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Plutonium chemistry and other actinides in aqueous solutions

Part 1

Actinide Family

Ph. MOISY

CEA/DEN/DMRC ; Marcoule

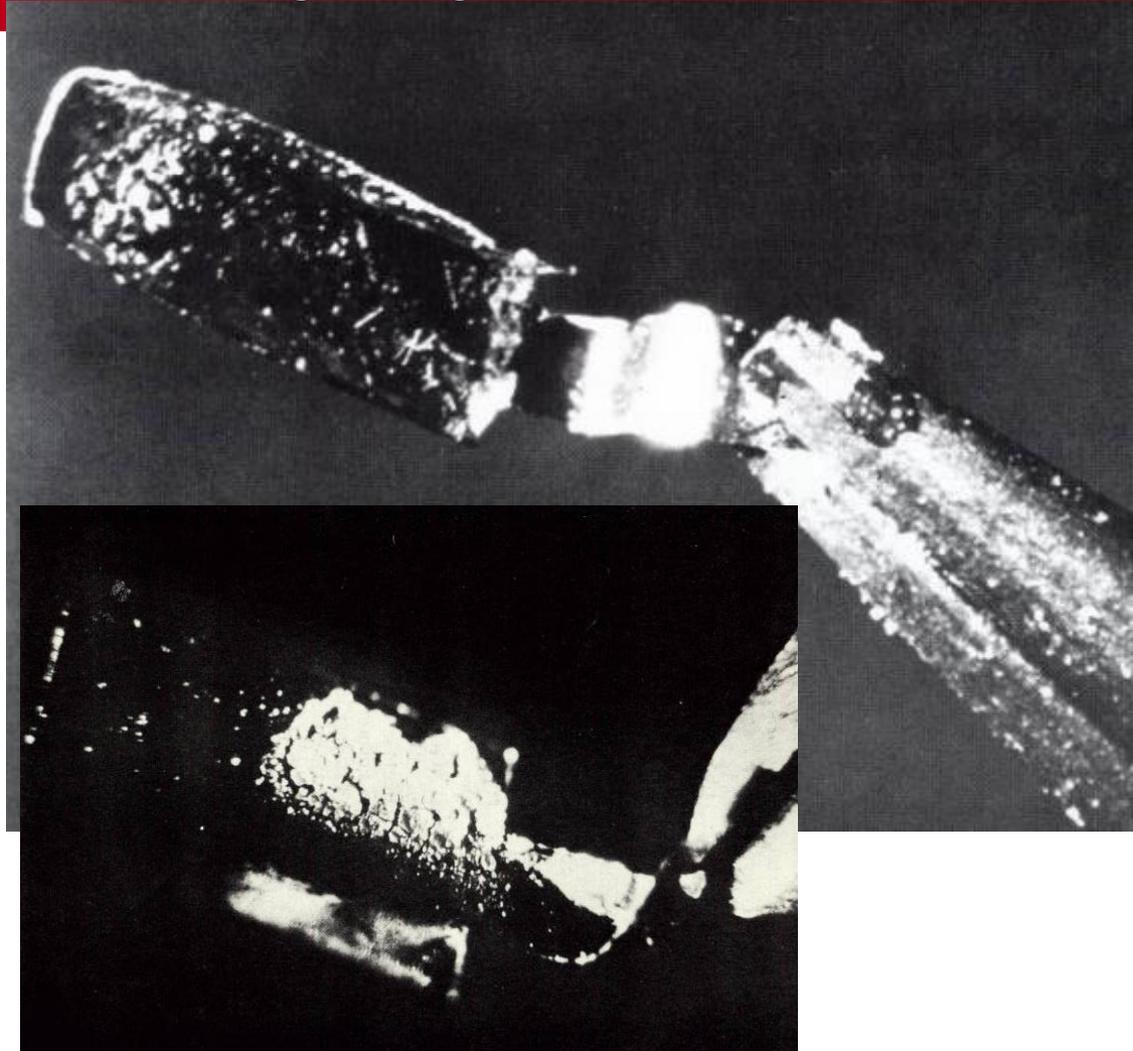
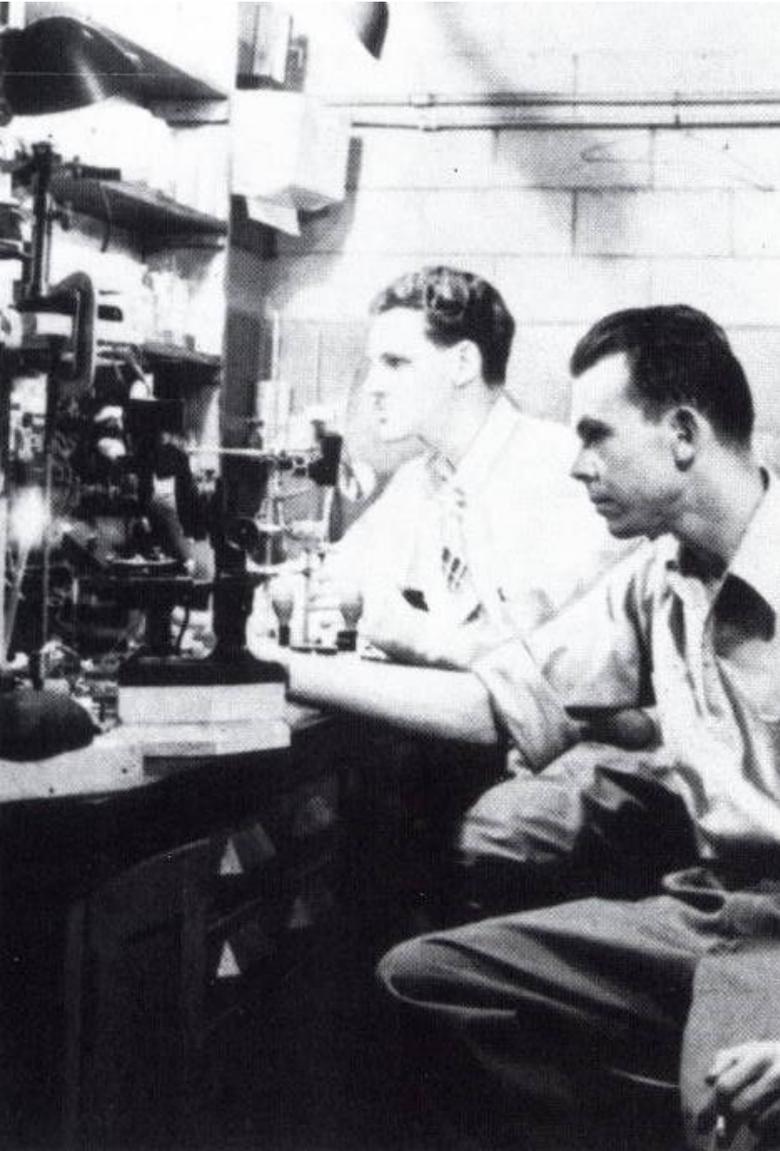
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GT Seaborg: 6 teams of 2 or 3 researchers + researchers specialists
microchemical for plutonium separation

