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THE CHEMISTRY BEHIND ANALYTICAL ACTINIDE SEPARATIONS

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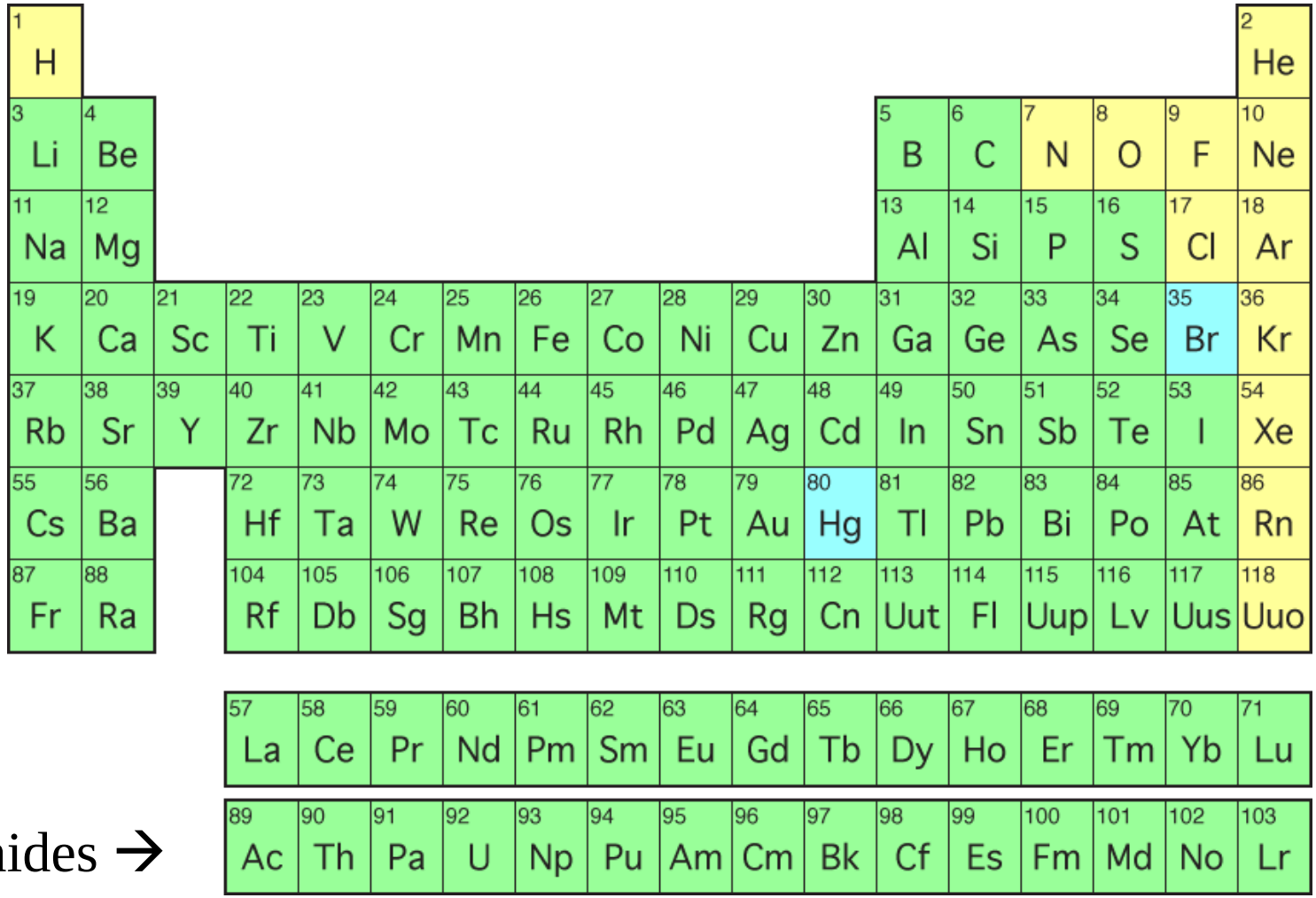
Laboratory of Radiochemistry

- 30 persons including 13 doctoral students
- Comprehensive master's program in radiochemistry
- Research areas:
  - Migration of radionuclides in geosphere related to final disposal of spent nuclear fuel
  - Selective separation of radionuclides from nuclear waste effluents
  - Radiopharmaceutical chemistry
  - Environmental radioactivy


1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37 Rb
38 Sr
39 Y
40 Zr
41 Nb
42 Mo
43 Tc
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
49 In
50 Sn
51 Sb
52 Te
53 I
54 Xe
55 Cs
56 Ba
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
87 Fr
88 Ra
104 Rf
105 Db
106 Sg
107 Bh
108 Hs
109 Mt
110 Ds
111 Rg
112 Cn
113 Uut
114 Fl
115 Uup
116 Lv
117 Uus
118 Uuo
57 La
58 Ce
59 Pr
60 Nd
61 Pm
62 Sm
63 Eu
64 Gd
65 Tb
66 Dy
67 Ho
68 Er
69 Tm
70 Yb
71 Lu
89 Ac
90 Th
91 Pa
92 U
93 Np
94 Pu
95 Am
96 Cm
97 Bk
98 Cf
99 Es
100 Fm
101 Md
102 No
103 Lr

