including the rare earths and Th also precipitate. Hold-back carriers are added to decrease the precipitation of Zr and alkaline earths. The fluoride precipitate is converted either to acid-soluble sulfates by evaporating until fumes of H_2SO_4 appear, or to hydroxides by metathesis with alkali hydroxide. Oxidation at room temperature with bromate yields fluoride-soluble Np(VI), but other actinides and lanthanides are not oxidized and, hence, are precipitated in a subsequent LaF_3 precipitation step. After removal of solids, Np is reduced to the tetravalent state and again coprecipitated with LaF_3. Pa is coprecipitated with manganese dioxide preceding the LaF_3 precipitation as required.[121] LaF_3 precipitation has been used to separate Np(IV) and Np(V) from Np(VI).[122]

Zirconium Phosphate. Tetravalent ions of Np, Pu, Ce, Th, and other elements are coprecipitated with zirconium phosphate. A variation of this method by Magnusson, Thompson, and Seaborg[121] is based on oxidation-reduction cycles. After zirconium ion and $NaBiO_3$ are added, the solution is heated to oxidize Np and Pu to the hexavalent state. H_3PO_4 is added to carry tetravalent ions. The supernatant solution is treated with excess hydrazine to destroy bismuthate and then with ferrous ion to yield Np(IV) and Pu(III); Np is carried with zirconium phosphate, but Pu(III) and U(VI) are not carried. The zirconium phosphate is dissolved in HNO_3 - HF, and Np is separated from Zr by coprecipitation with LaF_3.

Barium Sulfate. Ce, Ba, La, and Np(IV) in quantities from carrier-free trace levels to 1 mg are coprecipitated >99.7% by barium sulfate from strong sulfuric acid solutions containing potassium salts and hydrogen peroxide. This causes a separation from most other elements. Np was separated by dissolution of the barium sulfate and reprecipitation from concentrated sulfuric acid containing chromic acid; Np(IV) was not carried with the Ce, Ba, and La. The Np in the supernatant was reduced to Np(IV) with hydrogen peroxide and again coprecipitated with barium sulfate. After the precipitate was filtered, ^{239}Np was determined by gamma counting of the filter.[123] The method has been further modified[124] and also applied to a wide variety of environmental and biological samples[125] (Procedure 15, p176).

Hydroxides. Insoluble hydroxides coprecipitate all oxidation states of Np except Np(VII).[45,127-129] Generally, the trivalent and tetravalent states are carried most effectively. The choice of reagent for precipitation depends on the composition of the solution. Strong bases are used when the solution contains cations that are amphoteric (Al, Pb, Zn) or when the solution contains organic complexing ligands. When the solution contains cations that form ammine complexes or are insoluble in strong base (Cu, Co, Ni, Ca, Mg), ammonia is used as precipitant.

Other Inorganic Coprecipitants. Np(IV) is coprecipitated with bismuth phosphate and the double sulfate of lanthanum and potassium. Coprecipitation with lanthanum potassium double selenate gives results similar to those described for the double sulfate but does not have any advantages.[130]

The pentavalent cations of the transuranium elements are coprecipitated with potassium uranyl tricarbonate.[131]

Dupetit and Aten[132] described the coprecipitation of tetravalent actinides with thorium peroxide and uranium peroxide. Neptunium is completely carried by thorium peroxide, but results were poor with uranium peroxide. This was attributed to the presence of Np(V).

Other less common carriers for Np(IV) include thorium and lanthanum oxalates and zirconium, thorium, and ceric iodates.

Other Organic Coprecipitants. Zirconium phenylarsonate and zirconium benzenesulfinate are specific for coprecipitation of the tetravalent ions from solution. The transuranium elements are separated from other cations and from each other by a series of oxidation-reduction steps similar to those outlined for zirconium phosphate.[133]

Kuznetsov and Akimova[134] have proposed a number of organic reagents for concentrating the tetravalent cations of the transuranium elements from very dilute solutions. Np(IV) and Pu(IV) form hexanitrato species in nitric acid-nitrate salt solutions, and these cations are coprecipitated with the nitrate precipitates of heavy organic cations. Of the reagents studied, butylrhodamine was the most effective organic cation. In concentrated nitrate solutions, U(IV), Th(IV), and Ce(IV) coprecipitate with Np(IV) and Pu(IV). Other coprecipitation was with quaternary ammonium bases, dimethyl dibenzyl ammonium, and benzylquinolium compounds. Excellent separation from rare earths, iron, chromium, manganese, and copper was attained.[135]

With many organic reagents containing sulfonic groups, tetravalent elements form soluble cyclic salts that are coprecipitated with precipitates formed by the cation of a basic dye (arsenazo) and the cyclic organic reagent. Compared to the organic nitrates above, the precipitation is more complete but less selective.[136]

Np(VI) is carried with sodium uranylacetate.

Precipitation. Precipitation of macro quantities of Np is seldom used as an analytical or radiochemical method. If other cations that form insoluble compounds are present, these must be separated first. When the solution is relatively free from other ions, a method such as alpha counting is usually more rapid and offers less health hazard. A number of Np compounds have low solubilities in aqueous solution; however, indefinite stoichiometry or necessity for calcination to the oxide limits the usefulness of direct gravimetric determination.

Hydroxides. No information is available on Np(III) "hydroxide," probably because it is rapidly oxidized even in an inert atmosphere. Np(IV) is precipitated from mineral acid solutions by sodium, potassium, and ammonium hydroxides as the hydrated hydroxide or hydrous oxide. The brown-green gelatinous solid is difficult to filter; it is easily redissolved in mineral acids. No formal solubility studies are reported, but the solubility in 1M $NaNO_3$ - 1M NaOH is <1 mg/l.

Np(V) "hydroxide" is green. The solubility in dilute ammonium solution is 0.18 g/l; in 1M NaOH, 0.017 g/l; and in 2.2M NaOH, 0.014 g/l.[35] There was speculation in the early literature[38] that Np(V) might precipitate as $NH_4NpO_3 \cdot xH_2O$ or an analogous sodium compound as well as $NpO_2(OH) \cdot H_2O$; however, the exact nature of the precipitate has not been confirmed. Np(VI) is precipitated as dark brown $(NH_4)_2Np_2O_7 \cdot H_2O$ with excess ammonia from mineral acid solution; the solubility is given as 25 mg Np/l.[35] When sodium hydroxide is the precipitant, a brown compound with reported composition $Na_2Np_2O_7 \cdot xH_2O$ is precipitated. Studies on the variable composition of the uranates leave some question as to the composition of the neptunates given above.[137]

Fluorides. Grayish-lilac colored Np(III) fluoride is precipitated by adding a dilute HCl solution of Np(III) containing Rongalite to a solution of ammonium fluoride or hydrofluoric acid in dilute hydrochloric acid while sparging with argon. The dry compound was quite stable to oxidation.[32] Np(IV) fluoride hydrate is precipitated when hydrofluoric acid is added to an acid solution of Np(IV).

Ammonium Np(IV) pentafluoride precipitates as a bright-green granular solid when hydrofluoric acid is added to a solution of Np(IV) containing NH_4^+ ions. A similar precipitation in the presence of potassium ions yields a bright-green precipitate that X-ray diffraction indicates is KNp_2F_9. The supernatant 1M HF - 0.01M NH_4^+ from precipitation of the ammonium salt contained 1.1 mg Np/l two hours after precipitation; the solubility of the potassium salt was 1.7 mg Np/l after 16 hours in 0.5M H_2SO_4 - 0.5M K_2SO_4 - 2M HF.[38]

A double fluoride precipitate of La and Np with an approximate composition $La_2NpF_{10} \cdot xH_2O$ is obtained by adding hydrofluoric acid to an acid solution o equivalent amounts of La^{3+} and Np^{4+}. The solubility of the salt in water was 4 mg/l.[39]

Rubidium neptunyl(V) fluoride was prepared by injecting a chilled ∿0.1M HNO_3 solution of NpO_2^+ into a chilled solution of ∿12M RbF at 0°C. The gray-green precipitate was washed with small amounts of water, methanol, and acetone followed by air drying.[138]

Oxalates. Brown $Np_2(C_2O_4)_3 \cdot nH_2O$ (n ∿11) is precipitated by adding oxalic acid containing Rongalite into a dilute acid solution of Np(III) also containing Rongalite. The compound is appreciably oxidized within a few hours.[32]

After valence adjustment to Np(IV) with ascorbic acid,[40] bright-green $Np(C_2O_4)_2 \cdot 6H_2O$ is precipitated from solutions originally containing 5 to 50 g of Np(IV), (V), or (VI) in 1 to 4M HNO_3 by the addition of oxalic acid. The solubility varies as a function of the concentration of nitric acid and oxalic acid (Figure 3). At oxalic acid concentrations near 0.1M, the solubility varies between 6 and 10 mg/l as the nitric acid concentration is varied between 1 and 4M. The solubility is very dependent on maintaining all the neptunium in the tetravalent state. Significant separation from a number of cations is attained.

The salt $(NH_4)_4[Np(C_2O_4)_4] \cdot (NH_4)_2C_2O_4 \cdot xH_2O$ has been isolated.[139] The soluble aqueous complex was cooled to 0°C to remove excess ammonium oxalate. Ethyl alcohol addition produced an oily, dark-green liquid that yielded dark-green crystals when treated with 96% ethanol.

Green neptunyl(V) oxalate ($NpO_2C_2O_4H \cdot 2H_2O$) is precipitated when a solution of Np(V) in 1M HCl is treated with a 10% solution of oxalic acid in *tert*-butanol.[41]

Neptunyl(VI) oxalate ($NpO_2C_2O_4 \cdot 3H_2O$), a grayish-green crystalline solid, is precipitated from 2M HNO_3 - 0.05M $KBrO_3$ containing 20 to 40 g Np/l by adding oxalic acid until the solution is ∿0.3M $H_2C_2O_4$.[42] The solubility in 0.5M HNO_3 - 0.023M $H_2C_2O_4$ increased from ∿0.5 to ∿1.5 g Np/l over the temperature range 0 to 20°C. In 1M HNO_3 at 14°C, the solubility varied from ∿3.8 to

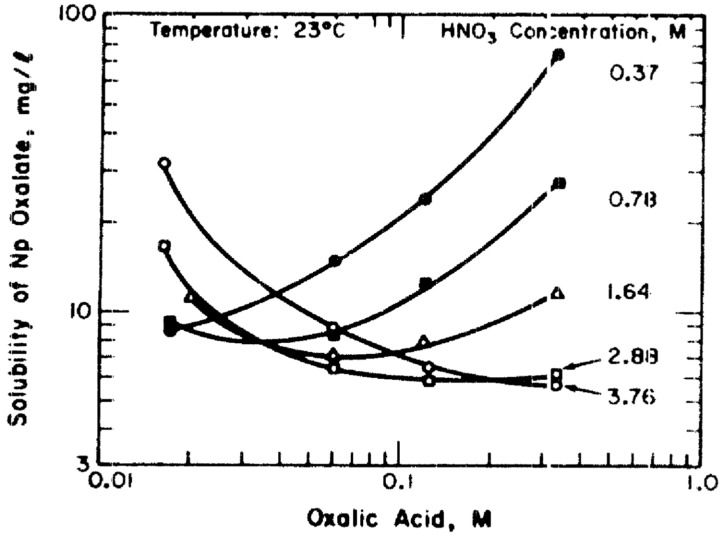

Figure 3. Solubility of Np(IV) Oxalate

~0.75 g Np/l as the oxalic acid concentration varied from ~0.002M to ~0.15M.

Peroxide. Np(IV) peroxide is precipitated from solutions containing Np(IV), (V), or (VI) in >3M HNO_3 by the addition of hydrogen peroxide.[140] The higher valence states are rapidly reduced to Np(IV), and gray-purple neptunium peroxide precipitates. The precipitation does not progress through the highly colored, soluble peroxy complexes that are characteristic of plutonium peroxide. Two crystalline forms were prepared depending on the acidity of the precipitation solution. The solubility is reported as a function of the concentrations of nitric acid and hydrogen peroxide. A minimum solubility of $\sim 10^{-4}$M neptunium occurred in solutions 1.5 to 2.5M HNO_3 and 4.5M H_2O_2. The solubilities were not readily reproducible at nitric acid concentrations of <2.5M.

Iodates. Precipitation of Np(III) iodate has not been reported. Np(IV) iodate, a tan-brown solid, is precipitated when HIO_3 or KIO_3 is added to a dilute mineral acid solution. The solubility in 1M HCl - 0.1M HIO_3 is 0.8 g/l; in 1M HCl - 0.1M KIO_3, 0.08 g/l.[35] These solubilities appear to be high, possibly because some Np was in higher oxidation states.

Acetate. Rose-colored $NaNpO_2(C_2H_3O_2)_3$ is precipitated when a sodium acetate - sodium nitrate solution is added to a dilute sulfuric acid solution that has been heated to 90°C in the presence of potassium bromate to give NpO_2^{2+}. The solubility is ~0.1 g/l in 0.5M H_2SO_4 - 0.07M $NaNO_3$ - 2M $NaC_2H_3O_2$.[38]

Carbonates. No simple carbonates of Np(III) and Np(IV) are reported. A light-colored precipitate of Np(V), $KNpO_2CO_3$, is precipitated by addition of solid alkali carbonate (to about pH 7) to a solution of Np(V) made by reduction of Np(VI) with iodide ion.[43]

Phosphate. A green gelatinous precipitate, $Np(HPO_4)_2 \cdot xH_2O$, is formed when phosphoric acid is added to Np(IV) in hydrochloric or nitric acid. The solubility in 1M HCl - 0.5M H_3PO_4 is ∿56 mg/l, and the solubility in 1M HNO_3 - 1M H_3PO_4 is ∿134 mg/l.[45]

Sulfates. Mefod'eva and Gel'man[32] report precipitation of Np(III) as the complex sulfates $K_5Np(SO_4)_4$ and $NaNp(SO_4)_2 \cdot nH_2O$. Np(III) is produced in dilute hydrochloric and sparged with argon at ∿50°C using Rongalite reductant. In the dry form, the complex sulfates are stable to oxidation even at increased temperature.[32] Np(IV) is crystallized from hot concentrated sulfuric acid as a bright-green compound, presumably $Np(SO_4)_2 \cdot xH_2O$. The solubility is ∿16 g Np/l. Sulfuric acid solutions of Np(V) and Np(VI) have been reported, but no data are given on solubility.[35] Although not reported, it is expected that Np(IV) compounds analogous to Pu(IV) compounds could be precipitated from a solution containing sulfate salts, alkali metal ions, and Np(IV).

Other Compounds. Several Np(IV) chloride complex salts have been prepared. Yellow Cs_2NpCl_6 was precipitated by mixing solutions of Np(IV) and CsCl in 2 to 11M HCl and saturating the resulting solution with hydrogen chloride. The solubility in $\sim$10M HCl is <0.01M and increases to $\sim$1.4M in $\sim$1M HCl.[141] A similar compound, $[(C_2H_5)_4N]_2NpCl_6$, was precipitated by adding tetraethylammonium chloride in 12M HCl to Np(IV) in 8 to 12M HCl.[142] Several other complex salts of Np(V) and Np(VI) have been reported. Yellow $[(C_2H_5)_4N]_2NpO_2Cl_4$ was precipitated by the same procedure used for the Np(IV) salt,[143] and Cs_2NpOCl_5 (bright yellow), $(Ph_4As)_2NpOCl_5$ (bright yellow), Cs_3NpOCl_4 (turquoise), and $Cs_2NpO_2Cl_4$ (dark yellow) were made by variations of the same procedure.[59]

The phenylarsonate and salicylate of Np(III) have been reported.[32] They are quite stable at ambient temperature when dry.

B. SOLVENT EXTRACTION

Solvent extraction of Np from aqueous solution into immiscible organic solvents is probably used most often for separation because of its rapidity, simplicity, and reliability. Solvent extraction of Np is usually made from nitrate systems. Generally the efficiency and specificity are decreased from chloride systems; other systems, such as fluoride, sulfate, and phosphate, form complex ions with neptunium, and extraction is inhibited.

There are examples of both ion association extraction and chelate extraction among the solvent extraction systems for Np.[144,145] In chelate systems, compounds such as TTA, cupferron, acetylacetone, and 8-hydroxyquinoline replace coordinated water from neptunium ions and form neutral, almost covalent, chelate compounds that are soluble in such organic compounds as hydrocarbons. In ion association systems, several mechanisms are possible by which uncharged, extractable compounds are formed by electrostatic attraction between oppositely charged ions. In one ion association system, an oxygen-containing organic compound such as ether is coordinated to Np(IV), and the complex cation is associated with nitrate ions to give an uncharged extractable species. Ion association solvents commonly used for Np extraction include TBP, hexone, diethylether, isoamyl alcohol, pentaether, and dibutyl carbinol. For solvents such as hexone and diethylether, which form coordination complexes with actinide nitrates, the order of extractability of the various oxidation states is usually (VI) > (IV) >> (III) and (V), with the last two states generally considered to be nonextractable. The (IV) oxidation state is poorly extracted by diethylether but is extracted into hexone and dibutyl carbinol. For TBP and chelating agents, which form coordination complexes with the metal nitrates, the stable oxidation state giving the strongest complex is usually extracted most efficiently. The tendencies of the actinides to form complexes is (IV) > (VI) > (III) and (V). Thus, TBP, TTA, and other complexing agents usually extract the (IV) state most effectively. An exception (Table 17) is Np(IV)-TBP; however, these exceptions may be the result of the instability of the oxidation state in the aqueous solution.

Groh and Schlea[146] and Schulz and Benedict[5] have reviewed production-scale neptunium processes, including solvent extraction.

Chelate Systems. A large number of bi-functional reagents that form strong coordination complexes with metal ions have been investigated. These complexes are more soluble in nonpolar organic solvents, such as benzene or CCl_4, than in the aqueous phase. Of these compounds, the fluorinated β-diketone, 2-thenoyltrifluoroacetone (TTA) has been most widely used for extraction of Np in radiochemical and analytical applications.[147,148] Many variations include TTA extraction as a part of the total separation scheme before the analysis of Np or the determination of its oxidation states.[127,132,149,150]

TABLE 17

VARIATION OF EXTRACTION COEFFICIENTS WITH OXIDATION STATE

Organic Phase	Aqueous Phase	Np(III)	Np(IV)	Np(V)	Np(VI)	Pu(III)	Pu(IV)	Pu(VI)	Am(III)	Am(VI)
19% TBP-kerosene	4M HNO_3		3.0	0.13	11.0	0.014	11.5	2.5	0.08	
0.5M TTA-xylene	1M HNO_3	10^{-6}	10^{4}	10^{-4}	10^{-3}	10^{-4}	10^{4}	0.004	10^{-8}	
Diethyl ether	6M HNO_3		0.1	0.3	4.6			2.3		
	1M HNO_3-sat NH_4NO_3							1.2		
Hexone	0.5M HNO_3-11.1M NH_4NO_3					0.14	1.7	9.8		
	6M HNO_3		0.3	1.7	3.5					>100

Some data for the extraction of Np and other cations into 0.5M TTA in xylene for a range of nitric acid concentrations are given in Table 18.

Shepard and Meinke have compiled a useful set of TTA extraction curves showing extraction as a function of pH for a number of elements.[150] The data show that by judicious pH control, TTA extraction is useful to separate neptunium from many other elements.

Basically, the TTA method depends on quantitative reduction of Np to the highly extractable tetravalent state while interfering ions are stabilized in inextractable oxidation states. (Procedures 1 and 2, p 138 and 141). Neptunium in 1M HNO_3 or 1M HCl is rapidly and completely reduced with ferrous sulfamate, hydroxylamine hydrochloride-potassium iodide, or hydroxylamine hydrochloride-ferrous chloride. Np(IV) is extracted into the TTA, and Pu(III) and U(VI) remain in the aqueous phase. If no interfering cations are present, the extract can be evaporated directly for counting. The efficiency of separation from other alpha emitters is verified by alpha pulse height analysis. Fe(III), Zr(IV), and Pa(V) are strongly extracted from 1M HNO_3, but separation is attained by stripping the Np(IV) from the TTA-xylene into 8M HNO_3. Trivalent actinides and lanthanides do not interfere. Sulfate, phosphate, oxalate, and chloride, if present in the aqueous phase, are complexed with Al^{3+} before extraction to prevent interference.

TABLE 18

EXTRACTION COEFFICIENTS FOR VARIOUS IONS INTO 0.5M TTA-XYLENE[149]

Ion	HNO_3 (M)	Extraction Coefficient at 25°C
Np(III)	1.0	$<3 \times 10^{-8}$
Np(IV)	1.0	1×10^{4}
	8.0	$<1 \times 10^{-2}$
Np(V)	0.8	$<5 \times 10^{-4}$
Np(VI)	0.8	$<1 \times 10^{-3}$
Pu(III)	1.0	1×10^{-6}
Pu(IV)	1.0	1×10^{4}
	8.0	$<1 \times 10^{-2}$
Pu(V)	1.0	$<1 \times 10^{-4}$
Pu(VI)	1.0	4×10^{-3}
U(VI)	1.0	3×10^{-5}
Fe(II)	1.0	$<1 \times 10^{-3}$
Fe(III)	1.0	375
Ce(III)	1.0	1×10^{-5}
Ce(IV)	1.0	1×10^{3}
Zr(IV)	1.0	1×10^{7}
	8.0	250
Am(III)	1.0	1×10^{-9}
Al(III)	1.0	1×10^{-20}
Na	1.0	1×10^{-20}
Nb(V)	1.0	4×10^{-1}
Th (IV)	1.0	3.0

The relative standard deviation for the analysis is ±2%. The nominal decontamination attained from plutonium is 10^3 to 10^4.[151,152] Some data on the extraction of Np from sulfate and perchlorate systems with TTA have been given by Sullivan and Hindman.[93]

TTA extraction preceded by a LaF_3 coprecipitation cycle has also been described.[153-156] Np has been separated from numerous special materials where a combination of methods including TTA extraction was used. Holcomb[157] has described a method for separating 17 gamma-emitting radionuclides, including ^{239}Np, from heavy water moderator by TTA solvent extraction and anion exchange. The individual nuclides were determined by gamma counting and gamma spectrometry.

8-Hydroxyquinoline forms the following chelates with Np: $Np(C_9H_6NO)_4$ with Np(IV) and $H[NpO_2(C_9H_6NO)_2]$ with Np(V). Extraction of a number of elements as a function of pH into 0.1M 8-hydroxyquinoline in $CHCl_3$ is shown in Figure 4. The trivalent actinides extract only at pH 4-6, and at this pH appreciable hydrolysis of the metal cation occurs.[153] Np(IV) cupferron is extracted almost quantitatively into chloroform from 1M HCl and is back extracted in 8M HCl.[158a]

Separation with acetylacetonate has been reported for U and Pu and probably has application for Np.

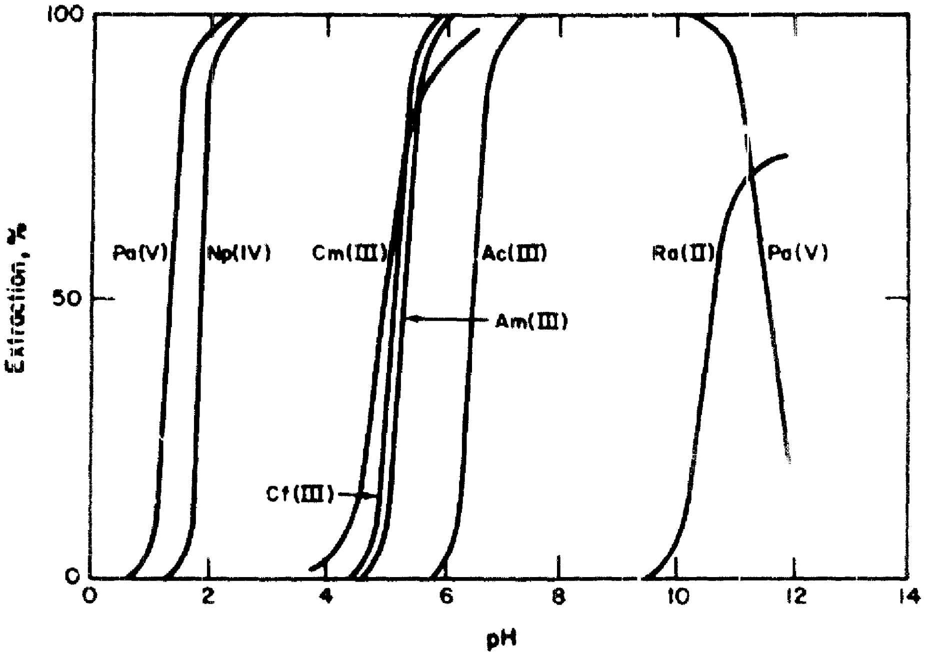

FIGURE 4. Percentage Extraction of Tracer Quantities of Ac(III), Am(III), Cm(III), Cf(III), Np(IV), and Pa(V) with 0.1M 8-Hydroxyquinoline /$CHCl_3$ and of Ra(II) with 1.0M 8-Hydroxyquinoline/$CHCl_3$ [μ = 0.1M (Na, NH_4, H)ClO_4, 25°C]. [C. Keller and M. Mosdzelenski, *Radiochim. Acta.* 7, 185(1967) Supplemented].

Extraction of plutonium dibenzoylmethane or salicylate has been reported.[159,160] Neptunium dibenzoylmethane is unstable in aqueous solution, so Pu and U, which form extractable complexes, can be separated.[159,161]

Chmutova *et al.* extracted Pu(IV) from 3M HNO_3 with a chloroform solution of N-benzoylphenylhydroxylamine; UO_2^{2+}, Am(III), (V), and fission products (except Zr and Nb) do not extract.[162]

Np(IV) is strongly extracted from 1 to 4M HNO_3 and 1 to 6M HCl with 4-benzoyl-3-methyl-1-phenyl-pyrazolin-5-one; under the same conditions, Np(V) and (VI) are not extracted.[163] Np is extracted at pH 9 to 10 with 1-nitroso-2-napthol in n-butanol and isopentanol and is separated from U and Pu.[164]

Ion Association Systems. The TBP-HNO_3 system is a useful system for large-scale processing but is not widely used for quantitative analytical separation. TBP forms an organic-soluble coordination complex with the metal nitrate, generally of the type $M(NO_3)_4 \cdot 2TBP$.[165] Increasing the nitrate concentration by adding nitrate salts of Al or Ca favors extraction. Other factors that affect the extraction include complexing ions, reagent purity, free TBP concentration, temperature, and mixing time. A summary of the early work with TBP has been given by Geary.[166] The physical and chemical properties of TBP as an extracting agent have been summarized by McKay and Healy.[167] Other discussions of the use of TBP are in References 168-170. Extraction coefficients for many elements for a variety of aqueous solutions and TBP concentrations have been reported by Schneider and Harmon;[149] data are shown in Table 19.

Np(VI) is almost completely separated from Al(III), Am(III), Cr(III), Fe(II), Fe(III), Na(I), Zn(II), and many other cations in one stage of TBP extraction. Separation of Np from Pu and U involves either oxidation of Np to the (VI) state for extraction and subsequent stripping of Np(V), or stabilization of inextractable Np(V) followed by extraction of Pu and U.

The following sequence of extractability has been found for the various oxidation states of the actinides: M(IV) > M(VI) >> M(III) > M(V). For the tetravalent actinides the sequence is Pu(IV) > Np(IV) > U(IV) > Th(IV), while among the hexavalent actinides the extractability decreases with increasing atomic number: U(VI) > Np(VI) > Pu(VI)[165] (Figures 5 and 6).