- Redox and fluoride precipitation
- Redox and precipitation bismuth phosphate
- H₂O₂ precipitation
- volatile fluorides
- fractional adsorption
- solvent extraction

End of July 1942: 150 kg of uranyl nitrate irradiated (cyclotron) ¼ mg Pu
U(VI) extraction with ether (C₂H₅OC₂H₅), then four fractions for separation
according to Redox way + precipitation fluoride (entrainment with LaF₃)



$^{239}\text{PuO}_2$ (2.77 μg) (September 10 1942)

End 1942: first graphite pile by E. Fermi → massive plutonium production (sports stadium of the University of Chicago.)

Construction of a second "graphite reactor" at Oak Ridge

End 1942: B. Goldschmidt in Montreal. Missions between Montreal and Chicago (transfer of 4 μg Pu early 1943 to Montreal)

1944: Development in Canada of a "D₂O reactor" and plutonium separation (Chalk River). June 1944: Some U-irradiated rods transferred to Montreal.

Mid 1945: 300 Solvent tests and selection triglycol dichloride (tri- ethylene glycol) (Cl-(CH₂)₂-O-(CH₂)₂-O-(CH₂)₂-Cl) as less volatile than Ether (C₂H₅-O-C₂H₅)

1949: 15 kg of Pu purified in Canada!