Actinides →

MOST RELEVANT ACTINIDES IN THE ENVIRONMENT AND/OR NUCLEAR WASTE

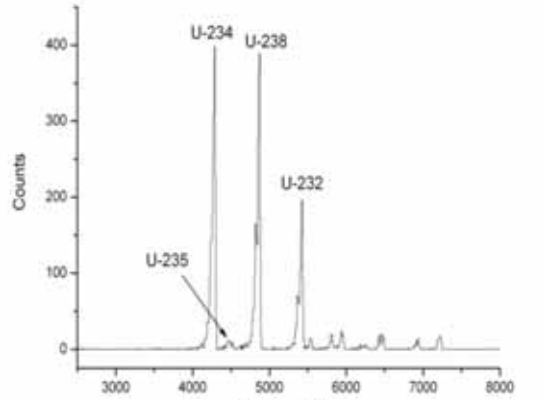
- Thorium (^{228,230,232}Th) – natural
- Uranium (^{234,235,238}U) – natural
- Neptunium (^{237}Np) – artificial
- Plutonium (^{238,239,240,241}Pu) – artificial
- Americium (^{241}Am) - artificial

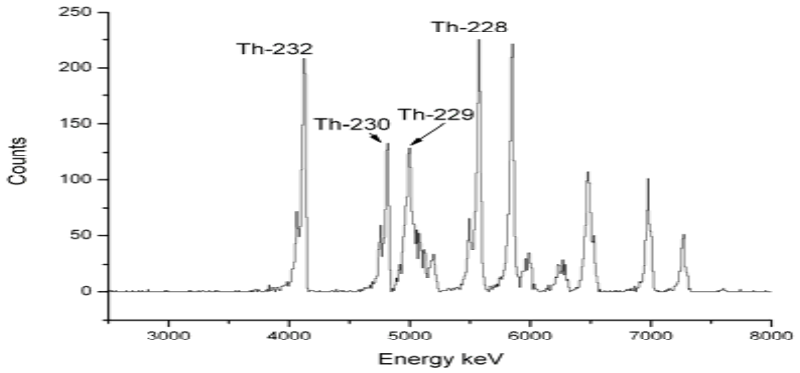
Activities and concentration of actinides in 10 cm surface soil in Finland

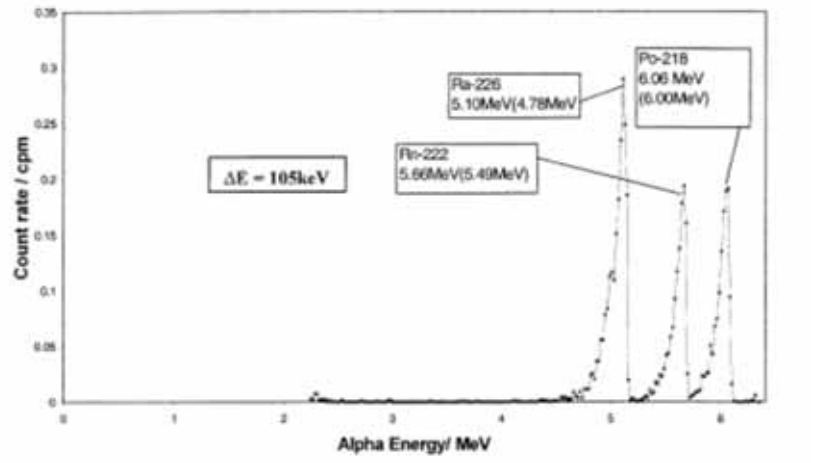
Nuclide	Bq/kg	g/kg	mol/kg
^{210}Po	30	2×10^{-13}	9×10^{-16}
^{226}Ra	20	5×10^{-10}	2×10^{-12}
^{228}Th	20	7×10^{-13}	3×10^{-15}
^{230}Th	20	3×10^{-8}	1×10^{-10}
^{232}Th	20	5×10^{-3}	2×10^{-5}
^{234}U	20	9×10^{-8}	4×10^{-10}
^{238}U	20	2×10^{-3}	7×10^{-6}
^{237}Np	0.002	7×10^{-11}	3×10^{-13}
^{238}Pu	0.02	2×10^{-14}	1×10^{-16}
^{239,240}Pu	0.5	2×10^{-10}	8×10^{-13}
^{241}Am	0.2	2×10^{-12}	6×10^{-15}

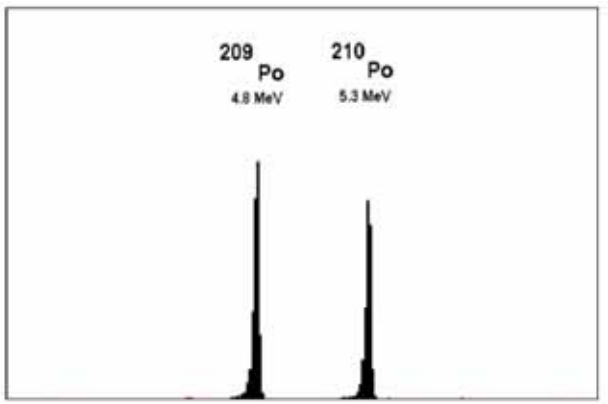
MEASUREMENT OF ACTINIDE CONCENTRATIONS AND ISOTOPIC COMPOSITION - 1

- Alpha spectrometry
  - Interferences from each other and from ^{210}Po and ^{226}Ra