The tetravalent and hexavalent actinides are extracted from HCl solutions with similar relative distribution coefficients as from nitric acid but exhibit no maxima. Lower distribution coefficients are observed for extraction from perchloric acid solutions because of weak complexing by the perchlorate ion. Strong complexing agents, such as, SO_4^{2-}, PO_4^{3-}, and F^-, reduce the extractability of all actinides appreciably; however, cations such as Al that form quite stable complexes with these anions partially negate the deleterious effect on actinide extraction. Distribution

TABLE 19

EXTRACTION COEFFICIENT DATA FOR TBP[149]

Ion	Solution	TBP (%)	Extraction Coefficient At 25°C
Am(III)	4.0M HNO_3	30	0.013
Al	4.7M	15	0.0003
Ca	4.7M	15	0.0003
Co(II)	2.14M $Co(NO_3)_2$	60	0.002
Cr(III)	3.0M HNO_3	100	0.0001
Cu(II)	3.0M	100	0.0004
Fe(II)	4.7M	15	0.005
Fe(III)	2.0M	12.5	0.003
Mg	4.7M	15	0.0003
Na	2.0M	12.5	0.003
Ni(II)	3.0M	100	0.00006
Np(IV)	4.0M	30	3.0
Np(VI)	4.0M	30	12.0
Th	4.0M	30	2.8
Pa	4.0M	50	2.8
Zn	2.0M $Zn(NO_3)_2$	12.5	0.0001
Ru	2.0M HNO_3	30	0.15
Zr	2.0M	30	0.09
Nb	2.0M	30	0.03
Rare earths	2.0M	30	0.02
Pu(III)	5.0M	20	0.012
Pu(IV)	5.0M	20	16.6
Pu(VI)	5.0M	20	2.7
U(IV)	4.0M	25	10
U(VI)	4.0M	25	23
HNO_3	2.0M	30	0.26

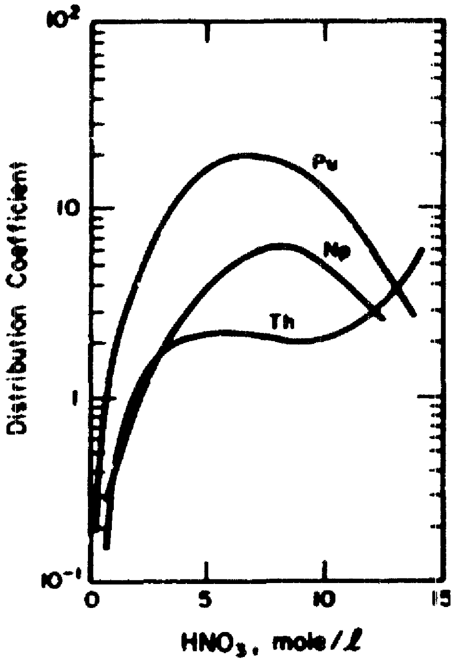

Figure 5. Distribution Coefficients for the Extraction of Tetravalent Actinides by 19 vol % TBP-Kerosene from Nitric Acid Solution.[165]

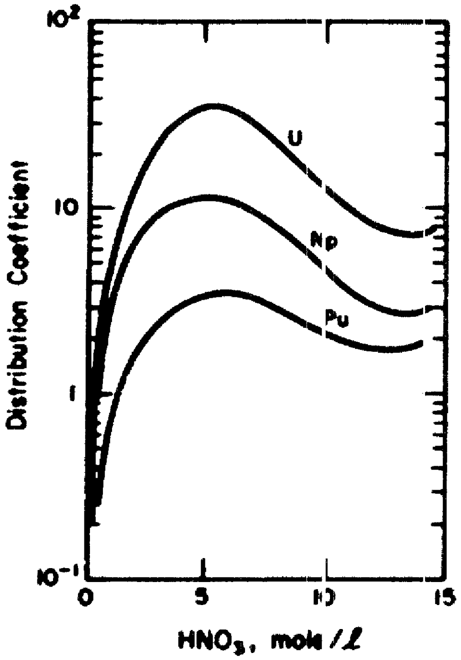

Figure 6. Distribution Coefficients for the Extraction of Hexavalent Actinides by 19 vol % TBP-Kerosene from Nitric Acid Solution.[165]

coefficients for Np(V) and trivalent actinides are appreciably lower[171] than for tetravalent and hexavalent actinides.

For NpO_2^+:

$$NpO_2^+{}_{(aq)} + NO_3^-{}_{(aq)} + TBP_{(org)} = [NpO_2(NO_3)\cdot TBP]_{(org)}$$

For analytical applications with small volumes, equilibrium is attained in less than five minutes with good mixing.

The extraction properties of many other organophosphorus compounds have been studied; however, few separation methods for Np have been defined. Higgins *et al.* working with the butyl series found the order to be phosphate ($(RO)_3PO$) < phosphonate ($R(RO)_2PO$) < phosphinate ($R_2(RO)PO$) < phosphine oxide (R_3PO).[172]

The distribution coefficients for the extraction of some tetravalent and hexavalent actinides with various trialkyl phosphates are given in Table 20.

Burger[174,175] and Petrov *et al.*[176] found that electronegative substituents in the alkyl chain, such as, chloride and phenyl, strongly depressed the extraction. Siddall[79] found that increasing the length of the alkyl chain in the phosphate series made little difference for up to eight carbon atoms for tetravalent and hexavalent actinides. The effect of branching the alkyl chain is to increase the extraction of U, Np, and Pu, but to strongly depress extraction of Th. The extraction mechanism of these compounds is generally the same as that for TBP, but the solvation number is not

TABLE 20

DISTRIBUTION COEFFICIENTS FOR THE EXTRACTION OF TETRAVALENT AND HEXAVALENT ACTINIDES WITH 1.9M TRIALKYL PHOSPHATE/ n-DODECANE FROM 2M HNO_3 AT 30°C[79]

	Distribution Coefficients[a]					
Extractant	Th	Np(IV)[b]	Pu(IV)[c]	U(VI)	Np(VI)[d]	Pu(VI)
Tri-n-butyl phosphate	2.9	3.2	16.1	26	15.6	3.5
Triisobutyl phosphate	2.4	2.7	11.8	22	15.9	3.4
Tri-n-amyl phosphate	2.9	4.2	15.6	32	19.3	4.1
Triisoamyl phosphate	4.2	4.7	17.8	34	18.9	4.4
Tri-n-hexyl phosphate	3.0	3.6	15.6	38	20.0	4.5
Tri-n-octyl phosphate	2.4	3.4	15.3	33	15.7	3.9
Tri-(2-ethylhexyl) phosphate	2.5	4.3	25	58	23	5.7
Tri-(2-butyl) phosphate	0.45	4.9	28	42	20	4.6
Tri-(3-amyl) phosphate	0.22	3.5	18.1	49	22	5.0
Tri-(3-methyl-2-butyl) phosphate	0.18	3.0	24	47	25	5.4
Tri-(4-methyl-2-amyl) phosphate	0.047	3.5	22	38	24	4.9

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a. For tracer amounts of the given elements.
b. The aqueous phase contains 0.01M $Fe(NH_2SO_3)_2$.
c. The aqueous phase contains 0.01M $NaNO_2$.
d. The aqueous phase contains 0.01M $(NH_4)_2Ce(NO_3)_6$.

necessarily the same for all elements.[173]

A method with mono[2-ethylhexyl]orthophosphoric acid in contact with 12M HCl + 0.1M hydroquinone has been effective for separating Np(IV) from U(VI), Pu(III), Am(III), Cm(III), and trivalent rare earths. The K value for Np(IV) is $\sim 10^3$, and for the other cations, $\sim 10^{-1}$; thus, separation is attained by a single contact followed by multiple scrubbing of the organic phase.[177] K. Kimura[178] has determined the acid dependency of the distribution coefficients for many elements extracted by 50 vol% bis(2-ethylhexyl)orthophosphoric acid (HDEHP) from HCl solutions (Figure 7). These data offer the basis for separating Np from many cations.

The distribution coefficients of Am(III), Pu(IV), Np(V), and U(VI) in HDEHP from HNO_3 are given in Figure 8.[179] The discontinuity in the Np(V) curve at high acid concentrations is probably due to disproportionation of Np(V) into Np(IV) and Np(VI), both of which are more extractable than Np(V).

Np(V) in dilute nitric acid has been separated from U(VI), Pu(IV), and Th(IV) by HDEHP extraction; however, there was evidence that a few percent of the Np(V) was reduced to Np(IV) and not separated by a single extraction.[180] Kosyakov *et al.*[179] used HDEHP to purify Am(III) from other actinides in higher valence states and to accomplish their mutual separation. Am(III), Pu, and U were extracted from 0.01M HNO_3 after stabilization of Np in the

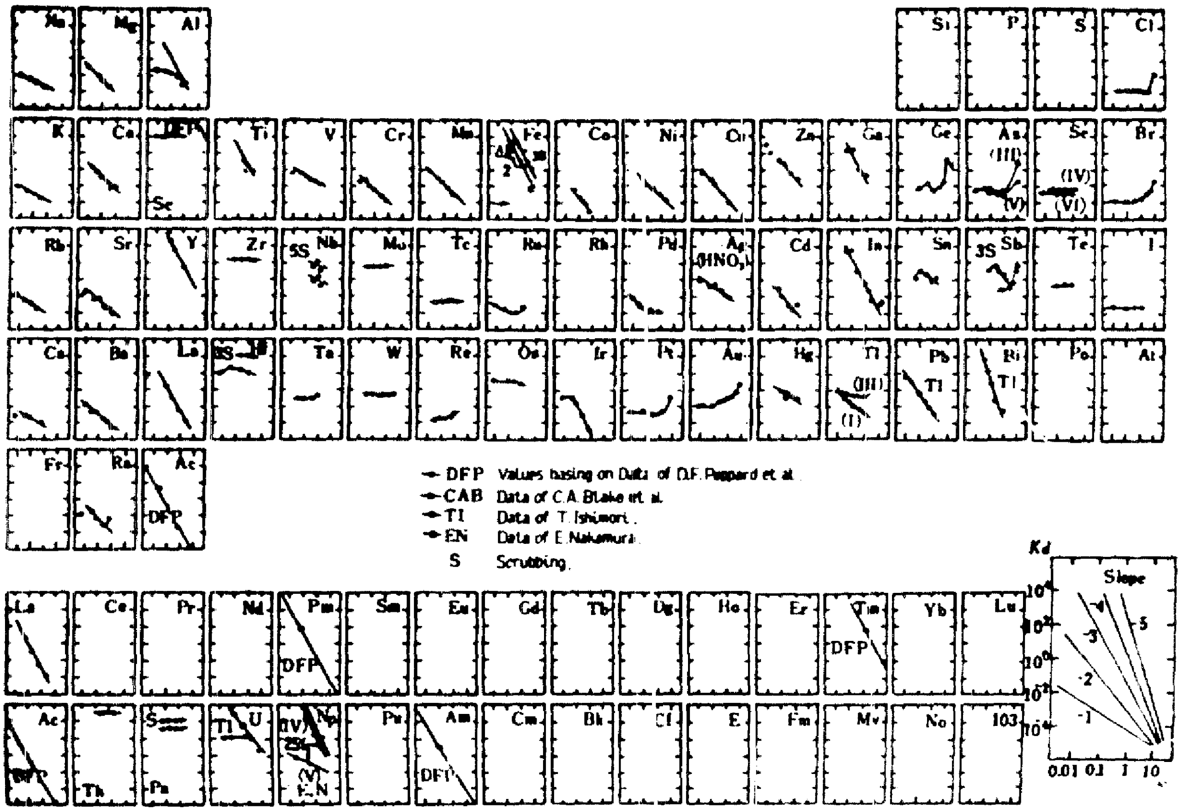

Figure 7. Extraction of Elements from HCl Solution by 50% HDEHP in Toluene as a Function of Acid Concentration.[178]

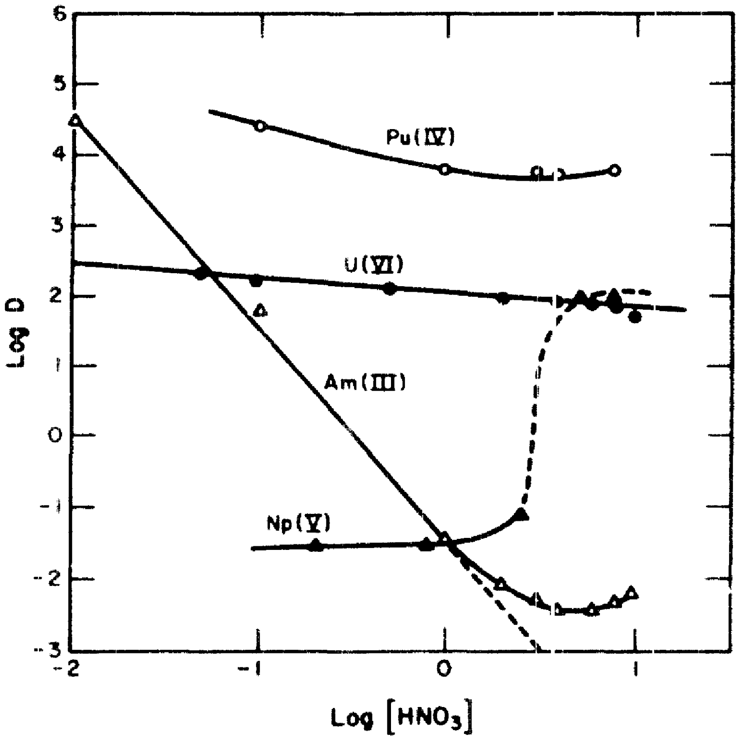

Figure 8. Extraction of Various Actinides into 0.5M HDEHP (isooctane diluent) from HNO_3 Solutions.[179]

pentavalent state with sodium nitrite. Np(V) was then oxidized to Np(VI) and extracted with HDEHP. Np(VI) was reduced to Np(V) and recovered from the organic phase by washing with 0.1M HNO_3. Am was back-extracted from the HDEHP with 3M HNO_3 and Pu was reduced to Pu(III) and recovered by back extraction with 3M HNO_3. U(VI) was recovered by back extraction with 1M $(NH_4)_2\ CO_3$.

Chudinov and Yakovlev[180] extracted U and Pu from Np(V) with HDEHP as a preliminary step in the colorimetric determination of Np(IV) with Arsenazo(III).

Peppard *et al.*[177,181] studied the extraction of several actinides by mono-2-ethylhexylphosphoric acid (H_2MEHP) from HCl solutions (Figure 9). The distribution coefficient for Np(IV) in 12M HCl was $\sim 10^3$, 10^4 times larger than the non-tetravalent species studied. Gindler *et al.*[182] used this method to purify ^{236}Pu for fission counting. The Np(IV) can be returned to the aqueous phase by addition of TBP to the organic phase, resulting in a great reduction in the distribution coefficient.

Kosyakov *et al.*[179] determined the distribution coefficients of Am(III), Np(V), Pu(IV), and U(VI) in H_2MEHP from nitric acid (Figure 10). They are generally higher for the same aqueous conditions than those for HDEHP.

White and Ross[183] have written a general review of the extractive properties of tri-n-octylphosphine oxide (TOPO).

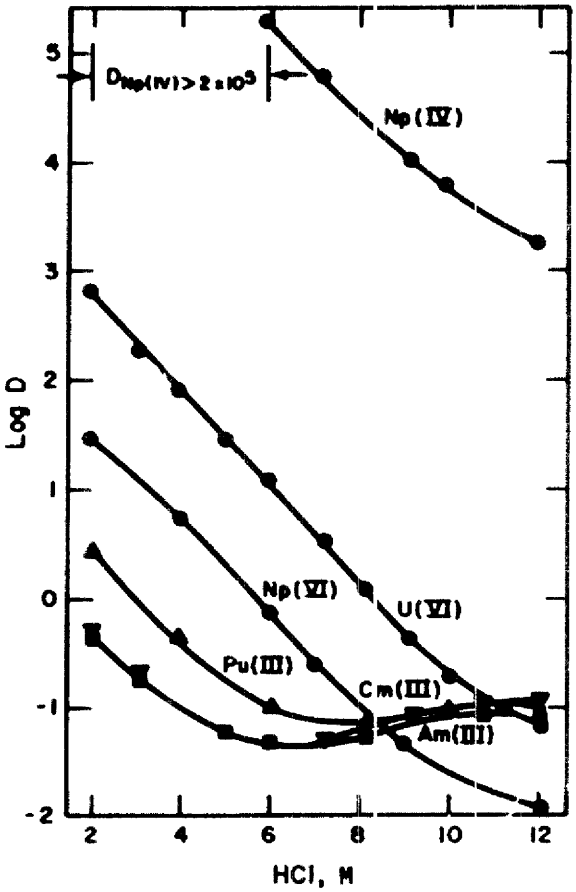

Figure 9. Extraction of some Actinide Cations into 0.48M H_2MEHP in Toluene as a Function of HCl Concentration.[177]

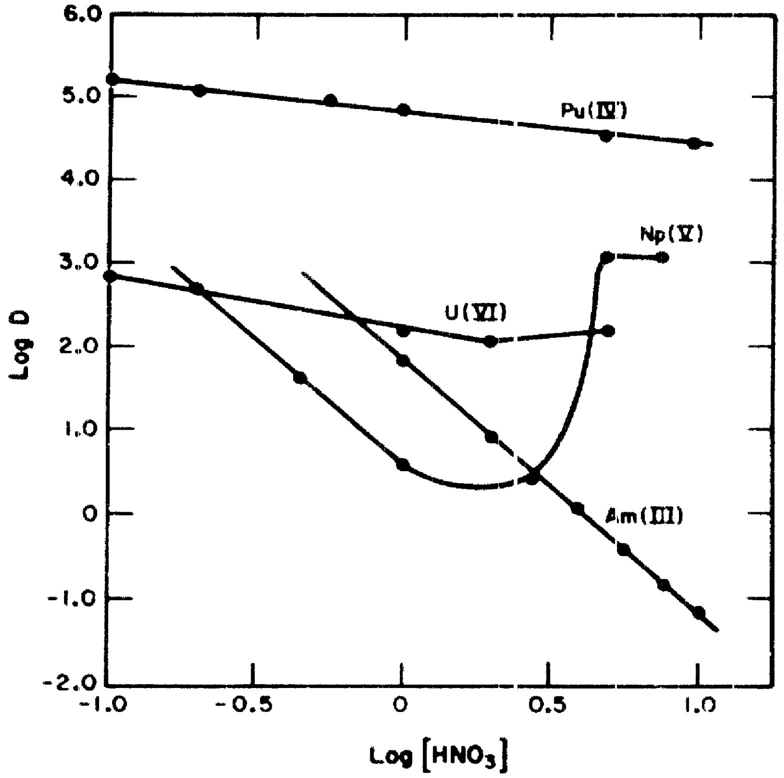

Figure 10. Extraction of Various Actinides into 0.2M H_2MEHP (Isooctane diluent) from HNO_3 Solutions.[179]

Extraction data for Np and other actinides into TOPO have been summarized by Weaver and Horner.[184]

Extraction with methyl isobutyl ketone (hexone) is based on the solvent power of hexone for the covalent nitrates of the (VI) oxidation states. Hexone was used for large-scale processing of irradiated nuclear fuels ("redox" process) but has been supplanted by other solvents both in plant and laboratory applications. A two-cycle extraction system for the separation of neptunium from uranium-fission product mixtures has been given by Maeck.[185] Hexone extraction of Np(VI) from acid-deficient $Al(NO_3)_3$ was followed by TTA extraction. Excellent separation from U, Pu, Ru, and Zr was attained. Also, Np has been separated from Pu and La. Np(VI) and Pu(VI) were produced by oxidation with $KBrO_3$; both were extracted into hexone from an $Al(NO_3)_3$ solution. Back extraction with an aqueous sodium nitrite solution yielded Np(V) and Pu(III), neither of which is soluble in hexone. The hydroxides were precipitated and dissolved in nitric acid, and ferrous sulfamate was added to give Np(IV) and Pu(III). Np was extracted into a solution of tributylamine in hexone, leaving the Pu in the aqueous phase.[129]

Extraction coefficients for ions into hexone from several different aqueous compositions are shown in Table 21.

Diethylether quantitatively extracts hexavalent Np, Pu, and Am from salted solutions containing a strong oxidant (Table 22).[186]

TABLE 21

EXTRACTION COEFFICIENTS OF VARIOUS SOLUTES INTO HEXONE AT 25°C[149]

Solute[a]	Salting Agent (M)		NO_3^- (M)	HNO_3 (M)	Extraction Coefficient
Na^+	$Al(NO_3)_3$	1.3	4.0	0.1	0.02
Al^{3+}		1.3	3.9	0.0	<0.0001
$Cr_2O_7^{2-}$		2.0	6.1	1.7 pH	0.011
Cr^{3+}		2.0	6.1	0.1	0.0003
U^{4+}		1.3	4.4	0.5	2.1
Am^{3+}		1.95	6.35	0.5	0.0018
Np^{4+}		1.3	4.4	0.5	1.5
Np^{5+}		1.5	5.0	0.5	<0.001
Np^{6+}		0.7	2.6	0.5	1.7
HNO_3		1.0	3.4	0.4	0.82
NO_3^-		1.5	4.5	0.0	1.1
Cs^+		1.0	3.5	0.5	0.009
Zr-Nb		1.0	3.25	0.25	0.01
Ru		1.0	3.1	0.10	0.10
Ce		1.3	4.1	0.20	0.12
F.P.[b]		1.4	4.6	0.4	0.10
Fe^{2+}	NH_4NO_3	8	8.2	0.2	0.004
Fe^{3+}		8	8.2	0.2	0.0005
Pu^{4+}		11.1	11.6	0.5	1.7
Pu^{6+}		11.1	11.6	0.5	9.8
Pu^{3+}		11.1	11.6	0.5	0.14
Pu^{6+}	$Al(NO_3)_3$	2.0	6.3	0.3	50.0
U^{6+}	$Al(NO_3)_3$	0.5	1.8	0.3	0.1
		1.0	3.3	0.3	2.0
		2.0	6.3	0.3	30.0
	NH_4NO_3	4.3	4.6	0.3	0.18
		8.7	9.0	0.3	2.0
		11.0	11.3	0.3	14.0

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a. Concentration of all solutes is 2 g/l

b. Gamma-emitting fission products after 144-day cooling period.

TABLE 22

EXTRACTION OF NEPTUNIUM, PLUTONIUM, AND AMERICIUM INTO VARIOUS SOLVENTS

Solvent	Aqueous Phase	% Extracted					
		Np (IV)[b]	Np (V)	Np (VI)	Pu (III)	Pu (VI)	Am (VI)
Ethyl ether	1M HNO_3; sat NH_4NO_3					[a]	100
	6M HNO_3	9	17	32		70	
	9M HNO_3	17	65	32		89	
Dibutyl	5M HNO_3	17	23	31		81	
carbinol	7 to 9M HNO_3	23	48	39		95	
DBBP,[c] 30%	4M HNO_3	91					
	7M HNO_3	15					
DBE,[d] 85%	2.4M $Ca(NO_3)_2$; 0.6M HNO_3					11	
	5.4M $Ca(NO_3)_2$; 0.05M HNO_3				0.3	41	

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[a] High efficiency; no value given.

[b] Np(IV) unstable in HNO_3.

[c] Dibutyl-butyl phosphonate, DBBP.

[d] Dibutyl ether, DBE, with 15% CCl_4.

Other elements that extract strongly are Ce(IV), Au(III), and Sc(III); P, Cr(VI), As(V), Hg(II), Tl(III), Th(IV), and Bi(III) are partially extracted. After back-extraction with dilute acid, ferrous ion and urea or hydrazine are added to reduce Np(VI) to Np(V); NH_4NO_3 is added for salting. A second extraction with diethylether further separates Np(IV) from U(VI).[127,186]

Distribution data for several of the actinides, including neptunium, as a function of nitric acid concentration into dibutyl carbitol are reported.[187,188]

Amine extractants, including long-chain alkyl or aryl primary, secondary, and tertiary amines, and quaternary amine salts react with acids to form an ion-association complex which is soluble in the organic phase. The mechanism is illustrated with a tertiary amine:

$$R_3N_{(org)} + H^+_{(aq)} + A^-_{(aq)} \rightarrow R_3NH^+ \text{---} A^-_{(org)}$$

A^- may be either a simple anion or the anion of a complex metal acid. The complex may undergo a further reaction with another anion in a manner analogous to anion exchange.

$$R_3NH^+ \text{---} A^-_{(org)} + B^-_{(aq)} \rightarrow R_3NH^+ \text{---} B^-_{(org)} + A^-_{(aq)}$$

The higher amines are excellent extractants for Np(IV), Pu(IV), and U. The advantage of amines over organophosphorus compounds is the greater stability to radiation and hydrolysis in radioactive solutions. The amines are usually dissolved in an organic solvent (xylene, benzene, or chloroform). To achieve rapid phase separation and to prevent formation of a third phase during extraction, a small amount (3 to 5 vol%) of a long chain aliphatic alcohol is added to the organic phase. The relative extractability of Np in nitrate solution is Np(IV) > Np(VI) > Np(V), although the selectivity depends on the structure of the amine and the composition of the aqueous phase. The extractive power of the amines in nitrate and chloride solutions varies in the order quarternary ammonium > tertiary > secondary > primary[189]; from H_2SO_4 solutions, the sequence is reversed. The distribution coefficient of tetravalent and hexavalent actinides from HCl and HNO_3 acid solutions decreases in the sequence Pu > Np > U > Pa > Th.

Keder *et al.*[190] have reported distribution coefficients for several actinide elements (more than one oxidation state) from nitric acid solutions with tri-n-octylamine (TOA) diluted with xylene (Figures 11, 12, and 13).

The tetravalent ions show a second power dependence on the amine concentration, indicating that the extracted complex involves two amine molecules. Extraction of Np(IV) and Np(VI) with trilaurylamine (TLA) from nitric acid is reported.[191,192] A review of liquid-liquid extraction with high molecular weight amines has been published.[193]

Np(IV) has been separated from U(VI), Pu(III), Am(III), and fission products by extraction of Np(IV) into tri-iso-octylamine

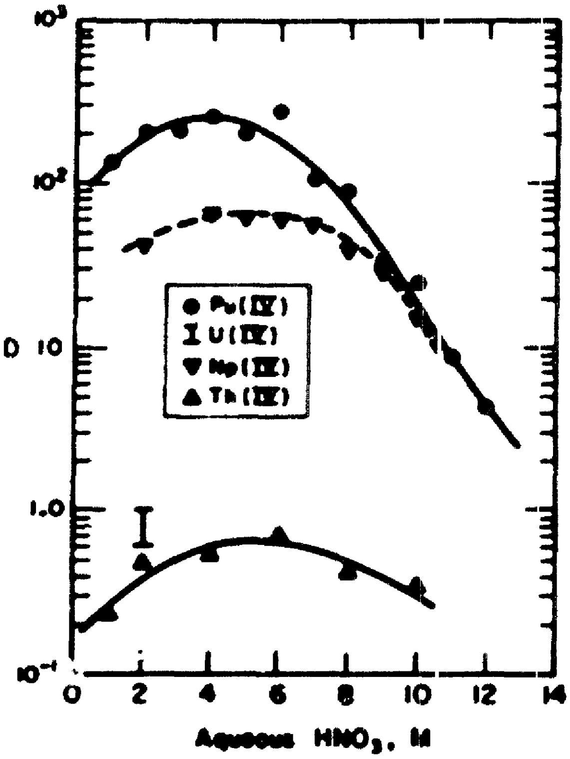

Figure 11. The Extraction of the Quadravalent Actinide Nitrates by 10 vol % TOA in Xylene.[190]

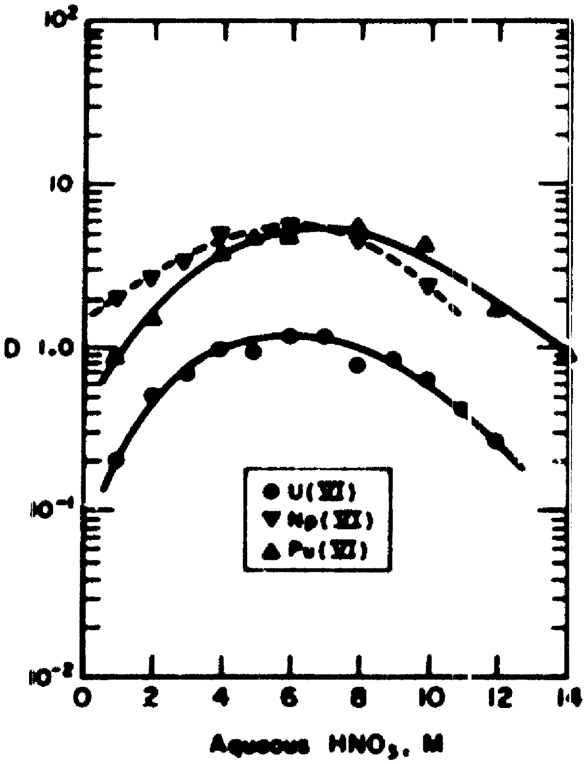

Figure 12. The Extraction of the Hexavalent Actinide Nitrates by 10 vol % TOA in Xylene.[198]

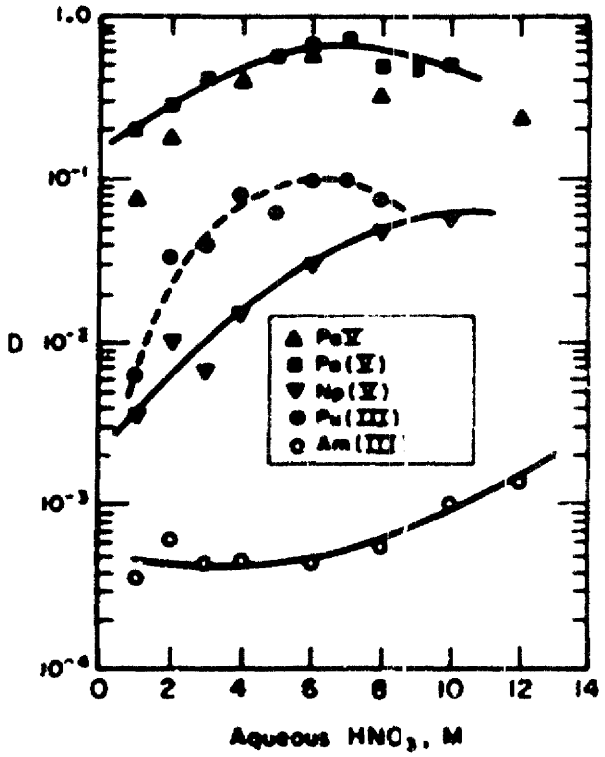

Figure 13. The Extraction of Pentavalent and Trivalent Actinide Nitrates by 10 vol % TOA in Xylene.[198]

(TIOA) in xylene from aqueous 5M nitric acid solution containing ferrous sulfamate. For further separation, the neptunium-bearing organic solution was scrubbed with 5M HNO_3 containing ferrous sulfamate. Final purification of Np was achieved with a TTA extraction.[194,195] ^{239}Np has been separated from ^{243}Am by extraction with TIOA.[196] Np(IV) was extracted ($K_d^O > 20$) from 0.1 to 10M HNO_3 with 0.1M tetraheptyl ammonium nitrate in xylene. The K_d^O was >2000 in 1M HNO_3.[197] Distribution data for a large number of elements in quaternary ammonium compounds from various solutions have been determined, and a procedure for separating Np and Pu with this system has been reported.[198]

Keder[199] has reported the distribution coefficients from tetra - and hexavalent Np, Pu, and U from HCl solutions into TOA (Figures 14 and 15). Pu(IV) is much more extractable than Np(IV) and U(IV) under the same conditions, and the hexavalent actinides are more extractable than the tetravalent in this system.