This is the period of secrecy and these are not listed!

We speak of the element 49 (instead of 94). Code names later become "silver" for item 93 (neptunium) and "Copper" to element 94 (plutonium).

By analogy with the solar system, the element 93 will be named neptunium (first planet after Uranus) and element 94 Plutonium.

Note 1: C. Tombaugh, discoverer of the planet "Pluto" hesitated to call Cronus (or Minerva - Roman). GT Seaborg has indicated it June 9, 1991 that Cronium (or Minervium) was not bad either!

Note 2: AC Wahl and Seaborg GT hesitated between Plutonium (Pu) and Plutium (Pl) for item 94 ...

Am and Cm are not easily oxidized to Oxidation State +VI, compare to Pu, Np and U.

In Berkeley, summer 1944:



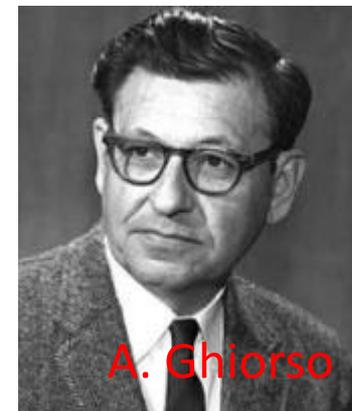
End of 44 : in a reactor, production of ²⁴¹-Am from ²³⁹-Pu,
L. O. Morgan, R. A. James et A. Ghiorso

The new elements bears a lot of similarities
with lanthanides. Separation with ion exchange resin.

Seaborg and his group at the University of California
(Berkeley) discovered 10 actinide elements: Pu, Am, Cm,
Bk, Cf, Es, Fm, Md, No, including element ¹⁰⁶Sg
(Seaborgium).



First americium sample
produced in 1944 on the
60-inch Berkeley cyclotron



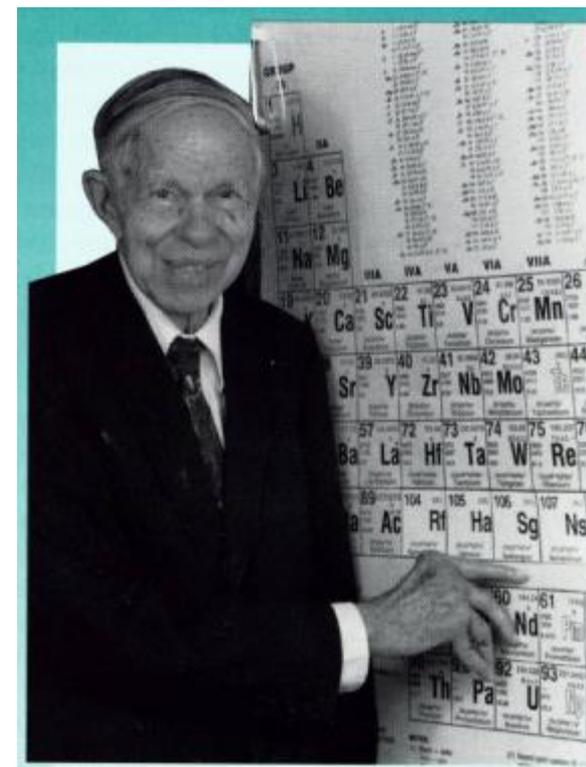
A. Ghiorso

Discovery of Am (radio Quiz le 11/11/1945)



With the development of transuranic chemistry, soon it become clear that they do not fit into Mendeleev Periodic Table of Elements:

- What is the relation of An to lanthanides and other chemical elements?
- What is their position in Table of Elements?



Glenn T. Seaborg

Theory of Actinides !

Seaborg's actinide theory resulted in a redrawing of the Periodic Table of the Elements into its current configuration with the actinide series appearing below the lanthanide series.

As a result of this concept, the transactinide and superactinide series of elements ($Z > 103$) were also properly placed within the d-block elements.

