

National Analytical Management Program (NAMP)
U.S. Department of Energy Carlsbad Field Office

Radiochemistry Webinars

Actinide Chemistry Series

▪ Neptunium Chemistry



*In Cooperation with our
University Partners*



Meet the Presenter...

Alena Paulenova



Dr. Alena Paulenova is Associate Professor in the Department of Nuclear Engineering and Director of the Laboratory of Transuranic Elements at the OSU Radiation Center. She is also Adjunct Professor at the Department of Chemistry at Oregon State University, a Joint Research faculty with Idaho National Laboratory, Division of Aqueous Separations and Radiochemistry and a member of the INEST Fuel Cycle Core Committee.

She received her Ph.D. in Physical Chemistry in 1985 from the Moscow/Kharkov State University. Until 1999, she was a faculty member at the Department of Nuclear Chemistry and Radioecology of Comenius University in Bratislava, then a visiting scientist at Clemson University and Washington State University in Pullman. In 2003 she joined the faculty at OSU as a Coordinator of the Radiochemistry Program at OSU Radiation Center to bring her experience to the task of helping to educate a new generation of radiochemists: <http://oregonstate.edu/~paulenova/>.

Her research interest has focused on application of radioanalytical and spectroscopic methods to speciation of radionuclides in aqueous and organic solutions and development of separation methods for spent nuclear fuel cycle processing, decontamination and waste minimization. The main efforts of her research group are fundamental studies of the kinetics and thermodynamics of the complexation of metals, primary actinides and fission products, with organic and inorganic ligands and interactions with redox active species, and the effects of radiolysis and hydrolysis in these systems.



Contact: (+1) 541-737-7070

E-mail: alena.paulenova@oregonstate.edu.

Neptunium Chemistry



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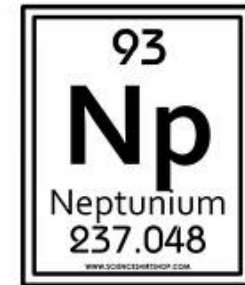
TRAINING AND EDUCATION SUBCOMMITTEE



Why to study Neptunium?

- Neptunium is one of actinides (“actinoids” by IUPAC), well known for being:
 - The first transuranic element ever synthesized
 - difficult to remove from other waste products
 - highly mobile in geological environments

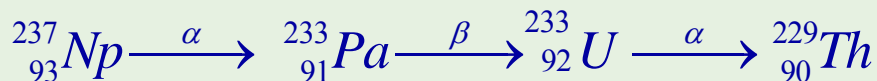
- Neptunium-237 ($T_{1/2} = 2.14$ million years):
 - the only neptunium isotope produced in the nuclear fuel cycle in significant quantity
 - byproduct of plutonium production; in breeder reactors about one part neptunium is produced for every 1,000 parts plutonium
 - Production ~ 3000 kg/year of ^{237}Np in used nuclear fuel (UNF)



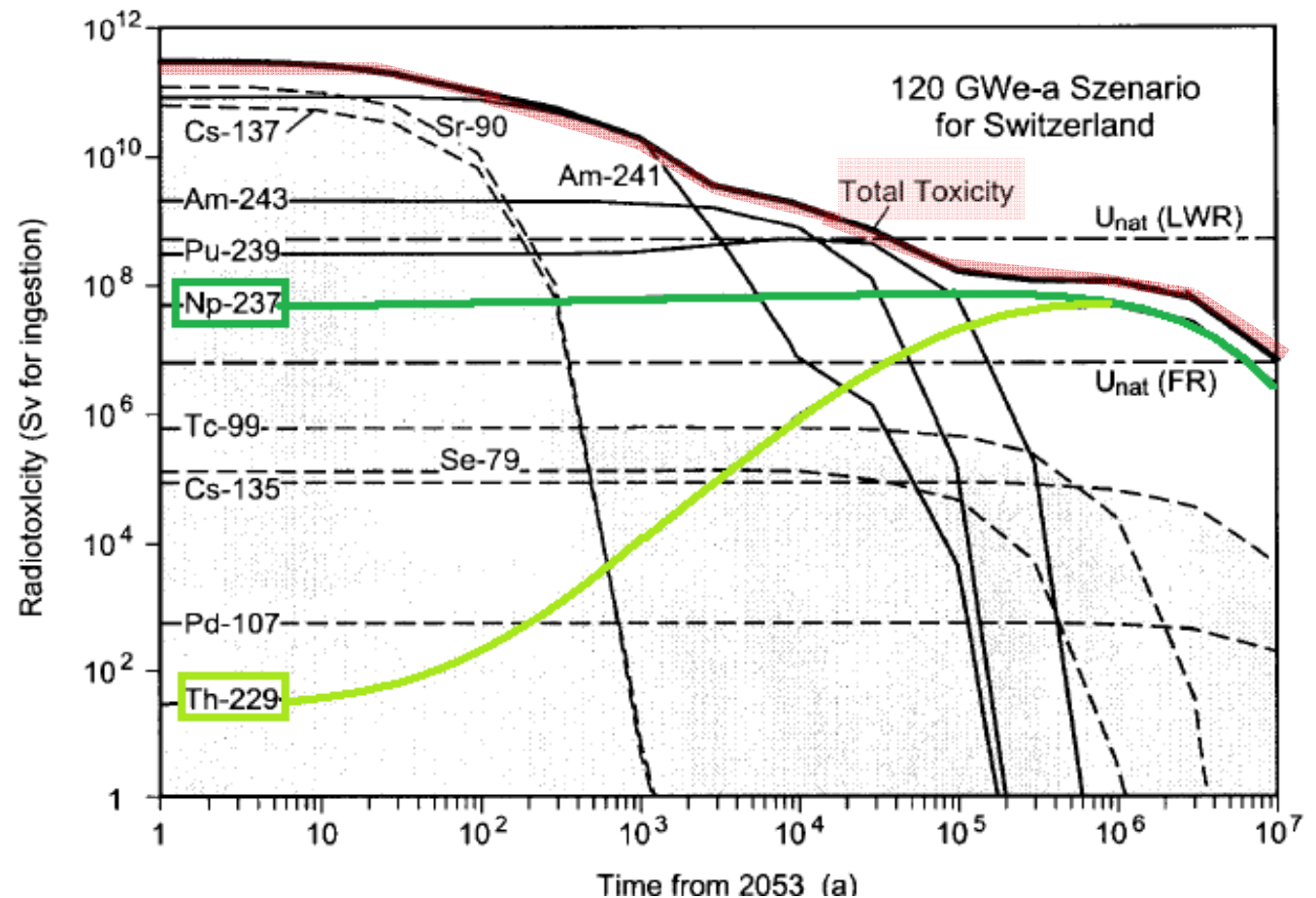
Atomic Symbol:	Np
Atomic Number:	93
Atomic Weight:	237.0482
Appearance:	silvery metal
Electron Configuration:	[Rn]7s ² 5f ⁴ 6d ¹
Radioactive Isotopes:	20 [atom/kaeri/re/kr]
Stable Isotopes:	0
Isomers:	> 5
Total Isotopes:	> 25
~ 5 isotopes important (A = 235-239)	

Np-237: long-term radiotoxicity

- main contributor to the long term toxicity of used nuclear fuel
- $T_{1/2} = 2\,177\,000$ yrs
- Over a long term, also formed as the decay product of Am-241 present in UNF
- Np-237 also decays to the fissile U-233



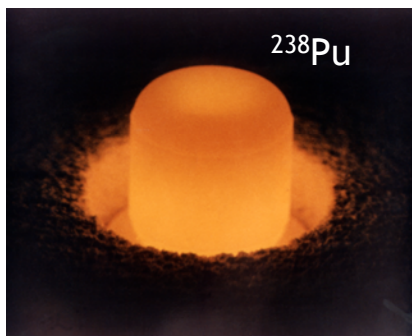
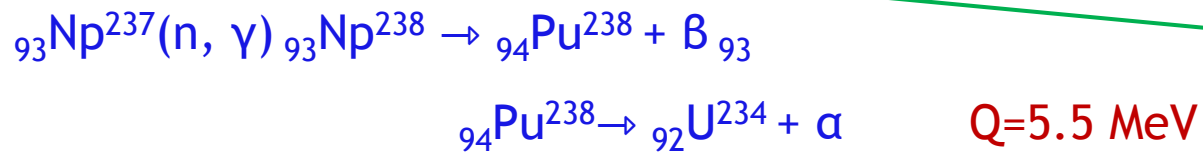
Radiotoxicity of LWR spent fuel after uranium and plutonium separation



Source: Actinide and Fission Product Partitioning and Transmutation, OECD NEA, 2001

Np-237 - needed in research and science

- ❑ Neptunium is considered useable in nuclear weapons (critical mass ~73 kg), although no country is known to have used it to make a nuclear explosive device.
- ❑ Although there are no major commercial uses of Np; Np-237 is needed for research and exploratory work:
 - As a component in neutron detection instrumentation
 - Production of Pu-236 by irradiation with bremsstrahlung of 23 MeV and 30 MeV electron beam [Yamana et al. (2001)] or protons ($E_p = 23.5$ MeV), [BARC-TIFR, Mumbai]
 - Production of Pu-238 for use in so-called RTGs (Radioisotope Thermoelectric Generators) to provide power for deep space missions in future space exploration: by neutron irradiation of **Np-237 targets** in the core of ORNL's High Flux Isotope Reactor:



ORNL (Radiochemical Eng. Development Center): Irradiated Np pellet is shown at center (surrounded by heat sink) prior to chemical dissolution in a hot cell.

Topics for today:

- Nuclear characteristics of neptunium
- Principal neptunium isotopes
- Important classes of Np compounds
- Neptunium in aqueous solutions
- Separation and analytical chemistry of Np

First Artificial Radioactivity

- U, Th, Pa and Ac are the only four naturally occurring actinides. Other An are artificial, being produced through various nuclear reactions.
- 1940 - Neptunium was the first transuranium element produced synthetically by bombarding uranium with slow neutrons in cyclotron:
- The newly found isotope of neptunium was created by absorption of neutron into the nucleus of U-238 (element 92) and a subsequent beta decay of U-239 to the element 93:
 - $${}_{92}\text{U}^{238} + {}_0\text{n}^1 \rightarrow {}_{92}\text{U}^{239} \rightarrow {}_{93}\text{?}^{239}$$
- ${}^{239}\text{Np}$ isotope (half-life 2.4 days) was discovered by Edwin McMillan and Philip H. Abelson in Berkeley.



- It was the first transuranium element observed ever.
- It was named Neptunium for the planet Neptune (the next planet out from Uranus, after which uranium was named).



Np, element 93 - great impact

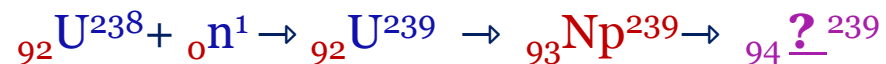


- E. McMillan was the first scientist ever to produce a transuranium element.
- He published his results already in 1939 but was not sure to call it a new element yet: *McMillan, E.: Phys. Rev.,55 (1939) 510*



- Together with Philip Abelson he repeated experiment, and a year later, a new element Np was claimed: *McMillan, E. and Abelson, P. H.: Phys. Rev., 57, (1940) 1185*

- The new element with A=239 and Z=93 was emitting beta particle of energy ~ 470 keV, so it lead to discussion about a daughter product with a mass number A=239 and Z=94:



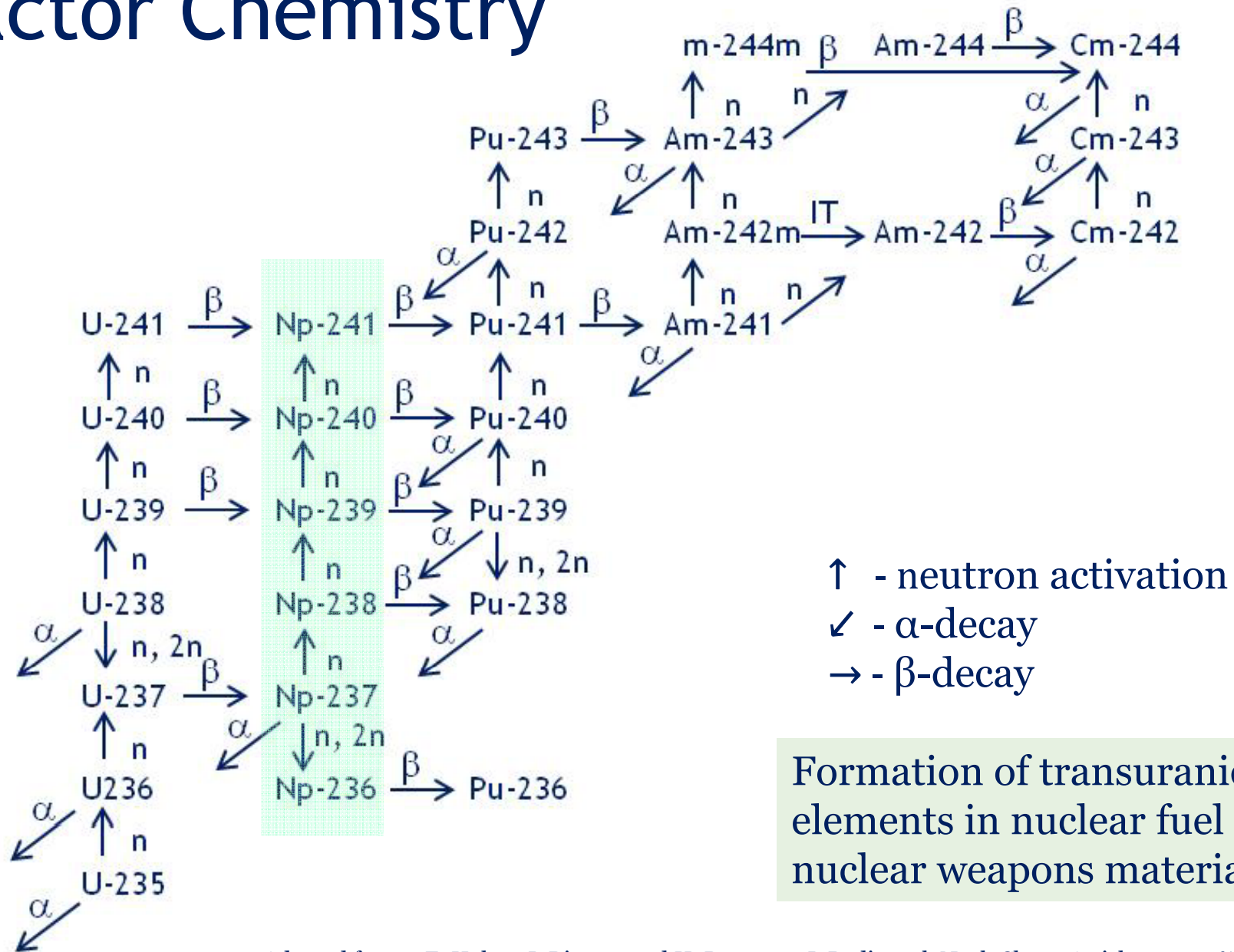
- McMillan immediately started bombarding U^{239} with deuterons to produce the element 94 but had to leave to MIT, so Glenn T. Seaborg joined McMillan's project and finished the work.



1941- Seaborg, Kennedy, Wahl and McMillan claimed discovery of plutonium (Pu, named after planet Pluto).

1951- **Nobel Prize in Chemistry**- G. Seaborg and E. McMillan - for "their discoveries in the chemistry of the first transuranium elements."

Reactor Chemistry

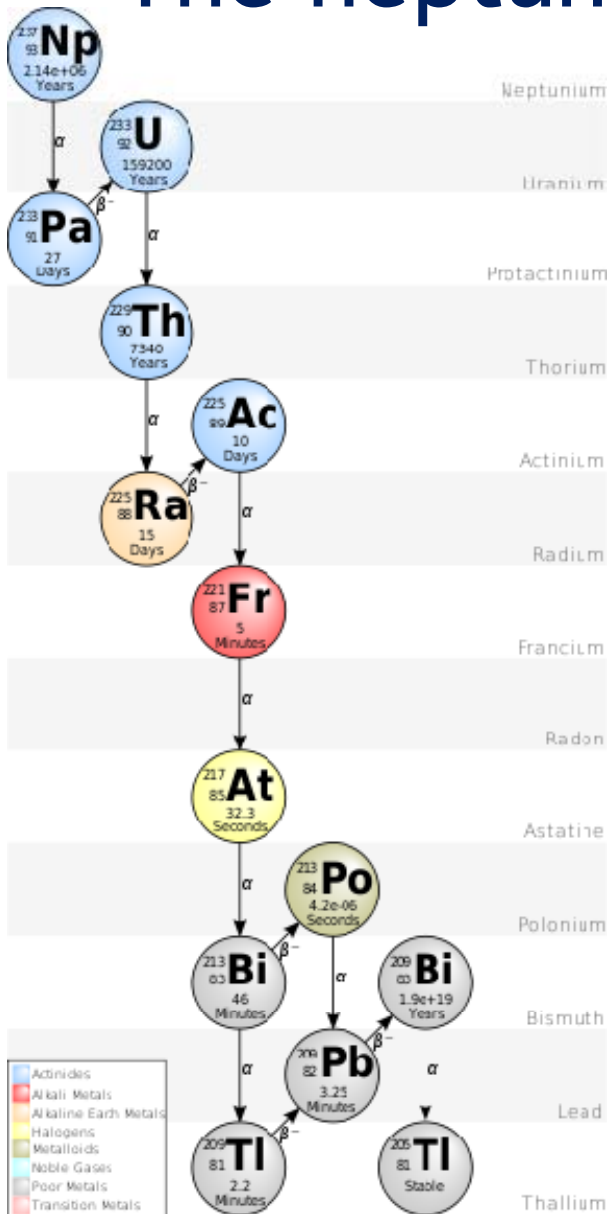


Radioactive Properties of Key Np Isotopes

Isotope	Nuclear reaction	Half-life	Decay mode	Alpha [MeV]	Beta [MeV]	Gamma [MeV]
Np-235	$^{235}\text{U}(p, 2n)^{235}\text{Np}$	396 d	EC (99.99%)	<	0.01	0.0071
Np-236	$^{235}\text{U}(d, n)^{236}\text{Np}$	1.54E5y	EC (87.3%), β (12.5%), α (0.2%)	5.02	0.21	0.14
Np-236m	$^{237}\text{Np}(n, 2n)^{236}\text{Np}$	22.5 h	EC(52%), β (48%)		0.55	0.6422
Pu-236	$^{236}\text{Np} \rightarrow ^{236}\text{Pu} + \beta$	2.9y	α	5.8	0.013	0.0021
Np-237	^{237}U(daughter): $^{235}\text{U}(n,\gamma)^{237}\text{U} \rightarrow ^{237}\text{Np} + \beta$ $^{238}\text{U}(n,2n)^{237}\text{U} \rightarrow ^{237}\text{Np} + \beta$ ^{241}Am (daughter): $^{241}\text{Am} \rightarrow ^{237}\text{Np} + \alpha$	2.177E6y	α	4.8	0.07	0.035
Pa-233	$^{237}\text{Np} \rightarrow ^{233}\text{Pa} + \alpha$	0.074y	β	-	0.2	0.20
Np-238	$^{237}\text{Np}(n, \gamma)^{238}\text{Np}$	2.1 d	β			
Np-239	$^{243}\text{Am} \rightarrow ^{239}\text{Np} + \alpha$ $^{239}\text{U} \rightarrow ^{239}\text{Np} + \beta$	2.36 d	β		0.722	

- 29 known Np isotopes and isomers: only 5 are important: with A = 235-239
- Pu-236 and Pa-233 also important, as they accompany the Np-236 and Np-237 decays.

The neptunium radioactive series



- $A = 4n + 1$
- Called after Np-237, the most stable radioactive isotope in the series; 2.14×10^6 years
- A series of [$\alpha + \beta + \alpha + \beta + \alpha \alpha \alpha$] between Np to Bi-213
- Bi-213 has two daughters: Po-213(β , 98%) and Tl-209 (α , 2%).
- Both daughters Po and Tl have simple decays to the same product Pb-209.
- The short-lived Pb-209 emits beta and decays to Bi-209.
- Bi-209 is practically stable; it decays to Tl-205 (stable) with a very-very long half-life of 1.9×10^{19} y.
- Since the half-life of Np-237 is three orders of magnitude shorter than the Earth's age, all primordial Np decayed long time ago and this decay chain no longer exists.

Figure adopted from Wikipedia.org

Sources of Neptunium

- ❑ **Used nuclear fuel (UNF):** after a few hundred thousand years Np-237 will be the prevailing transuranic element in UNF.
 - If Np-237 goes to the high-activity waste fraction for final disposal, concern arises not only because of its long half-life, but also because as the neptunyl ion NpO_2^+ it is fairly mobile in oxic conditions.
- ❑ **Radioactive Decay:** Np-237 is also formed by the alpha decay of Am-241, and therefore its activity in nuclear fuel and the environment is increasing.
- ❑ **Nuclear explosions:** Np-237 is formed with a total of about 2500 kg of Np released to the environment. Chemically, it is approximately the same amount as that of Pu isotopes, but because of its longer half-life, **specific activity** of Np-237 (Bq/g) is much lower.
- ❑ **Environmental release:**
 - Total release of Np-237 from the Chernobyl accident was about 5,000x lower than that from weapons tests fallout.
 - Release from UNF reprocessing plants: La Hague (France) and Sellafield (UK) together resulted in increased Np-237 levels in the nearby seas by a factor of as much as 1/1000 compared to the levels caused by the nuclear weapons tests fallout (10^{-15} to 10^{-14} g/L).
- ❑ **Conclusion:** Levels of Np-237 are high only in UNF. In the environment, the **activity levels** are very low compared to other actinides (Th, U, Pu, Am); determination of Np-237 from environmental samples requires a high separation efficiency and a sensitive measurement techniques.