Np(IV) and Pu(IV) were strongly extracted from sulfuric acid by the primary amine "Primene"* JM-T in xylene. In general, the order of extraction of Np(IV) and Pu(IV) from sulfate solution was primary >> secondary > tertiary amine.[200] Many more procedures for amine extraction have been reported for U and Pu, and these methods also offer potential for Np separation.[66,193,201]

Mixed Extractants (diluents). The term synergism is used to denote enhanced (or depressed) extraction of metals by mixed extractants (diluents) as compared to extraction by each extractant

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* Registered tradename of Rohm and Haas Co.

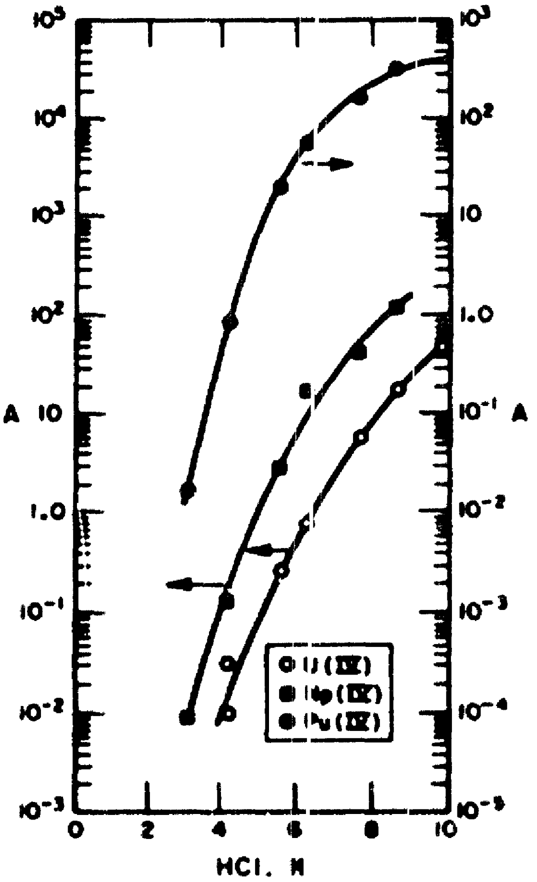

Figure 14. Extraction of U(IV) and Np(IV) by 10% TOA and Pu(IV) by 1.0% TOA from HCl Solutions.[199]

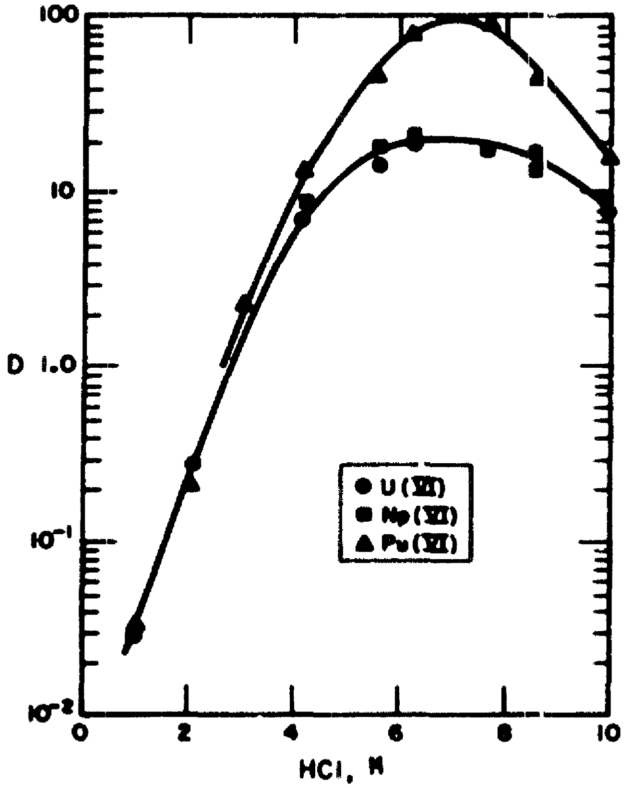

Figure 15. Extraction of Hexavalent U, Np, and Pu from HCl Solution with 1.0% TOA in Xylene.[199]

(diluent) taken separately. The range of phenomena described under the term synergism is diverse, complex, and not completely understood. A review of this subject is given by Marcus.[173] Although the subject has received considerable attention, only a few examples are reported for Np. Lebedev *et al.*[202] have reported a procedure to determine ^{243}Am through its daughter product ^{239}Np in solutions containing large quantities of curium and fission products. 0.1M 1-phenyl-3-methyl-4-benzoyl-pyrazolon-5 (PMBP) and 0.25M tributylphosphate (TBP) in benzene were used to separate Np(IV) from Zr, Nb, Cs, Ce, Am and Cm in 0.5M HNO_3 and 1M H_3PO_4. More than 99% of the Np was extracted with <0.1% of other elements. The ^{243}Am was determined by measurement of the gamma activity of the extracted ^{239}Np.

Taube[203] has discussed the influence of polarity in two-component diluent mixtures of chloroform, benzene and carbon tetrachloride on the extraction of Np(IV) and Np(VI) complexes with several phosphate and amine extractants. The results are interpreted in terms of the size of the complex species, the diluent structure, dipole interaction between complex and diluent, and other factors. Figures 16 and 17 show the effects of variation of diluent mixtures on the distribution of Np(IV) and (VI) into TBP and tetrabutylammonium nitrate from nitric acid.

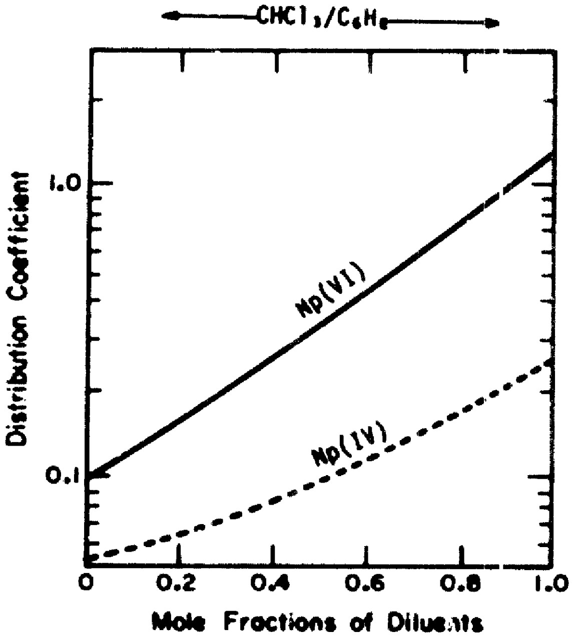

Figure 16. Neptunium Extraction with TBP from 5M HNO_3 into Diluent Mixtures.[213]

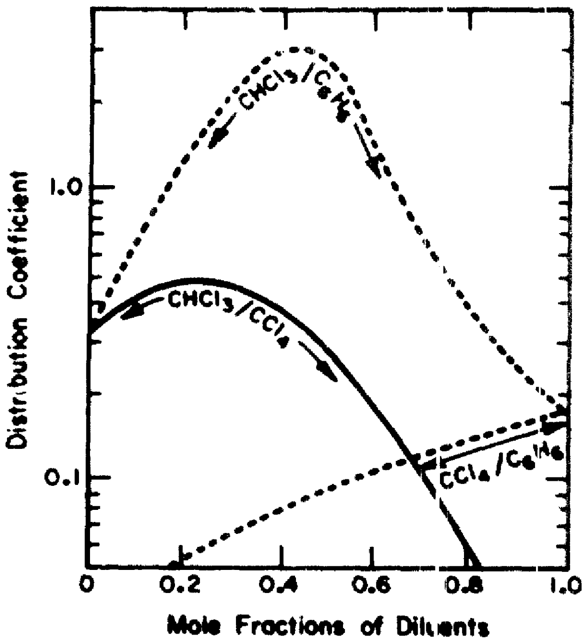

Figure 17. Distribution Coefficients for Np(IV) Extraction with 10^{-2}M Tetrabutyl-Ammonium Nitrate from 3M HNO_3 Using Mixtures of Different Diluents.[203]

C. ION EXCHANGE

Many variations of ion exchange are used for separating Np from other ions. Np ions in dilute mineral acids with no strong complexing ions are sorbed by strongly acidic cation exchange resins, such as sulfonated polystyrene. In general, the ability of cations to be sorbed on cation exchargers increases with increasing charge and decreasing hydrated radius. Thus, the order of sorbability on cation exchangers for Np is Np(IV) > Np(III) > NpO_2^{2+} > NpO_2^+. All Np species are sorbed at low acid concentrations and eluted with high concentrations of mineral acids; elution of NpO_2^+ proceeds first and Np(IV) is last. Some anions form neutral or anionic complexes with different oxidation states of Np, so that Np may be eluted by this mechanism. Both Np(V) and Np(VI) are slowly reduced to Np(IV) by common organic base resins. For this reason and because cation exchange of Np(IV) offers limited selectivity in the separation from other multivalent cations, this method has not been used widely for analytical applications.

Anion exchange is one of the techniques most used for separation of Np in analytical and process applications. The method is simple to perform and yields excellent separation from many other elements, including most of the fission products.

Ion exchange has been the subject of many reviews. The books of Helfferich,[204] Samuelson,[205] Amphlett,[206] and Rieman and

Walton[207] are good references to the theory and applications of ion exchangers. Other reviews of ion exchange include Massart,[208] Korkisch,[209,211] and Faris and Buchanan.[210]

Anion Exchange. Np(IV) forms anionic nitrate and chloride complexes that are strongly sorbed by anion resins; the anionic species provide separation from the cations of many other elements. The hexavalent state of the actinides also form strongly sorbed anionic chloride complexes. Greater separation of Np is attained from most other elements in the nitrate system than in the chloride system. The distribution coefficients of many elements over a wide range of nitric acid and nitrate concentrations have been reported.[212] Data are given in Figure 18.

In a typical anion exchange cycle, a sample containing Np is adjusted to 7 to 8M HNO_3 for optimum sorption of $Np(NO_3)_6^{2-}$ ions, and 0.01 to 0.05M ferrous sulfamate is added to ensure that all Np(V) and Np(VI) is reduced to Np(IV). The solution is heated to 55°C for 30 minutes or treated with sufficient sodium nitrite to react all the sulfamate and oxidize excess Fe(II) to Fe(III); this treatment is necessary to prevent excessive gassing in the resin bed. The resin is washed with strong nitric acid to remove Zr, Ru, Pa, Fe, Al, rare earths, U, transplutonium elements, and most other cationic contaminants. Th(IV) and Pu(IV) are not separated; however, washing with 5 to 15 bed volumes of 5 to 6M HNO_3-0.05M ferrous sulfamate-0.05M hydrazine reduces Pu(IV) to

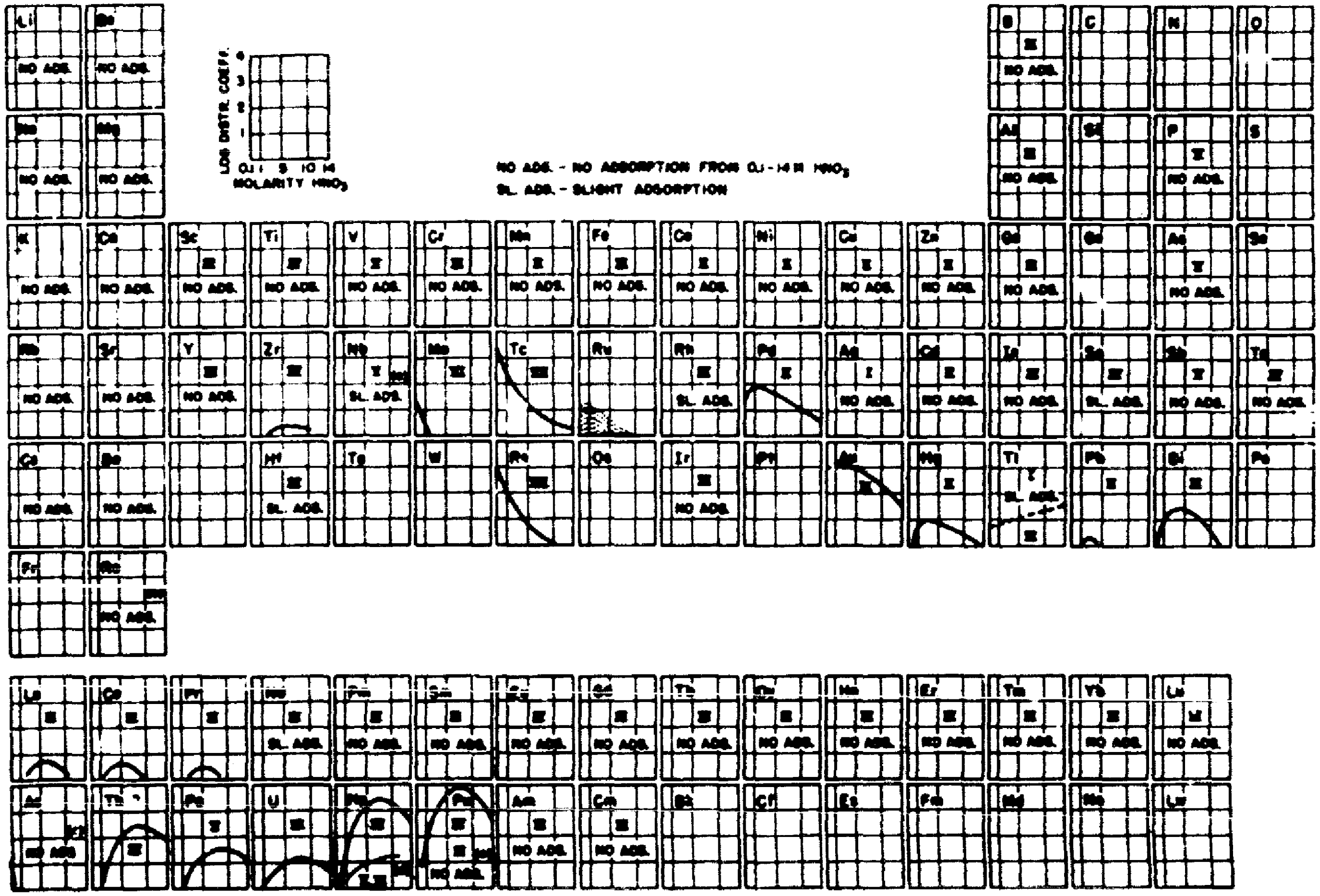

Figure 18. Sorption of the Elements from Nitric Acid Solutions by Strongly Basic Anion Exchange Resins.[212]

Pu(III), which is removed from the column. Washing with 8M HCl removes Th. The Np is eluted with 0.3M HNO_3. Cross-linking and particle size of the resin greatly influences the separation from other cations as well as elution of the Np.[152,213-215] Macroporous anion resin is superior to gel-type anion resin for separation of Pu from Np.[215a] A number of similar procedures with variations in acid concentration and substitution of semicarbazide or aminoguanidine for hydrazine have been reported.

The separation of tracer amounts of Np(VI), Th(IV), Am(III), and Pu(IV) in nitric acid by anion exchange has been reported.[216] The feed was adjusted to 7.2M HNO_3-0.05M $NaNO_2$ at 50°C to yield Np(VI) and Pu(IV). After sorption on "Dowex" 1-X4 resin, the column was washed with 7.2M HNO_3 to elute Am(III) and NpO_2^{2+}, then with 4M HNO_3 to elute Th(IV), and finally with 0.35M HNO_3 to elute Pu(IV). Other work with macro quantities of these cations has shown incomplete separation of Np probably because of some reduction to Np(IV). Also, Th(IV) and Pu(IV) were not completely separated. The separation of Np from fission products in 7.5M HNO_3 using ascorbic acid reductant is reported by Ichikawa.[217]

Radiochemically pure Np has been prepared for production of high purity metal with one nitrate anion exchange cycle and two chloride anion exchange cycles successively.[218]

The distribution coefficients of many elements over a wide range of hydrochloric acid concentrations have been reported.

These data are used to design separation systems for chloride anion exchange (Figure 19).[126,219] Np, Th, and Pu are separated by chloride anion exchange by sorbing the anionic chloro-complexes of Np(IV) and Pu(IV) in 8 to 12M HCl. Pu(III) is eluted with NH_4I in 8M HCl, NH_2OH-NH_4I in 12M HCl or $FeCl_2$ in 8M HCl; Th is not retained; and Np is eluted with 0.3M HCl.[156,220] Distribution data for 65 elements on "Dowex"*1-X8 from 2 to 17.4M acetic acid in water have been reported[221] (Figure 20). Examples of several separations including U and Np are given. Distribution data for 60 elements on cation exchange resin from 1 to 17.4M acetic acid in water have also been reported.[222] With Np(VI) in 7.9M $HC_2H_3O_2$, equilibrium was not reached even after 40 hours of mixing.

A method to separate and determine Np, Pu, U, Zr, Nb, and Mo in mixed fission products by anion exchange with HCl-HF solutions has been developed.[223] Trace quantities of Np have been separated from macro amounts of Zr and trace amounts of Nb by elution with HCl-HF solutions.[224] Also, HCl and HF solutions have been used to separate U, Pu, and Np from each other and from alkali metals, alkaline earths, rare earths, trivalent actinides, Al, Sc, Ac, Th, Y, and Ni (Figure 21).[225] Controlled elution with a series of solvent mixtures was used to separate Np, Pu, Zr, Nb, Mo, Tc, Te, and U from fission products.[226] The chloro complexes were sorbed on anion resin and sequential washes with 12M HCl-NH_2OH-NH_4I(Pu), 10M HCl-Aq H_2O_2(Np), 9M HCl-Aq H_2O_2(Np and Zr), 9M HCl-ethanol (1:1, Zr), 6M HCl-ethanol (1:1, Nb), ethanol-1M HCl(4:1, Te),

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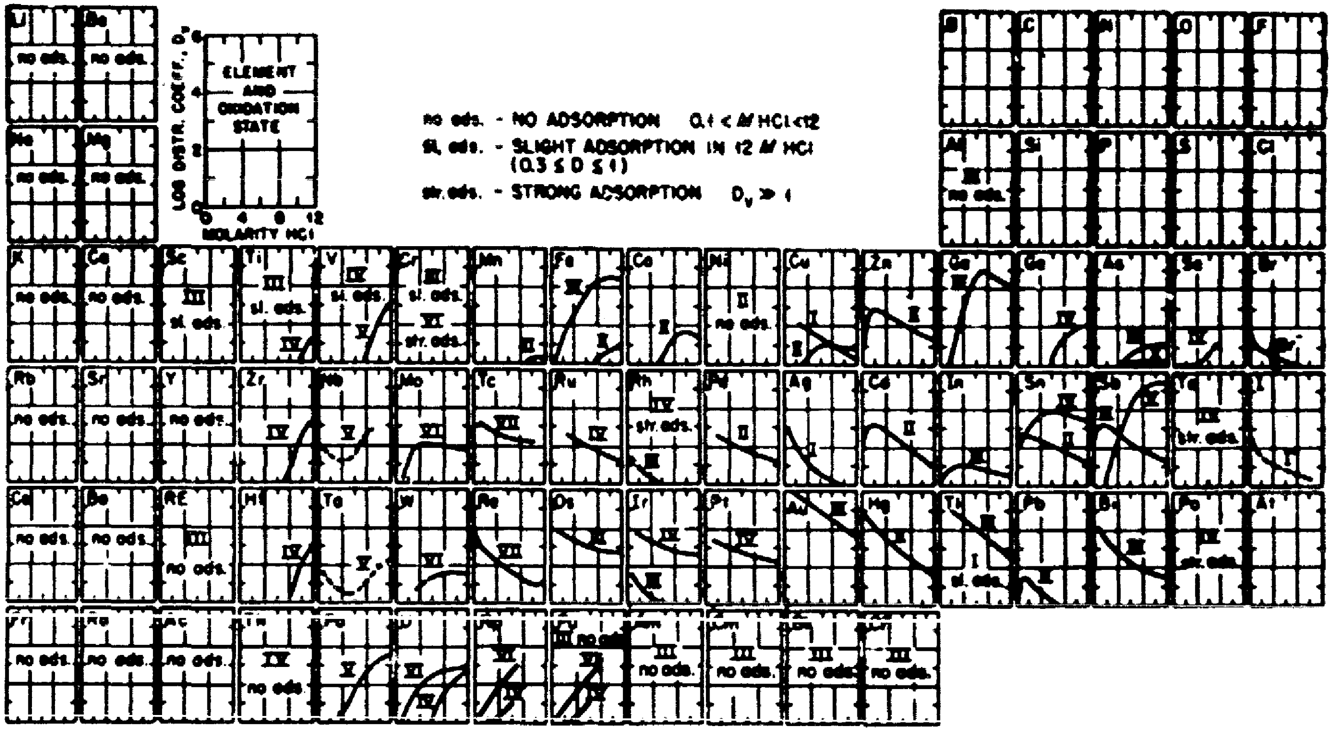

Figure 19. Sorption of the Elements from Hydrochloric Acid Solutions by Strongly Basic Anion Exchange Resins.[219]

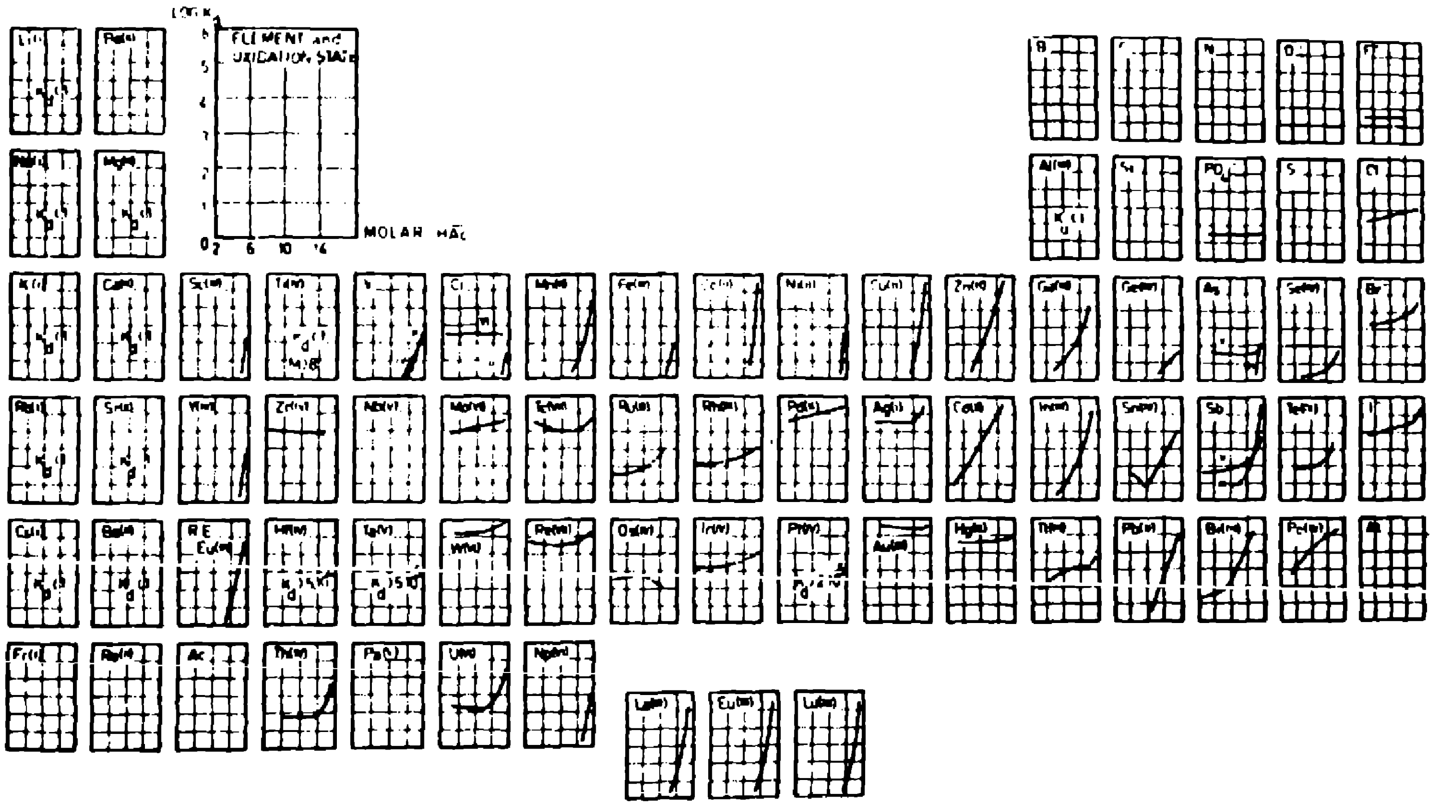

Figure 20. Sorption of the Elements from Acetic Acid Solutions by an Anion-Exchange Resin.[221]

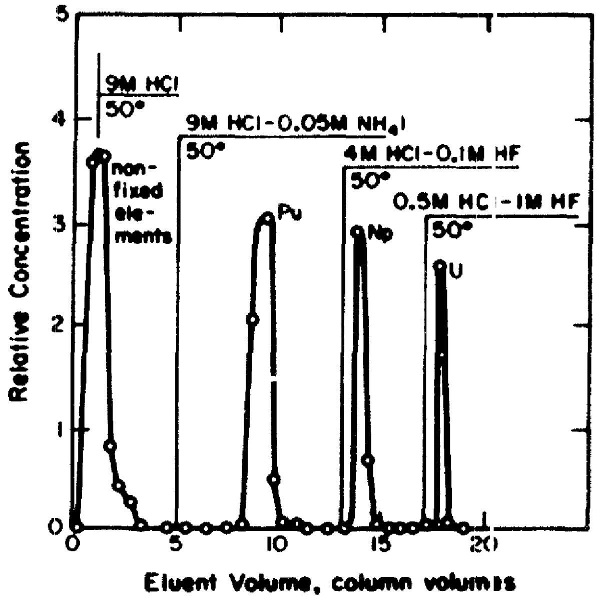

Figure 21. Uranium-Neptunium-Plutonium Separation by Anion Exchange ("Dowex" 1-X10, <400 Mesh, 0.25 cm^2 × 3 cm Column).[225]

ethanol-6M HCl(4:1, Mo), 0.1M HCl(U), and 4M HNO_3(Tc).