$s^1 s^2 g f^1 f^2 f^3 f^4 f^5 f^6 f^7 f^8 f^9 f^{10} f^{11} f^{12} f^{13} f^{14} d^1 d^2 d^3 d^4 d^5 d^6 d^7 d^8 d^9 d^{10} p^1 p^2 p^3 p^4 p^5 p^6$

1	H	He																																						
2	Li	Be	Métalloïdes	Non-métaux				Halogènes				Gaz rares										B	C	N	O	F	Ne													
3	Na	Mg	Métaux alcalins	Métaux alcalino-terreux				Métaux de transition				Métaux pauvres										Al	Si	P	S	Cl	Ar													
4	K	Ca	Lanthanides	Actinides				Superactinides				Éléments non classés										Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
5	Rb	Sr																							Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn								
7	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo								
8	Uue	Ubn	* Ute	Uqn	Uqu	Uqb	Uqt	Uqq	Uqp	Uqh	Uqs	Uqo	Uqe	Upn	Upu	Upb	Upt	Upq	Upp	Uph	Ups	Upo	Upe	Uhn	Uhu	Uhb	Uht	Uhq	Uhp	Uhh	Uhs	Uho								

↓

g^1	g^2	g^3	g^4	g^5	g^6	g^7	g^8	g^9	g^{10}	g^{11}	g^{12}	g^{13}	g^{14}	g^{15}	g^{16}	g^{17}	g^{18}
* Ubu Ubb Ubt Ubq Ubp Ubh Ubs Ubo Ube Utn Utu Utb Utt Utq Utp Uth Uts Uto																	

Theory of Actinide: Electronic Configuration

	Atom (g)	M ²⁺ (g)	M ³⁺ (aq)	M ⁴⁺ (g)		
6d ¹	Actinium	6d7s ²	7s			
	Thorium	6d ² 7s ²	5f6d			
	Protactinium	5f ² 6d7s ²	5f ² 6d		5f ¹	-
	Uranium	5f ³ 6d7s ²	5f ³ 6d	5f ³	5f ²	-
	Neptunium	5f ⁴ 6d7s ²	5f ⁵	5f ⁴	5f ³	-
	Plutonium	5f ⁶ 7s ²	5f ⁶	5f ⁵	5f ⁴	-
	Americium	5f ⁷ 7s ²	5f ⁷	5f ⁶	5f ⁵	-
	Curium	5f ⁷ 6d7s ²	5f ⁸	5f ⁷	5f ⁶	-
	Berkelium	5f ⁹ 7s ²	5f ⁹	5f ⁸	5f ⁷	-
	Californium	5f ¹⁰ 7s ²	5f ¹⁰	5f ⁹	5f ⁸	-
	Einsteinium	5f ¹¹ 7s ²	5f ¹¹	5f ¹⁰	5f ⁹	-
	Fermium	5f ¹² 7s ²	5f ¹²	5f ¹¹	5f ¹⁰	-
	Mendelevium	5f ¹³ 7s ²	5f ¹³	5f ¹²	5f ¹¹	-
	Nobelium	5f ¹⁴ 7s ²	5f ¹⁴	5f ¹³	5f ¹²	-
Lawrencium	5f ¹⁴ 6d7s ²	5f ¹⁴ 7s	5f ¹⁴	5f ¹³	-	

- Multiple oxidation states for the An ions are due to the close proximity of the energy levels of the 7s, 6d, and 5f electrons
- Oxidation states of An (particularly in the first half of the series “light actinides”) in solutions are more variable than those of the Ln

U(VI) hydrolysis

Espèces solubles
(UO₂)_i(OH)_j^(2i-j)

log β⁰_{ij} (I=0, t=25°C)
(Sélection OCDE)

UO₂²⁺

UO₂(OH)⁺

UO₂(OH)₂ (s)

UO₂(OH)₃⁻

UO₂(OH)₄²⁻

(UO₂)₂(OH)⁺

(UO₂)₂(OH)₂²⁺

(UO₂)₃(OH)₄²⁺

(UO₂)₃(OH)₅⁺

(UO₂)₃(OH)₇⁻

(UO₂)₄(OH)₇⁺

Espèce insoluble

log *K_S⁰ (I=0, T=25°C)
(Sélection OCDE)

UO₂(OH)₂·H₂O↓
= UO₃·2H₂O↓

(6,5)
(solubilité de UO₂(OH)₂·H₂O < 10^{-5.5} M)

8,8

(17,7)