Behavior in the Environment

- Typically, Np occurs in the environment as an **oxide**, although other forms can be present.
- It is generally most mobile from all other transuranic elements (Pu, Am, Cm), and it can move down with percolating water to underlying layers of soil.
- Np preferentially adheres to soil particles, with the concentration associated with sandy soil particles estimated to be about 5 times higher than in interstitial water (water in pore spaces between the soil particles);
- Np bonds more tightly to clay soils, where concentration ratios are typically higher (55x).
- Np is readily taken up by plants, and plant concentrations are typically similar to soil concentrations.

Neptunium in aqueous solutions

Analytical chemistry and spectroscopy of Np

Actinide Oxidation States

4 ⁺ g			5f ¹	5f ²	5f ³	5f ⁴	5f ⁵	5f ⁶	5f ⁷	5f ⁸	5f ⁹	5f ¹⁰	(5f ¹¹)	(5f ¹²)	(5f ¹³)
3 ⁺ aq			5f ²	5f ³	5f ⁴	5f ⁵	5f ⁶	5f ⁷	5f ⁸	5f ⁹	5f ¹⁰	5f ¹¹	(5f ¹²)	(5f ¹³)	(5f ¹⁴)
2 ⁺ g	7s	5f6d	5f ² 6d	5f ³ 3d	5f ⁵	5f ⁶	5f ⁷	5f ⁸	5f ⁹	5f ¹⁰	5f ¹¹	5f ¹²	(5f ¹³)	(5f ¹⁴)	(5f ¹⁴ 7s ²)
0	6d 7s ²	6d ² 7s ²	5f ² 6d 7s ²	5f ³ 6d 7s ²	5f ⁴ 6d 7s ²	5f ⁶ 7s ²	5f ⁷ 7s ²	5f ⁷ 6d 7s ²	5f ⁹ 7s ²	5f ¹⁰ 7s ²	5f ¹¹ 7s ²	5f ¹² 7s ²	(5f ¹³ 7s ²)	(5f ¹⁴ 7s ²)	(5f ¹⁴ 6d 7s ²)
7 ⁺					◆	◆									
6 ⁺				■	◆	□	◆								
5 ⁺			■	◆	■	□	□	◆							
4 ⁺		■	■	■	■	■	□	□	◆	◆					
3 ⁺	■	◆	◆	□	□	■	■	■	■	■	■	■	■	□	■
2 ⁺										◆	◆	◆	□	■	
An	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Importance: ■ > □ > ◆

The close proximity of the energy levels of the 7s, 6d, and 5f electrons almost guarantees multiple oxidation states for the actinide ions in the first half of the actinide series.

A variety of oxidation states (2⁺ to 7⁺) in aqueous solution possible, but the light actinides in aqueous acidic solutions are in III, IV, V and VI oxidation states

5+ and 6+ Oxidation States:

4 ⁺ g			5f ¹	5f ²	5f ³	5f ⁴	5f ⁵	5f ⁶	5f ⁷	5f ⁸	5f ⁹	5f ¹⁰	(5f ¹¹)	(5f ¹²)	(5f ¹³)	
3 ⁺ aq			5f ²	5f ³	5f ⁴	5f ⁵	5f ⁶	5f ⁷	5f ⁸	5f ⁹	5f ¹⁰	5f ¹¹	(5f ¹²)	(5f ¹³)	(5f ¹⁴)	
2 ⁺ g	7s	5f6d	5f ² 6d	5f ³ 6d	5f ⁵	5f ⁶	5f ⁷	5f ⁸	5f ⁹	5f ¹⁰	5f ¹¹	5f ¹²	(5f ¹³)	(5f ¹⁴)	(5f ¹⁴ 7s ²)	
0	6d 7s ²	6d ² 7s ²	5f ² 6d 7s ²	5f ³ 6d 7s ²	5f ⁴ 6d 7s ²	5f ⁶ 7s ²	5f ⁷ 7s ²	5f ⁷ 6d 7s ²	5f ⁹ 7s ²	5f ¹⁰ 7s ²	5f ¹¹ 7s ²	5f ¹² 7s ²	(5f ¹³ 7s ²)	(5f ¹⁴ 7s ²)	(5f ¹⁴ 6d 7s ²)	
7 ⁺					◆	◆										Importance: ■ > □ > ◆
6 ⁺				■	◆	□	◆									
5 ⁺			■	◆	■	□	□	◆								
4 ⁺		■	■	■	■	■	□	□	◆	◆						
3 ⁺	■	□	□	□	□	■	■	■	■	■	■	■	■	■	□	■
An	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

A variety of oxidation states (2⁺ to 7⁺) in aqueous solution possible, but the light actinides in aqueous acidic solutions are in III, IV, V and VI oxidation states

The 5⁺ oxidation state is well established for the elements Pa through Am; and the 6⁺ state in the elements U through Am.

The multiplicity of oxidation states, coupled with the hydrolytic behavior of the ions, make the chemical behavior of the elements from Pa to Am among the most complex of the elements in the periodic table.

Neptunium Ions in Aqueous Solution:

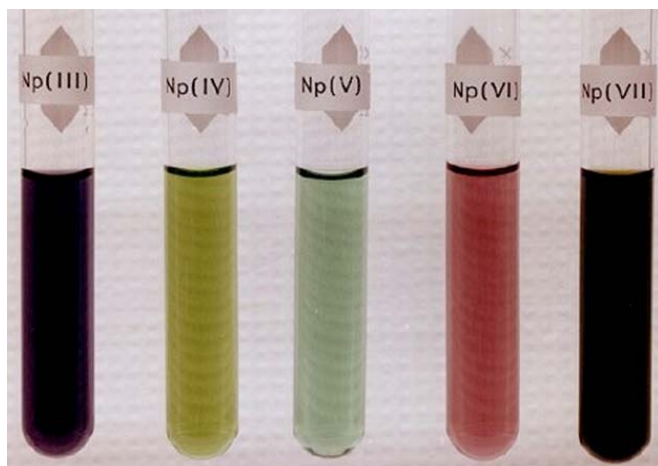
Actinides in the same oxidation state have essentially the same coordination environments, and in aqueous solutions (at pH < 3) they appear in four main structural ionic types:

- +III and +IV: simple cations An^{3+} or An^{4+} ; with a high charge density, they show a strong inclination to solvation, hydrolysis, and polymerization.
- +V and +VI: dioxocations AnO_2^+ and AnO_2^{2+} ; oxygenated species known as actinyl ions, formed by hydrolysis of metal cation of higher oxidation state in the hydration shell (see the first webinar).

Effective charge actinide cation is decreased by forming covalent bonds between two oxygen atoms $O=An=O$.

Cationic charge:	An^{3+}	An^{4+}	AnO_2^+	AnO_2^{2+}
Valence (oxidation state) of metal	3	4	5	6
Formal (“gross”) Charge of cation	3	4	1	2
Effective Cationic Charge	3.0	4.0	2.2	3.2
Strength order: “ionic potential” = charge/ionic radius	$AnO_2^+ < An^{3+} < AnO_2^{2+} < An^{4+}$			
	$NpO_2^+ < Np^{3+} < NpO_2^{2+} < Np^{4+}$			

Neptunium Stable Aqueous Species



Colors of neptunium:

Np(III) is violet (similar to promethium).

Np(IV) is yellowish green.

Np(V) is green-blue.

Np(VI) is rose.

Np^{3+} , Np^{4+} , NpO_2^+ , NpO_2^{2+} :

- Np^{3+} behaves analogically to Ln^{3+} : precipitates with OH^- , PO_4^{3-} , and F^-
- Np^{4+} behaves like Pu^{4+} : hydrolyzes and forms stable sulfate, fluoride and oxalate complexes
- Order of complex strength:
 - $\text{F}^- > \text{H}_2\text{PO}_4^- > \text{SCN}^- > \text{NO}_3^- > \text{Cl}^- > \text{ClO}_4^-$
 - $\text{CO}_3^{2-} > \text{HPO}_4^{2-} > \text{SO}_4^{2-}$
- NpO_2^+ forms cation-cation complexes: $\text{Fe} > \text{In} > \text{Sc} > \text{Ga} > \text{Al}$
- NpO_2^+ is not easily complexed, precipitated or extracted
- NpO_2^{2+} behaves like UO_2^{2+} and PuO_2^{2+} , forms similar complexes and is extracted by organic solvents

- In acid solution, 7+ oxidation state oxidize water rapidly, but An(VII) are more stable in alkaline aqueous solutions; containing in some cases the tetraoxo-species $\text{AnO}_4(\text{OH})_2^{3-}$. $\text{NpO}_4(\text{OH})_2^{3-}$ produced in 0.1-2 M LiOH (KOH) solution is extracted with various extractants such as TBP, TOPO, crown ether derivatives, HDEHP, etc. [Rozen et al., 1990].
- $\text{Co}(\text{NH}_3)_6\text{NpO}_5 \cdot 3\text{H}_2\text{O}$ - the only solid compound reported [Mikhailov, 1973].

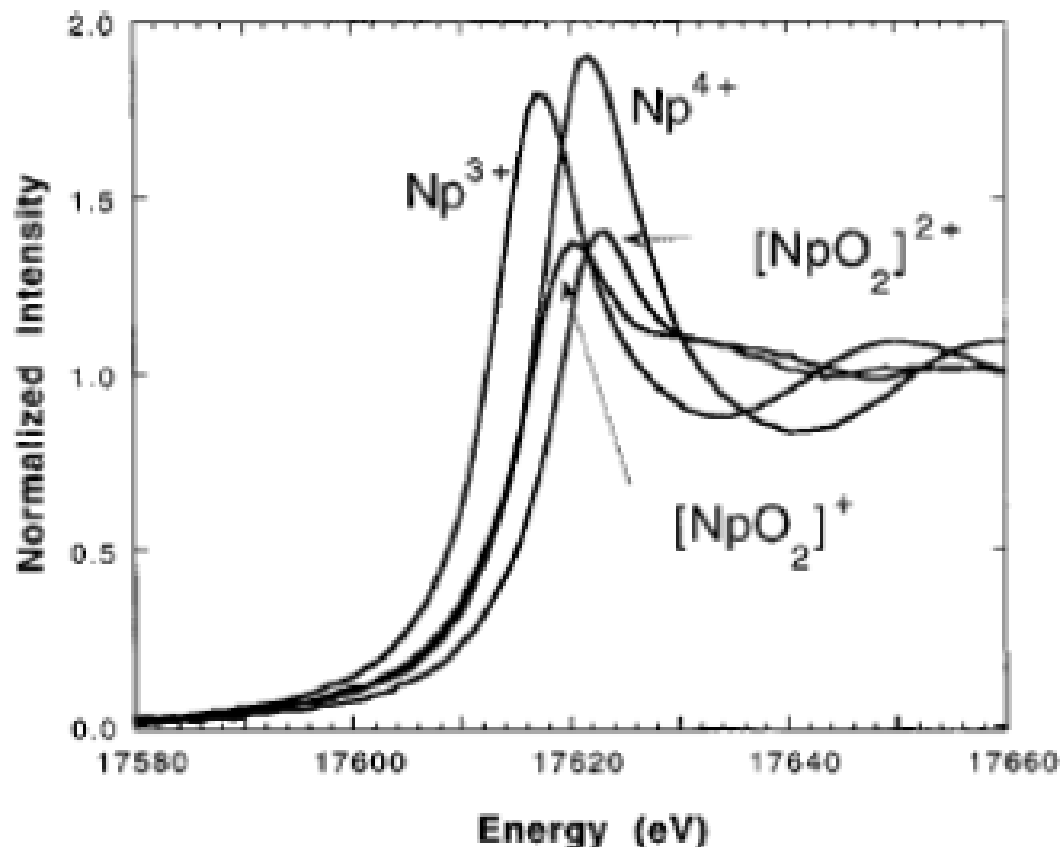
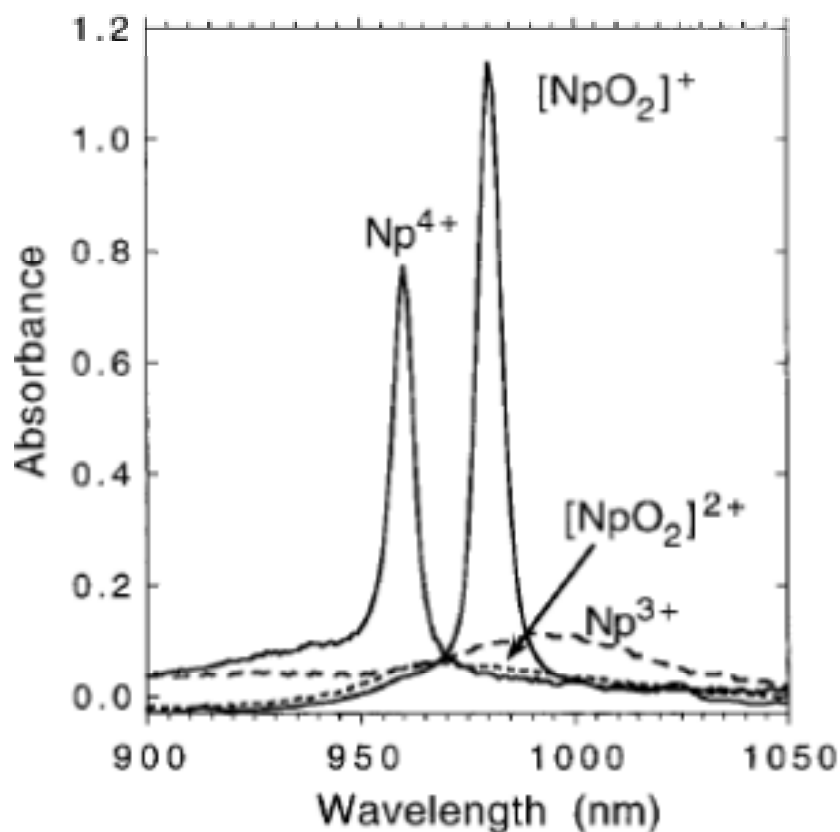
Redox Potentials of Np in Acidic Media

The standard redox potentials (V) for Pu and Np in 1M HCl or 1M HClO₄* [Edelstein, 2006]

		0.882		
Np ³⁺	→	Np ⁴⁺	→	NpO ₂ ⁺
		0.604		
			→	NpO ₂ ²⁺
				2.04*
			→	NpO ³⁺
		0.983		
Pu ³⁺	→	Pu ⁴⁺	→	PuO ₂ ⁺
		1.047		
			→	PuO ₂ ²⁺
				2.31*
			→	PuO ³⁺

- The redox couples in which **only an electron is transferred**, NpO₂⁺/NpO₂²⁺ (or Pu³⁺/Pu⁴⁺)
 - are electrochemically reversible and
 - their redox reactions are rapid
- Redox reactions that involve **forming or rupturing of the An-O bond**, Np⁴⁺/NpO₂⁺ (or Pu⁴⁺/PuO₂²⁺):
 - are not reversible
 - some of these are two-electron reductions
 - have a slower reaction rate because reorganization of the solvent shell

Np Redox Speciation



XANES spectra from the pure Np(III), Np(IV), Np(V), and Np(VI) states in HClO₄ under the same conditions and sequences used to obtain the optical spectra. [Soderholm et al., Anal. Chem. 1999, 71, 4622]

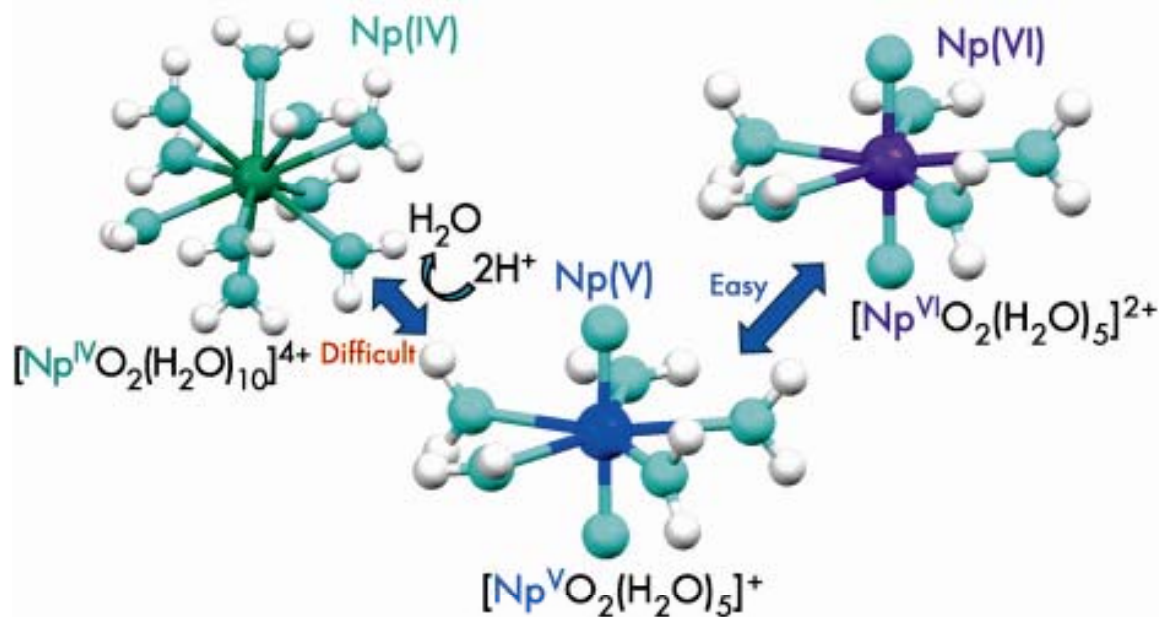
Optical spectra obtained for Np(III), Np(IV), Np(V), and Np(VI) with the sample in the spectroelectrochemical cell with controlled potentials of: -0.2, +0.4, +0.689, and +1.2 V. [Soderholm et al., Anal. Chem. 1999, 71, 4622]

in 1M HClO₄:



Np Redox in details

Structural determination of neptunium redox species in aqueous solutions



Structural rearrangement of Np hydrate species through the redox reaction

Adopted from:

A. Ikeda-Ohno (a,b), C. Hennig (a), A. Rossberg (a), H. Funke (a), A.C. Scheinost (a), G. Bernhard (a), T. Yaita (b), *Inorg. Chem.* 47, 8294 (2008).

EXAFS data confirm a structural rearrangement of Np hydrate species with oxidation state:

- Both **Np(V)** and **Np(VI)** ions exist predominately as penta-aquo neptunyl complexes $[\text{NpO}_2(\text{H}_2\text{O})_5]^{n+}$ where $n = 1$ [**Np(V)**] or $n = 2$ [**Np(VI)**]
- Np(IV) ion forms a spherically coordinated deca-aquo complex, $[\text{Np}(\text{H}_2\text{O})_{10}]^{4+}$.
- A drastic change in complex structure between **Np(IV)** and **Np(V)** makes the transition between these two redox states almost irreversible ($E \sim 0.9 \text{ V}$)
- Transition between **Np(V)** and **Np(VI)** requires no structural change, hence it is quasi-reversible ($E = \sim 0.2 \text{ V}$).

Role of Proton in Redox Chemistry

The **role of proton in redox processes** in aqueous solutions is crucial; for example:

- **Disproportionation** of Np between two oxidation states is appreciable only for the **Np(V)** oxidation state, and the reaction is favored by high concentration of acid:



- Obviously, the **synproportionation** reaction will be promoted by a lower acidity of solution:



- Both the tetravalent and hexavalent cations, having higher effective cationic charge, are more strongly complexed by ligands, thus the disproportionation reaction will be accelerated toward completion by an addition of complexing agents.
- **Control of redox species is very important consideration for analysis and experimental studies.**

Redox Chemistry in HNO₃ Solutions

- The oxidation of Np(V) by nitrate ion is favored by high HNO₃ and low concentrations of nitrous acid (HNO₂), and vice versa, Np(VI) is rapidly reduced to Np(V) at high concentrations of nitrous acid:



- It was found that oxidation of Np(V) to Np(VI) by nitric acid is very slow, but it can be accelerated by small concentrations of nitrous acid (Siddall, Dukes, 1959).
- However, under these conditions, the $\cdot\text{NO}_2$ radical is generated by synproportionation of HNO₂ and HNO₃:



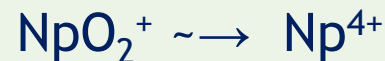
- Then, the accelerated oxidation of pentavalent neptunium may be due to reaction with the $\cdot\text{NO}_2$ radical, which actually acts as an oxidizing agent with Np(V), rather than the nitrous acid itself (Mincher, 2012):



Self-Radiolysis in Aqueous Solutions

Self-radiolysis may greatly affect the chemical equilibrium, redox and speciation of actinides in their solutions.