Other literature has included a study of the elution characteristics of Np, Pu, U, Pa, and Zr in HCl, HNO_3, and H_2SO_4 systems with "Dowex"-2 anion resin. Equilibrium data were given for each acid from 0.1M to concentrated, and possible separations based on equilibrium data were summarized.[227] Equilibrium data were given for a number of elements including Np in 0.1 to 30N H_3PO_4 with "Dowex"-2 resin. Separation of Np from Cs and Te was attained, but data were erratic.[228]

Np has been separated from Pa by elution with 12M HCl-0.5M HF with Pa eluting first.[219] Separation has also been achieved by elution with 5M HCl from anion resin, in which case Np elutes first.[229]

Np(IV) has been sorbed quantitatively on "Dowex"-1 from 0.1M Na_2CO_3 and eluted with NH_4Cl or dilute HCl.[230]

Np(VII) forms stable alkaline solutions as the NpO_5^{3-} ion. Novikov *et al.*[231] studied the anion exchange behavior of this soluble complex as a possible basis for separation from other elements. The sorption was irreversible for all experiments; this was attributed to the reduction of the Np(VII) by the resin.

An anion exchange method using the nitrate system has been reported for removal of Np before spectrochemical determination of cationic impurities[232] (Procedure 23, p 200).

In several reported instances, anion exchange resin exploded or ignited after use in nitric acid or strong nitrate solutions.[233] These accidents are thought to be due to nitration of the skeleton of the exchange resin, leading to the spontaneous reaction in the presence of heat. Anion exchange resin in the nitrate form should not be stored in the dry state, and temperature should be carefully controlled at <60°C when used in strong nitric acid. The nitric acid concentration should be <8.5M, and flow to the column should not be interrupted, particularly when high levels of radioactivity are in the column.

Cation Exchange. Sulfonic acid type resins have had limited applications for Np separations because both Np(VI) and Np(V) are reduced slowly by the resin.[234] Several separations have been reported for the pentavalent state of Np. Y. A. Zolotov and D. Nishanov[235] reported the separation of Np from U, Pu, and fission products by elution of Np(V) ahead of U(VI) with 1M HNO_3 from a cation resin in the hydrogen form. Np was initially oxidized to the hexavalent state with bromate. Separation of Np depended on reduction to Np(V) by the resin. Also, cation exchange has been used for partial separation of Np from Pu(IV), Th(IV), and Zr(IV). Np was oxidized to Np(V) in dilute nitric acid before sorption on the resin, but a few percent of the Np(V) was reduced to Np(IV) by the "Dowex"-50W resin and was not separated from the other cations.[236]

The distribution coefficients for many of the elements were determined in 0.1 to 12M HBr with "Dowex"-50 resin. Conditions for separation of U(VI) and Np(IV) and separation of Np(IV) and Pu(III) were given (Figures 22 and 23). Many other separation methods for Np could be devised from the distribution data (Figure 24).[237]

Np and Pu have been separated by elution from cation resin with HF after reduction to Np(IV) and Pu(III) with SO_2.[238] Np(IV) was eluted first with 0.02M HF[239], and then Pu(III) was eluted with 0.5M HF. Also, Np was separated from Pu by cation exchange with HBr followed by TTA extraction.[240]

Pressurized elution development chromatography on cation resin at 70 to 90°C with α-hydroxyisobutyric acid has been very useful for separation of trivalent actinide elements both in the laboratory and with macroscopic quantities.[241] Although no specific separations of this type for Np are reported, the method is useful for highly radioactive solutions.

Distribution data for many of the elements on "Dowex"-50 resin over a range of hydrochloric acid concentrations and also over a range of perchloric acid concentrations have been reported (Figures 25 and 26).[238]

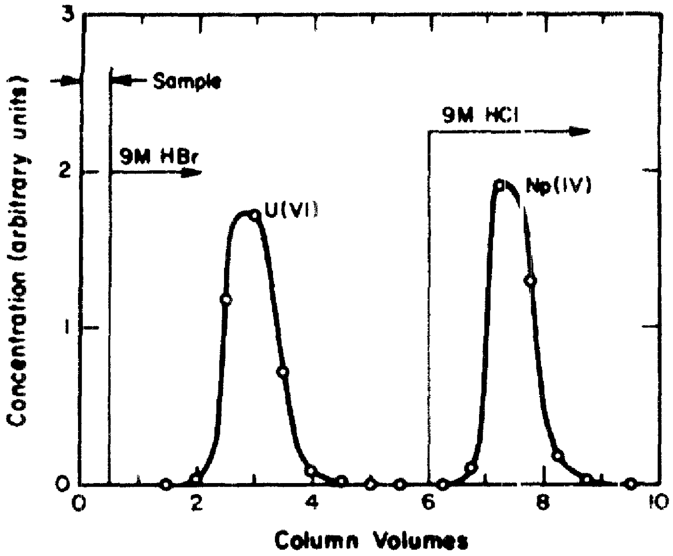

Figure 22. Separation of U(VI) and Np(IV) by Cation Exchange ("Dowex" 50-X4 0.2 cm² × 2 cm Column, 25°).[237]

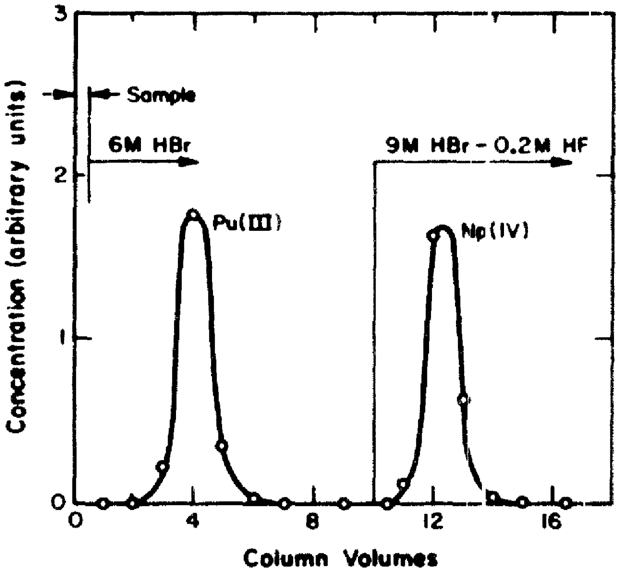

Figure 23. Separation of Pu(III) and Np(IV) by Cation Exchange ("Dowex"50-X4, 0.28 cm² × 3 cm Column, 60°).[237]

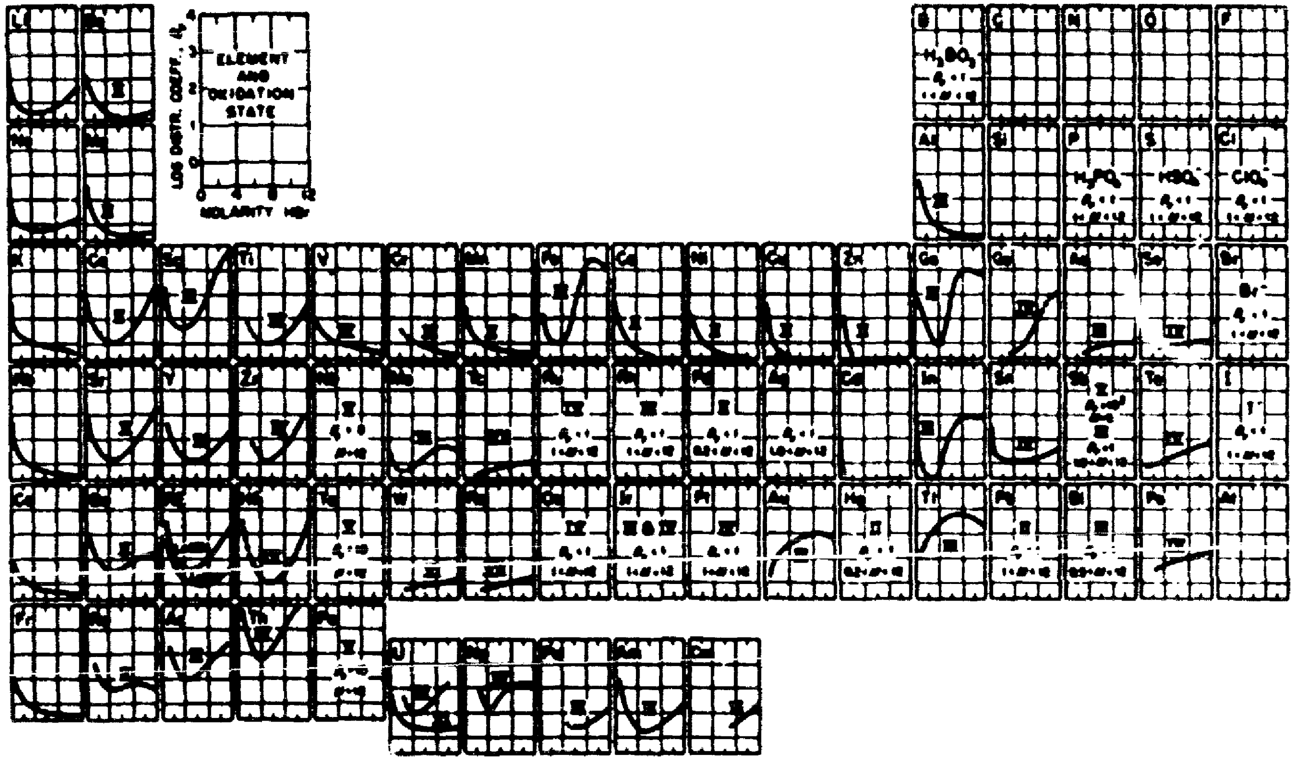

Figure 24. Sorption of the Elements from HBr Solutions by a Cation Exchange Resin.[217]

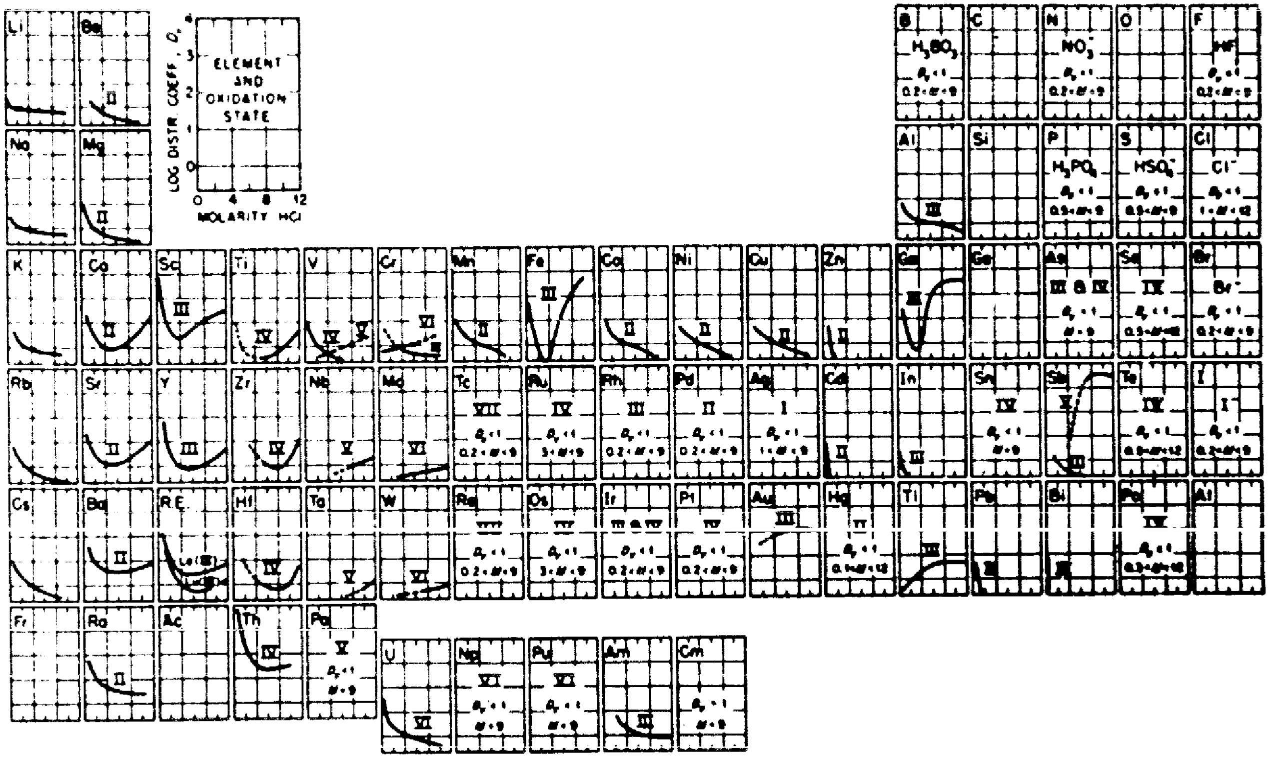

Figure 25. Sorption of the Elements from HCl Solutions by a Cation Exchange Resin.[238]

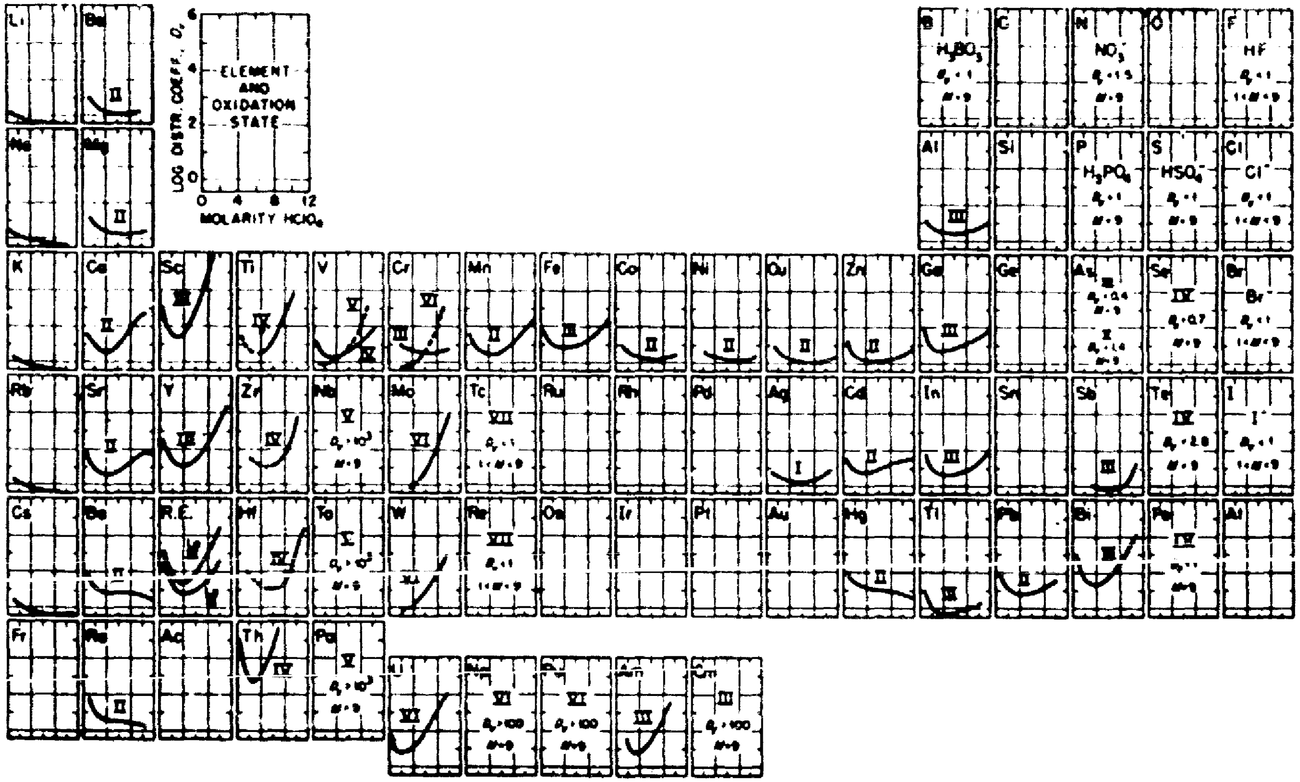

Figure 26. Sorption of the Elements from HClO$_4$ Solutions by a Cation Exchange Resin.[238]

Inorganic Ion Exchangers. Inorganic exchangers have been largely superseded by synthetic resins principally because of higher capacities and more useful physical characteristics of the synthetic resins. However, inorganic exchangers have the advantage of greater resistance to radiation damage. The distribution coefficients of 60 cations, including Np, on hydrous zirconium oxide, zirconium phosphate, zirconium tungstate, and zirconium molybdate have been measured.[242] Shafiev *et al.*[243] have studied the separation of Np, Pu, and Pm on zirconium phosphate. Np(V) is not retained while trivalent elements are readily eluted with 1M HNO_3. Pu(IV) is eluted with 0.5M HNO_3 containing reducing agents such as ferrous sulfamate or hydroquinone. Zirconium phosphate does not change the oxidation state of Np(V). The sorption of Np, Th, and U from HNO_3, H_2SO_4, and HF solutions on ammonium molybdophosphate (AMP) columns has been determined.[244,245] The sequence of sorption is Np(IV) > Th(IV) >> U(VI) >> Np(VI) > Np(V). These same workers demonstrated the separation of Th, U, and Np using columns loaded with AMP.[246] Tsuboya *et al.*[247] demonstrated conditions in a HNO_3 system for separating Np(IV) and U(VI) with a tungstic acid exchanger; Np(IV) is much more strongly retained than U(VI) from 0.5 to 2N HNO_3.

D. CHROMATOGRAPHY

Extraction Chromatography. Extraction chromatography has been applied to the separation of Np, Pu, Am, and U with 100% TBP sorbed on diatomaceous silica. The diatomaceous silica was initially exposed to dimethylsilane vapor, then treated with TBP, and used as the stationary phase. Nitric acid, with and without reducing agents, was used as the mobile phase.[248] Other workers[249] used this system for a similar separation of Np and found that modifications were required to prevent reduction of Np(VI) to Np(V) and to improve separation from some fission products. Eschrich[250] used the same system to determine the oxidation states of Np by eluting with 0.5 to 2M HNO_3. The order of elution was Np(V), Np(IV), and Np(VI). It is probable that some reduction of Np(VI) occurred.

^{239}Np was separated from fission products and U on a column of TTA sorbed on glass powder.[251] The chromatographic method gave much more effective separation than batch extraction; recovery was adequate so that isotopic dilution was not necessary. However, two column separations were necessary to separate Np from Zr. Wehner *et al.* [252] have also reported separation of ^{239}Np from fission and activation products on Poropak-Q impregnated with TTA-o-xylene.

Some workers have used "Kel-F"* or "Teflon"** powders coated with an organic extractant as the stationary phase for extraction

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* Registered tradename of M. W. Kellogg Co.

**Registered tradename of Du Pont.

chromatography separations. "Kel-F" powder coated with trilaurylamine nitrate has been used to separate Np from U, Pu, and fission products. The feed was adjusted to 2M HNO_3 - 0.1M $Fe(SO_3NH_2)_2$ and passed through the bed. After the column was washed with 1M HNO_3 containing $Fe(SO_3NH_2)_2$, the Np was eluted with H_2SO_4 - HNO_3. The method is very selective for Np(IV) and has yielded chemically pure ^{239}Np when the weight ratio of U to Np was $>10^{10}$ in the feed.[253] The separation requires one to two days. A similar method was developed for the coseparation of Np and Pu from U.[254]

Paper Chromatography. Paper chromatography R_f values for elements Ac through Am in many mixtures of either HNO_3 or HCl with methanol, ethanol, and butanol have been determined by Keller.[255] It was necessary to reduce Np(VI) to Np(V) or (IV) before starting the separation because Np(VI) is slowly reduced in the column resulting in poor separation of the bands. Neptunium(IV) was separated from Th(IV) with 12M HCl-butanol and >8M HNO_3-butanol mixtures. Also, good separation of Np(IV) from U(VI) was attained with >1M HCl-butanol; Np(V) was separated from U(VI) with 2M HCl-ethanol as developer.

Clanet[256] measured the R_f values for elements with atomic numbers 90 through 96 in mixtures of mineral acids with alcohols and discussed analytical applications.

R_f values for Np(IV), (V), and (VI) have been reported for paper treated with TOA using 0.5M HNO_3 developer solutions containing $LiNO_3$, NH_4NO_3, or $Al(NO_3)_3$. The values are well separated for the different oxidation states of Np and for the different actinides.[257] R_f values were also obtained for paper treated with solutions of tetrabutylhypophosphate in acetone-water (20:1) using developer solutions of nitric and perchloric acid.[258]

Twelve fission and neutron capture isotopes including ^{239}Np, have been separated from irradiated uranium with aqueous hydrofluoric and methylethyl ketone-hydrofluoric acid mixtures as developers.[259]

Thin Layer Chromatography. Rapid separation of different valence states of Np from each other and from other actinide elements by thin layer chromatography on "Teflon"-40 powder saturated with 0.1M tetrabutylhypophosphate solution has been demonstrated.[258]

Gas Chromatography. Effective separation of the transuranium elements by gas chromatography of their chlorides has been demonstrated.[260] The volatile chloride complexes were synthesized at ∿500°C by adding Al_2Cl_6 vapors into the carrier gas. The experiments were carried out in glass capillary columns maintained at ∿250°C with less than one microgram of each actinide. Cm, Am, and Pu were eluted in order of decreasing atomic number in about the same position as lighter lanthanide elements in a similar experiment. The retention times of Np, U, and Pa are much shorter; it is postulated that the tetrachlorides of these elements are produced. The chromatogram is measured by collecting fractions of Al_2Cl_6 condensate at the exit of the column. The actinide hydroxides are carried with La from strongly basic solution and separated from Al. Then the actinide is deposited, and the alpha spectrum is measured with a surface barrier detector and multichannel pulse height analyzer.

E. OTHER METHODS

Volatilization. Separation of more-volatile Np(IV) chloride from Pu(III) chloride and other less volatile chlorides has been reported.[261,262] The actinide chlorides were prepared by passing carbon tetrachloride vapor at 650°C over mixtures of plutonium-neptunium oxides or oxalates. The neptunium chloride sublimate was collected with a separation factor of $\sim 3 \times 10^3$ for Np initially containing 4% Pu; the yield was $\sim$96%. The method is useful for obtaining quite pure Np where a quantitative separation is not required.

NpF_6 is quite volatile, intermediate between UF_6 and PuF_6. Separation was attained from UF_6 by co-sorption of the hexafluorides on NaF. Then the $NpF_6 \cdot NaF$ complex was reduced, and the UF_6 desorbed. After refluorination, the NpF_6 was desorbed.[263]

Electrophoresis. Clanet[256] has developed an electrophoretic method on cellulose acetate membranes to separate the charged species formed by elements with atomic numbers 90 to 96 in 1 to

12M HCl and HNO_3. Mobility curves have been obtained for the acid concentration range for both acids. A large number of potential separations of these elements and the solution conditions are tabulated. Some of the separations of Np include Np(IV) or (V) from U(VI); Np(IV) from Pu(IV) or (VI); Np(IV), (V), or (VI) from Am(III) and Cm(III); and separation of the oxidation states of Np.

Electrodeposition. Although electrodeposition has been used to prepare mounts for radiometric measurement, electrolysis has not been used as a separation method. There has been one report that U, Pu, and Np were separated by electrolysis from HNO_3 by varying the pH. Optimum conditions were stated as current density 750 to 1000 mA/cm^2 with a plating time of 2 to 3 hours and solution volume of 20 to 30 ml. Np is completely deposited at pH > 9, and Pu and U are completely deposited at pH <6 and pH <3, respectively.[264] Other workers using different media for electrolysis have been unsuccessful in separating Np from other actinides. Although partial separation from a number of common cations has been attained, no useful separation method has been reported.

Miscellaneous. An analytical scheme has been described which yields sequential separation of the elements including Np remaining after neutron exposure of 1 mg of a fissile element.[265] The products were separated and isolated for determination of isotopic abundance by mass spectrometry using solvent extraction, ion exchange, extraction chromatography, and precipitation methods.

VIII. ANALYTICAL METHODS

A. SOURCE PREPARATION AND RADIOMETRIC METHODS

Counting. Because counting methods are more sensitive than chemical or spectrochemical methods, they are the primary methods for identifying and quantitatively determining Np. The two most common Np isotopes are ^{237}Np and ^{239}Np. ^{237}Np is usually determined by alpha counting its two major alpha transitions at 4.781 and 4.762 MeV. If ^{237}Np has decayed for a period of about 6 months or longer, it can be determined by gamma ray spectroscopy of its ^{233}Pa daughter. If ^{237}Np is separated from ^{233}Pa which has an 86.6-keV gamma ray, the ^{237}Np 86.6-keV gamma ray can be counted directly. ^{239}Np is determined by gamma counting its gamma transitions at 228 and 278 keV.[10]

The gross alpha activity of ^{237}Np can be determined with a proportional counter or plastic scintillation counter. If other alpha-emitting nuclides are present, an alpha pulse height analysis with a surface barrier detector allows a determination of the percentage of the total alpha counts attributable to ^{237}Np.

Liquid scintillation counting can be used to determine gross alpha activity with almost 100% efficiency and in many cases can be used to determine ^{237}Np in the presence of other alpha-emitting nuclides. The energy resolution in liquid scintillation is $\sim$600 KeV as compared to 15 KeV for surface barrier detectors.

Gamma-ray spectrometry with either a NaI scintillation detector or a Ge(Li) detector may be used to determine ^{239}Np. For ^{239}Np gamma rays (228, 278 KeV), the energy resolution of a typical coaxial Ge(Li) detector (about 1.0 KeV) is much better than for NaI (about 20 KeV). The efficiency of such Ge(Li) detectors relative to a 3 x 3 in. NaI detector is 3 to 15% for the 1.33-MeV gamma ray. Ge(Li) low-energy photon detectors (LEP) have an energy resolution of 0.5 KeV with lower efficiency.

An α-γ coincidence method for determinating ^{237}Np was developed which increased selectivity.[264] The resolving time of the coincidence system was taken as 8×10^{-8} sec.

A radioactivation method was developed to increase the sensitivity for determining ^{237}Np.[265] The activation product is short-lived ^{238}Np, which is determined by counting its 1.0 MeV gamma ray. To obtain maximum sensitivity, the Np should be purified before and after neutron irradiation.