22,8

23,0

11,3

22,4

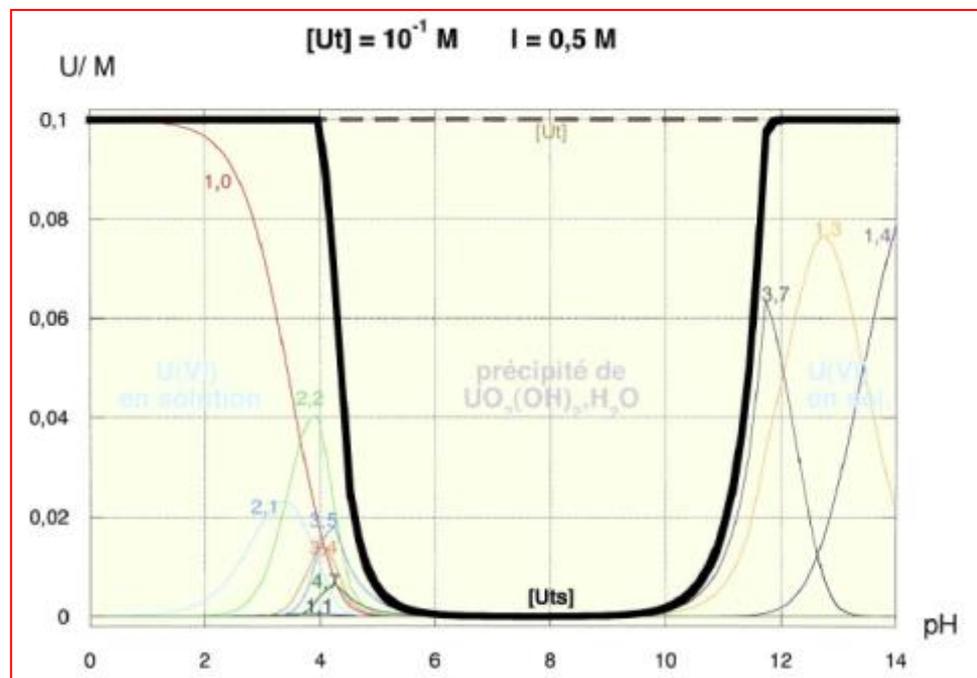
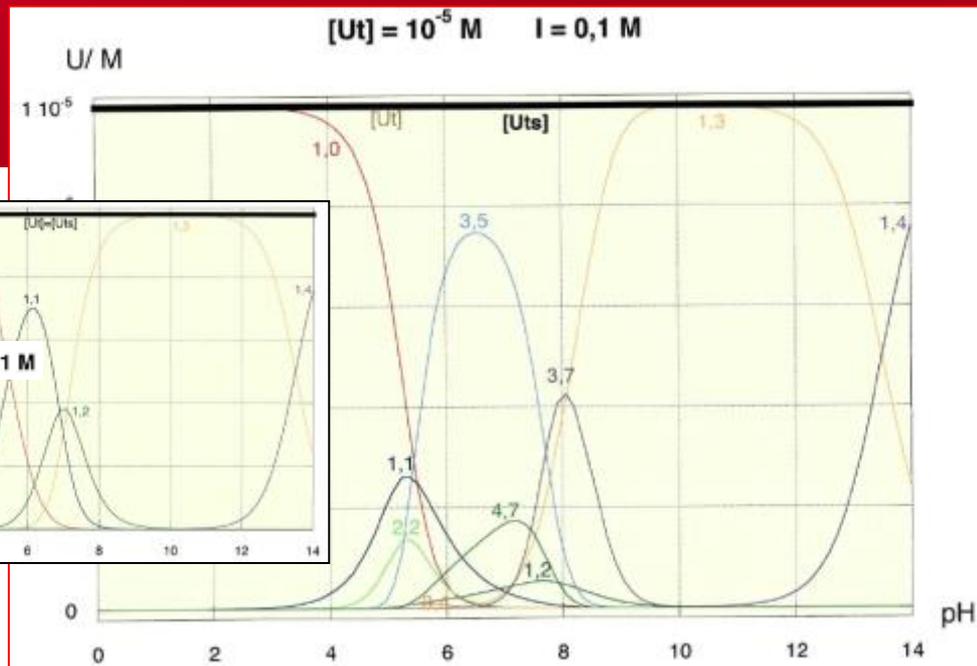
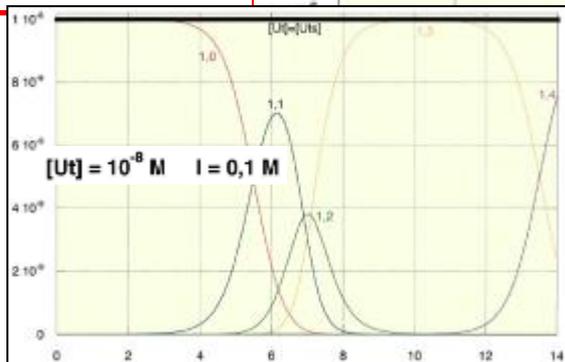
44,1