For example, ^{239}Pu :



- Intermediate Np (IV) is unstable in acidic solutions; it oxidizes to produce Np(V) and Np(VI); may repropportionate as well.
- In acidic solution of ^{239}Pu , the self-radiolysis results in changes of the oxidation state of PuO_2^{2+} which “degrades” by being reduced to Pu^{4+} at a rate of approximately 1.5% per day.
- However, in the case of longer lived Np-237, the hydrogen peroxide (and other radiolytic products from water) is produced in lower concentration than by ^{239}Pu .

Analysis and speciation

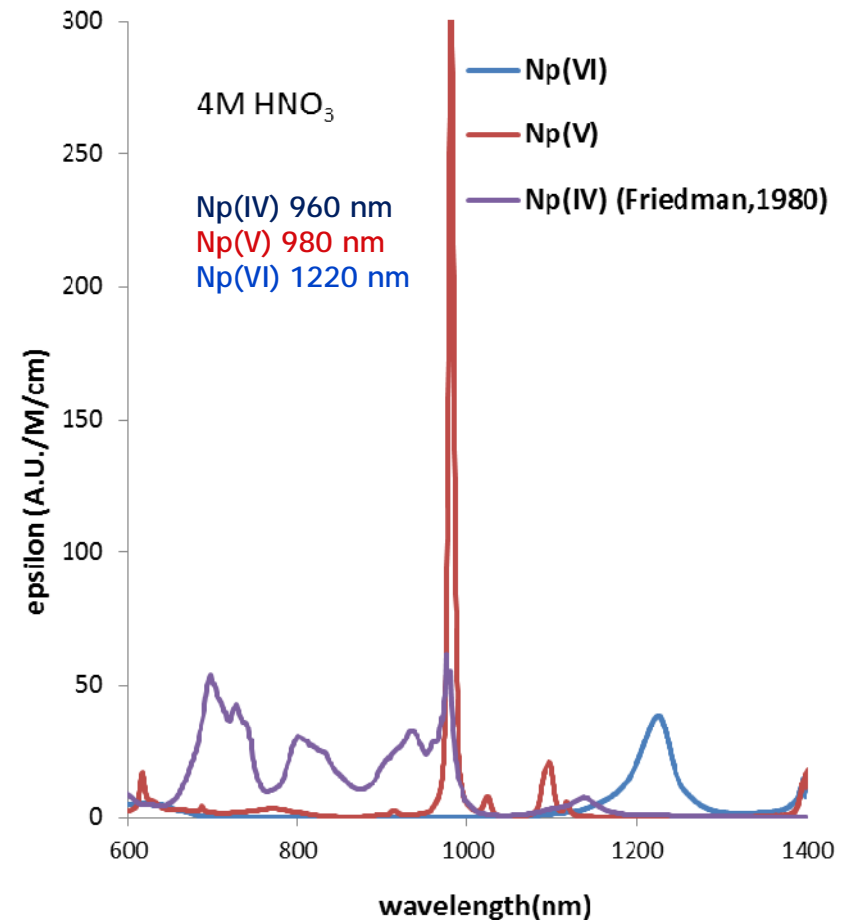
Chemical Speciation of Actinides

□ Aqueous/organic phase in processes:

- Spectrophotometry (UV, Vis, NIR)
 - Detection limit in 1 cm cell:
 - Np(III) 0.5mM, Np(IV) 0.1mM, Np(V) 0.05mM, Np(VI) 0.5mM
- Vibrational spectroscopy (FTIR, Raman)
- Nuclear Magnetic Resonance Spectroscopy
- X-Ray Absorption Fine Structure (XAFS) Spectroscopy
- Laser-Induced Fluorescence (LIF) Spectroscopy
- Etc.

□ Speciation Modeling:

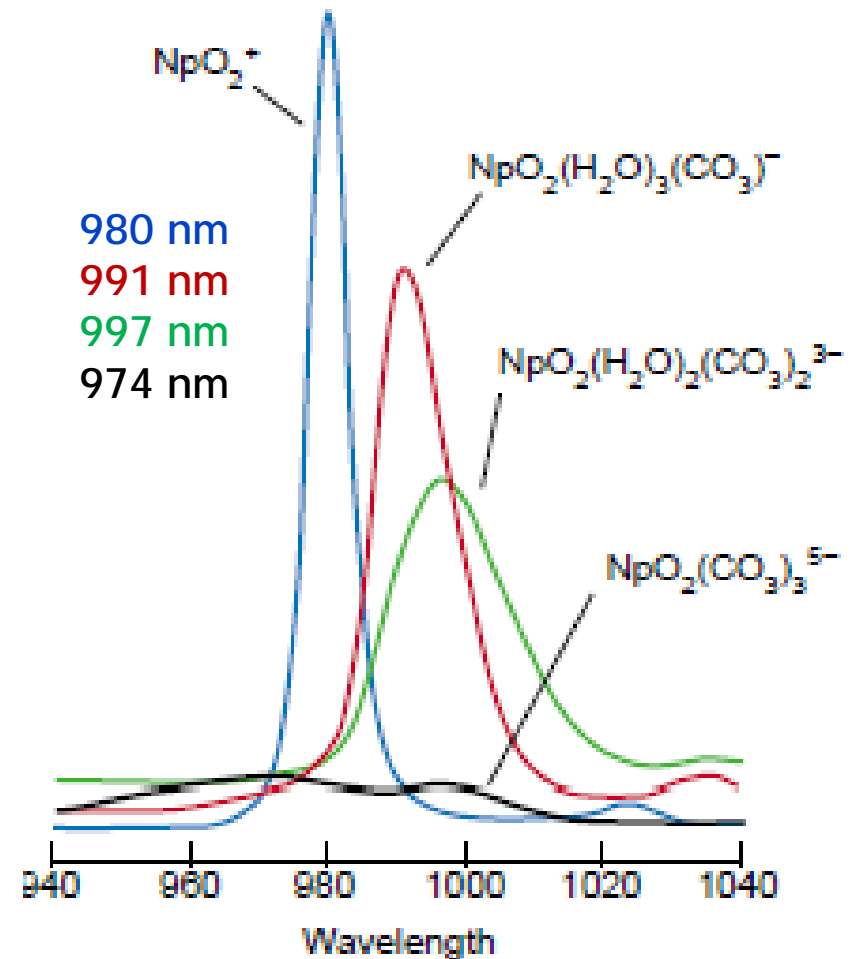
- Hyperquad (Peter Gans et al.)
- PHREEQC, FITEQL, MIEQL, etc.



Chemical speciation refers to the distribution of an element amongst chemical species in a system. [Precek, OSU, 2012]

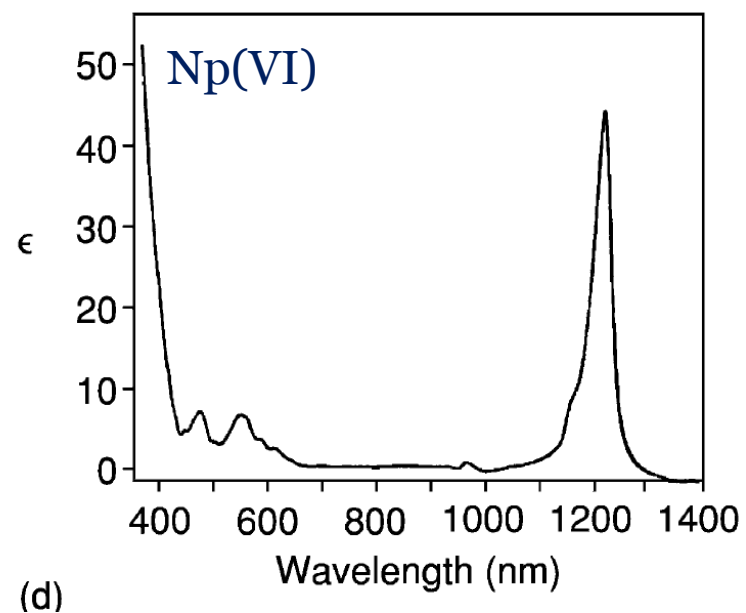
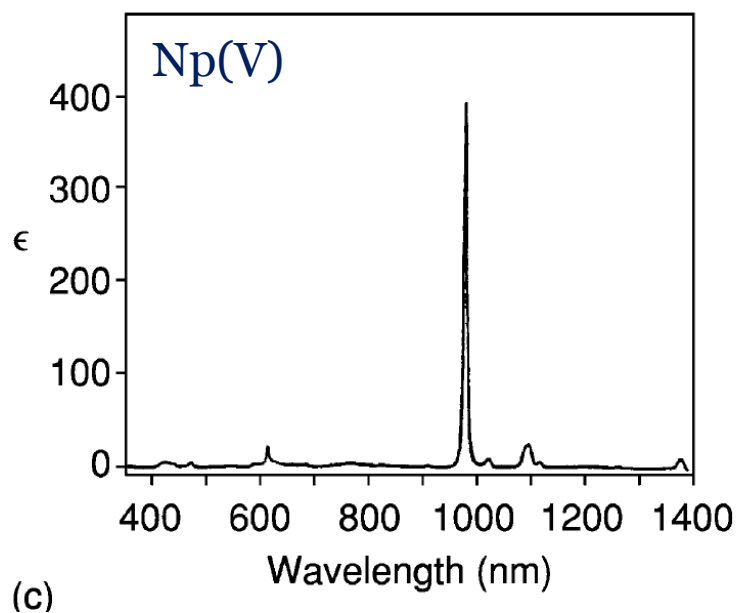
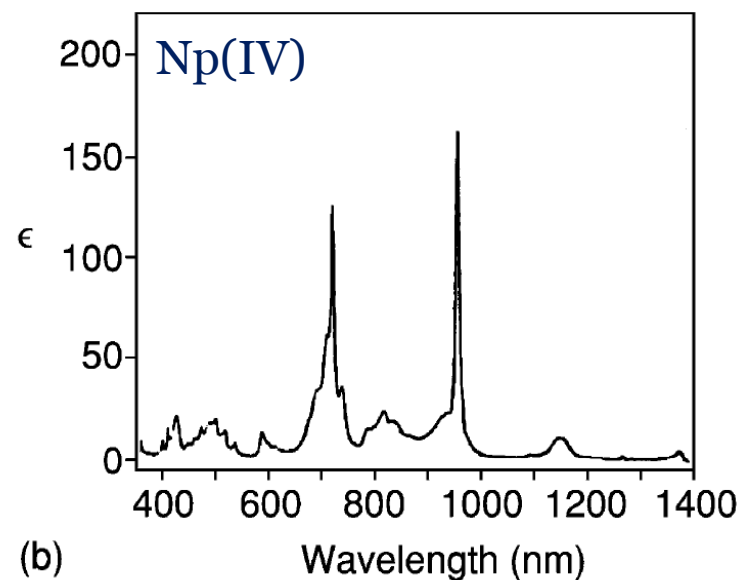
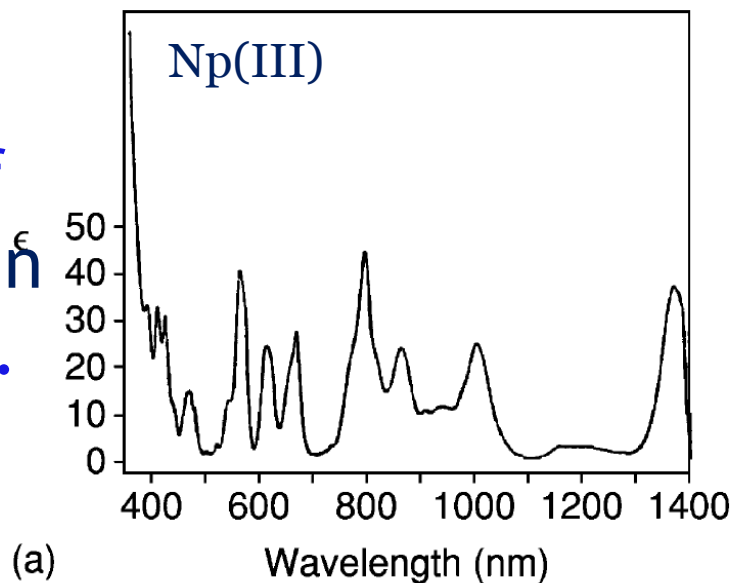
Speciation by Vis-NIR Spectroscopy

- Complexed ion can be tracked because the absorption band is shifted significantly with the addition of ligands
- For example, the non-complexed Np(V) aquo ion, penta-aquo ion, exhibits a strong absorbance at 980 nm.
- Addition of carbonate ligand instead of molecule of water shifts the peak in spectrum to higher wavelengths.
- Only the peak for the triscarbonato-Np (V) complex (with no water) is shifted back to lower wavelength (974 nm)
- Combining these spectroscopic results with those from XAFS experiments has given us insight into the molecular structures of environmentally relevant Np(V) complexes.

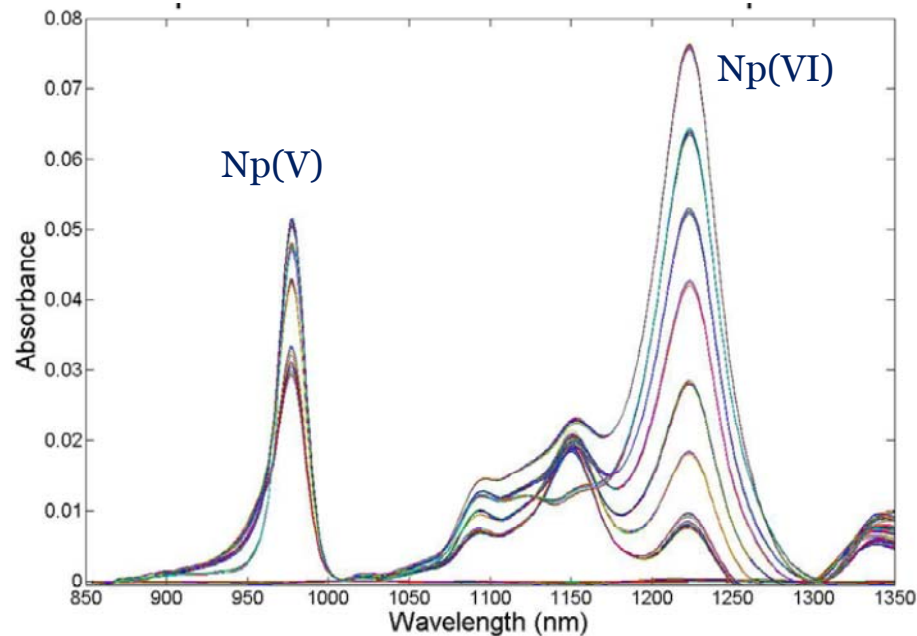


UV-vis-NIR Spectra of Np [Chemical Interactions of Actinides in the Environment, Runde, 2000]

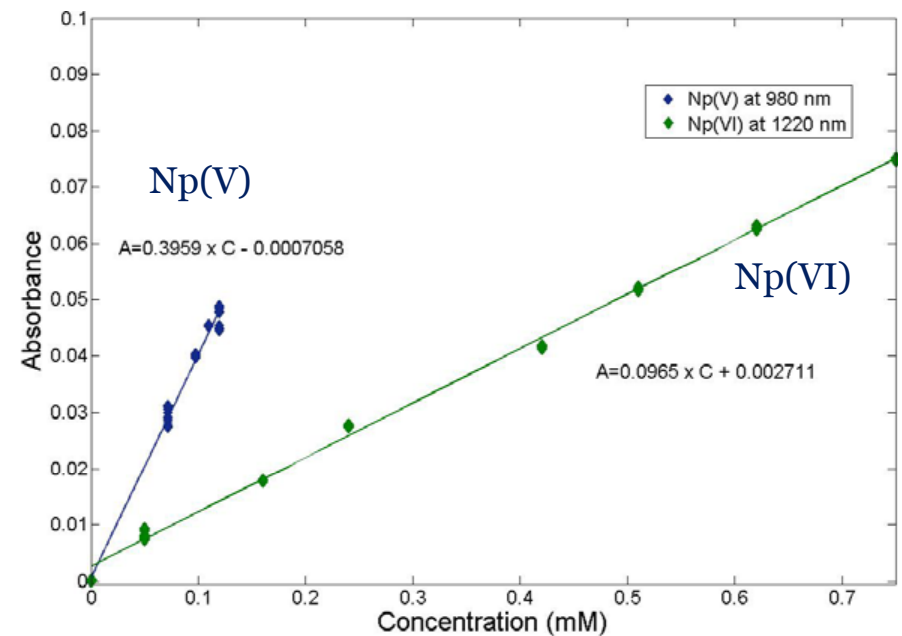
Spectra of
Np(III-VI) in
2 M HClO₄.



VIS-NIR chemometric analysis

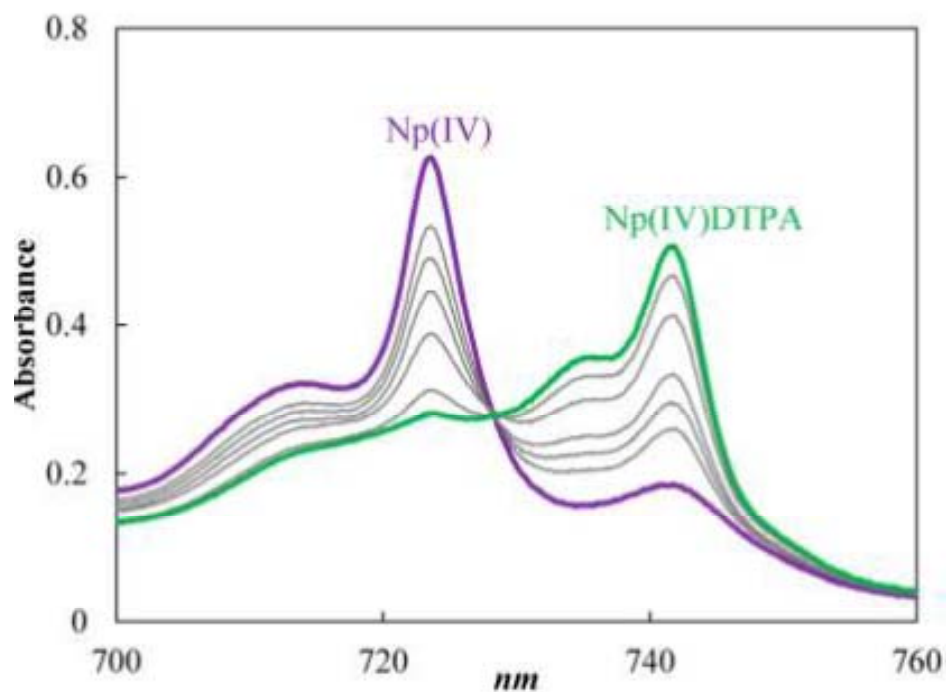


Standard Spectra Used for Chemometric Analysis for Neptunium (V, VI) .



Linear Calibration Plots for Neptunium (V, VI)

Np(IV) spectrophotometry



Np(IV) for spectrophotometry:

- from Np(V) stock in 2 M HCl
- electrochemically reduced using a platinum mesh cathode vs saturated calomel electrode (SCE) at -0.1 V for 20 min.
- Np concentration by LSC ($\sim 99\%$ det eff)
- γ spectroscopy
- Must be maintained under a constant nitrogen gas stream throughout the set of experiments
- periodically checked on consistency of the tetravalent oxidation state:

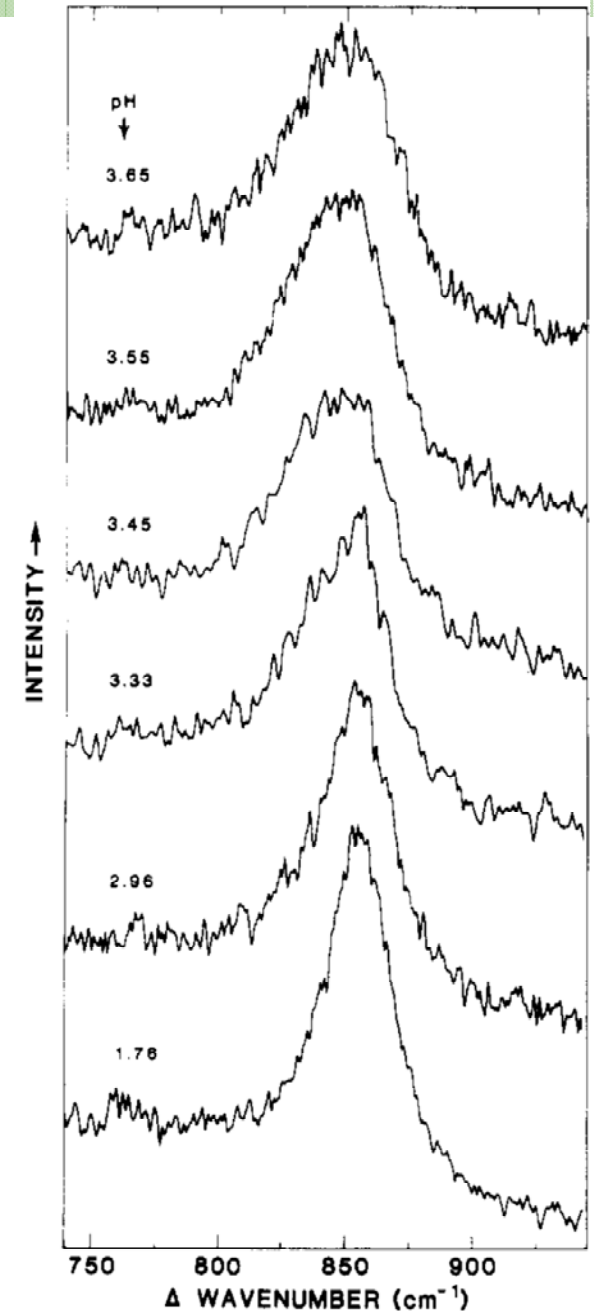
Purity of the tetravalent oxidation state:

- has absorption peaks at 724 and 960 nm
- absence of a Np(V) absorption peak at 980 nm confirms purity of the 4+ oxidation state

Raman spectroscopy of Np(VI)

Hydrolysis of NpO_2^{2+} :

- NpO_2^{2+} at 854 cm^{-1}
- Np(VI) hydroxocomplex: 834 cm^{-1}
- At pH 1.76 and 2.96: intensity and the shape of the 854-cm^{-1} NpO_2^{2+} band was found to be unchanged.
- Increase in pH causes broadening of the symmetrical stretching vibration at 854 cm^{-1} , and its maximum shifted toward a lower wavenumber
- this effect certainly corresponds to the appearance of a Np(VI) hydroxo complex in the solution having a characteristic band at a lower frequency at 834 cm^{-1}
- For pH values higher than 3.65, precipitation of a sodium neptunate occurred.