A summary of the sensitivity and selectivity of radiometric and radioactivation methods for determining Np is presented in Table 23. In summary, alpha counting is the most convenient method for ^{237}Np, and gamma spectrometric methods are preferred for ^{238}Np and ^{239}Np. Because of the continuing advancements in nuclear radiation detection systems, the sensitivity, precision, and accuracy of the radiometric methods discussed above could be

TABLE 23

SENSITIVITY AND SELECTIVITY OF RADIOMETRIC AND RADIOACTIVATION METHODS FOR DETERMINING NEPTUNIUM[66]

Isotope	Method	Sensitivity of Method	Interfering Element	Permissible Amount in Terms of		Duration of Analysis (min)
				Np Weight (mg)	Np Activity	
^{237}Np	α-Counting	0.05 to 0.1 μg	^{239}Pu	5×10^{-6}	0.02	10 to 60
			^{241}Am	1×10^{-8}	0.02	
			^{238}Np	--	10^{3}	
			U	20	0.02	
			FP[a]	--	10^{3}	
			SI[b]	50	--	
^{237}Np	α-Spectrometry	0.1 to 0.5 μg	^{238}Pu	0.2	10	50 to 100
			^{241}Am	4×10^{-3}	10	
			^{238}Np	--	10^{4}	
			U	50	0.05	
			FP	--	10^{3}	
			SI	50	--	
^{237}Np	γ-Spectrometry	0.01 to 0.1 mg	^{239}Pu	10	10^{3}	10 to 60
			^{238}Pu	--	0.02	
			^{241}Am	5×10^{-6}	50	
			$^{141+144}$Ce	--	0.1	
			U	100	1	
			FP	--	1	
			SI	10^{3}	--	
^{237}Np	α,γ-Coincidence (80 keV)	0.1 to 0.5 μg	^{239}Pu	20	2×10^{3}	60 to 200
			^{241}Am	5×10^{-6}	50	
			^{239}Np	--	10^{1} to 10^{4}	
			FP	--	10^{1} to 10^{4}	
			SI	50		
^{238}Np ^{239}Np	β-Counting	10^{-6} μCi	FP	--	0.02	10 to 60
			^{238}Pu	--	0.	
			U	(0.1 to 1)		
			SI	(0.1 to 1)		
^{239}Np	γ-Spectrometry (100 keV)	10^{-3} to 10^{-6} μCi	^{239}Pu	--	10	5 to 60
			^{241}Am	--	100	
			$^{141+144}$Ce	--	0.1	
			U	100	4	
			FP	--	3	
			SI	100		
^{238}Np	γ-Spectrometry (1000 keV)	10^{-3} to 10^{-1} μCi	^{238}Pu	(>1)	10^{3}	5 to 60
			^{237}Np	(>1)	$>10^{3}$	
			U	(>100)	$>10^{3}$	
			^{95}Zr + ^{95}Nb	--	0.1	
			^{140}La + ^{140}Ba	--	0.1	
			FP	--	1	
			SI	(100)		
^{237}Np	Radioactivation (by γ-spectrum of ^{238}Np)	10^{-3} μg [with flux of 10^{13} n/(cm^{2}-sec)]	^{239}Pu	1	10^{3} to 10^{6}	24 to 150
			^{235}U	1	--	
			^{238}U	>300	-	
			Other elements	>100	-	
			FP	--	0.1 to 1	

FP - Fission Product

SI - Stable Isotopes

improved with available advanced instrumentation.

Source Preparation. Direct evaporation is the simplest method for preparing sample aliquots for counting. The disadvantage for alpha pulse height analysis is the thickness of the deposit, which results in self absorption of the alpha particles. If a surfactant such as tetraethyleneglycol ($50\ \mu g/cm^2$) is added to the aqueous solution, the Np solution is evaporated from a film rather than a drop resulting in a more homogeneous deposit.[267,268] The surfactant polymerizes on heating and burns up when ignited. The diluted sample is transferred to a suitable counting plate, e.g. stainless steel disk, and slowly evaporated to dryness to prevent spattering. The direct mount is flamed to dull red heat, cooled, and coated with a thin layer of collodion solution, and the Np is counted.

Electrodeposition has been widely used to prepare high-quality sample mounts for precise alpha counting. The procedure is extremely useful when samples contain a mixture of alpha emitters that need to be resolved. Electrodeposition results in excellent sample mounts from organic solutions that evaporate very slowly or leave large amounts of residue and from aqueous solutions that contain large amounts of dissolved solids.

Np and other actinides can be deposited from a variety of electrolytes and under several conditions. Graves[269] described a semiquantitative method for depositing ^{237}Np from Li onto Pt. Ko[270] reported a method for quantitative deposition of Np from 0.2M $HClO_4$ - 0.15M NH_4COOH, and Mitchell[271] used NH_4Cl - HCl to obtain a yield of 94%. Some systems used by other workers[272-274] are formic acid-ammonium formate, ammonium oxalate, ammonium acetate, ethanol, isopropanol, and NH_4Cl with uranium carrier.

Donnan and Dukes[275] developed one of the fastest procedures for quantitative depositions by combining Mitchell's method with uranium carrier addition. ^{238}U is added as a carrier in three increments to the NH_4Cl electrolyte to ensure quantitative yield; only 20 minutes deposition time is required. An average recovery of 99.8% with a relative standard deviation of ±0.2% (n = 10) was obtained with Pu. Similar results were obtained with Np. Resolution of 20 keV is achieved consistently with electrodeposited mounts and a silicon surface-barrier detector.

Parker and Colonomos[276] reviewed electrodeposition procedures and described two new methods. One is a co-deposition method for alpha-spectrometry, and the other for preparation of carrier-free layers as fission detectors. In the co-deposition method with uranium carrier, ^{237}Np was deposited quantitatively in 10 min at 1700 V with stainless steel as the cathode.

In other recent work, Np was deposited quantitatively from ammonium oxalate or ammonium acetate solution or mixed ammonium

oxalate-ammonium chloride electrolyte.[277-280] Alcohol is an excellent plating medium for aqueous and organic samples. Methods have been reported for ethanol, isopropanol, and alcohol saturated with ammonium chloride.[281-283] Deposition from sulfuric, hydrochloric, perchloric, and oxalic acid has been reported by Palei.[284]
The effect of variables on the quantitative deposition on Np and other actinide elements has been reported by other authors.[285,286]

Other methods which have a lower efficiency but yield sources with excellent resolution include vacuum sublimation and electrospraying.[286-291] Both electrodeposition and electrospraying have several disadvantages. These methods take a longer time than evaporation and require special equipment including a specially designed electrolytic cell for electrodeposition, high voltage equipment, and special capillary with a needle electrode for electrostatic spraying.[266]

B. SPECTROPHOTOMETRY

Although different oxidation states of Np have sharp absorption bands, spectrophotometric analysis has had limited use because radiometric procedures are more sensitive. Further, alpha containment is required for the spectrophotometer, and operation within a glove box is tedious. Generally, procedures used for other actinides can be applied to the determination. Np is adjusted to a single oxidation state, and the concentration is calculated from the molar extinction coefficient and the absorption of the solution at the proper wavelength. When more than one oxidation state is present, appropriate equations may be formulated for the concentration of each component.[292]

Absorption Bands. Important absorption bands and molar extinction coefficients of the different oxidation states are listed in Table 24. Most of the sharp bands can be used for qualitative or quantitative work even though they only obey Beer's Law over a limited concentration range. The best band to use for analysis of Np(III) is at 786 mμ because this band obeys Beer's Law. The strongest bands for Np(IV) (960 mμ, 723 mμ) do not obey Beer's Law, but they can be used with appropriate calibration and constant slit width. The strongest band for Np(V) (at 980 mμ in 1M HNO_3) does obey Beer's Law;[298] a high-resolution monochromator (e.g., a double-grating monochromator) should be used. Cauchatier' and coworkers[298] have developed a method for determining Np in irradiated nuclear fuels by measuring the Np(V) band in 1M HNO_3. The pentavalent state is produced by adding hydrazine to a Np(V)-Np(VI) mixture obtained after evaporation of the nitric acid solution. Correction for Pu(VI) is necessary. The most useful band for Np(VI) is at 1.23 μm; Colvin developed a method using this band for measurements in nitrate solution.[299] In this method, Np is oxidized to the hexavalent state with sodium dichromate, and then the acidity is adjusted to 1 to 2M. The absorbance is measured at 1.23 μm

TABLE 24

IMPORTANT ABSORPTION PEAKS OF NEPTUNIUM[293-297]

	Absorption Band (mμ)	Molar Extinction Coefficient
Np(III)	552[a]	44.5
	602[a,d]	25.8
	661[a,d]	30.5
	786[b,d]	44 (50 to 60°C)
	849[b]	∿25
	991[b]	∿27
	1363[b]	∿39
Np(IV)	500[c]	∿15
	504[a,d]	22.9
	590.5[a,d]	16.1
	∿600[c]	∿ 7.5
	∿715[c,d]	∿ 3.7
	723[b]	127
	743[a,d]	43.0
	800[c]	∿21
	825[a,d]	24.5
	960[b]	162
	975[c]	∿32
Np(V)	428[a]	11.1
	617[b,d]	22
	∿617[c,d]	∿18
	980[b]	395
	∿990[c]	∿180
Np(VI)	476[a]	6.4
	557[a]	6.8
	1223[b,d]	45
	1230[c,d]	∿43
Np(VII)	412[e]	1370 ±40
	618[e]	382 ±10

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a. 1M $HClO_4$.
b. 2M $HClO_4$.
c. 1M HNO_3.
d. Obeys Beer's Law.
e. KOH Solution.

against a reference HNO_3 solution that is the same HNO_3 concentration as the sample. The method has a relative standard deviation of ±0.5% at 3 g/ℓ. A number of ions, including Pu, do not interfere when present in amounts ten times that of the Np. A study on heavy water solutions of neptunium salts in which numerous well-defined bands were found in the region 1.2 to 1.8 μm is reported by Waggener.[300]

Color Complexes. Spectrophotometric methods for Np lack sensitivity. Furthermore, the position of the band extinction coefficients are affected by some anions and by the Np concentration. These disadvantages are partially overcome when color complexes that have very high molar extinction coefficients are used. A method with arsenazo III [1, 8-dihydroxynapthalene-3, 6-disulfonic acid-2, 7-bis(azo-I) benzene -2-arsonic acid] is reported.[301-303] The intensity of the stable green complex of Np(IV) and arsenazo III is measured at 665 mμ. The color forms instantaneously, and its intensity is constant over the concentration range 4 to 6M HNO_3. The molar extinction coefficient at 665 mμ is $\sim 10^5$. Chudinov and Yakovlev separated U(IV), Pu(IV), and Th(IV), which form colored complexes, from NpO_2^+ by extraction with di-2-ethylhexylphosphoric acid (HDEHP) in carbon tetrachloride. After extraction, Np is reduced to Np(IV), and arsenazo III is added. The lower limit of detection is 0.04 μg/ml, and the relative accuracy is between 1 and 7%.

Bryan and Waterbury[302] separated Np from U and Pu by extraction with tri(iso-octyl)amine (TIOA) before determining the arsenazo III complex. They found that of 45 elements tested, only Pd, Th, U, Pu, and Zr interfered. The relative standard deviation was between 7.2 and 1.1% in 200-mg samples of 8.5 to 330 ppm of Np. (Procedure 20, p192.) Novikov *et al.* have studied the color complex of Np(IV) with Arsenazo M.[304] At 664 mμ the molar extinction coefficient is 1.18×10^5 in 7M HCl and 9.5×10^4 in 0.5M HCl.

Thorin was used by several workers to analyze Np.[305,306] The absorbance is measured at 540 mμ against a reference solution not containing Np. The molar extinction coefficient measured with a Beckman DU spectrophotometer is ∿14,500. The precision of the method at the 95% confidence limits is ±2.1% for 0.63 μg of Np/ml. Chudinov and Yakovlev used extraction to separate Np from U and Pu interferences. The thorin method has also been automated[307] with the Technicon AutoAnalyzer, and the precision has been improved.

Np reacts in weakly acidic solution (pH∿2) with xylenol orange to form a colored complex with an absorbance maximum at 550 mμ and molar extinction coefficient of 5.5×10^4.[308] Xylenol orange is three times more sensitive than thorin but only one-half as sensitive as arsenazo III as a reagent for Np(IV). The greatest advantage of xylenol orange is that uranyl ions do not interfere. Fe(III), Zr, Th, and Bi interfere.

Np(IV) forms a color complex with quercetin that is stable in the pH range 3 to 7 and obeys Beer's Law over a concentration range 0.4 to 4.0 μg/ml. The molar extinction coefficient is ∿2.3 x 10^4 at 425 mμ. This method requires an extensive purification to remove cations and traces of organic impurities.[309]

The color complex of Np(V) and arsenazo III exists over a narrow pH range and was studied by Chudinov and Yakovlev.[310] A method with the green-colored complex of Np(V) and chlorophosphonazo III was also developed by these workers.[311] Chemical separation or masking agents are required for a number of elements. Chudinov has studied spectrophotometrically the interaction of 12 organic dyes of different types with NpO_2^+.[312] He concluded that the most promising reagents for pentavalent neptunium are 1-(2-pyridylazo) resorcinol (PAR), arsenazo III, and chlorophosphonazo III. With PAR, the molar extinction coefficient is ∿4.3 x 10^4 at 510 mμ.

C. CONTROLLED POTENTIAL COULOMETRY

Determination of Neptunium Concentration. Alpha counting is generally superior to coulometry for determining less than a few micrograms of Np; however, controlled potential coulometry is an accurate and precise method for determining Np above the 10-μg level.[313] The electrolysis cell contains a platinum electrode at which the Np(V/VI) couple is titrated in 0.5M H_2SO_4. First, the Np is oxidized to Np(VI) with Ce(IV), the Np(VI) and Ce(IV) are electrolytically reduced to Np(V) and Ce(III), and then Np(V) is coulometrically oxidized to Np(VI). The integrated current in the last step is used to calculate the concentration of Np. The standard deviation ranged from 6% for 7 µg to 0.05% for about 1 mg of Np. As little as 2 µg was detected. Elements which significantly interfere are Au, Pt, Hg, Tl, and Cl ; Pu and Pd cause only slight interference. Stromatt's method was used successfully with a gold electrode instead of a platinum electrode to eliminate the $Pt/Pt(OH)_2$ reaction reported by Fulda.[314] Fulda obtained a precision of ±0.6% for 6 mg of Np. In another application of Stromatt's method, the precision was 0.1% (n = 8) for 9 mg of Np. Also, Buckingham[315] demonstrated a coefficient of variation for the coulometric method of ±0.8% for neptunium oxide and ±1.1% (n = 11) for neptunium nitrate solutions. Delvin and Duncan[316] used the same method in the presence of nitrate with H_2SO_4 electrolyte. Plock and Polkinghorne[317] used coulometry to analyze solutions of dissolved alloys for both U and Np without prior chemical separation. Propst[318] has reported a coulomteric method for Np using a conducting glass electrode in a thin-layer electrochemical cell. Organic contaminants interfered and were removed by bisulfate fusion before coulometry.

Determination of Oxidation States. This method applies to the (IV), (V), and (VI) states and was reported by Stromatt.[319] The analysis depends on the fact that Np(IV) is not oxidized, nor is Np(V) reduced at a significant rate at a platinum electrode in 1M H_2SO_4 electrolyte. The procedure is: (1) a potential is applied at the controlled potential electrode to reduce Np(VI) to Np(V); (2) Np(V) is electrolytically oxidized to Np(VI); (3) Ce(IV) is added to oxidize Np(IV) to Np(VI); (4) excess Ce(IV) and Np(VI) are electrolytically reduced to Ce(III) and Np(V); and (5) Np(V) is electrolytically oxidized to Np(VI). Np(VI) is determined in the first step. The difference between the integrated currents for the first and second titrations corresponds to Np(V), and the difference between the integrated currents for Step 5 and Step 2 corresponds to Np(IV).

Determination of Oxidation-Reduction Potential. The potential for the Np(V)/(VI) couple was measured in sulfuric, perchloric, and nitric acids with a platinum electrode.[92] The potential in HCl was not obtained because of reduction of Np(VI) by chloride. The inability of the method to measure irreversible couples, such as Np(IV)/(V), is a serious limitation. The potential for the Np(III)/(IV) couple was obtained with a mercury electrode.

D. POLAROGRAPHY

Alternating current polarography with square-wave or pulse polarographs has been applied to determine small concentrations of Np. Slee and others[128] have reported an analytical method with square-wave polarography to determine Np in Pu after preliminary separation from Pu by TTA extraction. Np is back-extracted from the TTA into 10M HNO_3. After several evaporations with nitric acid and wet ashing with mixed nitric and perchloric acid (to oxidize organic material), the final perchlorate residue is taken up in 1 ml of HCl. 2 ml of 5N hydroxylamine hydrochloride is added, and the solution is evaporated to reduce the volume to 0.5 ml. Then, 0.5 ml of 1M EDTA is added; the solution is adjusted to pH 5.5 to 6.5 with several drops of ammonia and diluted to 5 ml. Exactly 2 ml of the dilution are transferred to a polarographic cell and sparged with nitrogen. The Np peak is recorded at about -0.8V against the mercury pool electrode on the square-wave polarograph. Then an accurately measured aliquot of a standard Np solution prepared in EDTA is added to the cell, and the Np concentration in the original solution is calculated from the increase in peak height. Interference from the oxidation of chloride ions is decreased by adding EDTA to shift the half-wave potential of the Np peak. The potential for the reduction of the EDTA complex is about 700 mV more negative than for the reduction of neptunium ions; therefore, the peak is shifted well away from the anodic oxidation of chloride ions and is well defined. The authors report precision of ±2% and ±10% for concentration ranges of 500 and 25 ppm, respectively.

Cauchetier *et al.*[290] reported a method which makes use of the Np(IV)-Np(III) couple for determining Np in solutions of irradiated nuclear fuels and ^{237}Np targets. Np is reduced electrolytically to Np(IV), and the polarogram is taken. An aliquot of standard Np is added to the cell, and the procedure is repeated. The method was used to analyze solutions with a Np content >20 mg/ℓ containing Pu, U, Fe, Ni, Cr, and fission products, with a precision of ∿2%.

Polarography and other methods were used to compare the chemistry of U, Np, and Pu by Kraus, *et al.*[321] Jenkins used a manual polarograph to study the nature and stability of EDTA complexes with Np(III) and Np(IV).[322] Np(III) and (IV) were studied in chloride and perchlorate media by Hindman and Kritchevsky.[323]

Np was included in a review of electrochemistry of the actinides by Milner.[324] The sulfate complexes of Np(IV) were studied polarographically by Musikas.[97]

E. TITRATION

Potentiometric. 10- to 100-mg quantities of Np were determined by redox titration.[325] Ce(IV) is used to titrate Np(V) to Np(VI), and iron(II) perchlorate was used to titrate Np(VI) to Np(V). The methods can be used successively on the same aliquot of sample if HNO_3 is present (to give the required ceric oxidation potential) and chloride ion is absent (it would be oxidized to chlorine).

Stoppered weight burets were used for adding reagents, and a platinum-calomel system was used to detect the end points. Relative standard deviations for a single determination were 0.15% for ferrous titers and 0.59% for ceric titers.

Complexometric Titration. Np(IV) is titrated with a solution of EDTA at pH 1.3 to 2.0 with xylenol orange as indicator. The reaction of Np(IV) with EDTA is stoichiometric and the color changes from bright rose to light yellow at equal molar concentrations. The error for determining 1 to 4 mg of Np is 1 to 2%. Np(IV) is produced in 0.01 to 0.05M HCl with hydroxylamine reductant. Fe^{3+}, Zr^{4+}, Pu^{4+}, Th^{4+}, and ascorbic acid interfere. Reasonably large amounts of alkali, alkaline-earth, rare earth elements, Zn^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, and $UO_2{}^{2+}$ do not interfere.[326]

Chronopotentiometric. There has been little analytical chemistry done in molten salts, and so far the only useful results have been obtained from electroanalytical methods. Np(IV) was determined quantitatively in molten LiCl-KCl eutectic at 400 to 500°C with an accuracy of ±4%.[327]

F. EMISSION SPECTROMETRY

Np has a line-rich emission spectra with the more-sensitive lines at 4154.5, 4098.8, 3999.5, and 3829 Å.[328,329] Other methods are more useful for quantitative determination of Np than the spectrochemical method, which is generally used only for analyses of impurity elements. To prevent interference by the numerous spectral lines of Np, a chemical separation is usually made, or the carrier distillation method with gallium sesquioxide is used.

A quantitative method for determination of impurities in Np is reported by Wheat[232] (Procedure 23, page 200). The method is a modification of one reported by Ko for Pu.[330] The neptunium oxide is dissolved in HNO_3, reduced to the tetravalent state with hydrazine and sulfamic acid, and then sorbed on anion exchange resin. Two cycles of anion exchange are used to separate Np. The second effluent is evaporated to dryness to decompose hydrazine. The residue is made water soluble with aqua regia, evaporated to dryness, and dissolved in 6M HCl containing Co as the internal standard for the spectrographic analysis. The coefficient of variation for a single determination of a number of common metal ion impurities ranges from 9 to 24%. For a 50-mg sample, the minimum concentration of impurities that can be analyzed is 0.5 to 10 ppm.

G. GRAVIMETRIC METHODS

Precipitation of Np for gravimetric determination is not a useful method. If other ions which form insoluble salts are present, these must be separated first. When the solution is relatively free from other ions, alpha counting or some other method is usually more rapid and offers less health hazard. A number of Np compounds have low solubilities in aqueous solution; however, indefinite stoichiometry or necessity for calcination to the oxide limits the usefulness of direct gravimetric determination. Often the small quantity or low concentration of neptunium precludes the use of gravimetry.

Hydroxide. Np(IV) is completely precipitated from mineral acid solution by Na, K, or NH_4OH as the hydrated hydroxide or hydrous oxide. The brown-green gelatinous solid that forms is difficult to filter but is easily redissolved in acids. The solubility in 1M $NaNO_3$ - 1M NaOH is <0.1 mg/ℓ. Np(V) "hydroxide" is green; it is somewhat more soluble in a sodium nitrate-sodium hydroxide solution. Np(VI) is precipitated as dark brown $(NH_4)_2Np_2O_7\cdot H_2O$ with excess NH_4OH from mineral acid solution.[35]

Fluorides. Np(IV) is precipitated from mineral acid solution as green hydrated NpF_4 by adding excess HF. The compound dissolves readily in reagents which complex fluoride ion, such as Al^{3+} or boric acid. When K or NH_4F is used as the precipitant, the green double salt KNp_2F_9 or NH_4NpF_5 is produced.

Peroxides. Purple Np(IV) peroxide is precipitated when a large excess of H_2O_2 is added to a strongly acidic solution of Np(IV), Np(V), or Np(VI), because peroxide rapidly reduces Np to the tetravalent state. Reduction is much slower in dilute mineral acid. Np(IV) peroxide always incorporates some of the anion into the crystal and may have different crystalline forms depending on the acid concentration of the supernatant. Np is separated from many cations by precipitation of neptunium peroxide.[36]

Oxalates. Green Np(IV) oxalate hexahydrate is precipitated from dilute acid solution with oxalic acid. Because quantitative precipitation is not attained for Np(V) or Np(VI), a reducing agent, such as ascorbic acid, is used to ensure complete reduction to Np(IV). A granular, easily-filtered precipitate is produced under controlled conditions.[40] $(NH_4)_4Np(C_2O_4)_4$ and $NpO_2HC_2O_4$ have also been precipitated from Np(IV) and Np(V) solution.

Iodate. Light tan Np(IV) iodate is precipitated from dilute mineral acid by adding excess potassium iodate.[35]

Carbonate. The double carbonate of Np(V), $KNpO_2CO_3$, is produced by adding potassium bicarbonate to a dilute acid solution of Np(V), until the resulting solution is 0.1M in bicarbonate. The solution is heated at 90°C for 3 to 4 hours to produce the light tan double salt.[43]

Acetate. Sodium neptunium(VI) dioxytriacetate, $NaNpO_2(C_2H_3O_2)_3$, is pink by transmitted light and pale green by reflected light. Np is oxidized in dilute acid with $KBrO_3$ at 90°C to NpO_2^{2+}. Sodium neptunylacetate is precipitated by adding an equal volume of 4M $NaNO_3$ - 4M $NaC_2H_3O_2$ solution.[38]

Phosphate. Np(IV) di(monohydrogenphosphate) hydrate $[Np(HPO_4)_2 \cdot XH_2O]$, a pale-green gel, is precipitated by adding phosphoric acid to a dilute acid solution of Np(IV).[35]

H. SPOT TESTS

Spot tests for determining oxidation states of Np and Pu were obtained for 36 organic and inorganic reagents commonly used in paper chromatography.[331] The tests were made on Whatman No. 1

paper which was treated with 2M HCl in descending chromatography for 12 hours to remove traces of Fe, Mg, and Ca. The paper was treated with two successive 24-hour washings by migration with twice-distilled water. Because of hazards of these alpha emitters and the high sensitivity of radioactive measurement, very sensitive spot tests with an identification limit of less than 1 μg of actinide were selected. Observations were made in white and ultraviolet light for both acidic and basic media with each reagent. First the acidic media was allowed to dry; then ammonia was added and evaporated. A standard scale of colors was used for comparison. In most cases, a color reaction was obtained with less than 1 μg of actinide, but the color was the same for all oxidation states of both Np and Pu.

Diphenylcarbazide gives a color reaction with Np(VI) but not Np(V); however, Pu(VI) gives the same color reaction. In acid solution, sodium alizarinsulfonate or arsenazo give a color with Pu(IV) and Pu(VI), but no color with Np(V) and Np(VI). Four of the reagents, chromazural-S, arsenazo, 4,2-pyridyl-azo-resorcinol, and pyrocatechol, give fluorescent spots under ultraviolet light with all oxidation states of Pu and Np; kojic acid fluoresces only with Pu(III).

The oxidation states of Np and Pu were characterized from color reactions on chromatograms and electropherograms.[256]

The tetravalent states give characteristic colors with alizarin, arsenazo-I, and thorin-I; however, diphenylcarbazide was used for the hexavalent state.

I. MASS SPECTROMETRY

Subnanogram quantities of ^{237}Np were determined with a mass spectrometer by Landrum, et al.[332] The instrument was a double-focusing, 60-degree sector type, with a 12-inch radius. The source chamber contained a tantalum filament (from which the sample was volatilized) and a rhenium filament (on which gaseous species were ionized). After mass analysis, the ionized Np atoms were collected in a Faraday cup. The method uses isotopic dilution with ^{235}Np or preferably ^{236m}Np. This method is much more rapid than neutron activation, and the sensitivity is at least ten times greater. The standard deviation for 0.1 to 0.5 nanogram of Np was 1 to 2%. Isotope dilution with ^{239}Np has also been applied to determine ^{237}Np.[333]

Spark source mass spectrometry is useful for less quantitative measurements of many elements including Np; however, it is most often used for determining cationic impurities in Np and other actinides.[334]

J. X-RAY FLUORESCENCE SPECTROMETRY

The ease of production and simplicity of the X-ray spectra produced for elements of high atomic number allow mixtures of actinides to be analyzed by X-ray fluorescence spectrometry with considerable precision and accuracy. Either solid or liquid samples can be analyzed by the internal standard technique. Mixtures of U, Np, and Pu were analyzed at ratios as high as 1:1:1; results were comparable to standard counting. U, Np, and Pu in any combination of two elements were analyzed at ratios as high as 1:8 without seriously affecting accuracy. However, at ratios of 1:10, low results of 5 to 7% were obtained for the element present at lower concentration. The principal L series X-ray emission lines of elements with atomic numbers 92 through 96 are given by Kofoed.[335] Novikov *et al.*[336] used X-ray fluorescence to determine microgram amounts of Np in pure solutions or in solutions containing Pu. The sensitivity was 0.2 to 0.3 μg of Np. The relative standard error in determining 1 μg Np was 5%, and the analysis, including sample preparation, required 30 to 40 minutes. The $K\alpha_1$ and $K\alpha_2$ X-ray energies for Np, Pu, and Am were measured by Nelson, et al.[337]

K. NEUTRON ACTIVATION

Neutron activation was used to determine subnanogram quantities of ^{237}Np.[332] The unknown sample was irradiated with another Np sample of known Np content and comparable weight in the same average time-integrated neutron flux. After irradiation, the ^{238}Np was determined by gamma spectrometry. Conventional radiochemical separation methods were used. Isotopic dilution with mass quantities of ^{237}Np served to determine chemical recovery.

L. OTHER METHODS

Gamma counting ^{239}Np, the decay product of ^{243}Am, has been used to determine ^{243}Am in solutions containing large amounts of Cm. The ratio of the equilibrium amount of ^{239}Np to the amount of ^{243}Am was determined by separating (by TTA extraction) and analyzing (gamma counting) ^{239}Np from samples in which ^{243}Am and ^{239}Np were known to be in secular equilibrium. The method was compared to determining ^{243}Am by the isotope dilution-mass spectrometric method. The precision of the method was 7% at the 95% confidence limits (n = 16) for sample aliquots that contained 0.1 to 5 μg of ^{243}Am.[338] A similar approach was reported by Lebedev *et al.*[202]

^{233}Pa, the daughter of ^{237}Np decay, has more-abundant gamma rays, which are easier to measure than ^{237}Np. Cofield[339] used this as a basis for determining ^{237}Np-^{233}Pa in human lungs by *in vivo* gamma spectrometry with a large NaI scintillation detector in a low-background counting chamber.