54,45

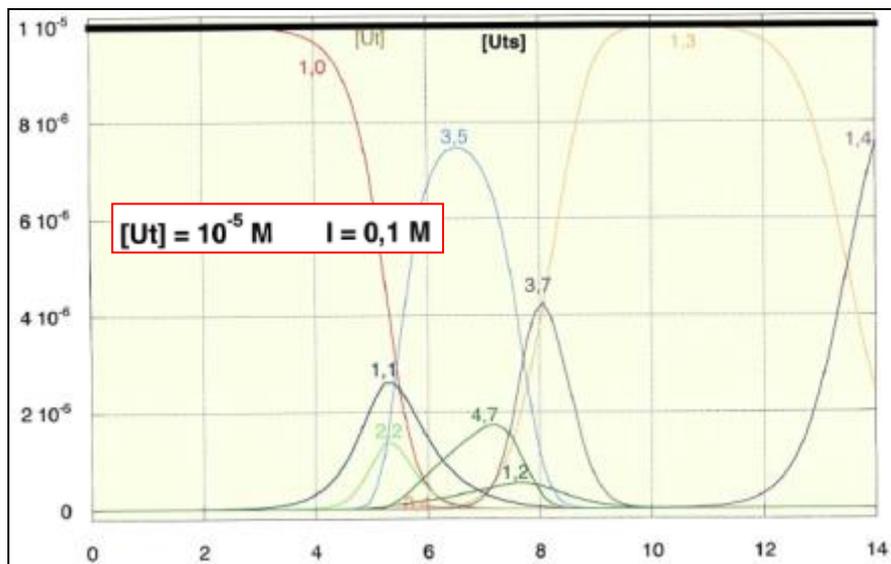
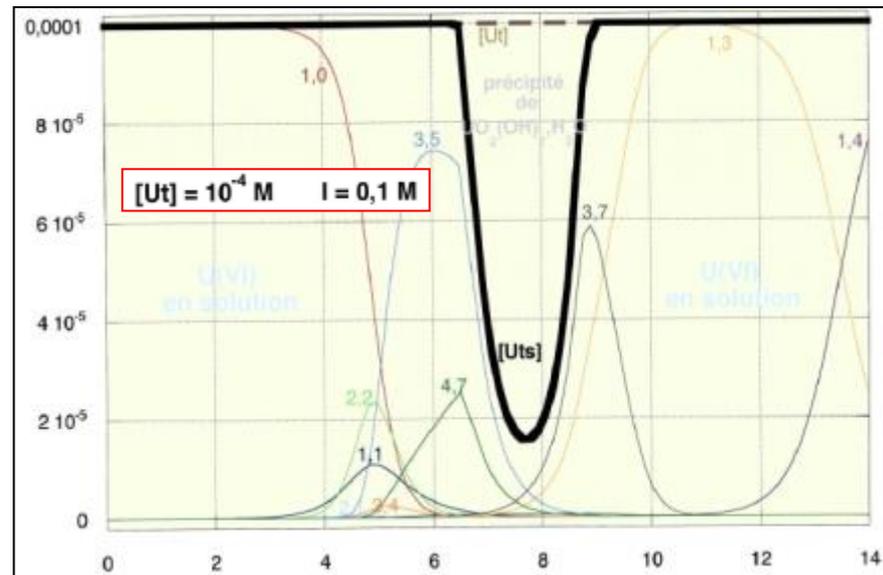
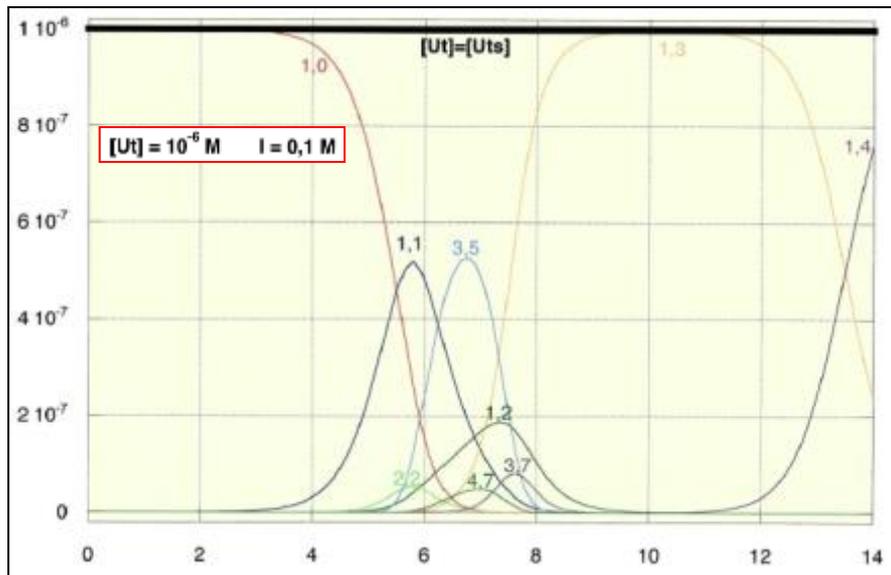
67,0