MEASUREMENT OF ACTINIDE CONCENTRATIONS AND ISOTOPIC COMPOSITION - 2

- Mass spectrometry
  - Interferences:
    - From isobars (^{238}Pu cannot be measured due to presence of ^{238}U)
    - From tailings (^{239}Pu cannot be measured if large excess of ^{238}U is present)
    - From polyatomic ions (^{238}UH interferes with ^{239}Pu measurement

→ RADIOCHEMICAL SEPARATIONS ARE NEEDED

- Precipitation
- Ion exchange
- Solvent extraction
- Extraction chromatography

Mass vs. activity – effect on separation

	activity (Bq)	mass (g)
^{238}U	20	2×10^{-3}
^{239}Pu	0.5	2×10^{-10}
Excess of U	40-times	10^{10}-times

If uranium is removed by a factor of 10000, its activity is only 0.4% of that of plutonium → uranium does not intefer with plutonium measurement by alpha spectrometry

If plutonium is to be measured ICP-MS, there is still 10^6-times excess of plutonium, which does not allow Pu measurement

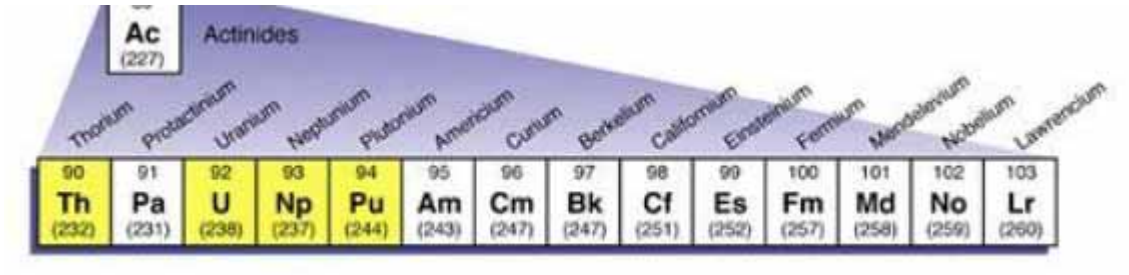
MAIN CHEMICAL PARAMETERS BEHIND ANALYTICAL SEPARATIONS OF ACTINIDES

- Complex formation with Cl^- and NO_3^-
- General trend: the higher the charge density of a cation the stronger the complex (coulombic interaction)
- Charge density of a cation increases with:
  - Smaller size
  - Higher charge

MAJOR PARAMETERS CONTROLLING THE CHARGE DENSITY OF ACTINIDES

- OXIDATION STATE → CHARGE
- ATOMIC NUMBER → SIZE

Chemical properties of actinides



- 5f elements - 5f orbitals are progressively filled
- Lighter actinides Th, Pa, U, Np and Pu behave like transition elements (several oxidation states → complex chemistry)
- Heavier actinides, from Am on, behave like lanthanides (prevailing oxidation state +III → An^{3+})

Oxidation states of actinides

	+II	+III	+IV	+V	+VI	+VII
Actinium		**X**				
Thorium		x	**X**			
Protactinium		(x)	x	**X**		
Uranium		x	x	x	**X**	
Neptunium		x	x	**X**	x	x
Plutonium		x	**X**	x	x	x
Americium	(x)	**X**	x	x	x	
Curium		**X**	x			
Berkelium		**X**	x			
Californium	(x)	**X**	(x)			
Essium	(x)	**X**				
Fermium	x	**X**				
Mendelevium	x	**X**				
Nobelium	**X**	x				
Lawrencium		**X**				