The neutron capture cross section of ^{238}U was measured by analysis of ^{239}Np produced [$^{238}\text{U}(n,\gamma)^{239}\text{U} \xrightarrow{\beta^-} {}^{239}\text{Np}$]. The procedure uses isotope dilution with ^{237}Np to determine chemical yield, TTA extraction for separation of Np and U, electrodeposition for

Np source preparation, and gamma counting[340] for analyses.

Characteristic isomer shift ranges have been measured for several valence states of Np using Mössbauer resonance of the 59.54-keV gamma ray of ^{237}Np. They extend from about -6.8 cm/sec to +5 cm/sec for the individual oxidation states of +7 to +3 and are clearly defined.[341,342] The isomer shift characteristic of each oxidation state is useful for study of bonding in Np compounds. Dunlop and Kalvius have also made significant contributions.[341a]

IX. RADIOACTIVE SAFETY CONSIDERATIONS

The Np isotopes emit high-energy alpha particles, medium-energy beta particles, and low-energy gamma rays. The tendency of Np to concentrate in the bones with a biological half-life of 7.3 x 10^4 years makes ingestion the primary hazard to personnel. Studies of the distribution of ^{239}Np in animal tissue showed 60 to 80% of the Np was deposited in the bones.[131] Studies have also been made of the inhalation, pulmonary absorption, gastro-intestinal absorption, and short-term retention of ^{237}Np in rats.[343] Because ^{237}Np ($T_{1/2} = 2.14 \times 10^6$y) is the only isotope of Np which is available in weighable amounts, it presents the only serious hazard. The radiation hazard is small due to the low specific activity of ^{237}Np and the low energy of its gamma radiation. Table 25 lists body burdens and maximum permissible concentrations of ^{237}Np and ^{239}Np for continuous occupational exposure.[344] In handling large quantities of ^{237}Np, standard gloved-boxes maintained at a negative air pressure with respect to the laboratory air[345] should be considered for containment.

Criticality is no problem for ^{237}Np because the bare critical mass for a sphere of density 20.45 g/m^3 is 68.6 kg.[346]

TABLE 25

HEALTH HAZARD DATA FOR NEPTUNIUM ISOTOPES[344]

			Maximum Permissible Concentration for 40-hr Week (μCi/cc)	
Isotope	Organ	Max Permissible Body Burden (μCi)	Water	Air
^{237}Np (sol.)	Bone	0.06	9×10^{-5}	4×10^{-12}
	Kidney	0.1	2×10^{-4}	7×10^{-12}
	Total Body	0.5	4×10^{-4}	2×10^{-11}
	Liver	0.5	6×10^{-4}	2×10^{-11}
	GI(LLI)		9×10^{-4}	2×10^{-7}
(insol.)	Lung			10^{-10}
	GI(LLI)		9×10^{-4}	2×10^{-7}
^{239}Np (sol.)	GI(LLI)		4×10^{-3}	8×10^{-7}
	Bone	30	100	4×10^{-6}
	Kidney	40	200	7×10^{-6}
	Total Body	70	300	10^{-5}
	Liver	100	500	2×10^{-5}
(insol.)	GI(LLI)		4×10^{-3}	7×10^{-7}
	Lung			2×10^{-6}

X. COLLECTION OF PROCEDURES

A. INTRODUCTION

The procedures are divided into three categories:

- Procedures for extraction, extraction chromatography, ion exchange, and carrier precipitation or some combination of these methods with highly radioactive samples. Most of these methods utilize alpha counting (alpha pulse height analysis), gamma spectroscopy, or possibly isotopic dilution. The method of determination is not detailed for all procedures.
- Procedures used for environmental and biological samples.
- Miscellaneous procedures for quantitative determination, including absorption spectrometry of color complexes, coulometry, and gamma spectrometry.

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Procedure 1. Separation of Np by TTA Extraction

F. L. Moore[148]

Outline of Method

Np is separated from fission products, U, Pu, transplutonium elements, and nonradioactive elements by extraction into thenoyltrifluoroacetone (TTA). After separation, an aliquot is suitably prepared for either alpha counting of ^{237}Np or gamma counting of ^{239}Np.

Reagents (C.P. Chemicals)

- HCl, 1M
- HNO_3, 10M
- Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) solution, ∿5M. Dissolve 69.5 g of reagent in 200 ml of distilled water and warm if necessary for dissolution.
- FeCl , ∿2M. Dissolve 40 g of reagent-grade $FeCl_2 \cdot 4H_2O$ tetrahydrate in 100 ml of 0.2M HCl. Store in a dark glass stoppered bottle.
- 2-Thenoyltrifluoroacetone-xylene solution, ∿0.5M. Dissolve 111 g of compound in one liter of reagent-grade xylene.

Equipment

- Extraction vessel with mixing device
- Hot plate
- Micropipets
- Stainless steel counting plates
- Counting plate heater
- Meeker burner

- Asbestos board
- Sample carrier
- Alpha proportional counter (or gamma counter)

Pretreatment

If interferences may be present in solution with the Np tracer, Np is adjusted to Np(IV) and carried on ∿1 mg of La precipitated as the hydroxide. The hydroxide precipitates are dissolved in 1M HNO_3, and LaF_3 is precipitated to carry Np(IV). The fluoride precipitates are dissolved in a few drops of 2M $Al(NO_3)_3$ and dilute HCl. While the extraction of Np(IV) from HNO_3 is usually very effective, HCl should be used whenever possible because there is a greater tendency to form extractable Fe(III) ion in the HNO_3 system.

It is desirable to measure the chemical yield if much chemistry is employed. A ^{237}Np spike is useful for determining ^{239}Np recovery; ^{239}Np may be used for determining ^{237}Np yield.

Procedure

1. Pipet a suitable aliquot of the sample into a separatory funnel or other extraction vessel.
2. Adjust the solution to 1M HCl - 1M $NH_2OH \cdot HCl$ - 0.25M $FeCl_2$. KI may be used as a reductant in place of $FeCl_2$.
3. Mix the solution for 5 min at ambient temperature.
4. Add an equal volume of 0.5M TTA and mix for 10 min.
5. Allow the phases to separate; then remove the aqueous phase and discard it.

6. Wash the organic phase by mixing with an equal volume of 1M HCl for 3 min. Allow the phases to separate and discard the aqueous wash.

7. Strip the Np from the organic phase by mixing with an equal volume of 10M HNO_3 for 2 min. (If the aqueous strip is too high in gamma activity for alpha measurement, the last traces of radioactive Zr and Pa may be removed by a 5 min re-extraction of the 10M HNO_3 strip solution with an equal volume of TTA.

   Ordinarily, the small amount of Fe in the TTA causes negligible self absorption in counting, and the TTA extract is mounted directly on the counting plate. If Fe is a problem, excellent separation is attained by stripping the Np into 10M HNO_3.

8. A suitable aliquot of the TTA extract or the 10M HNO_3 strip is prepared by conventional methods for either alpha counting for ^{237}Np or gamma counting for ^{239}Np.

Procedure 2. Separation of Np by TTA Extraction

R. S. Dorsett[151]

Outline of Method

Np is determined in the presence of Pu, U, fission products, and other alpha-emitting nuclides by extraction into thenoyltrifluoroacetone (TTA) followed by alpha counting of the TTA. The analysis consists of three parts: (1) the pre-extraction step in which acid and oxidation state are adjusted, (2) the extraction in which Np is quantitatively extracted into TTA, and (3) the mounting and alpha counting of the TTA extract. When additional purification is required, the Np is stripped from the TTA, acid and oxidation state are adjusted, and a second extraction is done. The precision of the method is dependent on the type and quantities of interferences. The interferences caused by sulfate, phosphate, fluoride, and oxalate ions are eliminated by addition of $Al(NO_3)_3$ which complexes these ions. A coefficient of variation of 2% is obtained with relatively pure solutions.

Reagents

- Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), 1M, is prepared by dissolving 69.5 g of C.P. grade compound and diluting to one liter.
- ($NaNO_2$), 1M, is prepared by dissolving 69 g of C.P. grade compound and diluting to one liter.
- 2-Thenoyltrifluoroacetone-xylene, 0.5M, is prepared by dissolving 111 g of the compound in one liter with C. P. xylene.

- Ferrous sulfamate [$Fe(NH_2SO_3)_2$], 2M, is prepared by dissolving iron powder in an excess of sulfamic acid with minimum heating. The solution is filtered after dissolution.
- Aluminum nitrate [$Al(NO_3)_3$], 2M, is prepared by dissolving 750 g of C.P. grade compound and diluting to one liter.
- (HNO_3) nitric acid solutions are prepared as required from C.P. grade stock.
- Collodion solution, 0.5 mg/ml, is prepared by dissolving 500 mg of collodion in one liter of 1-to-1 ethyl alcohol-ethyl ether.

Equipment

- Centrifuge cones (with caps)
- Vortex mixer
- Micropipets
- Stainless steel counting plates
- Counting plate heater
- Meeker burner
- Asbestos board
- Sample carrier
- Alpha proportional counter
- Alpha pulse height analyser

Pretreatment

Fluoride method. When it is not known what impurities are present in the solution, Np(Pu) can be carrier precipitated with $La(OH)_3$. The hydroxide is dissolved in HNO_3, and La is reprecipitated as the fluoride. The fluoride precipitate containing the actinides and lanthanides is dissolved in $Al(NO_3)_3$ and dilute HNO_3, and this solution is extracted with TTA.

Np in Tributylphosphate (TBP). If Np is present in TBP or other organic extractants, it is stripped with dilute HNO_3 (∿0.1M) and then analyzed by the procedure.

Separation of Np and U. Acid control is very important for this separation. In the analysis of low-level Np solutions that contain large quantities of U, the problem is complicated because ^{237}Np and ^{234}U have the same alpha energies. Also, the specific activity of ^{234}U is 10 times greater than ^{237}Np. An accurate analysis is assured by (1) close control of the extraction acidity, (1 ±0.1M), (2) a double extraction cycle, and (3) in extreme cases, a fluorophotometric determination of U content of the final TTA extract.

Procedure

1. Pipet 10^3 to 10^4 dis/min alpha of ^{237}Np into a 15-ml centrifuge cone.
2. Add sufficient water or HNO_3 so that at the end of Step 3 the acid is 1M. Mix.
3. Add 1 ml of 2M $Fe(NH_2SO_3)_2$ solution. Mix and let the solution stand for 5 min.
4. Add 3 ml of 0.5M TTA in xylene, and mix for 5 min in a vortex mixer.
5. Allow the phases to separate; then remove the aqueous phase and discard it. Add 4 ml of 1M HNO_3 to the organic phase, and mix for 2 min in the vortex mixer.

6. If the alpha activity due to Pu and U is $<10^3$ dis/min, proceed to Step 9. If the alpha activity is $>10^3$, proceed to Step 7.

7. Remove the aqueous phase from Step 5 and discard it. Add 1 ml of 8M HNO_3 to the organic phase, and mix for 5 min in the vortex mixer.

8. Discard the organic phase. Repeat Steps 2 through 5.

9. Turn on the counting plate heater, heat to 175° to 190°C, and place a clean stainless steel counting plate on the heater.

10. Pipet an aliquot from the organic phase that contains $\sim 10^3$ dis/min Np, and add it dropwise to the plate. Rinse the pipet twice with xylene, and add both rinses to the plate. Heat the plate until dry.

11. Heat the plate over a Meeker burner flame until the plate is a dull red color. Place the plate on an asbestos board to cool.

12. When the plate is cool, add 1 drop of collodion to cover the surface. Allow the plate to dry several minutes before counting.

Procedure 3. Determination of ^{239}Np in Samples Containing U, Pu, and Fission Products

H. L. Smith[347]

Introduction

The procedure for determining ^{239}Np affords excellent decontamination from milligram quantities of U, the fission products obtained from 10^{13} fissions, and Pu. The decontamination factor for Pu is about 10^4.

An initial fuming with H_2SO_4 is required to ensure exchange between the ^{237}Np tracer employed and ^{239}Np, and also to complex U(VI). If the sample is a dissolved U foil, HNO_3 must be added before the fuming step to convert U to the VI oxidation state. Np(IV) and (V) are carried by LaF_3 precipitations in the presence of Zr and Sr holdback carriers. The precipitations provide decontamination from the activities of Zr and Sr as well as from U. LaF_3 scavenging with Np in the VI oxidation state decontaminates from the lanthanides and partially from Pu.

The chemical yield is about 50%, and eight samples can be analyzed in one day.

Reagents

- La carrier: 5 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
- Sr carrier: 10 mg Sr/ml, added as $Sr(NO_3)_2 \cdot 4H_2O$ in H_2O
- Zr carrier: 10 mg Zr/ml, added as $ZrOCl_2$ in H_2O
- ^{237}Np standard solution: 5,000 to 10,000 counts/(min-ml) in 2 to 4M HCl or HNO_3

- HCl: 0.1M; 2M; concentrated
- H_2SO_4: concentrated
- HNO_3: concentrated
- H_3BO_3: saturated solution
- HF: 1:1 H_2O and concentrated HF
- HI-HCl: 1 ml 47% HI + 9 ml concentrated HCl
- $HF\text{-}HNO_3$: equal parts by volume of 2M solutions
- $NH_2OH \cdot HCl$: 5M (or saturated)
- $KMnO_4$: 10% solution
- NH_4OH: concentrated
- "Dowex" 1-X10 anion exchange resin:
  100 to 200 or 200 to 400 mesh, slurry in H_2O*

Procedure

Step 1. Pipet 1 ml of ^{237}Np standard into a clean 125-ml erlenmeyer flask, and then pipet in the sample. Wash down the sides of the flask with a little H_2O, add 10 drops of concentrated H_2SO_4,** and evaporate nearly to dryness on a hot plate. (No harm is done if the solution is permitted to evaporate to hard dryness.)

Step 2. Dissolve the residue by boiling briefly in a minimum of 2M HCl. Transfer the solution to a clean 40-ml Pyrex centrifuge

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* The resin is supplied by the Bio-Rad Laboratories, Richmond, Calif., who purify and grade the resins manufactured by the Dow Chemical Co.

** If the sample has been obtained from more than the equivalent of 50 mg of soil, do not add any H_2SO_4 since $CaSO_4$ will precipitate and carry Np to some extent.

tube; wash the flask once with H_2O, and transfer the washings to the tube. The volume of solution should be 5 to 10 ml. (Ignore any small residue.)

Step 3. Add 5 drops of La carrier and 3 drops of Zr holdback carrier. Add 2 drops of $NH_2OH{\cdot}HCl$ for each ml of solution, stir, and let stand for a few minutes. Add HF dropwise until the yellow color of the solution disappears and the solution becomes cloudy (LaF_3). Centrifuge. Remove and discard the supernate. Wash the precipitate with 1 to 5 ml of HF-HNO_3.

Step 4. Dissolve the precipitate by slurrying with 3 drops of saturated H_3BO_3 and adding 3 drops of concentrated HCl. (Ignore any small residue.) Add 3 ml of 2M HCl and precipitate $La(OH)_3$ by adding about 1 ml of concentrated NH_4OH. Centrifuge, and discard the supernate. Wash the precipitate by boiling it briefly with several milliliters of H_2O. Centrifuge and discard the supernate.

Step 5. Dissolve the precipitate in about 5 ml of 2M HCl. Reprecipitate LaF_3 by adding 10 drops of HF; centrifuge, and discard the supernate. Wash the precipitate with 1 ml of HF-HNO_3. If the precipitate volume is greater than 0.2 ml, repeat the hydroxide and fluoride precipitations until the volume of LaF_3 precipitate does not exceed 0.2 ml.

Step 6. Dissolve the fluoride precipitate in 1 drop each of saturated H_3BO_3 and concentrated HNO_3. Add 10 drops of $KMnO_4$, and allow to stand for 5 min. Add 2 drops of HF, and allow the solution to stand for a few minutes. Centrifuge, and transfer the supernate to a clean centrifuge tube. Wash the precipitate with 1 ml of HF-HNO_3, centrifuge, and add the supernate to the previous one. Discard the precipitate.

Step 7. Add 2 drops of La carrier to the solution, stir, centrifuge, and transfer the supernate to a clean centrifuge tube. Wash the precipitate with 1 ml of HF-HNO_3, add the washings to the previous supernate, and discard the precipitate.

Step 8. Add 5 drops of $NH_2OH \cdot HCl$ and 2 drops of Zr carrier, and let stand for a few minutes. Add 2 drops of La carrier, stir well, centrifuge, and discard the supernate. Wash the precipitate with 1 ml of HF-HNO_3, centrifuge, and discard the supernate.

Step 9. Repeat Steps 6 and 7.

Step 10. Add 5 drops of $NH_2OH \cdot HCl$ and 2 drops of Sr hold-back carrier, and let stand for a few minutes. Add 2 drops of La carrier, stir well, centrifuge, and discard the supernate. Wash the precipitate with 1 ml of HF-HNO_3, centrifuge, and discard the supernate.

Step 11. Dissolve the precipitate with 1 drop of saturated H_3BO_3 and 10 drops of concentrated HCl. Pass the solution through a "Dowex" 1-X10 anion exchange column, 3 cm × 3 mm, and wash the column with 1 ml of concentrated HCl. The Np, now in the IV oxidation state, is sorbed on the column. If necessary, remove Pu from the column with HI-HCl.* Add approximately 1 ml of 0.1M HCl to the reservoir of the column. Discard the first 2 drops that come off the column, and then collect approximately 0.25 ml in a clean, dry centrifuge tube. Use no air pressure when eluting the Np. Pick up the solution in a transfer pipet and evaporate by stippling on a 2.5 cm Pt plate. If possible keep the deposit within a 1.3 cm circle. Flame the sample to dull red in a burner, mount with double-sided Scotch tape in the center of an Al plate, and α- and β-count on 3 successive days.**

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* The procedure should remove 95% of the Pu initially present in the sample. If, at this point, there remains enough Pu to interfere with the determination of the Np yield, that is, more than 1% of the Np tracer, Pu may be removed more efficiently in the following way: Allow 1 ml of HI-HCl solution to drip through the column with no added pressure. Wash the column with several ml of concentrated HCl, and discard the effluent, which contains Pu in the III oxidation state, and proceed with the rest of Step 11. One elution step such as the one just described removes 99.5% of the Pu.

** Alpha-counting: The sample is counted in a 7.5 cm i.d. methane-flow proportional counter with a loop anode, operated in the α-plateau region. Beta counting: The sample is placed on the third shelf of a methane-flow proportional counter with a window thickness of 4.8 mg/cm^2. An absorber (about 5 mg Al/cm^2), placed on the first shelf, stops soft betas and alphas. The individual counts are corrected to t_0, using a half-life of 56.6 hr, and are then averaged.

Procedure 4. Determination of Np

J. Landrum[348]

Outline of Method

After the sample is dissolved, the volume is reduced by evaporation. Np and other hydroxides are precipitated with 50% NaOH to separate Al. The precipitate is dissolved in concentrated HCl, and Np is separated from many impurities by chloride anion exchange. Further separation is attained by performing in order: TTA extraction, cupferron extraction, and chloride anion exchange. The plate for counting is prepared by electrolysis.

Reagents

- 50% NaOH
- La carrier, 5 mg La/ml (as $La(NO_3)_3 \cdot 6H_2O$ in H_2O)
- Concentrated HCl
- 55% HI solution
- HCl gas
- Bio-Rad AG 1 x 8, 50 to 100 mesh resin
- 10M HCl - 0.5M HI
- 5M HCl
- 1M HCl
- 0.4M Thenoyltrifluoroacetone (TTA) in xylene
- 6% Cupferron
- $CHCl_3$
- Saturated NH_4Cl solution
- Concentrated NH_4OH

Procedure

1. To the sample add about 3 x 10^5 alpha counts/min ^{237}Np standardized tracer. Add ∿2 mg of La^{3+} carrier and 2 ml 55% HI (no inhibitor), and boil the solution until the volume has been reduced to about 10 ml. Transfer to a 40-ml cone. Add sufficient 50% NaOH to dissolve any Al that may be present. Heat in a water bath, centrifuge, and discard the supernatant liquid.

2. Wash the precipitate with 10 ml of 10M NaOH. Again heat, centrifuge, and decant. Wash the precipitate thoroughly with 30 ml of H_2O (to remove most of the Na^+ salts), centrifuge, and decant.

3. Dissolve the precipitate in 10 ml of concentrated HCl. Add 2 drops of 55% HI (no inhibitor).

4. Cool and saturate the solution with HCl gas. (If white salts precipitate, centrifuge them and decant.) Pass the solution through a "Dowex" 1-X8, 50 to 100 mesh column, 6 mm I.D. by 11 cm, pretreated with concentrated HCl - 0.5M HI. Discard the effluent. If ^{236}Pu is to be measured, save the effluent and note the time of Np-Pu separation.

5. Wash the column with 15 ml of 10M HCl - 0.5M HI, and collect the wash with the effluent.

6. Elute the Np with three 5-ml portions of 5M HCl, and allow a minute or so between elutions. Collect the eluate in a 125-ml Erlenmeyer flask.

7. Add 2 drops HI, and boil to near dryness. Transfer to a 40-ml cone with 1M HCl. Add 1M HCl to make approximately 15 ml.

8. Add 10 ml of 0.4M TTA in benzene, toluene, or xylene, and equilibrate for 30 min. Separate the layers by centrifuging, and transfer the organic layer into a clean 40-ml cone. Repeat the extraction with 5 ml of 0.4M TTA for 10 min. Combine the organic fractions. Discard the aqueous fraction.

9. Wash the organic with 5 ml of 1M HCl for 2 min. Centrifuge, and discard the aqueous.

10. Back-extract the Np by equilibrating the TTA with 2 ml of 9M HCl for 10 min. Separate the layers as before, and transfer the aqueous to a clean cone. Repeat the extraction with 1 ml of 9M HCl for 5 min. Combine the aqueous phases.

11. To the combined aqueous phases, add 2 drops of 6% cupferron and 5 ml of $CHCl_3$. Equilibrate for 30 sec. Discard the $CHCl_3$ (lower layer). Add 5 ml of $CHCl_3$ and repeat the extraction. Again discard the $CHCl_3$. This step is designed to remove troublesome Nb activity.

12. Transfer the solution to a 125-ml Erlenmeyer flask, add 1 ml concentrated HNO_3, and boil to near dryness. Add 5 ml of 9M HCl and 1 ml of concentrated formic acid. (CAUTION: The reaction between HNO_3 and formic acid may be violent if too much HNO_3 is present.) Warm the solution until the HNO_3 has been destroyed. This step oxidizes U(VI) and reduces Np(IV).

13. Add 5 ml of fresh concentrated HCl (final HCl concentration should be >10M, use HCl gas if necessary). Pass the solution through a "Dowex" 1-X8, 50 to 100 mesh, 6-mm I.D. x 5 cm column, pretreated with 10M HCl. Wash the column with 5 ml of 10M HCl. Discard the effluent and wash.

14. Elute the Np as in Step 6, but with 10 ml of 5M HCl. Collect in a 125-ml Erlenmeyer flask.

15. Repeat Steps 7, 8, 9, and 10. (TTA extraction)

16. Examine on a NaI detector for gamma contamination. If the sample is radiochemically pure, plate the sample.

Electroplating

Boil the solution from Step 10 to near dryness. Add 1 ml of saturated NH_4Cl and one drop of methyl red indicator, and adjust acidity with NH_4OH and 1M HCl so that one drop of 1M HCl turns the solution red. (Volume should be 3 to 4 ml.) Transfer the solution to an electroplating cell fitted with a Pt wire anode and a 1-in.-diameter Pt disc cathode. Pass approximately 1.5 amps through the cell for 15 min.

Add 1 ml of concentrated NH_4OH to the cell while electrolysis is in progress. Continue plating for another 15 to 30 sec. Remove the solution from the cell, and check it for activity in a well counter. If appreciable activity is present, repeat the plating procedure without the addition of NH_4Cl.

Dismantle the cell, flame the Pt disc to a dull red, and alpha count for chemical yield. Gamma and beta count for ^{239}Np and ^{238}Np.

Notes

1. Using this procedure, Np is separated from solutions whose contents underwent 10^{15} fissions (one week previous) and up to one gram of dissolved soil. Gamma-ray spectroscopy showed no activities other than ^{238}Np and ^{239}Np.

2. 10 to 12 hours is required for six samples.

3. The yield for this procedure is 30 to 60%.

ocedure 5. Determination of Small Amounts of Np in Pu Metal

L. J. Slee, G. Phillips and E. N. Jenkins[320]

Outline of Method

Pu metal is dissolved in HCl. The Np (10 to 2000 ppm) is parated from Pu by TTA extraction and determined with a square-ve polarograph.

Reagents

- Distilled water
- HNO_3, analytical-reagent grade
- Hydroxyamine hydrochloride ($NH_2OH \cdot HCl$) solution, 5M
- TTA solution, 0.5M in xylene: Dissolve 28 g of 2-thenoyltrifluoroacetone (TTA) in 200 ml of pure xylene, filter, and dilute with xylene to 250 ml.
- Ferrous chloride ($FeCl_2$)
- EDTA solution: Dissolve 37 g of disodium ethylenediaminetetraacetate (EDTA) in distilled water, adjust to pH 7 with ammonia solution, and dilute to 100 ml.

Procedure

1. Weigh $\sim$300 mg of Pu metal accurately.
2. Add 5 ml of distilled water and then slowly add 0.5 ml of 10M HCl. When the reaction subsides, add 1 ml of 10M HCl and 2 ml of 5M $NH_2OH \cdot HCl$ and warm the solution.
3. Dilute to 10 ml with distilled water, add 250 mg of $FeCl_2$, allow 5 min for oxidation state adjustment.
4. Transfer quantitatively to an extraction vessel, and add 5 ml of 0.5M TTA. Stir for 10 minutes, allow the phases to separate, and remove the organic phase.

5. Repeat the extraction with 5 ml of 0.5M TTA.

6. Combine the organic phases in the extraction vessel, add 1 ml of 1M HCl, and stir for 1 min (to remove entrained Pu. Remove the aqueous phase.

7. Add 5 ml of 10M HNO_3, and stir for 10 min to strip the Np.

8. Remove the aqueous phase into a clean vessel, and repeat Steps 7 and 8.

9. Evaporate the 10M HNO_3 to ∿3 ml and then add 5 ml of analytical-grade concentrated HNO_3.

10. Evaporate to ∿1 ml, and repeat evaporation with two more 5-ml portions of concentrated HNO_3.

11. Add 3 ml of analytical-grade perchloric acid (60%) and more concentrated HNO_3 and evaporate to complete wet oxidation of organic matter.

12. Heat until solid perchlorates remain but do not bake.

13. Dissolve the residue in 1 ml of warm 6M HCl and 1 ml of water.

14. Add 2 ml of 5M $NH_2OH \cdot HCl$ and evaporate slowly to ∿0.5 ml.

15. Add 0.5 ml of 1M EDTA and 4 to 7 drops of ammonia to adjust pH to 5.5 to 6.5.

16. Dilute to 5.00 ml, and mix thoroughly. Transfer 2.00 ml to a polarograph cell, and de-aerate with N_2 (pre-saturated with water) for ∿3 min.

17. Record the Np peak at about -0.8 V against the mercury-pool anode on the square wave polarograph.

18. Add ∿0.2 ml of a standard Np solution prepared in EDTA so that the original peak height is approximately doubled. Deduce the Np concentration of the original solution from

the increase in peak height. Interference from the oxidation of chloride ions is decreased by adding EDTA to shift the half-wave potential of the Np peak.

The precision is ±2 and ±10% for concentrations of 500 and 25 ppm, respectively.

Procedure 6. Determination of Np in Sample Containing Fission Products, U, and Other Actinides

A. Schneider[194]

Introduction

This procedure describes an analytical solvent extraction method for separating Np from Pu, Am, Cm, U, Th, and fission products using tri-iso-octylamine (TIOA) and thenoyltrifluoroacetone (TTA). Np is separated from Pu, Am, Cm, and fission products by extraction of Np(IV) into the amine from HNO_3 containing a reducing agent. Further purification is obtained by stripping Np from the amine with dilute HCl and then extracting the Np into TTA.