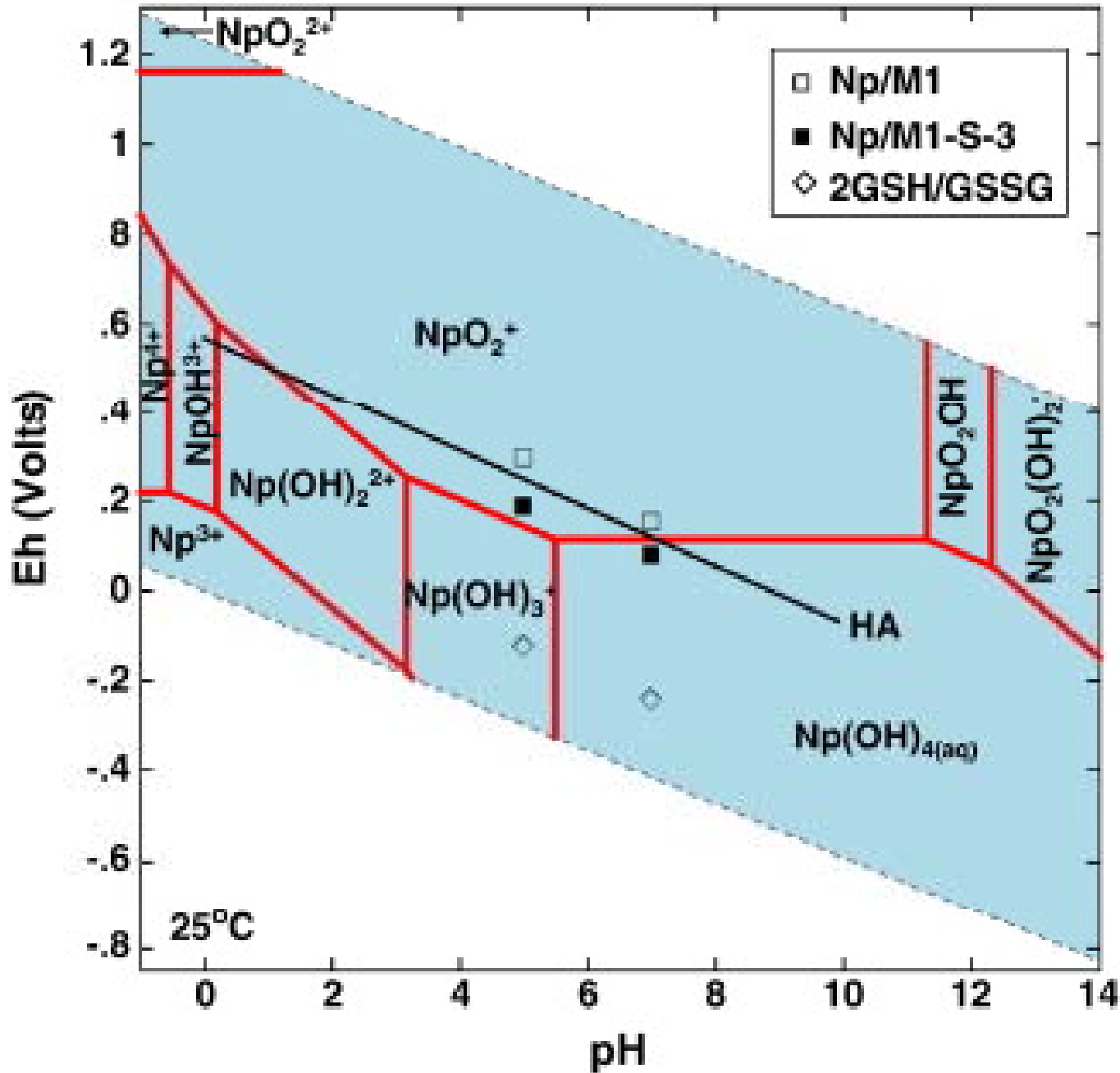
Np hydrolysis

- ❑ Np hydrolysis follows the effective cationic charge order:
$$\text{Np(IV)} > \text{Np(VI)} > \text{Np(III)} > \text{Np(V)}$$
- ❑ Np(III)
 - Stable in acidic solution below $\text{pH} \leq 4$; Oxidizes in air to Np(IV)
 - Neptunium(III) hydroxide is not soluble in water and does not dissolve in excess alkali; no K_{sp} data
- ❑ Np(IV)
 - Stable only in acidic solution; hydrolysis starts already at $\geq \text{pH} 1$
 - Hydrolyzed species may remain in solution, at higher concentration of metal precipitate. $K_{sp} = ?$
- ❑ Np(V)
 - Most stable Np species, not hydrolyzed at $\text{pH} \leq 7$
- ❑ Np(VI)
 - Not hydrolyzed at $\text{pH} \leq 3-4$
- ❑ Np(VII)
 - No data on hydrolysis as Np(VII) exist only under very basic conditions as anionic complex species

The inorganic aqueous and solubility-limiting species for Np(V)

Np(V) Reactions	log K
$\text{NpO}_2^+ + \text{OH}^- \rightleftharpoons \text{NpO}_2\text{OH}(\text{aq})$	2.7
$\text{NpO}_2^+ + \text{OH}^- \rightleftharpoons \text{NpO}_2\text{OH}(\text{s, am})$	8.8
$\text{NpO}_2^+ + \text{OH}^- \rightleftharpoons \text{NpO}_2\text{OH}(\text{s, aged})$	9.5
$\text{NpO}_2^+ + 2\text{OH}^- \rightleftharpoons \text{NpO}_2(\text{OH})_2^-$	4.5
$\text{NpO}_2^+ + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2\text{CO}_3^-$	5.0
$\text{NpO}_2^+ + 2\text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_2^{3-}$	6.4
$\text{NpO}_2^+ + 3\text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_3^{5-}$	5.3
$\text{Na}^+ + \text{NpO}_2^+ + \text{CO}_3^{2-} + 3.5\text{H}_2\text{O} \rightleftharpoons \text{NaNpO}_2(\text{CO}_3) \times 3.5\text{H}_2\text{O}(\text{s})$	11.1
$3\text{Na}^+ + \text{NpO}_2^+ + 2\text{CO}_3^{2-} \rightleftharpoons \text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$	14.2
$\text{K}^+ + \text{NpO}_2^+ + \text{CO}_3^{2-} \rightleftharpoons \text{KNpO}_2(\text{CO}_3)(\text{s})$	13.6
$3\text{K}^+ + \text{NpO}_2^+ + 2\text{CO}_3^{2-} + 0.5\text{H}_2\text{O} \rightleftharpoons \text{K}_3\text{NpO}_2(\text{CO}_3)_2 \times 0.5\text{H}_2\text{O}(\text{s})$	-4.8

Source: **Compliance Recertification Application for the Waste Isolation Pilot Plant**
 Title 40 CFR Part 191, Subparts B and C; Appendix SOTERM-2009; Actinide Chemistry Source Term



Summary of Np Chemistry

Predominant Species Diagram for Np as a function of pH and E_h based on the Np speciation data reactions

Source:
 Title 40 CFR Part 191, Subparts B and C
 Compliance Recertification Application for the
 Waste Isolation Pilot Plant
 Appendix SOTERM-2009
 Actinide Chemistry Source Term

Analysis of Neptunium

Analytical methods and detection limits

Analytical methods for the determination of ^{237}Np and their detection limits:

<i>Method</i>	<i>Detection limit</i>	<i>Refs.</i>
Alpha spectrometry	0.014–0.05 ng 3.7×10^{-4} –0.013 Bq	Germain et al. (1987)
ICP–MS	2×10^{-4} Bq	Scott et al. (1991)
Luminescence spectrometry	5 ng g ⁻¹ (0.13 Bq g ⁻¹)	Novikov et al. (1975)
High resolution ICP–MS	10 fg	
Neutron activation analysis	1×10^{-4} –100 ng g ⁻¹ (2.6×10^{-6} –2.6 Bq g ⁻¹)	Germain et al. (1987)
X-ray fluorescence	200–300 ng (5.2–7.8 Bq)	Burney and Harbor (1974)
Laser induced photo-acoustic spectroscopy	2.37×10^3 ng mL ⁻¹ (61.8 Bq mL ⁻¹)	Klenze and Kim (1988)
Laser ablation ICP–MS	0.5 ng g ⁻¹	Gastel et al. (1997)
Resonance ionization mass spectrometry	4×10^8 atoms (1.6×10^{-13} g)	Riegel et al. (1993)
Accelerator mass spectrometry	10^5 atoms (4×10^{-17} g)	Fifield et al. (1997)
Glow discharge mass spectrometry	80 pg/g	De las Heras et al. (2002)

Analytical methods

- ❑ Environmental levels
 - General levels 1E-15 g/L
 - Elevated levels up to 1E-11 g/L
- ❑ Radiometric methods
- ❑ High-resolution gamma spectrometry for Np-237 (Pa-233)
$$\text{Np-237} \rightarrow \text{Pa-233} + \alpha$$
 - Np-237 directly: (29 keV, 86 keV)
 - Np-237 indirectly (via Pa-233): (312 KeV)
 - Determination of Np-237 via Pa-233 gives a more sensitive detection method, but assumes equilibrium is established between parent and daughter. Unless processing of the material has been undertaken within the last 270 days this is a reasonable assumption.
- ❑ Neutron activation analysis/gamma
 - Formation of ^{238}Np , 170 barns, 2.117 day half life for ^{238}Np ; 500x more sensitive than alpha spectroscopy; 984.5 keV in gamma spectrum
- ❑ Alpha spectrometry
 - 2.6E7 Bq/g; Isolation from seawater; hydroxide co-precipitation, ion-exchange, LaF_3 ; alpha: 4.8 MeV in alpha spectrum interferes with 4.8 MeV of U-238 → separation from U-238 by solvent extraction (TTA) or extraction chromatography
- ❑ Liquid scintillation method: 99.9% detection efficiency; separation needed

Separations for Np Analysis

- Adjustment of Oxidation state
- Solvent Extraction
- Chromatography
- Extraction Chromatography
- Rapid and Combined Methods

Adjustment of the Oxidation State

- The role of oxidants and reductants is paramount
- Besides electrolysis, also a variety of **reductants** and **oxidizers** were tested for adjustment of the oxidation states.
- *Nitrite*
- A special role of NO_2^- - NaNO_2 is added to adjust the oxidation state of plutonium to IV+, or Np to V+.
- It is very useful since it can both oxidize tetravalent neptunium to the **pentavalent** state and, at the same time, reduce hexavalent neptunium.
- Since both neptunium and plutonium can exist in several oxidation states at the same time, nitrite is an important agent when only one oxidation state is needed.

Adjustment of Oxidation States

Generating an unusual oxidation state opens new separation opportunities:

- For example, typically pentavalent Np, a non-extractable species of Np, if oxidized to hexavalent Np-species, NpO_2^{2+} , behaves as a chemical analog of UO_2^{2+} , or if reduced to Np^{4+} behaves as a chemical analog of Pu^{4+} and can be separated from the initial aqueous phase

Heptavalent An:

14

- Increase from 1 M acid to 10 M base causes a change in redox potential of 2 V and makes possible the oxidation of Np(VI) to Np(VII).



Hexavalent neptunium (15 mM) prepared electrolytically in 4M HNO_3 in H-cell with a Pt electrode (OSU, Nov 2009).

Slide 41

I4

I don't understand increase from 1 M acid to 10 M base, you want to say a decrease in the acidity I suppose from 1M acid to 10 M base?

INL, 1/28/2013

Agents and Procedures for Adjusting the Np Oxid. State

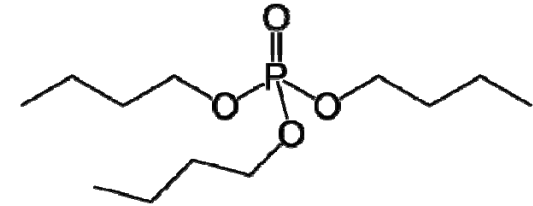
<i>Oxidation states of neptunium ion</i>		<i>Procedures</i>	
<i>Before treatment</i>	<i>After treatment</i>	<i>Agents</i>	<i>Conditions</i>
Oxidative treatment			
Np(III), Np(IV), Np(V)	Np(VI)	Ce(IV) MnO ₄ ⁻ Ag(II) BrO ₃ ⁻ HClO ₄ Cl ₂ O ₂ (air)	HNO ₃ , H ₂ SO ₄ HNO ₃ , H ₂ SO ₄ 1 M HClO ₄ fuming 1 M HCl (348 K)
Np(III)	Np(IV)		
Reductive treatment			
Np(V), Np(VI)	Np(IV)	Fe ²⁺ I ⁻	H ₂ SO ₄ 5 M HCl (373 K)
Np(VI)	Np(V)	NH ₂ NH ₂ NH ₂ OH NO ₂ ⁻ H ₂ O ₂ Sn ²⁺ SO ₂	1 M H ⁺ 1 M H ⁺ 1 M HNO ₃ 0.5 M HNO ₃ HCl H ₂ SO ₄
Np(IV), Np(V), Np(VI)	Np(III)	Zn(Hg) H ₂ (Pt black)	

From: Z. Yoshida, et al.; Neptunium, see full reference in the end

Solvent Extraction

TBP (PUREX)
CMPO (TRUEX)
TTA
MBIK
others

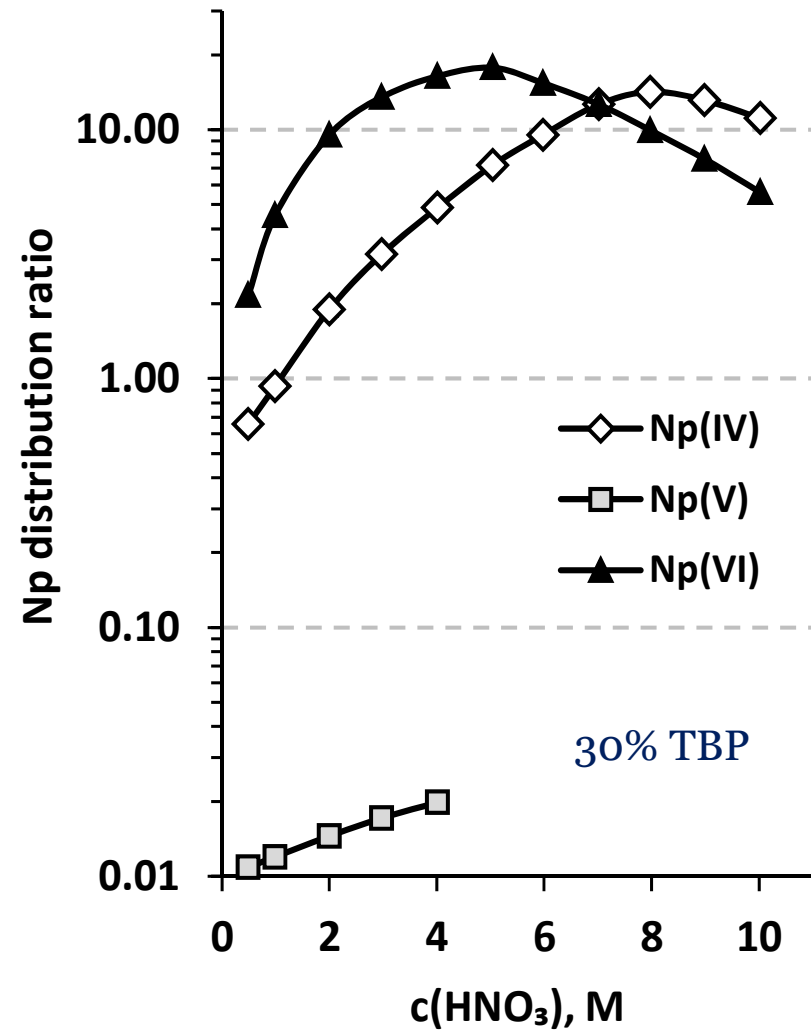
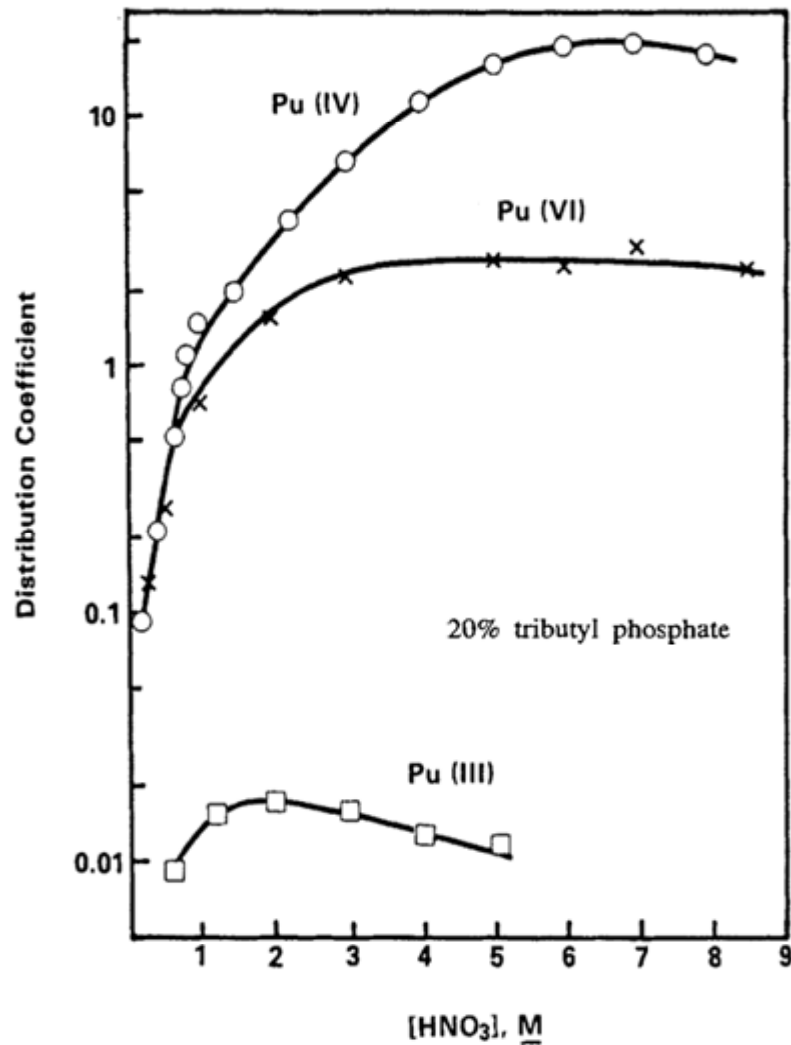
Np solvent extraction