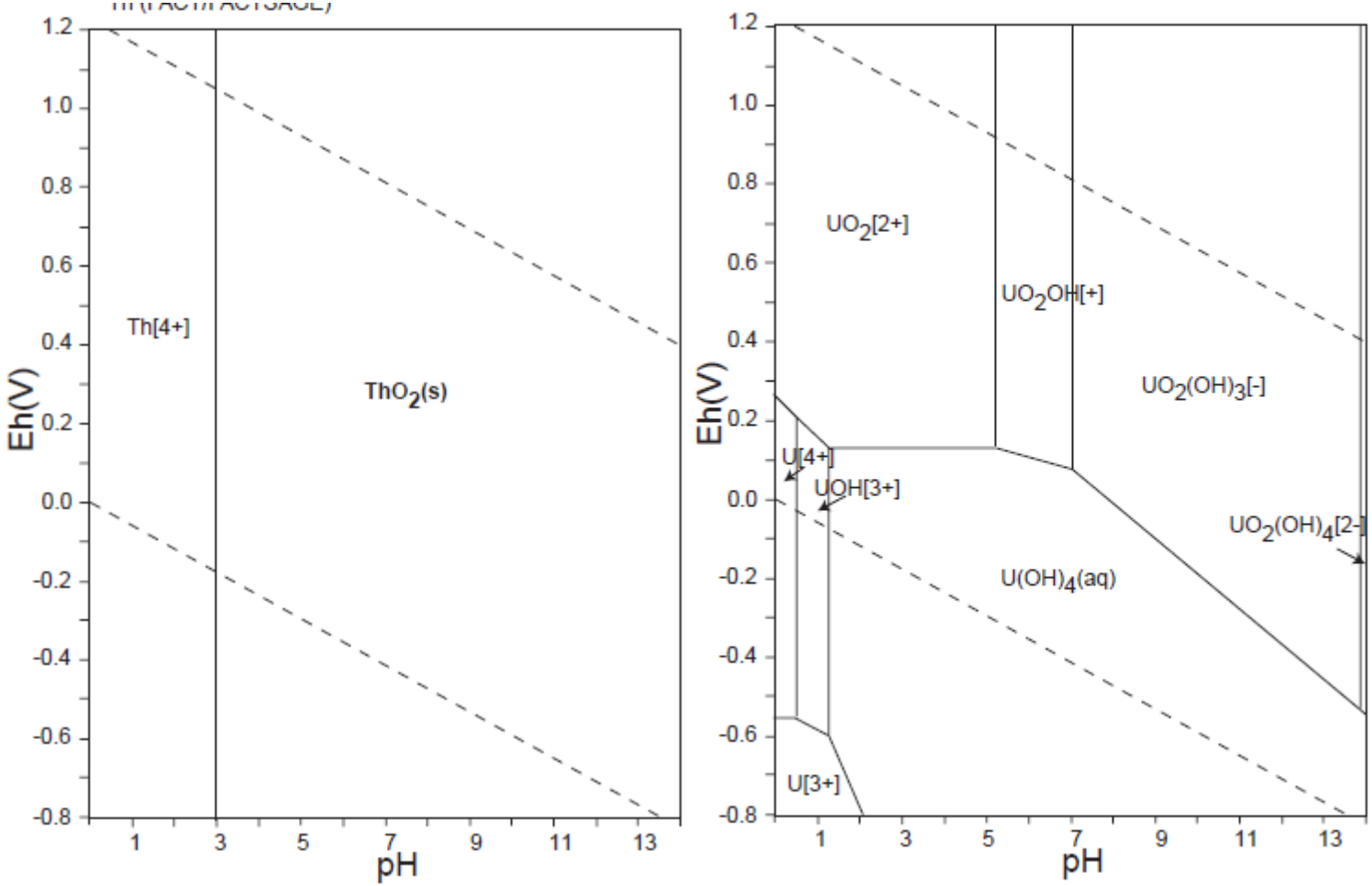
OXIDATION STATES

- Th^{4+}
- U^{4+}, UO_2^{2+} (VI)
- Np^{4+}, NpO_2^{+} (V)
- $Pu^{3+} \leftrightarrow Pu^{4+}$, PuO_2^{+} (V), PuO_2^{2+} (VI)
- Am^{3+}

Interfering elements in separations for alpha spectrometry:

- Po^{4+}
- Ra^{2+}

Eh – pH diagrams (Pourbaix diagrams)



Chemical forms of actinides at various oxidation states

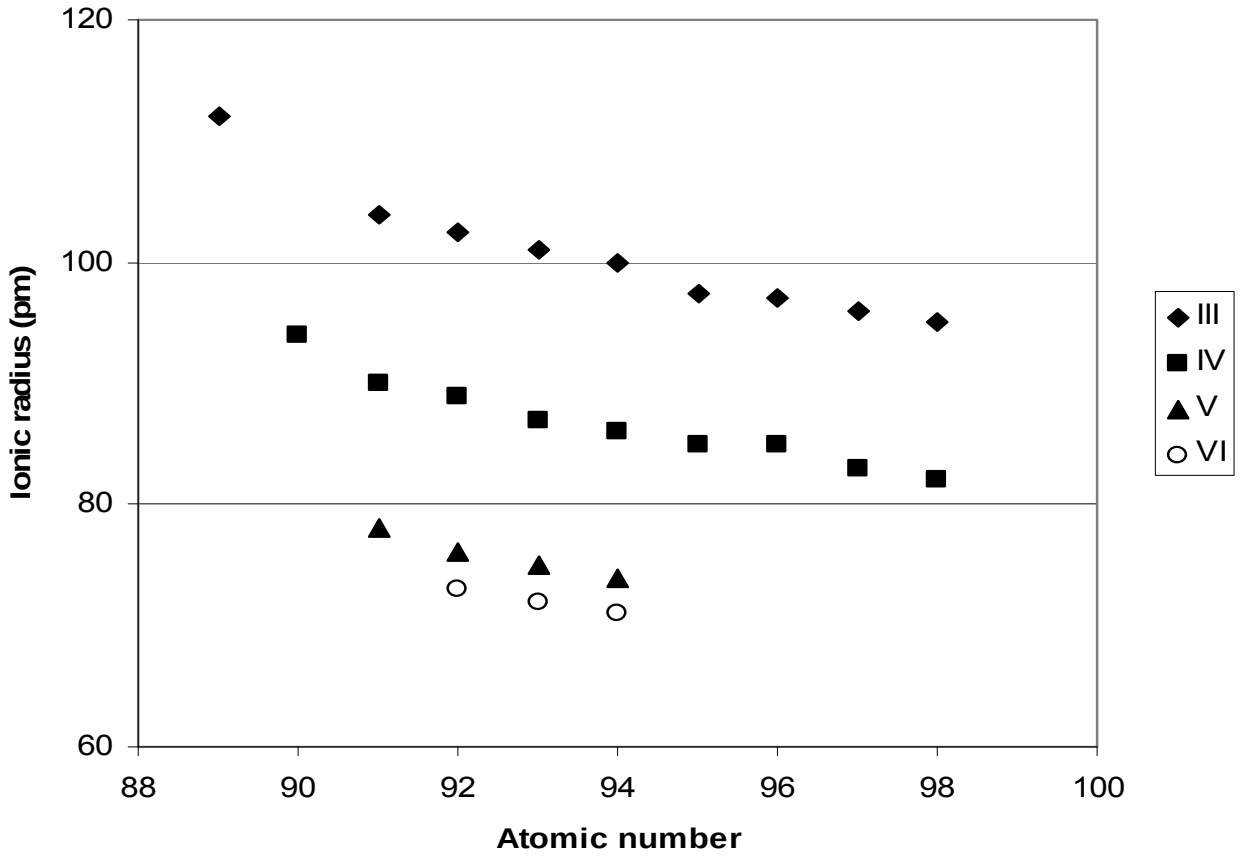
+III: An^{3+}
+IV: An^{4+}
+V: AnO_2^{+} $(O=An=O)^{+}$
+VI: AnO_2^{2+} $(O=An=O)^{2+}$