Reagents

- 5M HNO_3
- 3M [Ferrous Sulfamate], $Fe(NH_2SO_3)_2$
- 5.5M [hydrazine], N_2H_4
- 10 Vol% tri-isooctylamine (TIOA) in xylene
- 1M HCl
- 5M [hydroxylamine hydrochloride] ($NH_2OH \cdot HCl$)
- 0.5M TTA in xylene

Procedure

1. To a 5-ml extraction vial add 1.5 ml of 5M HNO_3 and a glass-covered magnetic stirring bar.
2. Pipet the sample (not to exceed 200 µℓ) into the HNO_3 and stir.

3. Add 3 drops 2M $Fe(NH_2SO_3)_2$ and 1 drop of 5.5M N_2H_4. Stir and allow to stand for 5 min at room temperature.

4. Add 1.0 ml of 10% TIOA in xylene and stir for 3 min to produce an emulsion. Allow the phases to separate. Separate the phases, and discard the aqueous.

5. Transfer the organic phase from the original vial to a clean vial containing 1.5 ml of 5M HNO_3, 3 drops of $Fe(NH_2SO_3)_2$, and 1 drop of N_2H_4. Stir for two minutes, allow the phases to separate, and discard the aqueous phase.

6. Transfer exactly 0.75 ml of the organic phase to a clean vial containing 2.5 ml of 1M HCl and 1.5 ml of xylene. Rinse the 0.75-ml pipet in the xylene phase of the new vial. Stir for 3 min and allow the phases to separate. Discard the organic phase.

7. Transfer exactly 2.0 ml of the aqueous HCl phase to a clean vial. Add 3 drops of 5M $NH_2OH{\cdot}HCl$ and 3 drops of 2M $Fe(NH_2SO_3)_2$. Stir and heat at 65°C for 3 min. Remove from the bath, and let stand for 3 min.

8. Add 1.0 ml of 0.5M TTA in xylene. Stir for 4 min to give a complete emulsion. Allow the phases to separate. The organic phase contains the purified Np. This phase is mounted for alpha counting for measurement of ^{237}Np.

Notes

1. The presence of fluoride, sulfate, oxalate, and phosphate lower the extraction coefficient of Np(IV) into TIOA; Chloride ion does not interfere. The deleterious effect of these anions is circumvented by reducing the sample size or by adding Al ion.

2. For U-free samples, the combined system yields 96 ±2% recovery. For U-bearing samples, the recoveries are dependent on the amount of U taken. The extraction conditions are reproducible, and for control analyses the recovery factors are included in the calculations.

3. In routine use, the combined extraction system achieves a separation from common fission products (Ce, Ru, Nb, Zr, Cs and Sr) of about 1×10^6 and a Pu separation factor of 5 to 50×10^5.

4. Control of the method for samples of unknown composition is maintained by spiking a portion of the sample solution with ^{237}Np or ^{239}Np and evaluating the recovery of the spike. An alpha pulse height analysis may be necessary if large amounts of Pu are initially present in the sample.

Procedure 7. Determination of Np in Samples of U and Fission Products

W. J. Maeck, G. L. Booman, M. C. Elliott, and J. E. Rein[185]

Introduction

This procedure describes a method for separation and determination of Np in solutions of U and fission products using methyl isobutyl ketone and thenoyltrifluoroacetone (TTA) extractants. Np is oxidized to the hexavalent state and quantitatively extracted as a nitrate complex into methyl isobutyl ketone from an acid-deficient $Al(NO_3)_3$ solution containing tetrapropylammonium nitrate. Np is stripped from the ketone with 1M HCl containing reductants and then quantitatively extracted into TTA-xylene to complete the separation.

Reagents

- $Al(NO_3)_3$ salting solution: Dissolve 1050 g of $Al(NO_3)_3 \cdot 9H_2O$, add 135 ml of concentrated NH_4OH with mixing, and cool to 50°C. Add 50 ml of 10% tetrapropylammonium hydroxide reagent, and stir the solution until all solid is dissolved. Dilute the solution to one liter with water.
- Reducing-strip solution: 1M HI - 0.5M $NH_2OH \cdot HCl$ and 0.25M $FeCl_2$ solution.
- 0.25M $KMnO_4$
- Methyl isobutyl ketone
- 0.5M TTA in xylene
- Ethylenediamine

Procedure

1. Add 6 ml of $Al(NO_3)_3$ salting solution to a tube containing 0.1 ml of 0.25M $KMnO_4$. Then pipet 1 ml or less of the sample into the tube and mix.
2. Add 3 ml of methyl isobutyl ketone, and mix for 3 minutes.
3. Centrifuge to separate the phases.
4. Remove 2 ml of the organic phase, and transfer to another tube containing 4 ml of the reducing strip solution. Mix for 10 min and allow the phases to separate.
5. Transfer 3 ml of the aqueous phase to a 30-ml separatory funnel; add 3 ml of 0.5M TTA, and stir vigorously for 10 min.
6. Let the phases separate, and discard the aqueous phase. Add 3 ml of reducing-strip solution, and scrub for 5 minutes.
7. Remove an aliquot of the organic phase, and dry it on a counting plate under a heat lamp. Cover the residue with 2 to 3 drops of ethylenediamine, evaporate to dryness, ignite, and count.

Notes

1. Extraction from acid-deficient $Al(NO_3)_3$ with methyl isobutyl ketone yields very good separation from Zr, and extraction with TTA gives good separation from Pu and U. The extraction of U and Pu is <0.1 and 0.01%, respectively. Ru and Zr, the only 80-day cooled fission products that follow Np, are separated by $>10^4$.
2. An alpha scintillation counter is used for gross counting, and a Frisch-grid chamber, 256-channel analyzer system is used for pulse height analysis.

Procedure 8. Extraction Chromatographic Separation of ^{239}Np From Fission and Activation Products in the Determination of Micro and Submicrogram Quantities of U

H. Wehner, S. Al-Murab, and M. Stoeppler[252]

Introduction

This procedure describes extraction chromatographic separation of ^{239}Np from fission and activation products after neutron irradiation. The system is Poropak-Q resin impregnated with TTA-xylene. It is suggested that radioactive samples are more easily analyzed with extraction chromatography than with TTA extraction.

Reagents

- Poropak-Q resin, 100 to 120 mesh
- 0.4M TTA in xylene (small amount of n-pentane added)
- 2M HCl
- 1M $FeCl_2$
- 3M $NH_2OH \cdot HCl$
- 10M HNO_3

Procedure

1. Dissolve sample in 2M HCl or convert to chloride with HCl.
2. Add 3 ml of freshly prepared 1M $FeCl_2$ and 4 ml of 3M $NH_2OH \cdot HCl$ mix, and let stand for 15 min.
3. Transfer the adjusted solution to a column (5 cm long and 0.6 cm I.D.) of Poropak Q impregnated with TTA-xylene at ~1 ml/(cm^2-min).

4. When the feed has passed through the column, wash with 2 ml of 1M HCl and then a few drops of distilled water. Discard the effluents.

5. Pass 5 ml of 10M HNO_3 through the column to strip the Np.

6. Count the HNO_3 solution containing the ^{239}Np immediately after separation with a 3 x 3 in. NaI(TL) detector connected to a 512-channel pulse-height analyzer and evaluate the 0.106-MeV photopeak.

Notes

1. The method was suggested for determining low concentrations of U by irradiating a standard sample of known U content at the same time as the unknown and then determining the ^{239}Np content of both samples. A sensitivity of 1 μg of U was determined for a ∿1 hour irradiation, at a thermal neutron flux of 2×10^{13} n/cm^2-sec with a cooling period of ∿20 hours. With a longer irradiation, a detection limit of 0.5 μg is suggested.

Procedure 9. Separation of U, Np, Pu, and Am by Reversed Phase Partition Chromatography

H. Eschrich[248]

Introduction

This procedure describes extraction chromatographic separation of U, Np, Pu, and Am. The system is Hyflo Super-Cel (diatomaceous silica) impregnated with tributyl phosphate (TBP) and aqueous HNO_3 solutions of the actinides.

Reagents and Materials

- Hyflo Super-Cel
- Purified tributyl phosphate (TBP)
- HNO_3
- Sodium dichromate solution ($Na_2Cr_2O_7$)
- Dichloro-dimethylsilane
- Glass column

Procedure

1. Add $Na_2Cr_2O_7$ to 1 to 2M HNO_3 containing the actinides, and heat at 75°C for five hours to yield hexavalent U, Np, and Pu.
2. Wash the packed column with ~10 column volumes of ~1M HNO_3 at relatively high flow and pressure to remove any air and nonsorbed TBP.
3. Add the sample volume (not greater than 1/10 of the total column volume and containing a maximum of 1 mg TBP-extractable species per 100 mg of silaned Hyflo Super-Cel) at a flow of 0.4 to 0.8 ml/(min-cm^2).

4. Wash the column with 1.7M HNO_3 to remove (in order) Am(III), Cr(VI), and Pu(VI).
5. After Pu(VI) elution, switch to 1.7M HNO_3 - 0.1M N_2H_4 wash. (Np is reduced to Np(V) and elutes immediately, and U(VI) is removed.)

Note

If U, Np, and Pu are present, no oxidation step is required. The feed is adjusted 0.7M HNO_3 - 0.02M $Fe(SO_3NH_2)_2$ to yield Pu(III), Np(IV), and U(VI), and the same composition wash solution is used. The order of elution is Pu(III), Np(IV), and U(VI).

Procedure 10. An Analytical Method for ^{237}Np Using Anion Exchange

F. P. Roberts[214]

Outline of Method

This method separates Np from Pu, U, Am, Cm, and fission products by anion exchange in HNO_3 solutions to permit ^{237}Np estimation by gamma spectrometry. The sample is spiked with ^{239}Np tracer to permit yield corrections and loaded onto a small column of "Dowex" 1-X4 (100 to 200 mesh) resin from 8M HNO_3 containing $Fe(NH_2SO_3)_2$ and semicarbazide. After washing with 30 to 40 column volumes of 4.5M HNO_3 containing $Fe(NH_2SO_3)_2$ and semicarbazide, the Np is eluted with dilute HNO_3 containing 0.005M $Ce(SO_4)_2$. Np recovery is ∿95% with a Pu decontamination factor of 5 x 10^4. Decontamination factors from U, Am, Cm, and gross fission products are all >10^4. Uranium at concentrations up to 180 g/ℓ in the feed does not interfere. The Pu decontamination factor can be increased 10 to 100 by following the HNO_3 wash with 12M HCl - 0.1M NH_4I. Np is then eluted with 6.5M HCl - 0.004M HF. The method is applicable to samples containing high salt concentrations.

Reagents (C.P. Chemicals)

- Concentrated HNO_3
- ∿2M $Fe(SO_3NH_2)_2$
- Semicarbazide
- ^{239}Np tracer

Materials

- "Dowex" 1-X4, 100-200 mesh
- Glass column, 0.3 cm x 7 cm with 10-ml reservoir

- Counting equipment

Procedure

1. Adjust an aliquot of sample to ∿8M HNO_3 with concentrated HNO_3.
2. Add an equal volume of 8M HNO_3 - 0.02 $Fe(NH_2SO_3)_2$ - 0.2M semicarbazide and mix.
3. Add ^{239}Np tracer (∿10^5 dis/min).
4. Pass the adjusted sample through the column at 3 to 6 drops/min.
5. Rinse the reservoir several times with a few drops of 8M HNO_3, pass through the column, and discard.
6. Pass 15 to 20 ml of 4.5M HNO_3 - 0.1M semicarbazide - 0.01M $Fe(NH_2SO_3)_2$ through the column at 3 to 6 drops per minute (Pu fraction).
7. Pass 2 ml of 8M HNO_3 rinse through the column.
8. Elute the Np with 2 ml of 0.005M $Ce(SO_4)_2$ in 0.25M HNO_3. Catch the eluate in a 2-ml volumetric flask.
9. Mount an aliquot of the Np product on a Pt disc for alpha counting and alpha energy analysis. (The yield is determined by comparative counting of the 0.23 MeV ^{239}Np gamma from the disc with that of a standard ^{239}Np disc.)

Procedure 11. Separation of U, Np, and Pu Using Anion Exchange

F. Nelson, D. C. Michelson, and J. H. Holloway[225]

Outline of Method

This method utilizes anion exchange in HCl for separating U, Np, and Pu from "non-adsorbable" elements which include alkali metals, alkaline earths, trivalent actinides, rare earths, and a number of other elements such as Al, Sc, Y, Ac, Th, and Ni.

Sorption of the uranides by anion exchangers from HCl solutions can occur in either the +4 or +6 oxidation states but not in the +3 or +5 states. In this procedure, U is sorbed as +6, while Np and Pu are sorbed in the +4 oxidation state. Pu is selectively reduced to Pu(III) and eluted, while U^{6+} and Np^{4+} remain sorbed. The latter are then eluted in separate portions with HCl - HF mixtures.

Reagents (C.P. Chemicals)

- 9M HCl
- 9M HCl - 0.05M NH_4I
- 4M HCl - 0.1M HF
- 0.5M HCl - 1M HF

Materials

- "Dowex" 1-X10, -400 mesh anion resin
- Column, 0.6 cm I.D. and 12 cm in length, with heating device.
- Resin bed, 0.28 cm^2 x 3 cm long.
- Plastic test tubes

- "Teflon" evaporating dishes
- Plastic transfer pipettes

Procedure

1. Evaporate sample to near dryness.
2. Add 1 ml of 9M HCl - 0.05M HNO_3 and heat for 5 min. Do not boil.
3. Heat column to 50° and maintain throughout elution.
4. Pretreat resin bed with 3 column volumes of 9M HCl. Use air pressure to obtain flow of 0.8 cm^3/min.
5. Pass sample through resin bed at 0.8 cm/min.
6. Wash bed with 4 column volumes of 9M HCl.
7. Wash bed with 8 column volumes of 9M HCl - 0.05M NH_4I (Pu fraction).
8. Wash bed with 4 column volumes of 4M HCl - 0.1M HF (Np fraction).
9. Wash bed with 3 column volumes of 0.5M HCl - 1M HF (U fraction).
10. Regenerate the column with 3 column volumes of 9M HCl.

The total time for the column operation is about 80 min.

Procedure 12. Separation of Zr, Np, and Nb Using Anion Exchange

J. H. Holloway and F. Nelson[224]

Outline of Method

This procedure is used to separate trace amounts of Np and Nb from micro-amounts of Zr. It makes use of the fact that Zr(IV) in HCl - HF media at high HCl concentrations is essentially non-sorbable by anion exchange resin under conditions where Np(VI) and Nb(V) are strongly sorbed.

Reagents

- 6M HCl - 1M HF - Cl_2
- 6M HCl - 1M HF
- 0.5M HCl - 1.0M HF
- 4M HNO_3 - 1M HCl - 0.2M HF

Materials

- "Dowex" 1-X10, -400 mesh anion resin
- Column, 0.9 cm I.D. x 12 cm in length containing 2 ml of resin
- "Teflon" evaporating dishes
- Plastic transfer pipettes
- Plastic test tubes
- Chlorine gas

Procedure

1. Dissolve the sample, and evaporate it to near dryness.
2. Add 1 ml of 6M HCl - 1M HF - Cl_2, and warm.
3. Transfer the sample to a plastic tube and bubble Cl_2 gas through it for ∿3 min.

4. Chlorinate the resin, and add it to the column.

5. Wash the bed with 2 column volumes (~4 ml) of 6M HCl - 1M HF - Cl_2. Then pass the sample through the bed. (Control the flow with air pressure at ~0.8 cm/min. When the sample has passed, wash with an additional 3.5 column volumes of 6M HCl - 1M HF - Cl_2 (Zr fraction).

6. Wash with 3 column volumes of 0.5M HCl - 1M HF to elute Np.

7. Wash with 3 column volumes of 4M HNO_3 - 1M HCl - 0.2M HF to elute Nb.

8. Regenerate with 3 column volumes of 6M HCl - 1M HF - Cl_2.

The total time for the column operation is ~30 min.

Procedure 13. Separation of Np and Pu by Anion Exchange

N. Jackson and J. F. Short[349]

Outline of Method

This procedure describes separation of macro amounts of Pu and Np. It is based on the fact that Pu(III) is not sorbed on anion exchange resin, while Np(IV) is strongly sorbed at high HCl concentrations. The valence adjustment is done before sorption on the column by dissolving the hydroxides in a concentrated HCl solution that has been saturated with NH_4I. The Np is removed from the column with 2 M HCl. The separation is quantitative and complete.

Procedure

The purification of 2.3 g of Np^{237} from approximately 50 mg of Pu^{239} was then undertaken. The Np and Pu were precipitated as hydroxides, centrifuged, and dissolved in 210 ml of concentrated HCl saturated with NH_4I. The solution was allowed to stand for 30 min and poured onto a Deacidite FF*anion column 20 cm long and 2.5 cm diameter, while a flow rate of 1 ml/min was maintained. The first 200 ml of effluent were pale blue [Pu(III)]. The column was then washed with 100 ml of concentrated HCl, and wash was collected separately. No activity was found in a drop collected at the end of the washing.

The Np was eluted with 2M HCl. It was possible to follow the dark green band of the Np down the column, and the first 40 ml of eluate was included with the concentrated HCl wash. All the Np

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*Deacidite is supplied by Permutit Co. Ltd., England.

was collected in the next 50 ml of eluate. No activity was found in any eluate after this stage. Some β-γ activity was detected on the glass wool at the top of the resin column and was assumed to be ^{233}Pa, the daughter of Np^{237}.

Procedure 14. Separation of Np and Pu by Cation Exchange

V. D. Zagrai and L. I. Sel'chenkov[239]

Outline of Method

Np(IV) and Pu(III) are adsorbed on the cation resin KU1 or KU2 from 0.25M HCl solution after reduction with SO_2 at boiling water temperatures. Np is eluted with 0.02M HF, and Pu stripped with 0.5M HF.

Procedure

1. To 6 to 8 ml of 0.25M HCl containing μg amounts of Np and Pu, add about half of the resin in the hydrogen form required to fill the plexiglass column (1 mm diameter × 90 mm high) and 1 to 2 ml of water.
2. Pass SO_2 gas through the solution vigorously for 15 to 20 min, while the solutions heating on a boiling water bath.
3. Allow the solution to cool to room temperature, and transfer the resin to the column with a pipette. Plug the top of the column with cotton, and pass the remaining solution through the column.
4. Wash the resin with 10 ml of 0.25 M HCl, followed by 10 ml of H_2O.
5. Elute the Np into a Pt dish or a "Teflon" beaker with 40 to 60 ml of 0.02M HF.
6. Elute the Pu with 4 to 5 ml of 0.5M HF.

Procedure 15. Separation and Radiochemical Determination of U and the Transuranium Elements Using Barium Sulfate

C. W. Sill[123,124,125]

Introduction

Large trivalent and tetravalent ions are precipitated with $BaSO_4$ while monovalent and divalent cations are not precipitated. This procedure outlines the separation of U and transuranium elements both from other elements and from each other. The oxygenated cations of the hexavalent state are too large to fit into the $BaSO_4$ lattice and are not carried. The $BaSO_4$ precipitate can be alpha counted directly with 92% counting efficiency, or the radionuclides can be electrodeposited for alpha spectrometry.

Reagents and Equipment

- Concentrated H_2SO_4
- C.P. K_2SO_4
- Concentrated HNO_3
- Concentrated perchloric acid ($HClO_4$)
- C.P. KNO_3
- C.P. potassium dichromate ($K_2Cr_2O_7$)
- 30% hydrogen peroxide (H_2O_2)
- Erlenmeyer flask
- Centrifuge and special tubes
- Counting supplies and equipment

Procedure

1. Add 3 g of anhydrous K_2SO_4, 2 ml of concentrated H_2SO_4, 6 drops each of concentrated HNO_3 and $HClO_4$, and 2.00 ml of 0.45% solution of $BaCl_2 \cdot 2H_2O$ (5 mg of Ba) to the solution containing the elements to be precipitated in a 250-ml Erlenmeyer flask and evaporate until fumes of H_2SO_4 appear. (If there is any question about removal of organic matter, add HNO_3 and/or $HClO_4$ and re-evaporate.
2. Heat the solution over a blast burner with swirling until the excess H_2SO_4 and $HClO_4$ are volatilized and a clear pyrosulfate melt is obtained.
3. Cool the melt, add 2 ml of concentrated H_2SO_4, and heat to boiling or until the pyrosulfate melt is dissolved. Do not volatilize much H_2SO_4.
4. Cool and add ~10 mg of solid $K_2Cr_2O_7$, and mix to ensure complete oxidation of Np. Do not heat because Pu will be oxidized and the excess dichromate will be thermally decomposed.
5. Cool to ~40°C and add ~20 ml of water; boil for 1 minute.
6. Cool, centrifuge, and wash the precipitate; the Np and U are in the supernate.
7. Add 0.5 ml of 30% H_2O_2 and 2.00 ml of 0.45% $BaCl_2$ to the supernate, and evaporate until fumes of H_2SO_4 appear to reduce any Pu that may have followed the Np.
8. Heat the H_2SO_4 to boiling, cool for 2 minutes, and add ~10 mg of $K_2Cr_2O_7$ to reoxidize the Np.
9. Add 20 ml of water and boil for 1 minute; cool, centrifuge, and combine the supernate with that from Step 6.
10. Add 0.5 ml of 30% H_2O_2 to reduce Np to the quadrivalent state, and evaporate to 25 ml.

11. Cool and add $BaCl_2$; then boil, centrifuge, wash, and mount the $BaSO_4$ which contains the ^{237}Np. The U remains quantitatively in the supernate.

Notes

1. Several other shorter procedures for Np are given when Np is to be separated from one or two other cations.
2. Details are given in the reference article for depositing the precipitate on a stainless steel disc that fits into a specially designed centrifuge holder and also into a specially designed counting holder. An alternative procedure uses electrodeposition of the radionuclides for alpha spectrometry.

Procedure 16. The Low-Level Radiochemical Determination of ^{237}Np In Environmental Samples

R. W. Taylor[350]

Introduction

Np, along with Pu and U, is removed from 8M HCl by anion exchange to triisooctylamine (TIOA). Each element can be individually removed from the TIOA. Pu is stripped first with 8M HCl - 0.05M NH_4I. Np is removed next with 4M HCl - 0.05M HF, and U is removed last with 0.5M HNO_3.

Most environmental samples contain large quantities of Fe that will extract with the actinide elements into TIOA. Much of the Fe will be stripped from the TIOA along with Np, but it is easily removed from 8 M HCl by isopropyl ether. If the sample is known to contain no Fe, the ether extraction step may be omitted.

Final decontamination of Np is accomplished by solid ion exchange. Np is finally electrodeposited for radioassay by alpha pulse height analysis.

When the sample contains large quantities of U, some of it may follow the Np and be electrodeposited on the plate. ^{234}U and ^{237}Np have the same alpha energy (4.75 MeV) and cannot be distinguished from one another. The Np can be converted to ^{238}Pu by neutron irradiation for verification of ^{237}Np. Also, when the Np activity is very low, conversion to ^{238}Pu will decrease the counting time. Two-hour irradiations at a flux of 1×10^{13} n/(cm^2-sec) result in a ^{238}Pu activity level about 7 to 10 times greater than the original activity due to Np.

Reagents

- HNO_3, 16M, 1M
- HCl, 12M, 8M
- H_2O_2, 30%
- NH_4OH, 1.5M
- KOH, 12M
- 8M HCl - 0.05M NH_4I: This reagent must be prepared fresh just prior to use. Discard any unused reagent at the end of the day.
- 10% TIOA (triisooctylamine): 10% volume/volume TIOA in xylene. Clean the reagent by shaking in a separatory funnel with half its volume of 0.5M HNO_3. Repeat the HNO_3 wash, and wash finally with distilled water. Store the cleaned TIOA in a glass flask.
- 4M HCl - 0.05M HF
- Isopropyl ether
- "Dowex" 2-X8 anion exchange resin, 200 to 400 mesh

Procedure

1. Adjust the sample to be analyzed to 8M HCl. Soluble samples may be dissolved directly; insoluble materials may be leached with hot 8M HCl; aqueous samples may be evaporated to near dryness and brought up in 8M HCl. The sample should be adjusted to a convenient volume of from 200 to 400 ml.
2. Add 5 ml of 30% H_2O_2 to the sample and heat at about 80°C until effervescence ceases. Cool the sample to about room temperature.

3. Transfer the sample to a 500-ml separatory funnel. Add an amount of 10% TIOA equal to one-fourth the amount of the original sample. Shake the funnel for one minute. Allow the phases to separate, and drain the bottom (aqueous) phase. Retain for other analyses.

4. Add 10 to 20 ml 8M HCl (according to volume of original sample) and shake one minute. Allow phases to separate, drain, and discard the aqueous.

5. To strip Pu from the TIOA, add to the separatory funnel an amount of 8M HCl - 0.05M NH_4I equal to one-half the volume of TIOA. Shake one minute and then allow phases to separate. Drain the aqueous and retain for Pu analysis. Repeat the Pu strip with a fresh portion of 8M HCl - 0.05M NH_4I. Combine the two strips, and save for Pu analysis.

6. To remove Np from the TIOA, add to the separatory funnel an amount of 4M HCl - 0.05M HF equal to one-half the volume of TIOA and shake for one minute. Allow the phases to separate, and drain the aqueous which contains Np. Repeat the strip with a fresh portion of 4M HCl - 0.05M HF, and combine the two strips. U can now be stripped from the TIOA with 0.5M HNO_3.)

7. Add an equal amount of 12M HCl to the combined strips, and transfer to a clean separatory funnel. Add 25 ml isopropyl ether and shake one minute. (CAUTION: Vent the separatory funnel frequently while shaking.) Drain the aqueous, and retain. Discard the ether in accordance with safety regulations. Repeat the ether extraction with a fresh portion of ether.

8. Evaporate the aqueous phase from Step 7 to dryness. Place in a muffle furnace at 400°C for at least 4 hours. Wet oxidize the sample two or three times with 3 or 4 ml

$16M\ HNO_3$ and 30% H_2O_2. Add 2 or 3 ml 12M HCl and evaporate to dryness. Repeat the 12M HCl evaporation.

9. Dissolve the sample in 10 ml of 8M HCl and pass through a "Dowex" 2-X8, 200 to 400 mesh, anion exchange column. The resin bed should be 50 mm long and 6 mm in diameter; it must be pre-conditioned with 5 ml of 8M HCl. After the sample passes through the column, pass an additional 5 ml of 8M HCl through it. Elute the Np from the column with 10 ml of 0.1M HCl. Evaporate to dryness.

10. Add 2 ml of 16M HNO_3 to the sample, and evaporate to dryness. Repeat the HNO_3 evaporation. Add 2 ml 1M HNO_3 to the sample, and heat gently to ensure dissolution. Cool, and transfer the sample to an electrodeposition cell. Rinse the beaker twice with 2 ml of distilled water, and transfer the rinse to the cell. Add 2 ml of 1.5M NH_4OH to the cell, and add distilled water until the cell is full.

11. Electrodeposit the sample at 10 V and about 200 mamp for three hours. Maintain the pH of the solution between 1 and 3 during electrodeposition. At the end of the electrodeposition period, add 1 ml of 12M KOH and plate for 1 min. Empty the cell, rinse with distilled water and remove the plate. Dry the plate and flame it.

12. Count the plate by alpha pulse height analysis. If there is no U present and if there is sufficient ^{237}Np present, radioassay can be accomplished directly. In the presence of U or when there is very little ^{237}Np present, increased sensitivity can be achieved by conversion of ^{237}Np to ^{238}Pu by neutron irradiation. The absence of ^{238}Pu is verified by the initial count.

13. Irradiate the Np sample for approximately two hours at a flux of 1×10^{13} n/(cm^2-sec). Allow the plate to

cool long enough to permit decay of induced Pt activities and to allow ^{238}Np to decay to ^{238}Pu. Recount the plate by alpha pulse height analysis. Correct the amount of ^{238}Pu now present by any originally present on the plate, if necessary. Calculate the amount of Np present before irradiation from the activation formula.

Procedure 17. Radiochemical Procedure for the Separation of Trace Amounts of ^{239}Np from Reactor Effluent Water

R. W. Perkins[155]

Introduction

This procedure accommodates a relatively large volume of reactor effluent water, and emphasis is placed on speed of separation and high radiochemical purity rather than high yield.