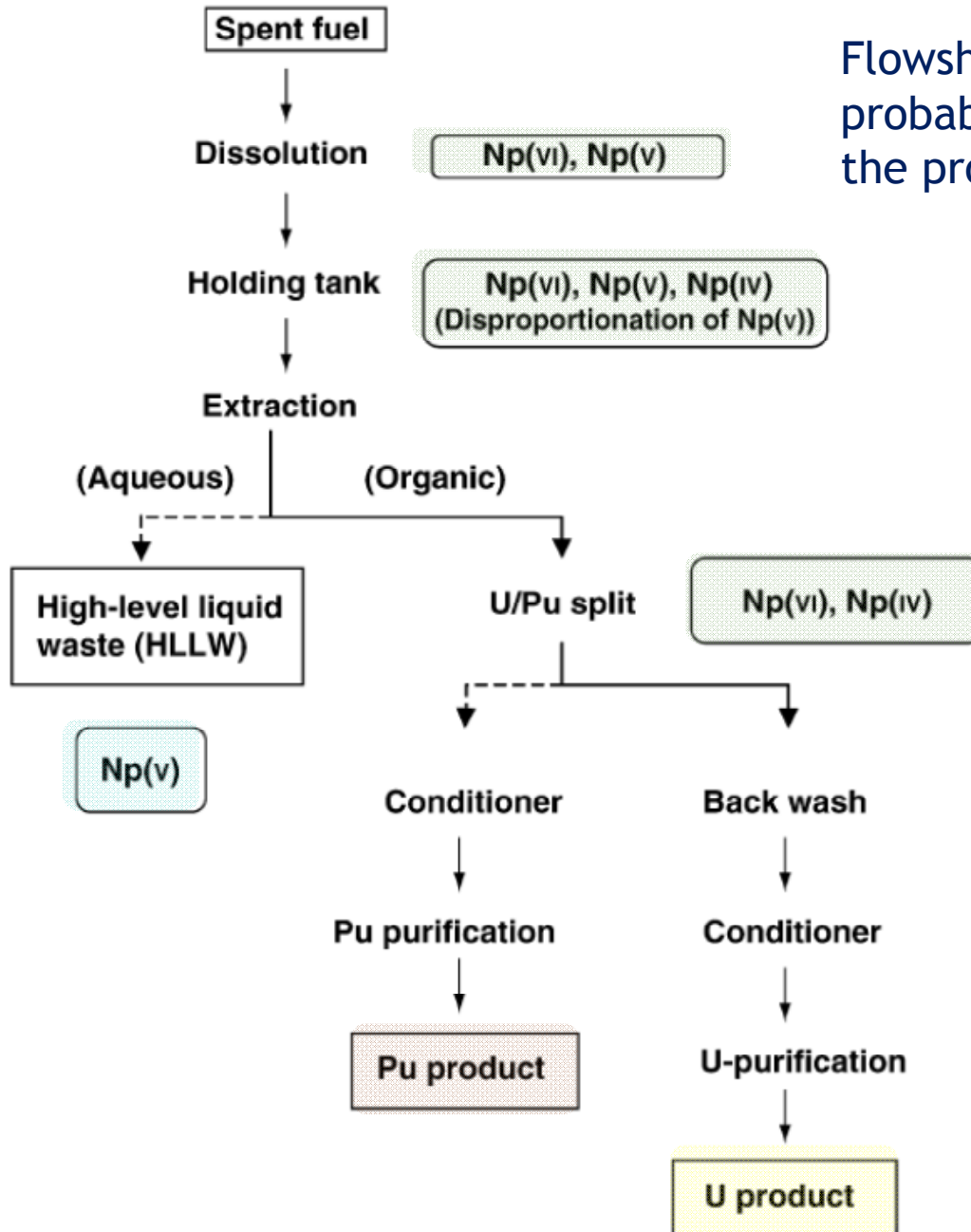


□ PUREX extraction:

- Tetra- and hexavalent Np are coordinated with organic ligand TBP (n-tributylphosphate)
- TBP is diluted with n-alkane (30 vol%), metal dissolved in nitric acid
- Np(V) must be either reduced to Np(IV) (analog of Pu⁴⁺) or Np(VI) (analog UO₂²⁺); hexavalent Np has better distribution ratios, so better if oxidized to Np⁶⁺
- Extracted species are the adduct complexes with TBP: NpO₂(NO₃)₂(TBP)₂ and Np(NO₃)₄(TBP)₂
- Extraction yields increase with increase concentration of TBP and nitric acid/nitrate
- Recovery from the organic phase also with oxidation state adjustment: reduction of Pu (to 3+) and Np (to 5+) by acetohydroxamic acid, Fe(II) sulfamate, etc.
- Np(IV) can be recovered also by complexation with aq ligands: EDTA, oxalate, carbonate

Extractability of the Pu and Np Cations





Flowsheet of the Purex process and the probable oxidation state of neptunium ion in the process solution.



- Experimental results at the THORP miniature pilot plant indicated that only 30% of the total neptunium was found in the HLW.
- The remaining neptunium was extracted with uranium and plutonium in the solvent product.

Advanced PUREX process

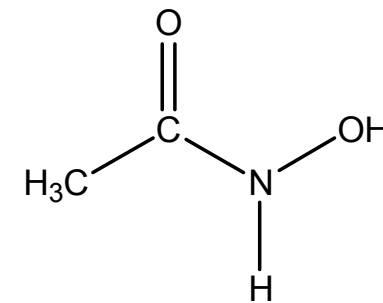
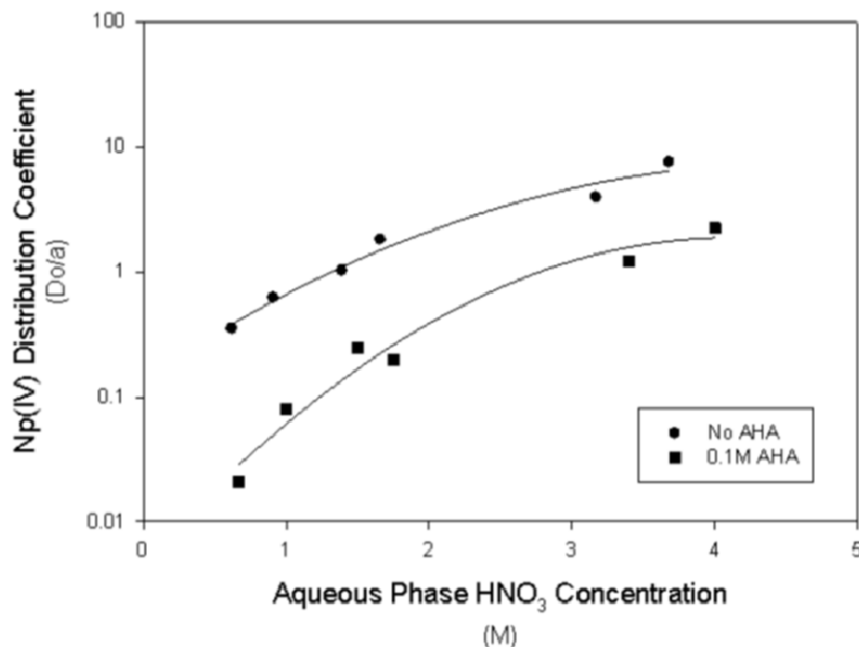
- Np(V) not extracted in PUREX
 - Np(V) slowly oxidizes to Np(VI)
 - Np(V) slowly disproportionates in high acid and extractable Np(IV) and Np(VI) are formed (previous slide)



- Np redox speciation is defined by the redox potential and acid (proton) concentration
- Several scenarios for the control of neptunium in the flowsheet are recommended, i.e., all neptunium is led to:
 - the HLW stream
 - the Pu fraction or
 - the U fraction followed by the isolation from uranium or
 - the recovery in the Np fraction before the U/Pu split process.
- In all cases, the method to control neptunium behavior is based on precise control of the oxidation state of the ion. Such appropriate redox reagents must be chosen to fulfill all criteria including:
 - kinetics of redox reaction
 - decomposability after the use and
 - stability toward high acidity and radiation.

Np in UREX (advanced PUREX)

- Np redox speciation is defined by the redox potential and acid (proton) concentration
- Back-extraction of Np(V) can be used to separate from Pu and U:
 - Reduction of Np(VI) possible by a variety of organic and inorganic compounds: hydrazine derivatives, N-butyraldehyde, hydroxamic acids
 - Acetohydroxamic acid (AHA) in the UREX-demonstration (Argonne NL)
 - AHA strips both Np and Pu back to aqueous phase by reducing Np(VI) to nonextractable Np(V) and binding Pu(IV) into stable acetohydroxamate complexes in aqueous phase.



Acetohydroxamic acid

Distribution of Np(IV) in 30 Vol% TBP from AHA/HNO₃ Solutions

TRUEX (CMPO Extraction)

- CMPO (n-octyl(phenyl)-N,N-diisobutyl-carbamoyl methylphosphine oxide) is an effective extractant for the separation of actinide ions from acidic solutions [Kolarik and Horwitz, 1988].
- The mixed organic solvent of (0.1-0.2) M CMPO + (1.2-1.4) M TBP in dodecane is usually employed.
- Extraction of Np(IV), Np(VI), Pu(IV), and U(VI) from HNO₃ compared with several extractants (diluent dodecane) [Mathur et al., 1996]:
 - CMPO
 - DBDA (dibutyldecanamide)
 - DHDA (dihexyldecanamide)
 - BEHSO (bis-2-ethylhexylsulfoxide)
- The extraction ability of extractants is in the order of:
 $CMPO > BEHSO > DHDA > DBDA$
- Extraction ability of CMPO is in the order of:
 $Np^{4+} > Pu^{4+} \sim NpO_2^{2+} > Pu^{3+} > NpO_2^+$

Np extraction with CMPO



Distribution ratios of neptunium and plutonium ions between solution of nitric acid and 0.1M CMPO + 1.4M TBP (dodecane) [Mincher, 1989]

HNO ₃	0.5 M	1.0M	2.0M	3.0M	4.0M	5.0M
NpO ₂ ⁺	0.001	0.02	0.04	0.07	0.12	0.18
NpO ₂ ²⁺	43	100	114	133	150	150
Np ⁴⁺	0.55	6	113	670	1500	2200
Pu ⁴⁺	16	40	76	110	144	174
Pu ³⁺	1.6	3.0	5.2	7.1	10	14

- For the separation of Np and Pu, the oxidation states are adjusted to Np(IV) and Pu(III) with 0.1 M Fe(II) sulfamate and Np(IV) is then extracted into the CMPO/TBP phase.
- Pu(III) is recovered by stripping with 0.01 M HNO₃ in the presence of 3% hydroxylamine nitrate.
- Np is recovered from the organic phase by an aqueous solution containing complexing agents such as oxalate, carbonate, or EDTA.

Np separation chemistry: TTA

- Most analytical methods exploit extraction with solvent extraction with HTTA (2-thenoyl trifluoroacetone).
- Procedures developed for ICP-MS, alpha spectrometry or neutron activation analysis
- TTA method developed for Pu(IV), so Np must be reduced to Np(VI)
- Solvent: 2-thenoyltrifluoroacetone (0.5 M in organic diluent).
- Necessary steps:
 - Initial aqueous phase: reduction to Np(IV)
 - Extraction Np(IV) from 0.5 M HNO₃
 - Stripping (back extraction) with 8 M HNO₃ or with 1 M HNO₃ (it oxidizes Np to Np(V))
 - Very reliable method, used for redox speciation of Pu and Np in aqueous solutions.

Np solvent extraction: HDEHP

- ❑ **HDEHP (di-2-ethylhexylphosphoric acid)**
 - Acidic, not very selective extractant
 - In 1 M HNO_3 with addition of NaNO_2 to keep Np(V) and not extracted
 - U, Pu, Np, Am are in their most stable oxidation states
 - Np is oxidized to Np(VI) then extracted
 - It reduces to Np(V) and is stripped with 0.1 M HNO_3

- ❑ **Tri-n-octylamine**
 - Used for separation of Np from environmental samples
 - Extracted from 10 M HCl; back extracted with 1 M HCl+0.1 M HF

- ❑ **Diisodecylphosphoric acid (DIDPA)**
 - Also extracts trivalent lanthanides at fairly low acidity (0.5M HNO_3)
 - Even Np(V) is extracted: addition of H_2O_2 promptly reduces Np to Np(IV) and increases extraction with DIDPA; Np strips well with oxalic acid (together with Pu).

Chromatography

Ion-exchange chromatography:

Cation exchange

Anion exchange

Extraction chromatography

Extraction chromatography:



Np chromatography

- Various methods based on ion-exchange chromatography have been used for the separation of neptunium ions (Burney and Harbour, 1974).
- **Cation-exchange** chromatography of NpO_2^{2+} , NpO_2^+ , and Np^{4+} with dilute acid solutions has been developed:
- The adsorption of ions of different oxidation states differ from each other so that the distribution ratio follows the order NpO_2^{2+} , NpO_2^+ , and Np^{4+} , which enables the mutual separation of neptunium ions of different oxidation states.
- Utilization of cation-exchange methods is limited because NpO_2^{2+} , NpO_2^+ are often reduced to Np^{4+} when in contact with the resin; the adsorption behavior of Np^{4+} is not so selective from other coexisting cations.
 - $\text{Np}^{4+} \gg \text{NpO}_2^{2+} \gg \text{NpO}_2^+$

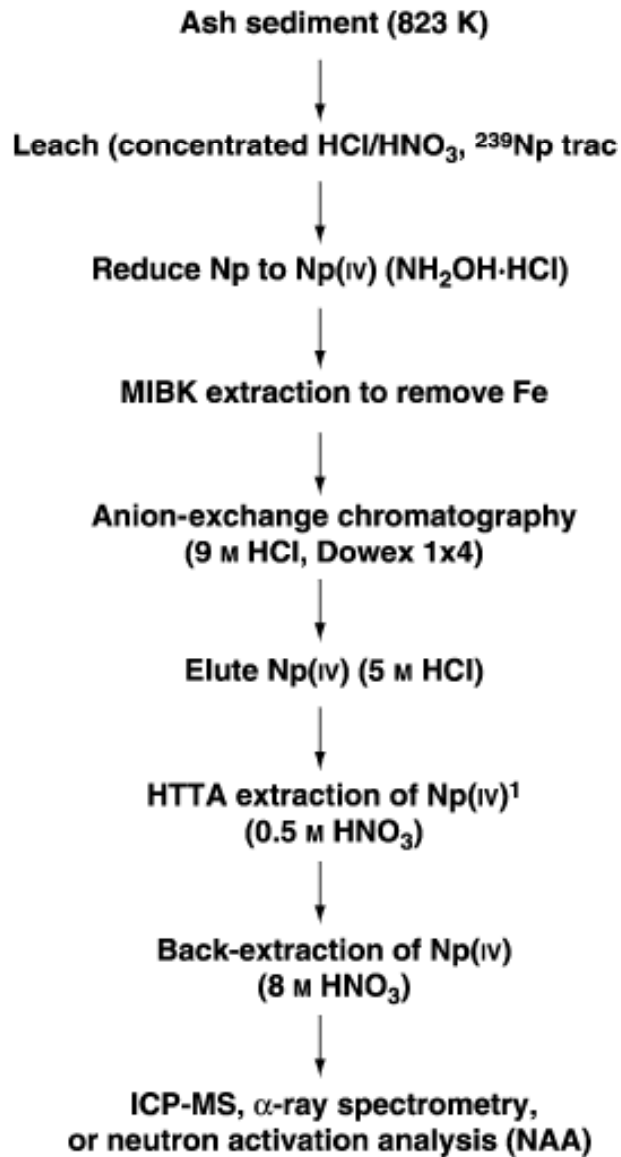
Ion-exchange chromatography

- Np(VI) and Np(IV) in **anion-exchange** chromatography:
- Np(VI) and Np(IV) form **anionic chloride or nitrate** complexes in aqueous solutions containing high concentration of chloride or nitrate ions
- Their anionic complexes formed are strongly adsorbed on **anion-exchange resins at 7-8 HNO₃**.
- Elute with 0.3 M HNO₃ (switch to cationic form)
- Well-established anion-exchange chromatographic methods are available and have been utilized for the isolation of neptunium from other actinides and fission product elements.
- From the viewpoint of the **selectivity** among neptunium ions and the other ions, nitrate media are preferable to chloride media.

Anion-exchange chromatography: Np

- Anion exchange can be used to separate ^{237}Np in both HNO_3 and HCl media, where tetravalent neptunium forms anionic complexes $\text{Np}(\text{NO}_3)_6^{2-}$ and NpCl_6^- .
- For both media, neptunium is first reduced to $\text{Np}(\text{IV})$ with ferrous sulfamate, for example. This reduces all plutonium species to $\text{Pu}(\text{III})$.
- In HNO_3 , the solution is loaded into an anion exchange column at an acid concentration of 7-8 M (the nitrite ions present in concentrated nitric acid oxidize $\text{Pu}(\text{III})$ to $\text{Pu}(\text{IV})$).
- $\text{Np}(\text{IV})$, $\text{Th}(\text{IV})$, and $\text{Pu}(\text{IV})$ are retained in the column, while $\text{Am}(\text{III})$ and $\text{U}(\text{VI})$ pass through and are completely removed by rinsing the column with 8 M HNO_3 .
- Next, thorium is eluted with 8 M HCl , $\text{Th}(\text{IV})$ does not form a strong anionic complex with chloride.
- The Pu in the column is then reduced with hydrazine hydrochloride in 8 M HCl to $\text{Pu}(\text{III})$ and then eluted out.
- Finally, neptunium is eluted out with dilute nitric acid.
- To carry out ion exchange in HCl media, neptunium is first reduced to $\text{Np}(\text{IV})$ and plutonium to $\text{Pu}(\text{III})$, and the solution is introduced into the column at an acid concentration of 9 M, where $\text{Th}(\text{IV})$, $\text{Pu}(\text{III})$, and $\text{Am}(\text{III})$ are not retained in the column.
- $\text{U}(\text{VI})$ is then rinsed out with 8 M HNO_3 , and finally $\text{Np}(\text{IV})$ is eluted with 0.5 M HCl .

Anion-exchange chromatography (1)



Separation of Np from environmental (sediment) samples with anion-exchange chromatography after solvent extraction with HTTA:

- Adjustment of neptunium to Np(IV) with hydroxylamine
- Bringing Np(IV) nitrate complex in 7 to 8 M HNO₃ solution
- Np(NO₃)₆²⁻, adsorption of hexanitrate complex of Np(IV), i.e. Np(NO₃)₆²⁻, on the anion-exchange resin
- Anionic nitrate complexes of Pu(IV) and Th(IV) are also adsorbed on the Dowex resin.
- Pu(IV) is eluted as Pu(III) with a mixture of 6 M HNO₃ + 0.05 M Fe(II) sulfamate + 0.05 M hydrazine
- Th(IV) is eluted with 8 M HCl. Np(IV) is then recovered by elution with 0.3 M HNO₃

Anion-exchange chromatography (2)

- Maiti et al. (1992) developed another method for the sequential separation of actinides by anion-exchange chromatography:
 - Np(IV), Pu(IV), and U(VI) in 9 M HCl-0.05 M HNO₃ solution are adsorbed on the anion-exchange resin
 - Am(III) is not adsorbed under these conditions
 - Pu(IV), Np(IV), and U(VI) are eluted successively using 9 M HCl-0.05 M NH₄I, 4 M HCl-0.1 M HF, and 0.5 M HCl-1 M HF, respectively.
 - The Pu(IV) is eluted by the reduction of Pu(IV) to Pu(III).