Effective charges:

$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+}$

+4 +3.2 +3 +2.2

IONIC RADII OF ACTINIDES



How the effective charge and ionic radius affect chemical properties

The smaller the ion, the stronger the tendency to hydrolyze and form complexes:

+III: $Ac^{3+} < Pu^{3+} < Am^{3+} < Cm^{3+} < Bk^{3+}$ etc

+IV: $Th^{4+} < U^{4+} < Np^{4+} \sim Pu^{4+}$

+V: $PaO_2^{+} > NpO_2^{+} < PuO_2^{+}$

+VI: $UO_2^{2+} < PuO_2^{2+}$

The higher the effective charge, the stronger the tendency to hydrolyze and form complexes:

$PuO_2^{+} < Pu^{3+} < PuO_2^{2+} < Pu^{4+}$

SEPARATIONS BY ION EXCHANGE CHROMATOGRAPHY

Formation of negative complex in strong HCl or HNO_3, e.g.

$$Pu^{4+} + nNO_3^- \rightarrow PuNO_3^{3+} \rightarrow Pu(NO_3)_2^{2+} \rightarrow Pu(NO_3)_3^{+} \rightarrow Pu(NO_3)_4 \rightarrow Pu(NO_3)_5^-$$

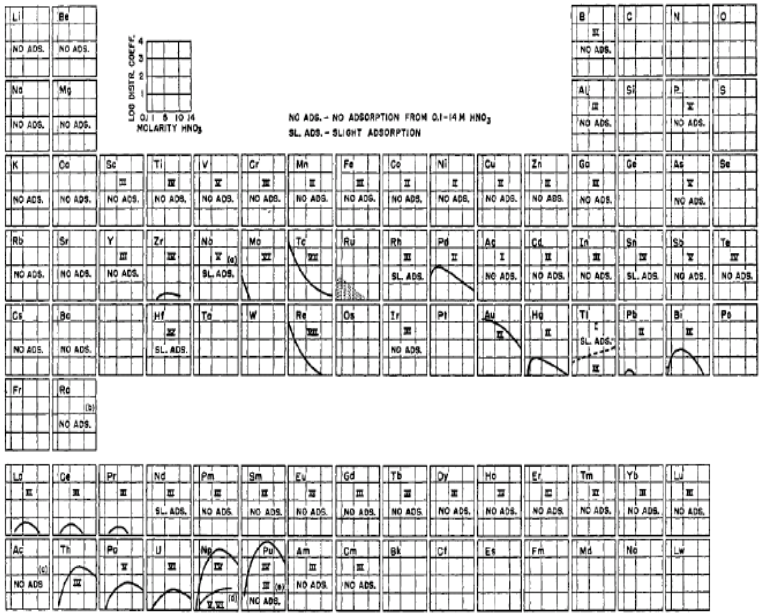
Ion exchange:

$$R\text{–}N(CH_3)_3NO_3 + Pu(NO_3)_5^- \Leftrightarrow R\text{–}N(CH_3)_3Pu(NO_3)_5 + NO_3^-$$