76,1

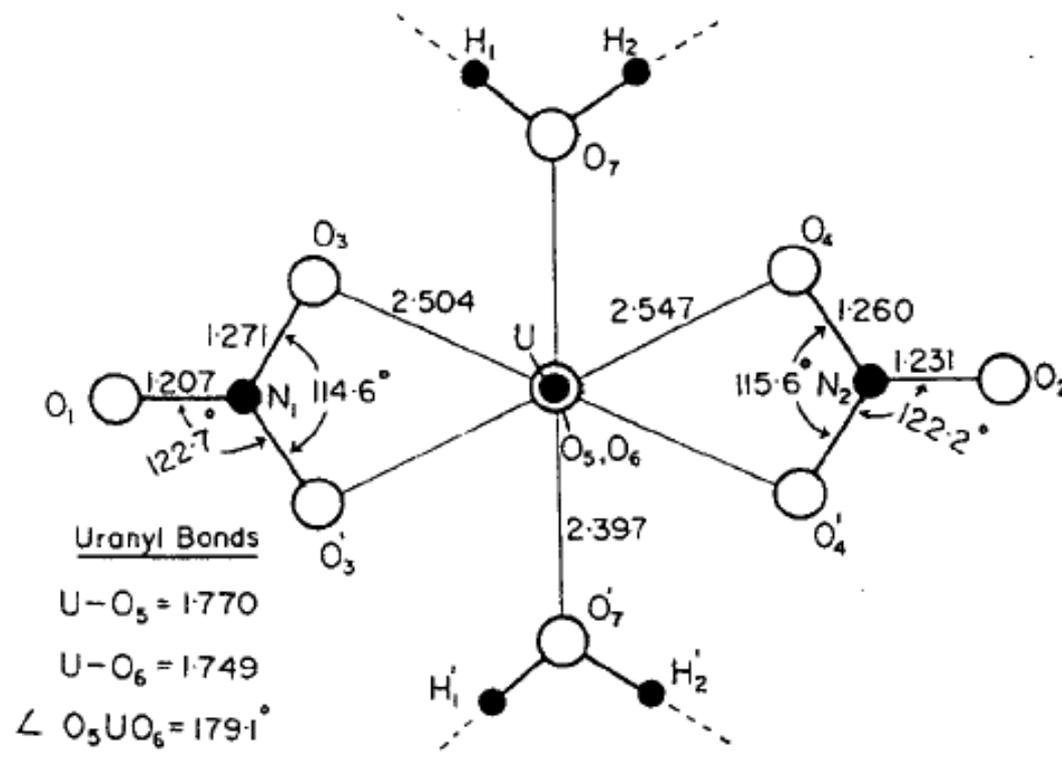
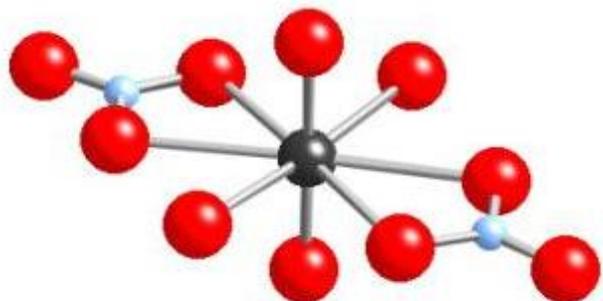
(6,5)