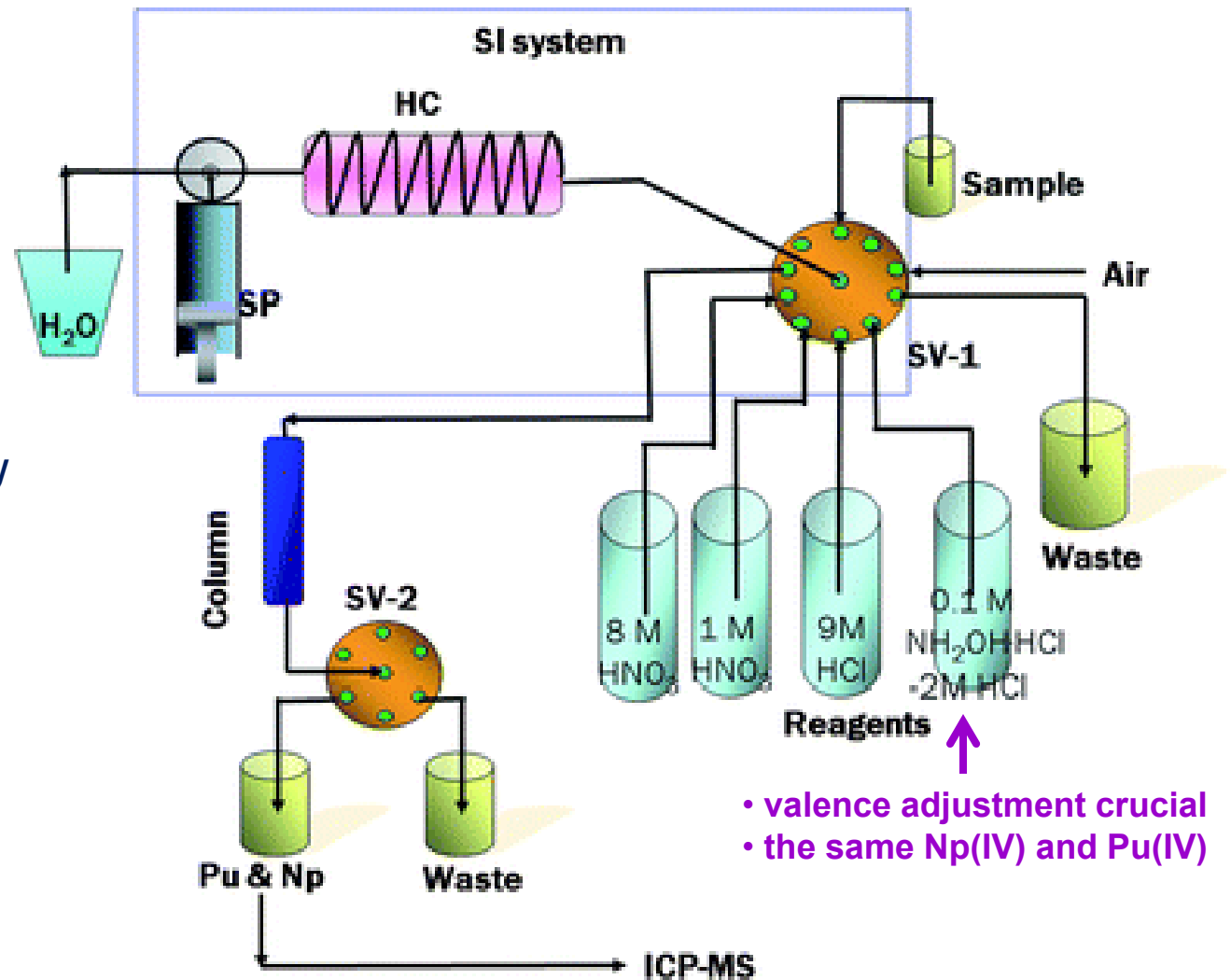
Rapid and simultaneous methods for determination Np

PERALS

ECX with sequential injection analysis and ICP-MS

Automated Analysis: ^{239}Pu , ^{240}Pu and ^{237}Np

- Rapid (1.5h) and simultaneous determination
- environmental samples (10g soil or 20g seaweed)
- Np-237 and Pu-239/240
- Extraction chromatography
- Pu(IV) and Np(IV) on TEVA column
- Sequential injection analysis (SI) and
- ICP-MS



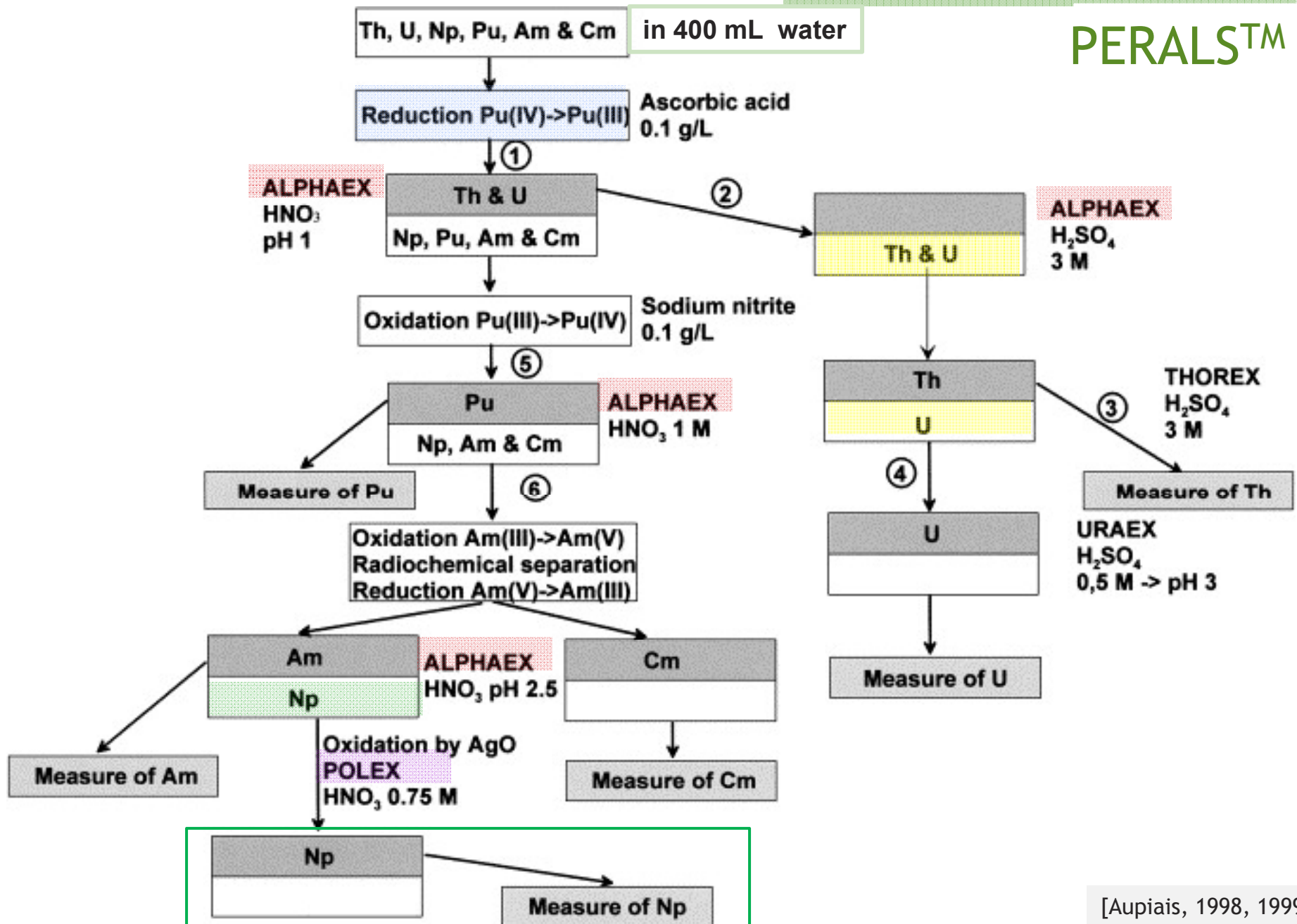
PERALS™ with extractive LSC cocktails

- PERALS™ - **Photon-Electron-Rejecting-Alpha-Liquid Scintillation System**, developed and tested at Brookhaven National Laboratory (BNL).
 - PERALS™, with a 99% alpha detection efficiency, can electronically filter out unwanted beta/gamma signals present in a sample to be counted by LSC (liquid scintillation counter).
 - Several extractive liquid scintillation cocktails with a combined detection /extraction performance in one step were designed by adding a suitable extractant molecule to the solvent containing scintillating fluors:

Cocktail	ALPHAEX	THOREX	URAEX	POLEX
Extractant added	HDEHP (di-2-ethyl-hexyl phosphoric acid)	1-nonyldecyl amine sulfate	TNOA (tri-n-octylamine sulfate)	TOPO (tri-octyl-phosphine oxide)

- Application of such cocktails for processing and counting Np-237 in water samples with such cocktails requires [Aupiais, 1999]:
 1. Oxidation of Np(V) to Np(VI) with bivalent silver (AgO),
 2. Extraction of Np(VI) from 0.5 to 0.75M HNO₃ solution into the extractive scintillation cocktail (POLEX) and
 3. Liquid scintillation counting with rejection of gamma emitters (PERALS)
(See the next slide for Np in a mixture of six radionuclides.)

PERALS™



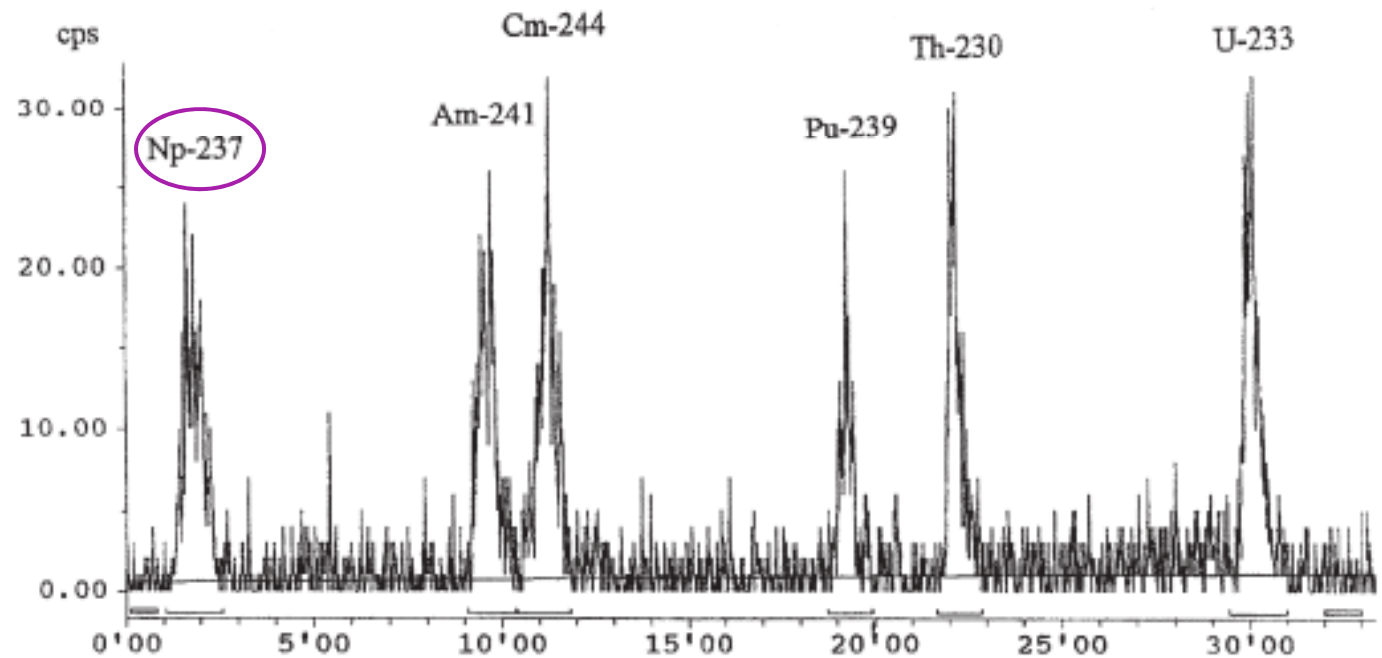
Rapid methods for Np (cont.)

- PERALS
- It is possible to use pulse decay analysis (PDA) or pulse shape analysis (PSA) to discriminate between alpha- and beta- or gamma-decay events in the same sample.
- Events originating from **alpha-particle** interactions with scintillation cocktail have **35-40 ns longer decay lifetimes** than events originating from **beta-particle** or gamma interactions.
- This is a result of the longer deexcitation and light emission processes in scintillation fluors after particle interactions.
- In pulse shape analysis (PSA) or pulse shape discrimination (PSD), the area of the tail of a pulse is compared to the total pulse area, which provides a method of assigning a pulse to that of an **α pulse (long pulse)** or **β - γ pulse (short pulse)**.
- Such pulse discrimination for **α - β** analysis requires two multichannel analyzers (MCAs), where pulses of longer decay times originating from **α** -events are registered in the **α** -MCA and those of shorter decay times are registered in the **β** -MCA as originating from **β** or **$\beta(\gamma)$** events.

Rapid methods for Np (cont.)

Separation procedures with HPLC and HPIC linked to flow scintillation analysis with alpha/beta discrimination.

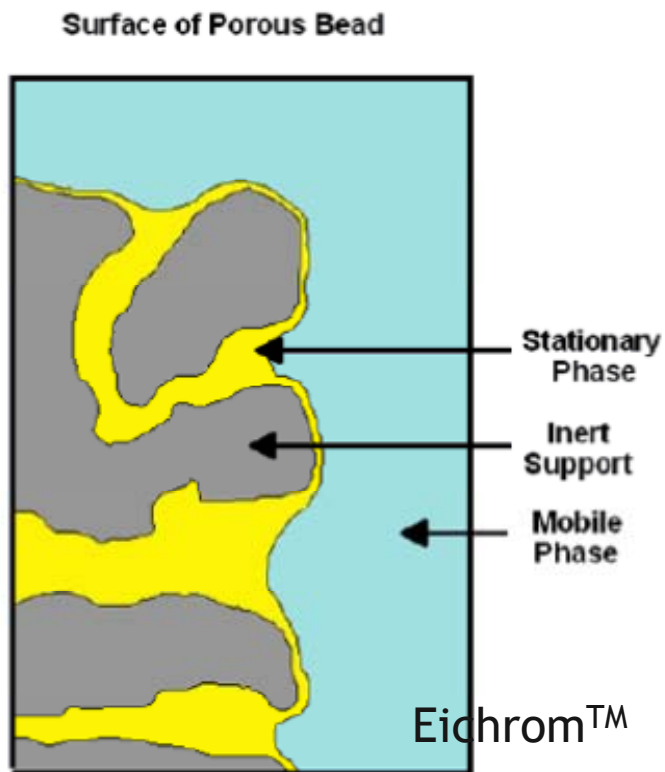
[Bradbury et al., 1990; Reboul and Fjeld, 1994, 1995], Devol [1995, 1995, 2002]



A typical ion chromatogram of select actinides using cationic elution.
[Reboul and Fjeld, 1995]

- An excellent separation procedure for **six common actinides** by HPIC and on-line flow cell measurements is displayed in this scheme. [Reboul and Fjeld, 1995].
- However, when radionuclides are not clearly separated analysis of gross alpha and gross beta activity with flow cells is possible.
- Chromatographic applications with hybrid scintillating extraction resins (TEVA-sci, others) are being developed by Dr. Devol's group at Clemson University [1995-present]

Extraction Chromatography ECX

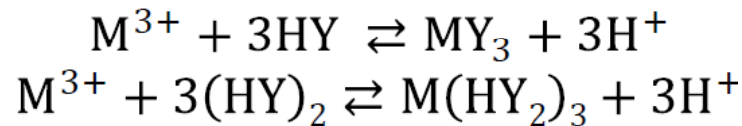


- Resins with metal complexing groups packed into chromatographic columns
- extraction-filtration disks
- EXC-resin produced by Eichrom™ (Darien, IL) are solid phase particles of a macroporous inert support resin, impregnated with an organic extracting solvent.
- Eichrom products and applications became the standard technology in the field of radiochemistry with methods used by accredited laboratories and regulatory agencies worldwide.
- Extraction resins based on silica gel or polymer substrates to which the selective ligand has been chemically attached are the SuperLig resins produced by IBC Advanced Technologies, Inc., US.

Examples of EXC Resins by Eichrom™

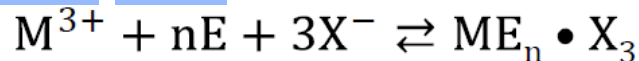
Acidic

ACTINIDE



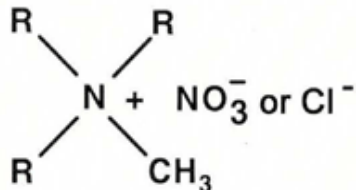
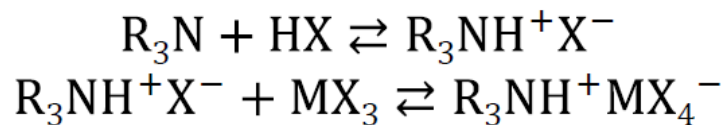
Neutral

TRU **DGA**

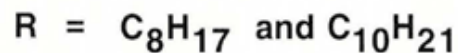


Basic

TEVA



TEVA Aliquat 336 (trialkylmethyammonium chloride or nitrate)

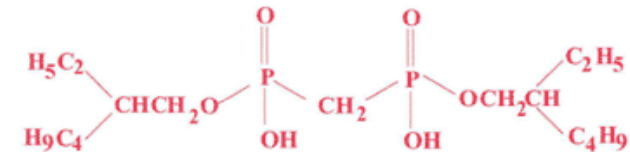


- extracts metals in anionic form (TcO_4^- , $Pu(NO_3)_6^{2-}$ or $Np(NO_3)_6^{2-}$)

ACTINIDE resin

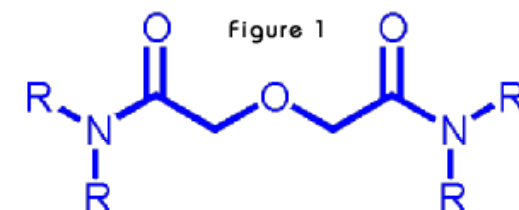
DIPEX® Extractant

P,P'- di(2-ethylhexyl)methanediphosphonic acid



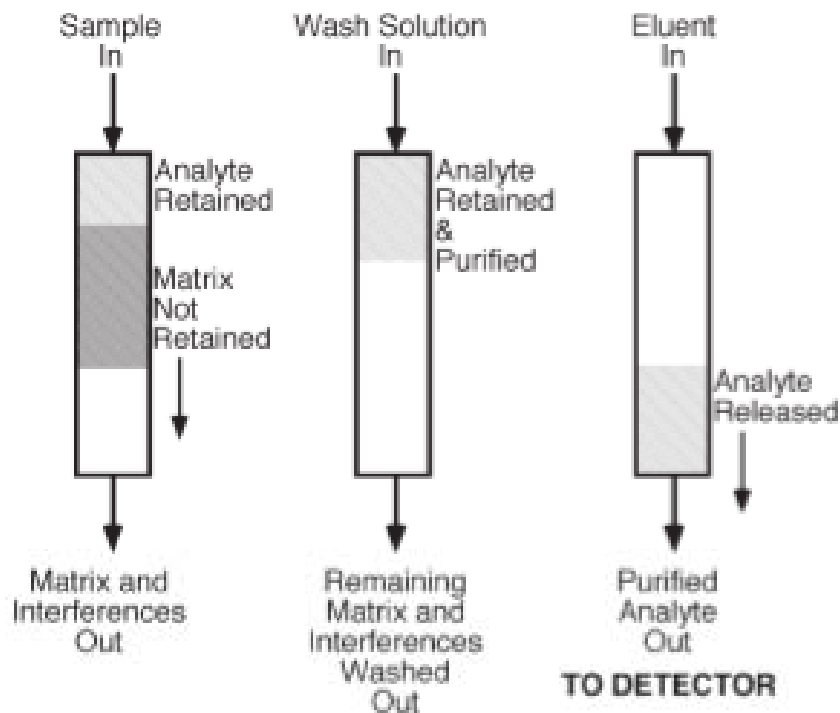
H₂DEH[MDP]

Horwitz, et al. (HP197)

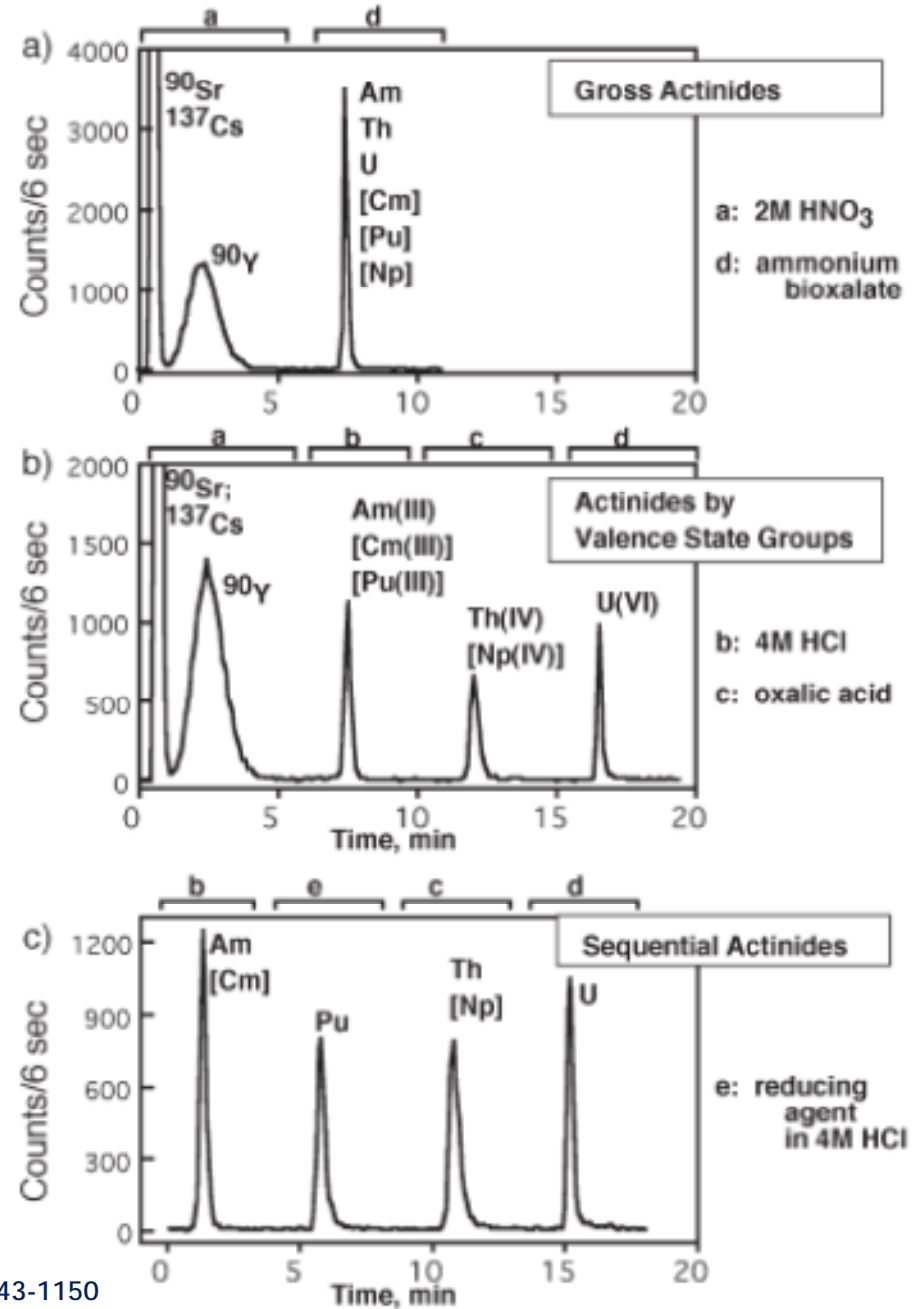


DGA diglycoamide

Extraction chromatography

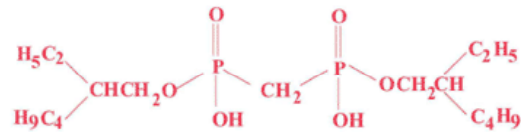


(Egorov et al., 2001; Grate and Egorov, 1998; Grate et al., 1999).