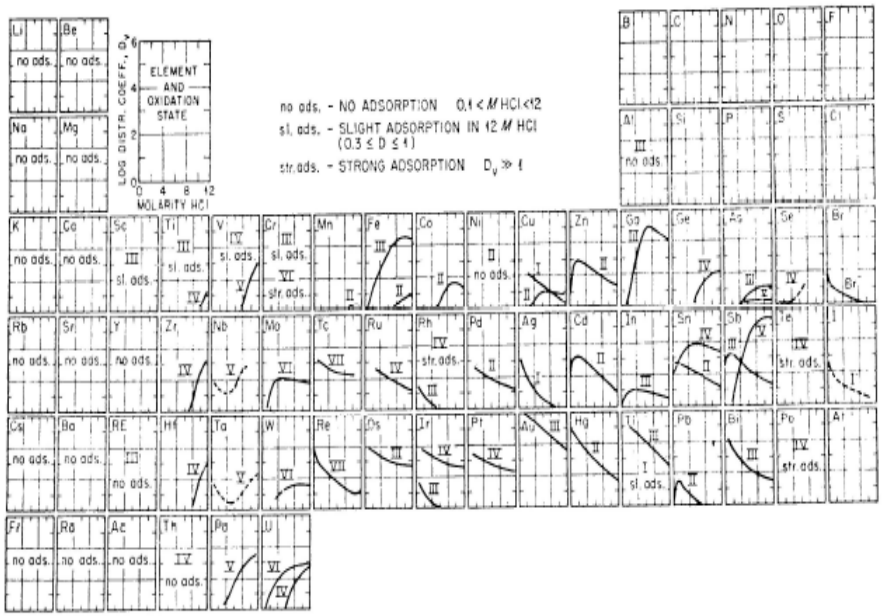
Distribution coefficients

$$K_d\ (D) = \frac{\text{concentration in the exchanger}}{\text{concentration in the solution}}$$

HCl

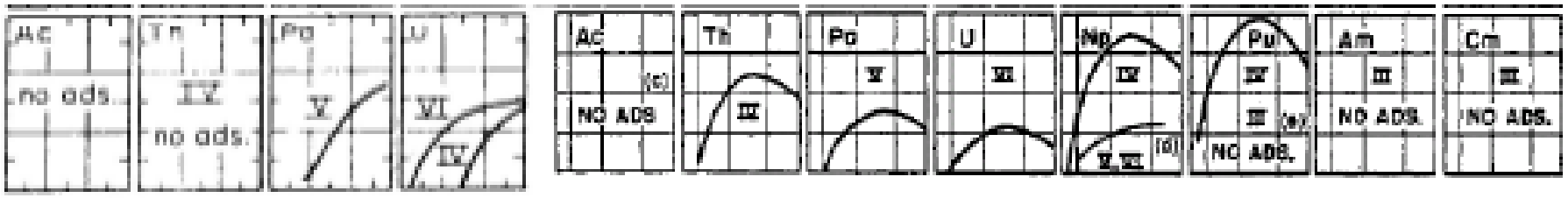


HNO_3



Distribution coefficients for actinides

HCl HNO_3



Ac Th Pa U Ac Th Pa U Np Pu Am Cm

Major points:

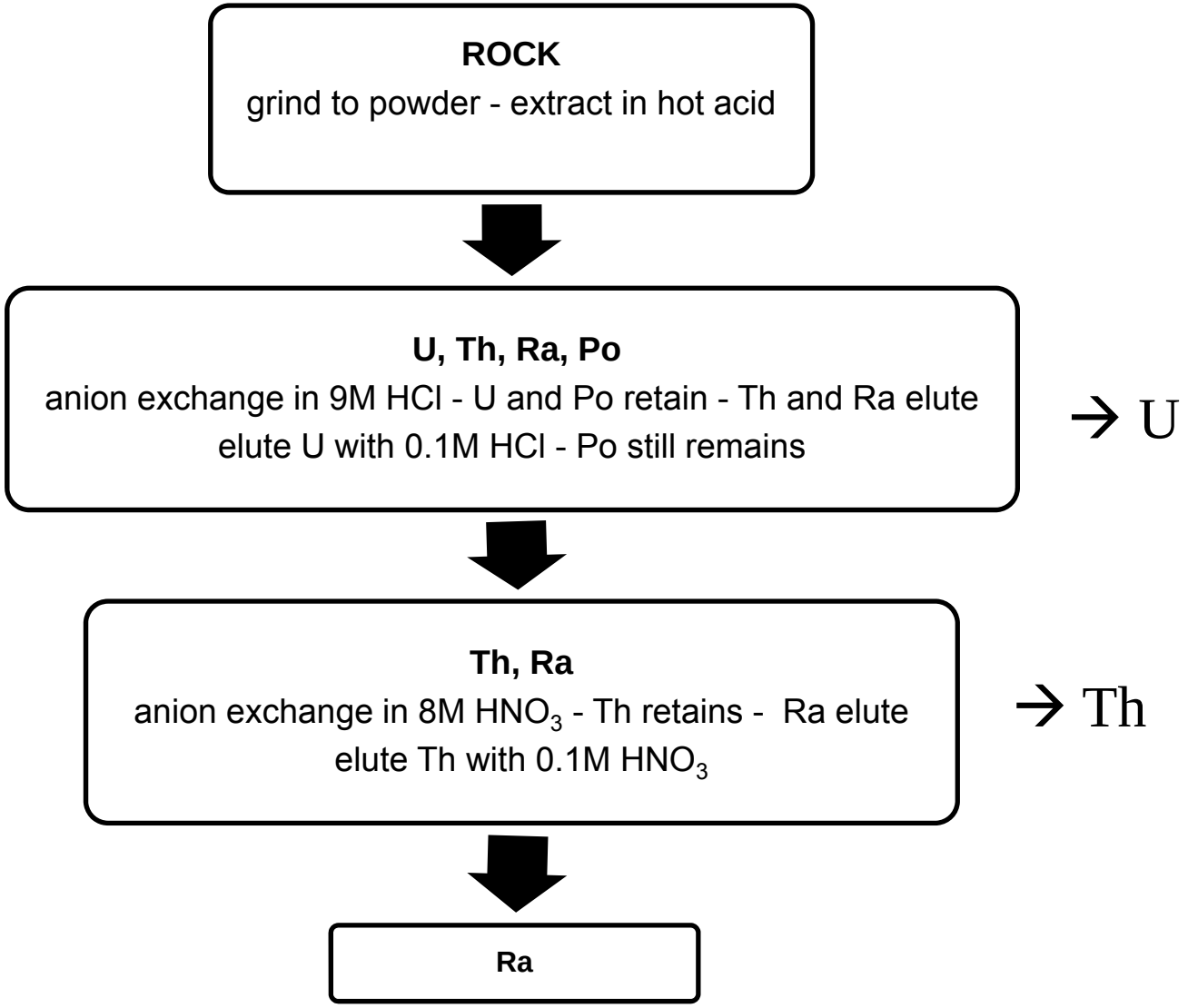
-Th forms a strong negative nitrate complex but no chloride complex