U(VI) hydrolysis



Nitrato complexes of An(VI)



The most well known !

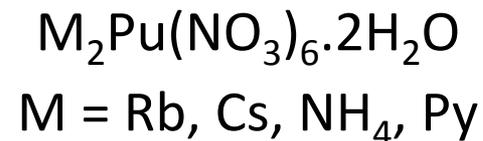
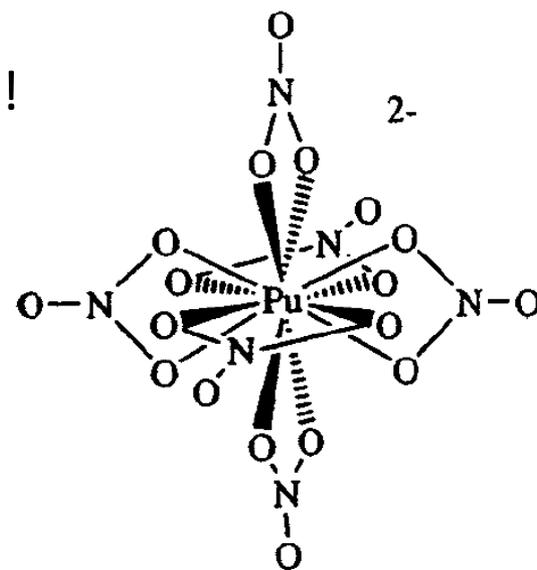
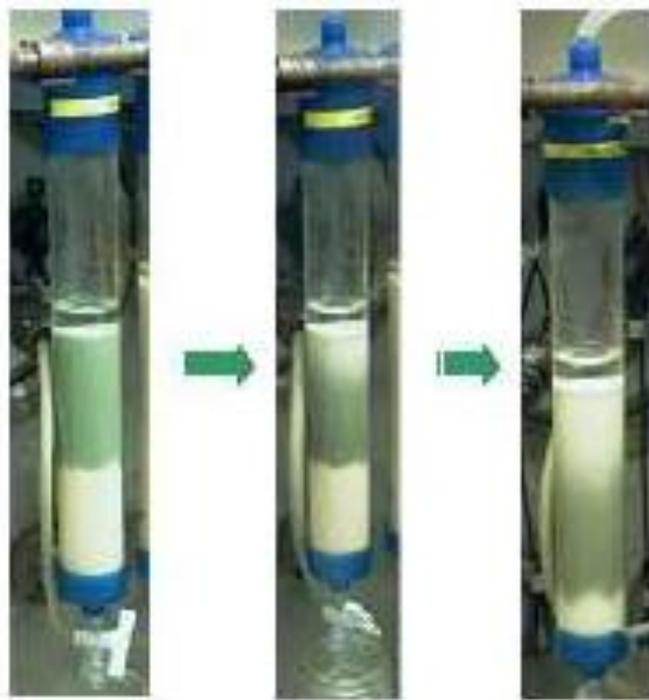
Uranyl nitrate $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$

Only $\text{PuO}_2(\text{NO}_3)^+$ known in aqueous solution

Nitrato complexes of An(IV)

In solution: $\text{Pu}(\text{NO}_3)_n^{4-n}$ (with $n = 1 - 6$): CN = 12 !
but $n=3$ and 5 are never characterized in solution !

$\text{Pu}(\text{NO}_3)_6^{2-}$ used in ion exchange resin for
Pu purification



Another important series for extraction: $\text{An}(\text{IV})(\text{NO}_3)_4$