Np on Actinide resin

P,P'- di(2-ethylhexyl)methanediphosphonic acid

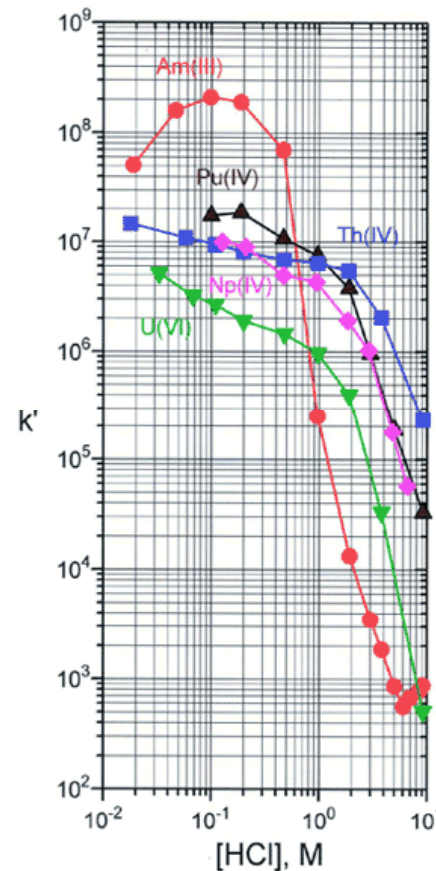


H₂DEH[MDP]

Horwitz, et al. (HP197)

Figure 2.

The uptake of actinide elements by Actinide Resin



Horwitz, et al. (HP197)

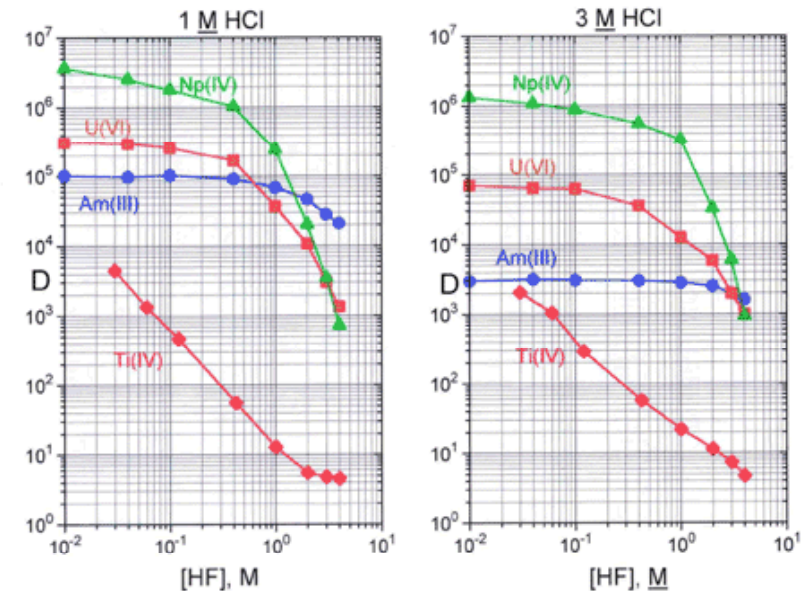
Retention of Np on Actinide Resin:

- decreases with increase [H⁺]
- metal in cationic form

Controlled by charge of cation:

- best for Np(IV)
- reduction Np(V) → Np(IV)
- Fe(II) sulfamate
- ascorbic acid
- hydroxylamine

Figure 9
Effects of HF on the uptake of Actinides in HCl Solutions



Horwitz, et al. (HP197)

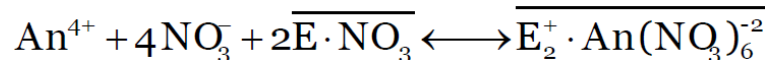
Np on TEVA resin

TEVA resin:

- Aliquat 336 (tetraalkylammonium- or trialkylmethyl ammonium- based extractant)

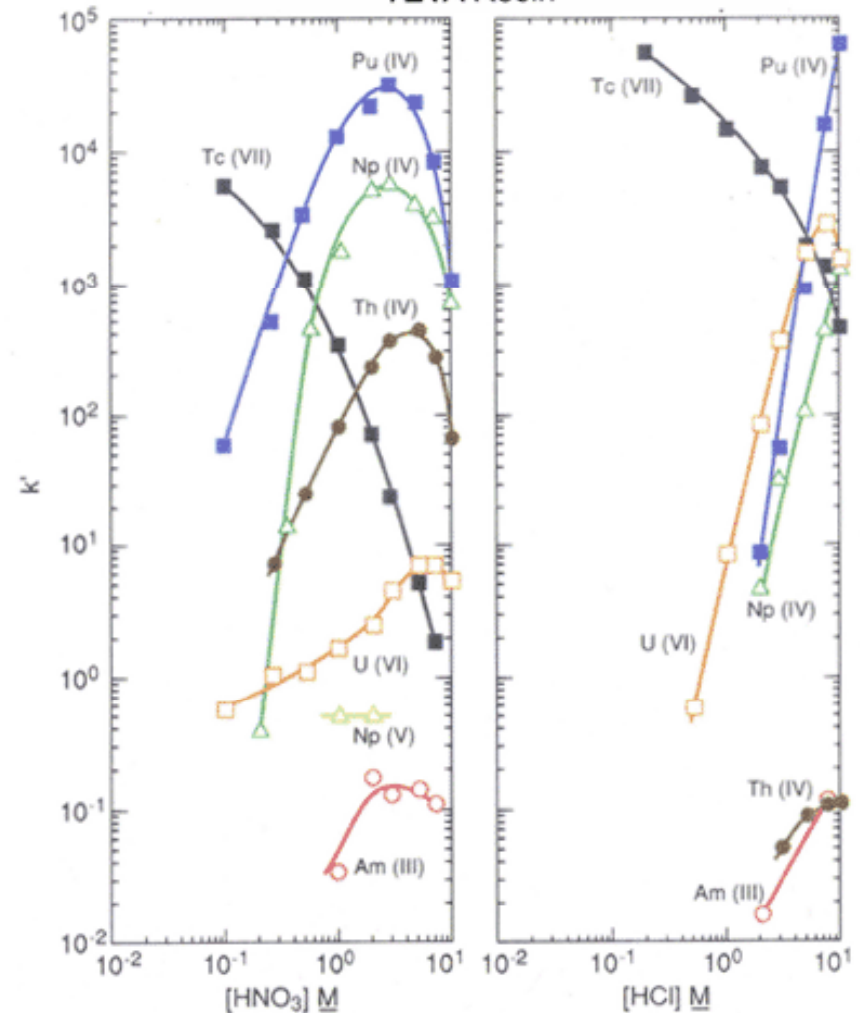
Np separation:

- Np(V) not extracted
- Np(VI) extracted, but less than Np(IV)
- Np(IV) extracted in both media (in HNO_3 better than in HCl)
- Hexanitrate complexes of An(VI) are retained the best
- Np(V) must be reduced to IV+
 - Fe(II) sulfamate
 - ascorbic acid
 - hydroxylamine



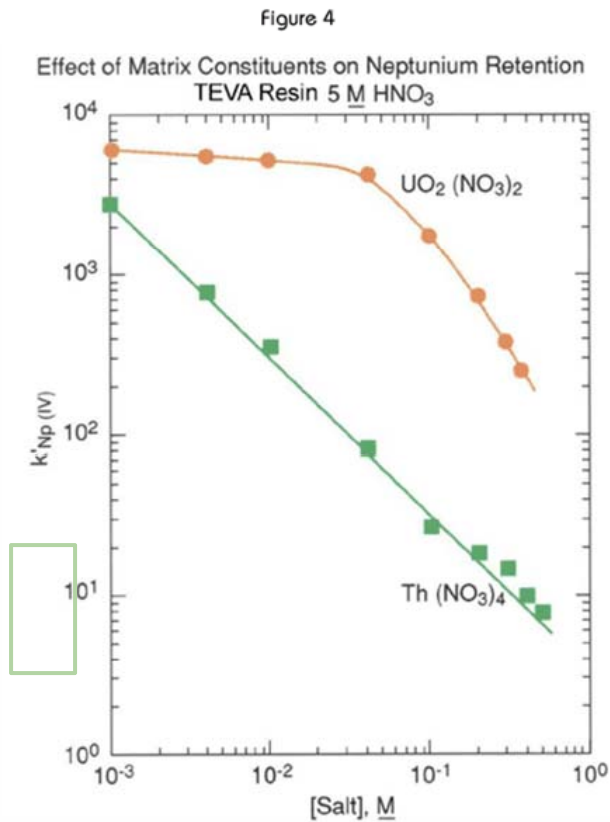
Figures 2 & 3

Acid dependency of k' for various ions at 23°C.
TEVA Resin



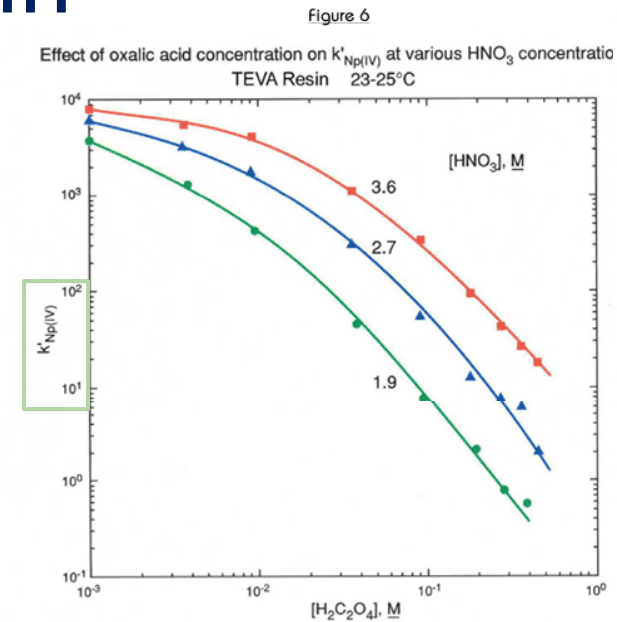
Horwitz, et al. (HP195)

Np on TEVA resin



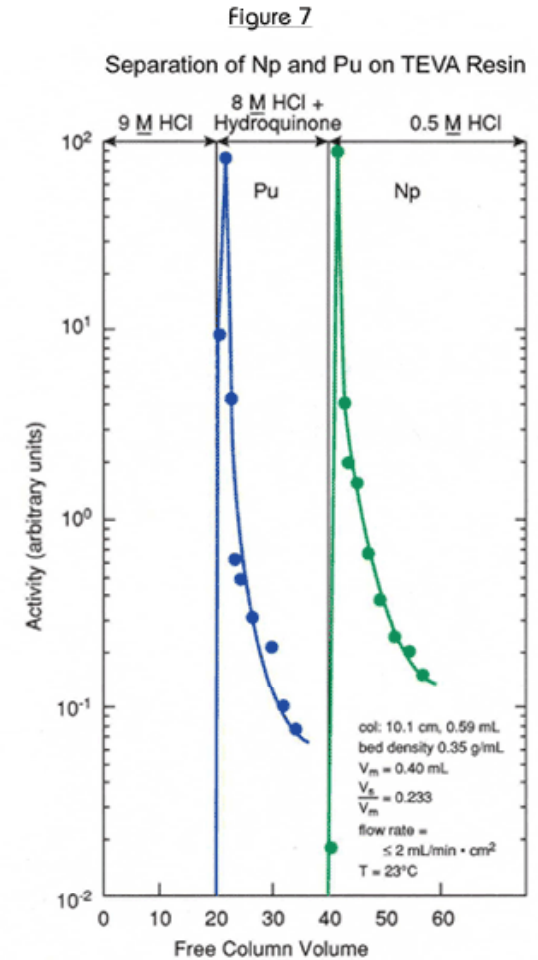
Horwitz, et al. (HP195)

Np(IV): Effect of added uranyl and thorium nitrates



Horwitz, et al. (HP195)

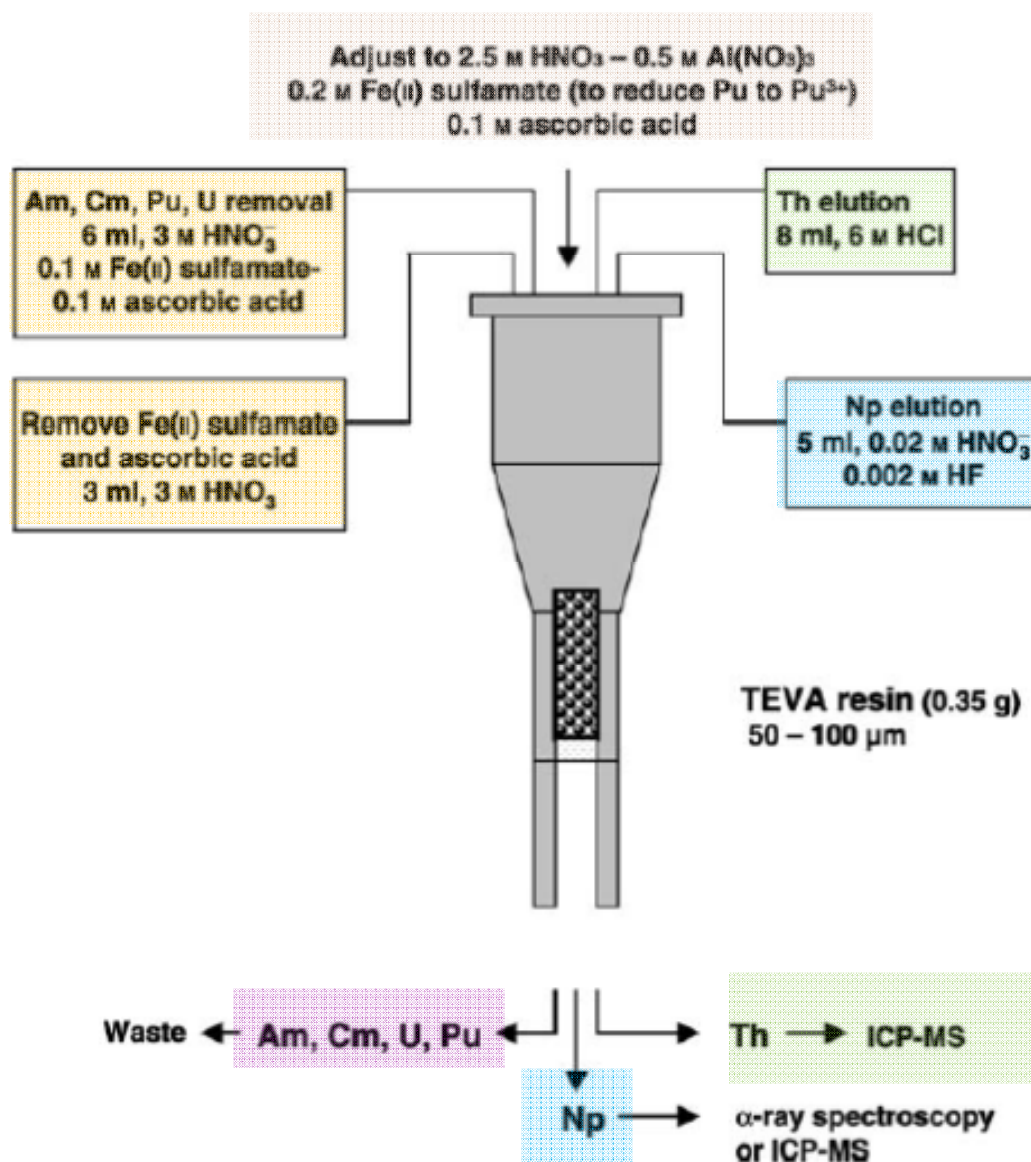
Np(IV): Effect of oxalic acid



Effect of [HCl] and hydroquinone

Elution profiles adopted from Eichrom™

TEVA resin for Np [from a mixture of An]



Maxwell (1997) developed a rapid method for the separation of Np using a resin loaded with Aliquat™ 336, which is called TEVA resin:

The oxidation states of Np and Pu are adjusted to Np(IV) and Pu(III) by reduction with Fe(II) sulfamate and ascorbic acid.

Np(IV) is retained on the resin while >99.9% Pu(III) is eluted and removed.

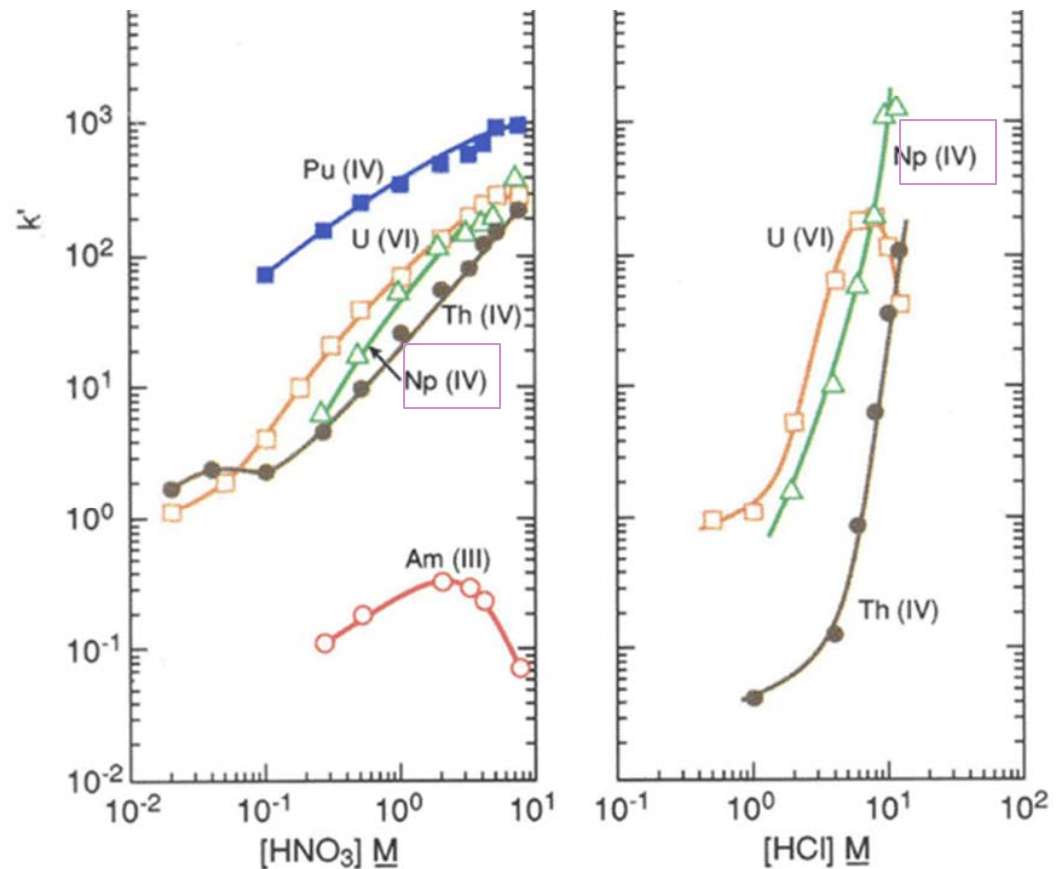
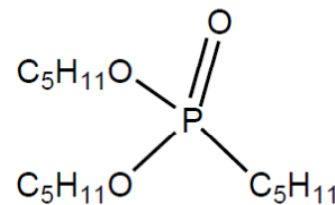
Thorium doesn't form anionic chloride complexes, so it elutes with HCl.

This method can be applied to such samples as nuclear materials process samples, waste solutions, and environmental samples

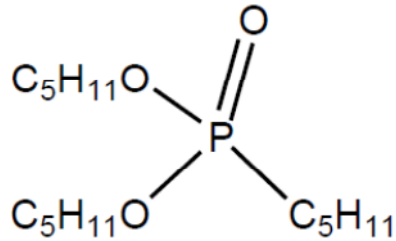
Np on UTEVA

- The DP[PP] extractant diamyl, amyolphosphonate forms **complexes** with the actinide elements.
- The formation of these complexes is driven by the concentration of nitrate in the sample solution.
- Uptake of the actinides increases with increasing nitric acid concentration.
- A similar dependence is observed also for chloride complexes.