-Trivalent actinides (Pu^{3+}, Am^{3+}) do not form negative complexes

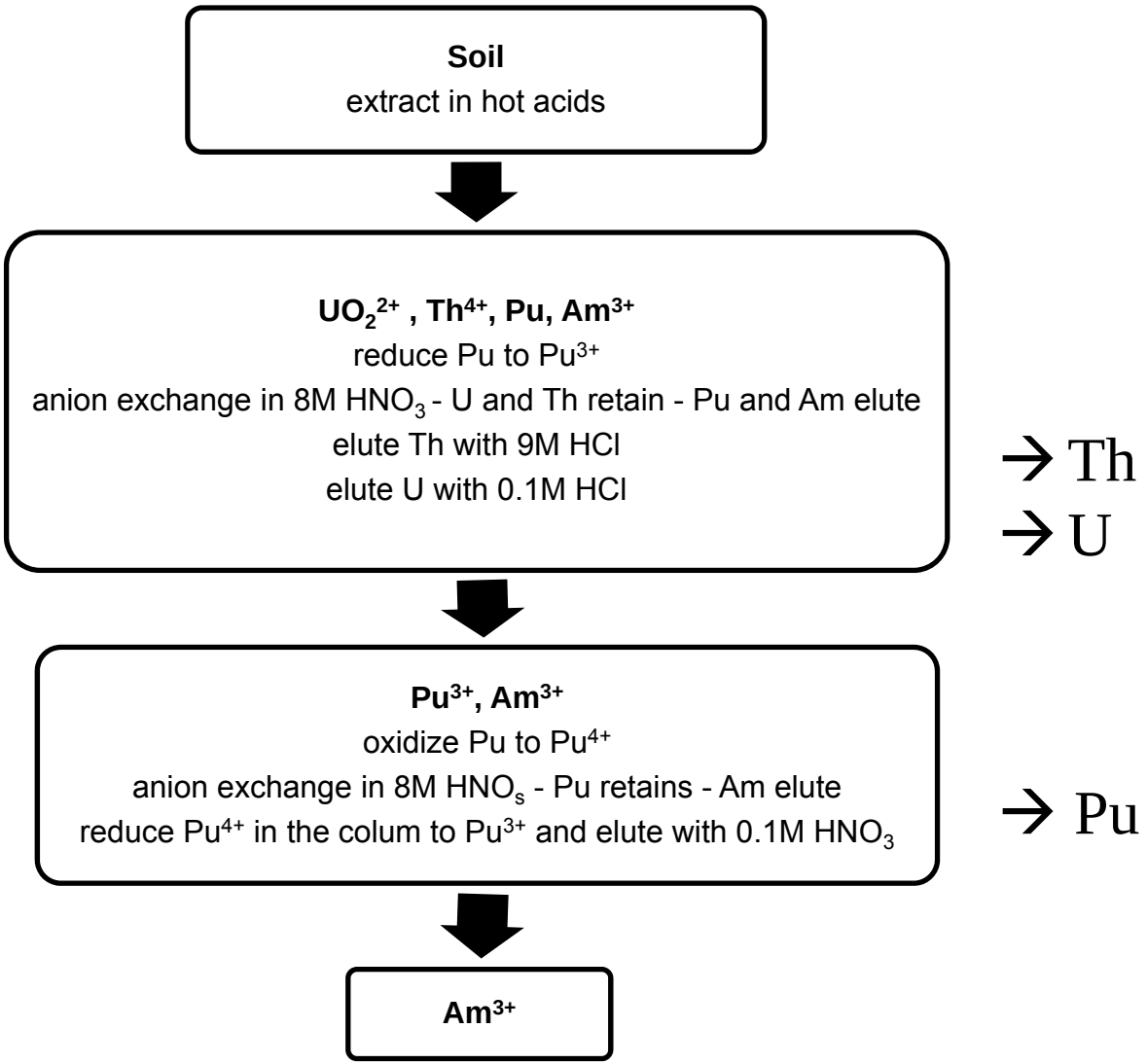
-Tetravalent Th^{4+}, Np^{4+}, Pu^{4+} and hexavalent UO_2^{2+} form strong (or intermediate) complexes in HNO_3 and HCl (exception Th in HCl)