Procedure

1. Add 20 mg of La carrier and 5 ml of concentrated HCl to one gallon of reactor effluent water, and evaporate to ∿50 ml.
2. Cool the solution, dissolve 0.25 g of $Fe(NH_2SO_3)_2$, and let stand for 5 min.
3. Transfer to a 100-ml plastic tube, add 5 ml of concentrated HF, stir, and let stand 5 min.
4. Centrifuge, and discard the liquid phase.
5. Dissolve the precipitate in 20 to 50 ml of 1M HCl, and dilute to 75 ml with 1M HCl.
6. Add 5 ml of concentrated HF, stir, and let stand for 5 min.
7. Centrifuge and discard the liquid phase.
8. Repeat Steps 5 through 7.
9. Transfer the precipitate to a 50-ml beaker containing 3 ml of concentrated $HClO_4$, and evaporate to dryness.
10. Dissolve the residue in 20 ml of 1M HCl by boiling. Cool the solution and dissolve 0.25 g of $Fe(NH_2SO_3)_2$.
11. Transfer the solution to a 125-ml separatory funnel and mix. Add 20 ml of TTA in benzene, and extract for 10 min. Discard the aqueous phase.

12. Wash the organic phase with three 20-ml portions of 1M HCl for 5 min each. Discard the aqueous solutions.

13. Back-extract the ^{239}Np with 10 ml of 8M HNO_3 for 10 min.

14. Place the aqueous in a 50-ml beaker containing 3 ml of concentrated $HClO_4$, and evaporate to dryness under a heat lamp.

15. Cool the beaker, add ∿5 ml of 8M HNO_3, and heat to boiling.

16. Dilute the solution to a measured volume and analyze by gamma counting.

Note

The analysis requires ∿6 hours, and the yield is >90%.

Procedure 18. Determination of Np in Urine

F. E. Butler[351]

Outline of Method

Urine is wet ashed with HNO_3 and H_2O_2 to destroy organic matter. The salts are dissolved in 8M HCl and extracted with TIOA (tri-isooctylamine). The Np is then back extracted, and the alpha activity is determined by direct planchetting and counting on low background solid-state counters.

A variation of the procedure provides for sequential determination of actinides in biological and environmental samples. Pu, Np, and U are extracted from 8M HCl to TIOA. The residual 8M HCl containing Th, Am, Cm, Bk, Cf, and Es are extracted from 12M HNO_3 to DDCP (dibutyl N, N-diethylcarbamyl phosphonate). The actinides of interest are back-extracted sequentially for quantative determinations.

Preparation of Sample

Urine collected in polethylene bottles is transferred to an Erlenmeyer flask with concentrated HNO_3 (200 ml of acid per liter). Acid is added to the urine in the polyethylene bottle to remove the Np, which may be adsorbed on the walls of the container. The acidified sample is evaporated to dryness, and the residue is wet ashed with HNO_3 and H_2O_2. Nitrates are metathesized to chlorides by evaporation to prevent interference with Pu (III) removal.

Reagents and Equipment

The liquid anion exchanger, TIOA (Bram Chemical Co.) is diluted to 10 vol % with xylene and washed with half its volume of 0.1M HCl before use.

The alpha-detection equipment are 2Π solid-state counters. The counters are equipped with detectors that have an active area of 350 mm^2 and are capable of accepting 1-in. stainless steel planchets.

All other reagents used in the procedure are prepared from analytical grade chemicals.

Procedure

1. Wet ash urine with HNO_3 and H_2O_2; then add 10 ml of 8M HCl to the white salts twice and evaporate the solution to dryness each time.
2. Dissolve the salts in freshly prepared 8M HCl - 0.05M NH_4I (50 ml of acid/250 ml of urine in sample), and heat to complete solution.
3. Transfer a 50-ml aliquot of the solution with 25 ml TIOA-xylene into a separatory funnel and shake for 1 min. (For urine samples of 250 ml or less, rinse the flask twice with 10 ml of 8M HCl, and add the rinses to the funnel.)
4. Drain and store the aqueous (lower) layer for Pu, Th, Am, Cm, and Cf analysis.
5. Rinse the organic phase with 25 ml of 8M HCl - 0.05M NH_4I at 80°C and shake for 1 min. Discard the rinse solution or combine with solution stored for other actinide analysis.

6. Add 25 ml of 4M HCl - 0.02M HF to the funnel and shake vigorously for 10 sec. Drain the Np strip to a 100-ml breaker. Repeat a second time and combine the two 25-ml solutions. Discard the organic phase or strip with 0.1M HCl for uranium analysis.

7. Evaporate the Np strip to dryness. Wet ash with HNO_3 and H_2O_2. Rinse sides of breaker with 4M HNO_3 and evaporate solution to dryness.

8. Add 1 ml 4M HNO_3 and transfer solution to stainless steel planchets and evaporate to dryness under an infrared lamp. Complete transfer with 3 rinses of 4M HNO_3.

9. Flame the dried planchet to dull red, cool, and count on low-level solid state alpha counters.

10. Calculation:

    Np activity on planchet is determined as follows:

$$\text{dis/(min-planchet)} = \frac{\text{total count - Bkgd}}{\text{(t)(counter eff.)}}$$

where: Bkgd. = counter background (3 to 10 counts/24 hr)

t = counting time in minutes

counter eff = counter efficiency as a fraction (normally 0.30)

The sensitivity of this analysis is 0.02 ± 0.01 dis/(min-sample). The recovery efficiency is determined by adding a known amount of Np standard to an aliquot of urine sample and following the same procedure for analysis.

Procedure 19. Determination of ^{237}Np by Gamma Ray Spectrometry

W. O. Granade[352]

Introduction

A gamma spectrometric method was developed that allows for the rapid determination of Np in process solutions containing fission products. The method is unaffected by highly salted, corrosive, or organic media. ^{237}Np is determined by gamma spectrometry using a thin lithium-drifted germanium [Ge(Li)] semiconductor detector to resolve the 86.6-keV ^{237}Np gamma ray.

Apparatus

The detector system consists of an Ortec model 3113-10200, low-energy photon detector with cooled FET preamp and a resolution of 900-keV full width at half maximum (FWHM) at 86.6-keV. A 4096-channel pulse height analyzer is used for the accumulation and storage of the gamma spectra. The data are read onto magnetic tape or printed out directly from a high-speed digital printer. Data reduction is performed using an IBM 360 system and FORTRAN programs developed to calculate nuclide abundances from multichannel gamma ray spectra.[1]

Procedure

Calibration. ^{233}Pa, the daughter of ^{237}Np, has a 0.017 abundant gamma ray at 86.6-keV that interferes with the measurement of the ^{237}Np gamma ray of the same energy. ^{233}Pa also has a 0.34 abundant gamma ray at 311.9-keV that is not associated with a ^{237}Np gamma ray. In order to determine the ^{233}Pa contribution to the 86.6-keV ^{237}Np photopeak, a pure standard solution of ^{233}Pa is required. ^{233}Pa is purified by passing an equilibrium solution of ^{233}Pa-^{237}Np through a diatomaceous earth column which sorbs ^{233}Pa. The ^{233}Pa is eluted, and the ^{237}Np contaminant level is determined by alpha counting (^{233}Pa does not decay by alpha emission). Aliquots of ^{233}Pa are pipetted into a standard gamma counting geometry. A series of counts of the ^{233}Pa are made to determine the ratio of gamma counts at the 86.6-keV peak to counts at the 311.9-keV peak. The ratio is used to calculate the ^{233}Pa contribution to the total counts detected at the 86.6-keV peak.

The efficiency of the Ge(Li) detector for 86.6-keV gamma rays is determined by calibration with known gamma standards between 43.5 and 511.6-keV.

Analysis

The standards and sample are counted in a holder which ensures a reproducible geometry at 2 cm. The deadtime correction (always <20%) was found to be accurate to <1%. The gain setting of the amplifier is adjusted to provide a peak width of 7 to 10 channels (FWHM) to allow reliable integration of the photopeak area. For a Gaussian distribution, 99% of a peak area is contained in 2.1 x FWHM. Therefore a peak area of 24 channels is used with a gain setting giving 10 channels FWHM.

The net counts per minute of ^{237}Np is calculated by subtracting the Compton background and the ^{233}Pa contribution from the 86.6-keV total photopeak area. The contribution of underlying Compton background is assumed to be linear over the peak area. An average of the counts from 4 channels on each side of the peak is used to determine the background correction. For an analysis above the determination limit (the relative standard deviation is less than 10% of the measured value), the peak area minus the background should be greater than[2]:

$$50\left\{1 + \left[1 + \frac{\text{Bkg. Sum}}{12.5}\right]^{\frac{1}{2}}\right\}$$

The absolute disintegration per minute value of ^{237}Np is obtained by dividing the net counts per minute by the product of the gamma ray abundance (photon/disintegration) and the detector efficiency at 86.6-keV.

A comparison of ^{237}Np results obtained by gamma spectrometry and TTA extraction[3] agreed within 3%. An aliquot of 1.06×10^5 alpha dis/(min-ml) ^{237}Np standard solution was extracted using TTA. A standard geometry sample was made from the TTA (organic) phase and one from the aqueous phase. The resulting gamma counting showed that 97% of the ^{237}Np had been extracted into the TTA phase. Close agreement between the two methods demonstrated the reliability of the gamma pulse height analysis. Samples can be counted in organic media with no adverse effects. A lower limit of detection of 1×10^4 d/m/ml at a confidence level of 95% was determined from a series of counts using a diluted standard ^{237}Np solution.

References

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2. M. A. Wakat and E. K. Dukes, *J. Radioanalyt. Chem.* *4*, 109 (1970).
3. B. F. Rider. *Selected Analytical Methods for Purex Process Control.* USAEC Report KAPL-890 (1953).

Procedure 20. Spectrophotometric Determination of Np

R. G. Bryan and G. R. Waterbury[302]

Outline of Method

Np is measured spectrophotometrically as the arsenazo III complex after separation from Pu and impurity elements by liquid-liquid extraction. U is removed first by extraction from 4M HCl into triisooctyl amine (TIOA)-carbon tetrachloride, while Np(IV) and Pu(III) are stabilized in their nonextractable oxidation states by Fe(II) and ascorbic acid. Then Np(IV) is extracted from 8M HCl into TIOA and back-extracted into 0.1M HCl. The Np-arsenazo III complex is formed in 6.1M HCl, and the absorbance is measured at a wavelength of 665 nm.

Reagents

- Arsenazo III, 0.2% [1,8-dihydroxynapthalene -3, 6-disulfonic acid-2, 7-bis (azo-2)-phenylarsonic acid]. Dissolve 1 g of arsenazo III in 500 ml of water containing two KOH pellets.
- Ascorbic acid, 5%. Dissolve 6 grams of ascorbic acid in 120 ml of 8M HCl.
- Carbon tetrachloride, (CCl_4) reagent grade.
- HCl, 12M, reagent grade.
- HCl, 8M, 4M, and 0.1M.
- Np stock solution. Dissolve high purity Np metal in 12M HCl.
- Phosphoric acid, (H_3PO_4) 15.9M, reagent grade.
- KOH, pellets, reagent grade.

- Reducing solution, 5% ascorbic acid and 0.5% Fe(II) ion in 4M HCl. Dissolve 2.5 g of ascorbic acid and 1.75 g of $Fe(NH_2SO_3)_2$ in 50 ml of 4M HCl.
- Tri(iso-octyl)amine-xylene (TIOA in xylene), 5%. Dissolve 31 ml of TIOA in 500 ml of reagent-grade xylene.
- Tri(iso-octyl)amine-carbon tetrachloride (TIOA-CCl_4), 5%. Dissolve 31 ml of TIOA in 500 ml of CCl_4.

Equipment

- Extractors (see figure in Reference 302).
- Laboratory glassware (beakers, pipets, syringes, and volumetric flasks).
- Spectrophotometer, Beckman model DU or equivalent, with matched fused-silica cells having 1-cm light paths.

Pretreatment

The sample of metal or alloy is inspected, and extraneous material is removed. Cutting oil is removed by washing with methyl chloroform. For each Pu metal sample, take two accurately weighed portions, each not greater than 200 mg and containing less than 60 µg of Np. Make duplicate determinations on each sample, on a solution containing a known quantity of Np, and on the reagent blank solution.

Procedure

1. Place each accurately weighed sample in a glass extractor and add 1.5 ml of 12M HCl. When the sample has dissolved, add 1 ml of the reducing solution and 2.5 ml of water.

2. Prepare reagent blank solutions by adding 1 ml of reducing solution and 4 ml of 4M HCl to each of two extractors.

3. Prepare known Np solutions by adding an aliquot of standard Np solution that contains an amount of Np approximately equal to that expected in the sample and 1 ml of reducing solution to each of two extractors. Dilute the solutions to 5 ml with 4M HCl.

4. Add 5 ml of TIOA-CCl_4 to each of the solutions prepared in previous steps, mix the phases for 2 min, and then allow the phases to separate for 1 min.

5. Separate the TIOA-CCl_4 layer and discard.

6. Repeat Steps 4 and 5.

7. Add 5 ml of 12M HCl and 10 ml of TIOA-xylene to each extractor, mix the phases for 3 min and allow the phases to separate for 1 min. Remove the aqueous phase containing the Pu.

8. Wash the inside of the extractor with 5% ascorbic acid-8M HCl, mix the phases for 2 min, and allow the phases to separate for 1 min. Remove the aqueous phase.

9. Wash the inside of the extractor with 8M HCl. Mix the phases for 2 min, and allow to separate for 1 min. Remove the aqueous phase.

10. Add 4 ml of 0.1M HCl to each extractor. Mix the phases for 3 min, and allow to separate for 1 min.

11. Remove the aqueous phase into a 25-ml volumetric flask containing 0.6 ml of H_3PO_4, 1 ml of 5% ascorbic acid-8M HCl, and 12.7 ml of 12M HCl.

12. Repeat Steps 10 and 11.

13. Add 2.5 ml of 0.2% Arsenazo III solution to the volumetric flask, and dilute to 25 ml with water. Stopper and mix the contents of the flask.

14. Measure the absorbance of the solution in cells having 1-cm light paths at a wavelength of 665 nm.

15. $$\text{Np, ppm} = \frac{(\text{As-Ab})\ (\text{Wk, } \mu\text{g of Np})}{(\text{Ak-Ab})\ (\text{sample wt in grams})}$$

Ab = absorbance of blank
Ak = absorbance of known Np solution
As = absorbance of unknown sample
Wk = μg of Np in known Np solution

Relative standard deviations range between 7.2 and 1.1% in measuring 8.5 to 330 ppm of Np in 200 mg samples. Of 45 elements tested only Pd, Th, U, and Zr cause serious interference, but only if present in concentrations greater than 0.8%. However, initial extraction from 4M HCl into TIOA removes some U, and Th is not significantly extracted from HCl solution. Also, H_3PO_4 complexes up to 1 mg of Zr without affecting the analysis. HF and HNO_3 cause low results unless removed by volatilization. The method tolerates the intense radioactivity from quantities of ^{238}Pu as large as 100 mg.

Procedure 21. Microvolumetric Complexometric Method for Np with EDTA

A. P. Smirnov-Averin, G. S. Kovalenko,
N. P. Ermoloev, and N. N. Krot[326]

Outline of Method

Np(IV) is titrated with a solution of EDTA at pH 1.3 to 2.0 with xylenol orange as indicator. The reaction of Np(IV) with EDTA is stoichiometric, and the color changes from bright rose to light yellow at equal molar concentrations. The determination takes approximately two hours; the error is ±0.03 mg.

Reagents and Equipment

- HCl, reagent grade
- Test solution, 10 mg Mn^{2+} and 50 mg $NH_2OH{\cdot}HCl$ per ml
- 30% KOH
- 10% NaCl in 4M HCl
- 0.1% xylenol orange
- Centrifuge tubes
- Micro or semimicroburet

Procedure

1. Add 1 to 4 ml of Np solution and 2 ml of test solution containing 10 mg Mn^{2+} and 50 mg of $NH_2OH{\cdot}HCl$ per ml into a centrifuge tube.
2. Dilute to 6 to 8 ml, and heat to 60°C; add 30% KOH with mixing until the pH >10.
3. Centrifuge the precipitate, and discard the solution.
4. Add 10% NaCl in 4M HCl dropwise until the precipitate is dissolved.

5. Add 1 to 1.5 ml of 4M HCl containing 50 mg of $NH_2OH \cdot HCl$ per ml, and heat the solution for 20 min on a boiling water bath.

6. Cool the solution, dilute to ∿100 ml with water, and add 1 to 2 drops of 0.1% xylenol orange.

7. Titrate with 2×10^{-3}M EDTA from a microburet until the color changes from rose to bright yellow.

Notes

1. HCl solutions are preferred in order to reduce all the Np to the tetravalent state with $NH_2OH \cdot HCl$. Ascorbic acid is not suitable, since its decomposition products interfere with the titration.

2. Doubly charged readily hydrolyzable ions (Mn^{2+}, Ni^{2+}, UO_2^{2+}), which do not interfere with the titration, are used as carriers.

3. Np can be determined with an error of ±0.03 mg in the presence of large amounts of alkali, alkaline earth, and rare earths elements, Mn^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+} (up to 20 mg), Ni^{2+}, Co^{2+} and UO_2^{2+}. Anions which are separated by strong base precipitation include NO_3^-, CH_3COO^-, SO_4^{2-}, $C_2O_4^{2-}$, $Cr_2O_7^{2-}$, and $EDTA^{4-}$. Pu is reduced to Pu(III) and does not interfere up to 2 mg. Zr^{4+}, Th^{4+}, and Fe^{3+} interfere because they are cotitrated with Np(IV).

Procedure 22. Photometric Determination of Np as the Peroxide Complex

Yu. P. Novikov, S. A. Ivanova, E. V. Bezrogova, and A. A. Nemodruk[353]

Outline of Method

Np(V) forms an intensely colored complex in alkaline solutions (pH >8). The ratio of Np(V) to H_2O_2 in the complex is 1:1; the molar absorptivities of the complex at 430 and 370 nm are 5010 ±210 and 7950 ±350, respectively. The method is highly selective for Np.

Reagents and Equipment

- NaOH, CP grade
- H_2O_2, CP grade
- Spectrophotometer and cells.

Procedure

1. Add the dilute acid (HNO_3, HCl, or $HClO_4$) solution, ∿2.5 ml containing 5 to 50 μg of Np into a test tube.
2. Adjust to Np(V) by adding 0.1 ml of 30% H_2O_2, and keep in a boiling water bath for 10 min.
3. Cool the solution, and add 0.1 ml of 0.5M H_2O_2.
4. Neutralize to pH 1 to 3 with NaOH, and add an extra 1 ml of 4M NaOH.
5. Dilute to exactly 4 ml with water, and mix thoroughly.
6. Measure the absorbance in a 1 cm cell at 430 or 370 nm realtive to a blank.
7. Determine the Np content using a calibration curve.

Notes

1. Np(V), but not Np(IV) or Np(VI), gives a color reaction with H_2O_2.
2. The stability of the colored Np(V) peroxide complex increases as the pH is increased. In 0.1M NaOH solution, the absorbance remains unchanged for two hours.
3. Increasing the H_2O_2 concentration to >7 x 10^{-3}M does not change the absorbance. At higher H_2O_2 concentrations, the time for constant absorbance increases.
4. When the solution contains U, 7 to 10 mg of $(NH_4)_2HPO_4$ is added before the NaOH. Greater amounts of the phosphate reduce absorbance of the Np(V) complex.
5. Fluoride reduces the absorbance of the Np(V) peroxide complex. Tartrate, carbonate, and sulfate ions to 0.1M have no effect. When iron is present, $Fe(OH)_3$ precipitates and is removed by centrifugation. Up to 300-fold amounts of Fe do not interfere. Four-fold amounts of Pu do not interfere.

Procedure 23. Separation of Np for Spectrographic Analysis of Impurities

J. A. Wheat[232]

Outline of Method

Np compounds are dissolved in concentrated HNO_3, and the solution is heated to dryness. The residue is dissolved in dilute HNO_3, and Np oxidation state adjustment is made with N_2H_4 and sulfamic acid. The hexanitrato anionic complex of Np(IV) is sorbed on strong base anion resin; the cationic impurities are not sorbed by the resin. The cycle is repeated, and the effluents are evaporated and baked at 400°C. The residue is dissolved in 6M HCl, and the cationic impurities are determined by emission spectroscopy.

Reagents and Equipment

- Double-distilled HNO_3
- "Dowex" 1-4 100 mesh
- Hydrazine (N_2H_4)
- Sulfamic acid
- Cobalt solution
- Small glass column
- Spectrograph

Procedure

1. Dissolve 50 mg of sample in concentrated HNO_3, and evaporate to dryness.
2. Dissolve solid residue in 2 ml of 0.35M HNO_3 and add one-fourth ml of 11M aqueous solution of N_2H_4. Wait at least 30 min for valance adjustment.

3. Add one-half ml of 3M sulfamic acid and 2.5 ml of 16M HNO_3, and mix the solution.

4. Pass the adjusted solution through a 3 ml bed of 100-mesh "Dowex" 1-X4 resin at <3 ml/(min-cm^2), and collect the effluent.

5. Wash the resin with $\sim$10 ml of 8M HNO_3, and combine the effluent with that from Step 2.

6. Elute Np from the resin with 0.35M HNO_3, and condition the column with 8M HNO_3 for reuse.

7. Evaporate the sorption and wash effluents to dryness, and repeat Steps 2 through 6. (99.96% of the Np was removed with two cycles of anion exchange).

8. Evaporate the sorption and wash effluents from Step 7 to dryness and bake at 400°C to expel hydrazine.

9. Dissolve the residue in 1 ml of aqua regia, and evaporate to dryness.

10. Dissolved the last residue in 1 ml of 6M HCl containing 100 μg of Co, which serves as an internal standard.

11. Evaporate two hundred μℓ of the solution to dryness on top of a 1/4-inch-diameter flat-top electrode.

12. Excite the sample for 30 sec by a 10-amp dc arc using a large Littrow spectrograph in the 2500 to 3500 A wavelength region. The slit width is 10 μm, and a two-step neutral filter 100%/35% is inserted in the slit. SA-2 emulsion is used.

Because of the relatively large volume of reagents used, a reagent blank should be carried through the procedure. Doubly distilled HNO_3 was used.

Recovery was 88 to 106% for all elements except Ni which was 65%.

The coefficient of variation for a single determination of the several elements varies from 9 to 24% with an average of 17%. The precision is affected by large volumes of reagents and incomplete removal of cationic impurities from the resin column. The method was applied to determination of Fe, Cr, Ni, Mn, Cu, Al, and Mg.

Procedure 24. Photometric Determination of Np as the Xylenol Orange Complex

N. P. Ermoloev, G. S. Kovalenko, N. N. Krot, and V. J. Blokhin[308]

Outline of Method

Np(IV) reacts in weakly acidic solution (pH $\sim$2) with xylenol orange to form a color complex with an absorbance maximum at 550 nm and molar extinction coefficient of 5.5×10^4. Xylenol orange is three times more sensitive than thorin but only one-half as sensitive as Arsenazo III as a reagent for Np(IV). The greatest advantage of xylenol orange compared to thorin and Arsenazo III is the relatively minor interference of U.

Reagents and Equipment

- HCl
- 30% KOH
- Test solution, 10 mg Mn^{2+} and 50 mg of $NH_2OH \cdot HCl$ per ml
- 100 mg $NH_2OH \cdot HCl$ per ml in 7M HCl
- 2M NH_4OH
- 0.05% xylenol orange
- pH meter
- Spectrophotometer
- Centrifuge tubes

Procedure

1. **Add solution containing 5 to 20 µg of Np to a centrifuge tube, and dilute to 5 to 8 ml; then add 30% KOH until pH >10.**
2. **Add 1 ml of test solution containing 10 mg of Mn^{2+} and 50 mg of NH_2OH-HCl into the centrifuge tube.**

3. Mix and centrifuge the precipitate. Discard the liquid; then dissolve the precipitate in 2 ml of 7M HCl containing 100 mg $NH_2OH \cdot HCl$ per ml.

4. Heat the solution to almost boiling on a water bath for 25 min to obtain Np(IV).

5. Dilute to ~15 ml with water, add exactly 1 ml of 0.05% xylenol orange, and adjust to pH 2.0 to 2.2 with 2M NH_4OH.

6. Transfer the solution quantitatively to a 25 ml volumetric flask, and dilute to volume with water.

7. Mix and measure the optical density of the solution on an FE'K-M Instrument fitted with a green filter and using cells with a path of 5 cm at 550 nm. The reference solution is the same pH and reagent composition as the Np solution.

Notes

1. The Np concentration is determined from a standard calibration curve.

2. The determination requires ~3 hours, and the error usually is <±1μg.

3. Np can be determined by the above method in HCl, HNO_3, $HC_2H_3O_2$, and H_2SO_4 solutions and also in solutions containing other anions that are removed by the strong base precipitation; fluoride and phosphate interfere.

4. Alkali, alkaline-earth, rare earths, and Zn^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, and Cr^{3+} can be tolerated at 100 times the weight of Np. Hexavalent U up to 10 mg does not interfere. Pu(III) up to 200 μg does not interfere unless stored for a period of time which results in oxidation to Pu(IV). Fe^{3+}, Zr^{4+}, Th^{4+}, and Bi^{3+} ions form intensely colored species that interfere unless separated.

Procedure 25. Analysis for Np by Controlled Potential Coulometry

R. W. Stromatt[313]

Introduction

Controlled potential coulometry is useful for detecting as little as 2 μg of Np, and 7 μg can be determined with 6% standard deviation. The general procedure is to first oxidize all the Np to Np(VI) with Ce(IV), then the Np(VI) and excess Ce(IV) are electrolytically reduced to Np(V) and Ce(III). Finally the Np(V) is coulometrically oxidized to Np(VI) to determine the concentration of Np.

Reagents and Equipment

- 1M H_2SO_4
- Mercury metal
- Mercuric sulfate
- Pure helium gas
- Sodium silicate solution
- Controlled potential coulometer
- Titration cell (working electrode Pt gauze, isolated electrode Pt wire and saturated calomel reference)

Procedure

1. Add the Np sample and the titration medium into the cell, and adjust the hydrogen ion and sulfate ion concentrations to ∿1N. (The hydrogen ion concentration is not critical between 0.4 to 2N but the electrode potential of the Np(V/VI) couple is affected by the sulfate concentration).
2. Add Ce(IV) solution until there is an excess as evidenced by a persistent color.

3. De-aerate the solution with He for 5 min. [If during this time the excess Ce(IV) has reacted, add additional Ce(IV)].

4. Apply the potential to reduce the Np(VI) and excess Ce(IV) to Np(V) and Ce(III) until the current becomes constant.

5. Apply the potential to oxidize the Np(V) to Np(VI). The oxidation is continued until a constant current is obtained. Make several readings of the integrated current, and extrapolate the integrated current curve to zero time.

6. Prepare a blank solution containing the same amount of Ce(IV), and after 5 min of de-aeration perform reduction and oxidation titrations at the same potentials as used for the Np titration. After constant current is reached for oxidation, read the integrated current several times and extrapolate to zero time.

7. Subtract the zero-time integrated current of the blank from that for the Np titration, and calculate the amount of Np based on the instrument calibration. (For highest accuracy, the Np lost in the de-aeration and from migration in the cell are taken into account.)

Notes

1. The Np(V)/(VI) couple can be titrated quantitatively and reversibly in HNO_3, $HClO_4$, and H_2SO_4; however, more reproducible results are obtained with H_2SO_4. Also, the potentials of the Pu(III)/(IV) and Np(V)/(VI) couples are separated better in H_2SO_4.

2. Ce(IV) ion is used for oxidation because oxidation of Np is rapid and quantitative, and Pu(IV) is not oxidized significantly in H_2SO_4.

3. Coulometric titrations in solutions containing organic contaminants are often slow and yield low values.

4. The concentration of Np in the different oxidation states can be made using the Pt electrode cell. The Np(V)/(VI) couple can be titrated without interference from oxidation of Np(IV).

   Np(VI) is determined by coulometric reduction to Np(V). The Np(V) is then oxidized coulometrically, and the difference between these two titrations is the Np(V) initially present. The total Np concentration is determined as previously discussed, and Np(IV) is calculated from the difference between the concentrations of Np(V) plus Np(VI) and the total Np.

5. Propst[318] has reported a coulometric method for Np utilizing a conducting glass electrode in a thin-layer electrochemical cell. Organic contaminants interfered and were removed by a bisulfate fusion procedure.

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