Acid dependency of k' for various ions at 23-25°C.
UTEVA Resin From: Eichrom.com



Np on UTEVA

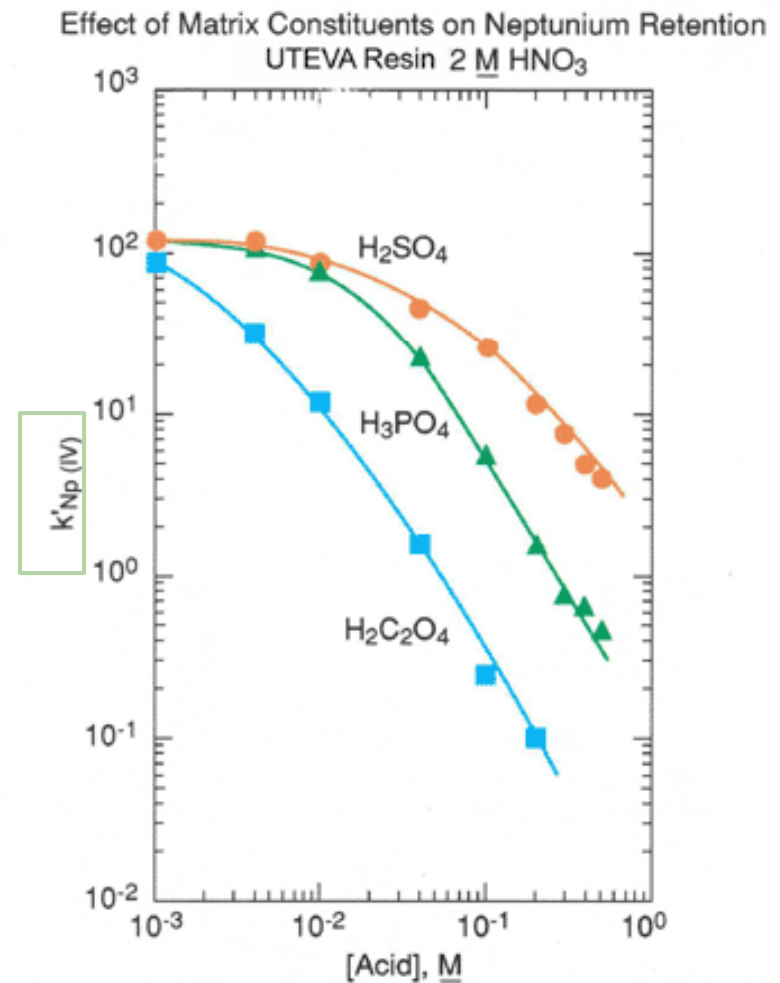


Diamyl Amylphosphonate (DAAP)
a.k.a. Dipentyl Pentylphosphonate (DPPP)

Np(IV):

- Effect of oxalic acid, sulfuric and phosphoric acid on k'
- Np(VI) in 2M HNO_3

Figure 4



Unpublished data (Horwitz, et al.)

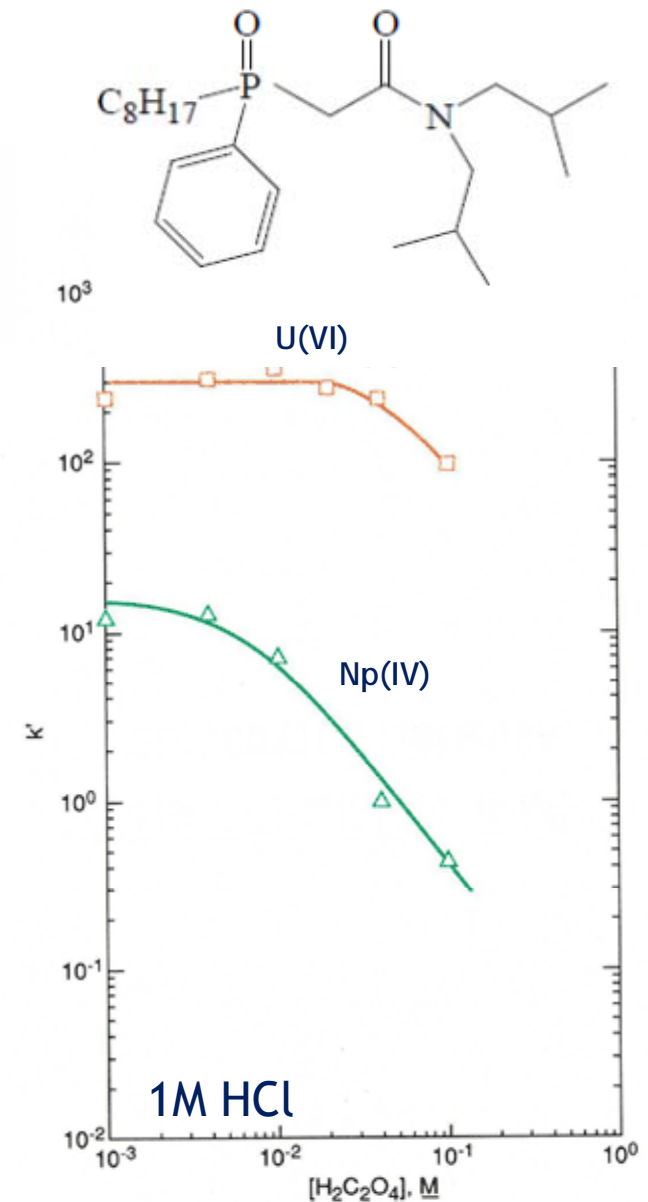
Np on TRU resin

- TRU resin:
 - CMPO (n-octyl(phenyl)-N,N-diisobutyl-carbamoyl methylphosphine oxide)
 - TBP (n-tributylphosphate)

- Retention of metals:
 - U(VI) retained 10x better than Np(IV)
 - Np(VI) retained 10x better than Np(IV)
 - Np(VI) well extracted
 - Np(V) partially extracted

- Effect of Presence of U(VI)

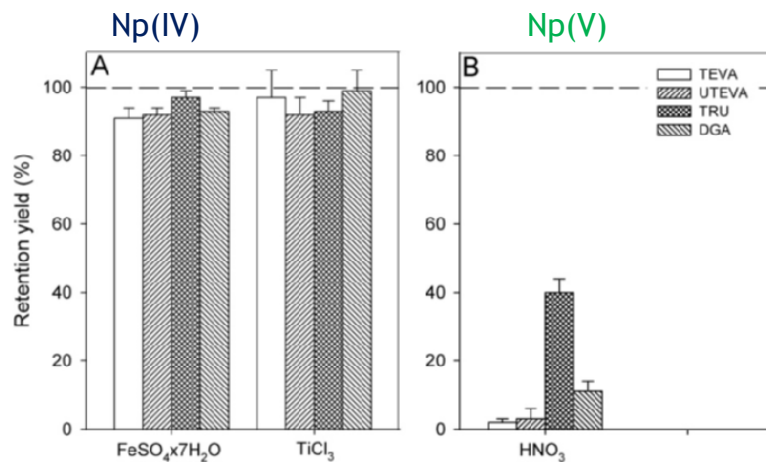
- Separation of Np controlled by valency:
 - Np(V) → Np(IV) reduction: Fe(II), ascorbic acid, hydroxylamine
 - Np(V) → Np(VI) oxidation: AgO, KBO₃, O₃, KMnO₄
 - **Elution** with oxalic acid



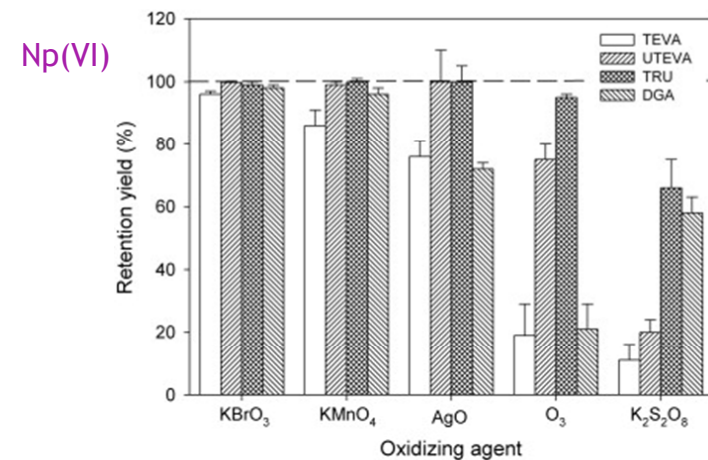
Np(IV) : effect of oxalic acid

Np Retention on EXC resins (Eichrom)

- The presence of U is detrimental to Np detection by either alpha (4.8 MeV) or ICP-MS analyses.
- General separation strategy with TEVA resin:
 - separating Np and U in 2-3M HNO₃ retention of U(VI) is lower than the one of Np(IV)
 - this approach requires the reduction of Np(V) to Np(IV), which is not well-suited for automation
 - oxidizing Np(V) into Np(VI) in 2-3M HNO₃ is also problematic, since both k_0 for Np(VI) and U(VI) on TEVA resin are within one order of magnitude and sample volumes are large.

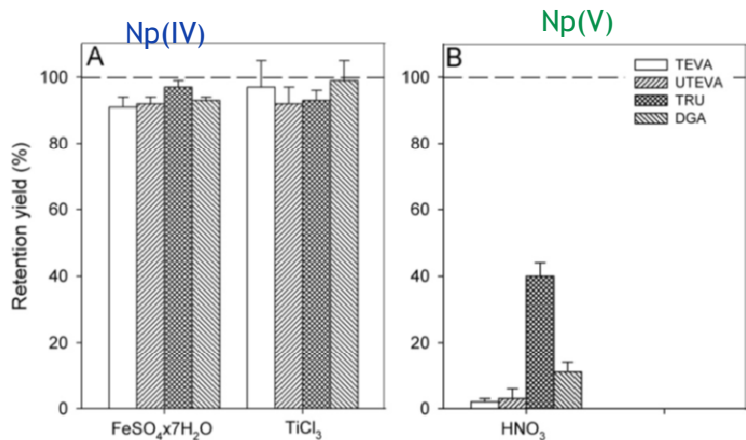


Left: Np retention yield (%) for various reducing agents on TEVA, UTEVA, TRU, and DGA resins in 2M HNO₃. [Guerin, et al, 2010]

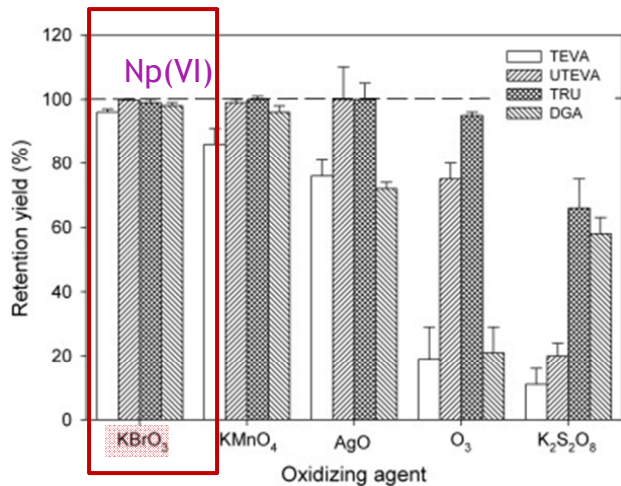


Np retention yield (%) for various oxidizing agent on TEVA, UTEVA, TRU, and DGA resins in 2M HNO₃. [Guerin, et al, 2010]

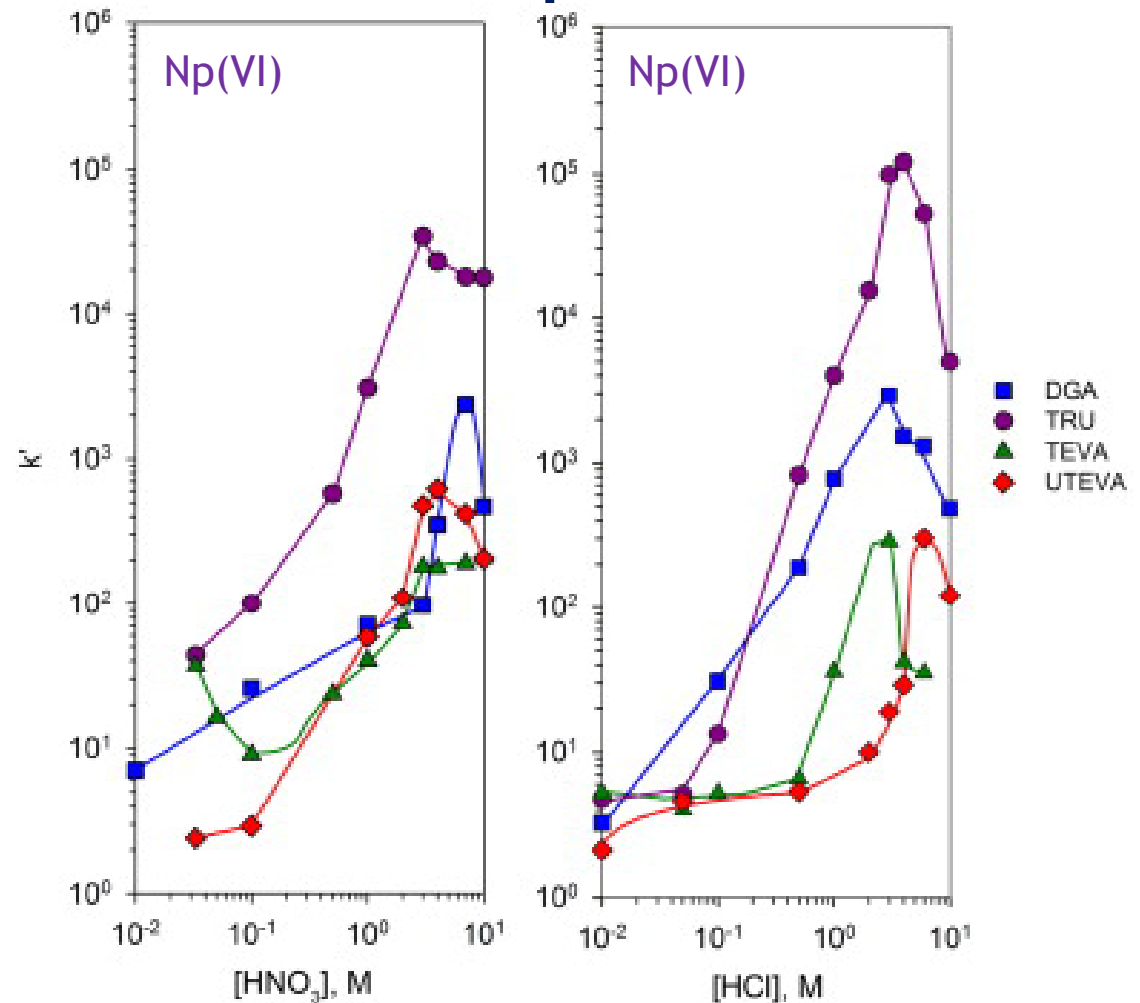
Np on EXC: optimal retention parameters



Np retention yield (%) for Ti(III) and Fe(II) reducers on TEVA, UTEVA, TRU, and DGA resins in 2M HNO₃. [Guerin, 2010]



Np retention yield (%) for various oxidizing agent on TEVA, UTEVA, TRU, and DGA resins in 2M HNO₃. [Guerin, et al, 2010]

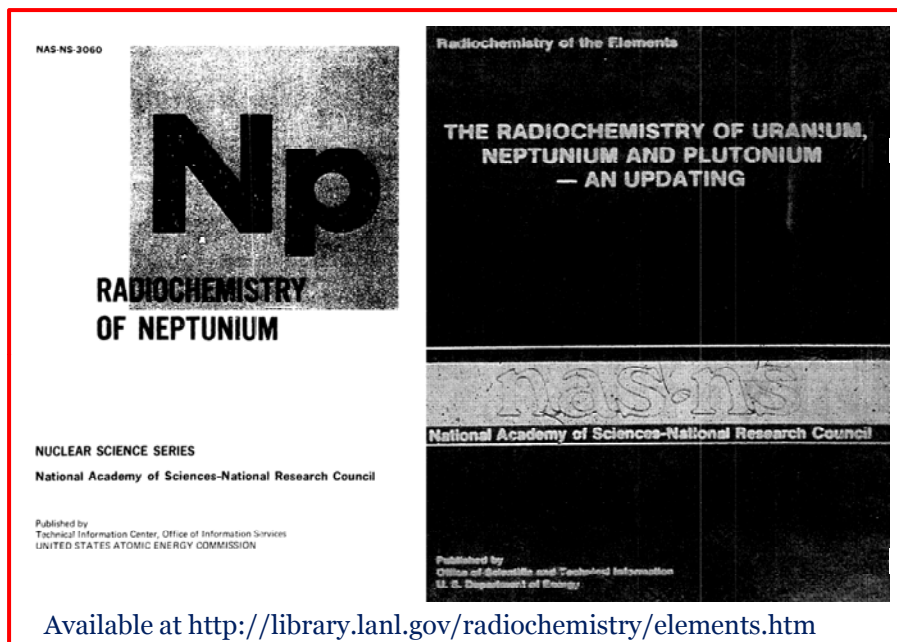


Retention capacity of Np(VI) as a function of [HCl] and [HNO₃] on DGA, TRU, TEVA, and UTEVA resins after oxidation with 1% (w/v) KBrO₃. [Guerin, et al, 2010]

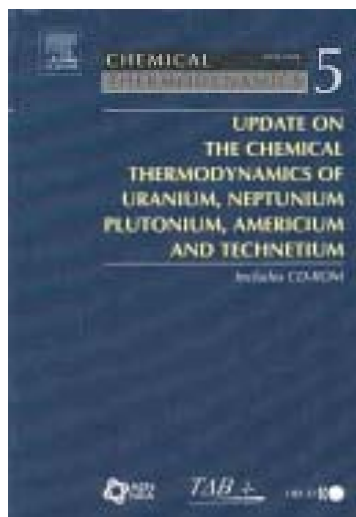
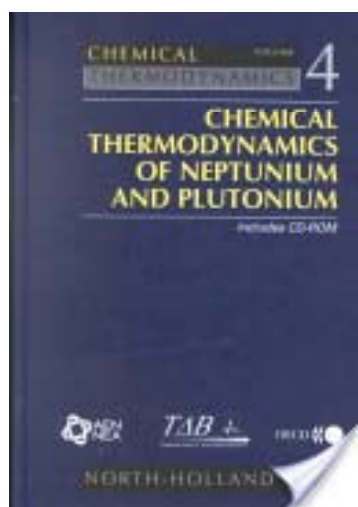
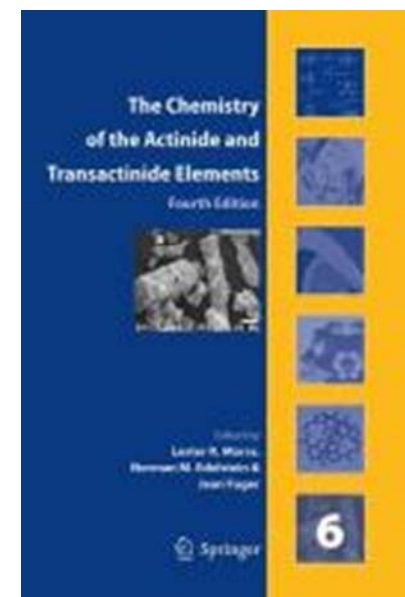
Np-237 in the presence of U-238:

- The presence of U is detrimental to Np detection by either alpha (4.8 MeV) or ICP-MS analyses.
- General separation strategy with TEVA resin:
 - separating Np and U in 2-3M HNO₃ retention of U(VI) is lower than the one of Np(IV)
 - this approach requires the reduction of Np(V) to Np(IV), which is not well-suited for automation.
 - oxidizing Np(V) into Np(VI) in 2-3M HNO₃ is also problematic, since both k_0 for Np(VI) and U(VI) on TEVA resin are within one order of magnitude and sample volumes are large.
- Since the retention of Np(V) is quite low on UTEVA resin, U/Np separation can be solved with tandem columns:
 - The first UTEVA resin would be used to remove a large proportion of natural interferences, especially U(VI).
 - Then, the loaded solution containing the unretained Np(V) could be oxidized to Np(VI) before being introduced into a second UTEVA resin.
 - TEVA and DGA resins have demonstrated similar k_0 to UTEVA at 2M HNO₃ so could also be used.
 - TRU resin has a higher k_0 and would be a potential candidate; however, the high retention of Np(V) and that TRU resin cannot be reused for complex matrices such as biological fluids and environmental samples makes this approach less attractive from an automation point of view.

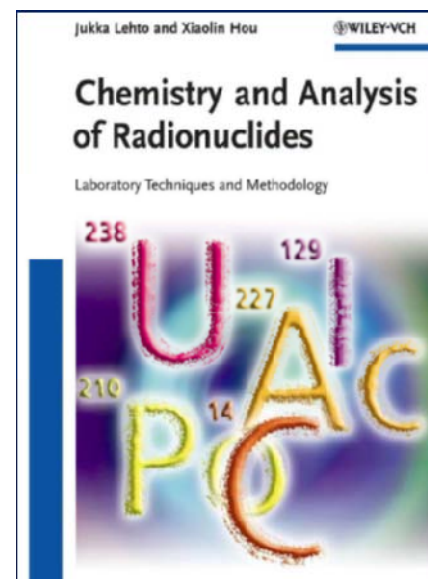
Recommended Reading:



Z. Yoshida et al.
 “Neptunium”, Chapter 6
 in “The Chemistry of the Actinide and Transactinide Elements”, edited by N. M. Edelstein, J. Fuger and L. R. Morss, Springer, (2006-2010). ▶ ▶



Chapter 15 in “Chemistry and Analysis of Radionuclides” by J. Lehto, J. and X. Hou (Wiley-CH, 2011)



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