- Po forms very strong complexes – Ra forms no complexes

Separation of Th and U from rock (no Np, Pu, Am)



Separation of Th, U, Pu and Am (surface soil)



Separations by extraction chromatography (solvent extraction)

Formation of neutral complex in strong HCl or HNO_3, e.g.

$Pu^{4+} + nNO_3^- \rightarrow PuNO_3^{3+} \rightarrow Pu(NO_3)_2^{2+} \rightarrow Pu(NO_3)_3^{+} \rightarrow Pu(NO_3)_4$

Transfer into organic phase (extractant R-X):

$R–X + Pu(NO_3)_4 \Leftrightarrow R–X\text{-}Pu(NO_3)_4$

Differences of ion exchange and solvent extraction chromatographies

- In ion exchange negative complexes are taken up by the resin
- In extraction chromatography complexes are neutral → lower acid concentrations are needed
- In ion exchange only one type of resin is used – strongly basic quaternary amine resin
- In extraction chromatogprahy several types of resins are used – also resins which take up trivalent metals

EXTRACTION CHROMATOGRAPHY RESINS

RESIN	***USE***	***EXTRACTION REAGENT***	***SEPARATION PROCESS***
Nickel Resin	Ni	dimethylglyoxime (DMG)	precipitation
Pb Resin	Pb	crown ether (18-crown-6)	extraction
Sr Resin	Sr, Pb	crown ether (18-crown-6)	extraction
MnO_2 Resin	Ra	MnO_2	ion exchange
Diphonix® Resin	Actinides and transition metals	diphosphonic and sulfonic acid	ion exchange
Ln Resin	Lanthanides, Ra-228	di(2-ethylhexyl) orthophosphoric acid (HDEHP).	extraction
Actinide Resin	Group actinide separations/gross alpha measurements	DIPEX	extraction
DGA Resin	Actinides, lanthanides, Y, Ra	N,N,N',N'-tetra-n-octyldiglycolamide	extraction
TEVA® Resin	Tc, Th, Np, Pu, Am/lanthanides	aliphatic quaternary amine	extraction/ion exchange
TRU Resin	Fe, Th, Pa, U, Np, Pu, Am, Cm	octylphenyl-N,N-diisobutyl carbamoylphosphine oxide (CMPO)	extraction
UTEVA® Resin	Th, U, Np, Pu	diamyl, amylphosphonate (DAAP)	extraction

Extraction chromatography resins for actinide separations

- TEVA resin retains tetravalent actinides Th^{4+}, (U^{4+}), Np^{4+}, Pu^{4+}
- TRU retains both tri and tetravalent actinides Th^{4+}, (U^{4+}), Np^{4+}, Pu^{4+}, Pu^{3+}, Am^{3+} and hexavalent uranium UO_2^{2+}
- UTEVA resin retains tetravalent actinides Th^{4+}, (U^{4+}), Np^{4+}, Pu^{4+} and hexavalent uranium UO_2^{2+}

Extractants:

- TEVA: aliphatic quaternary amine
- TRU: octylphenyl-N,N-diisobutyl carbamoylphosphine oxide (CMPO)
- UTEVA: diamyl, amylphosphonate (DAAP)

SUMMARY

- **Thorium** exists solely as Th^{4+} which forms a strong nitrate complex but no chloride complex.

- **Uranium** can exist as U^{4+} and UO_2^{2+} but only the latter one is relevant in radiochemical separations. Uranyl ion forms an intermediate nitrate complex and a strong chloride complex.

- **Neptunium** occurs both as Np^{4+} and NpO_2^{+} the latter one prevailing in most oxidizing conditions. For the radiochemical separation Np is reduced to Np^{4+} at which oxidation state it forms strong complexes especially with nitrate.

Summary

- **Plutonium** occurs at four oxidation states as Pu^{3+}, Pu^{4+}, PuO_2^{+} and PuO_2^{2+}. In the tetravalent state Pu forms a very strong complex with nitrate and as such can be efficiently retained in the separation medium. To separate Pu from tetravalent (Th, Np) and hexavalent (U) actinides it is reduced to trivalent state which does not retain in most separation media while for the separation of Pu from trivalent actinides (Am, Cm) it is oxidized to Pu^{4+}.
- **Americium** occurs solely as trivalent Am^{3+} which is not retained in separation media taking up tetra and hexavalent actinides.