



HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

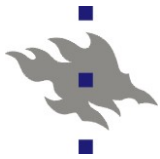
RADIOCHEMICAL SEPARATION METHODS

Jukka Lehto

Laboratory of Radiochemistry

University of Helsinki

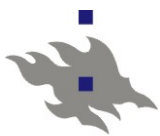
19.11.2009



SCOPE

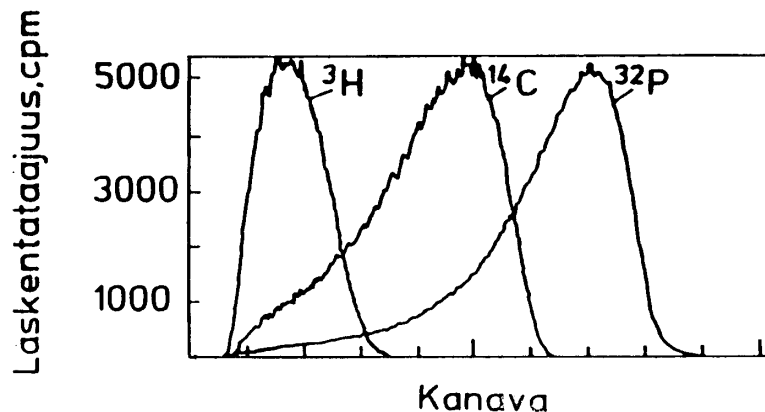
- NEEDS FOR RADIOCHEMICAL SEPARATIONS

- RADIOCHEMICAL SEPARATION METHODS:
 - Precipitation
 - Ion exchange
 - Solvent extraction
 - Extraction chromatography



REASONS FOR RADIOCHEMICAL SEPARATIONS

- Many beta and alpha decaying radionuclides emit also gamma rays – if these have high enough intensities and energies, they can be detected directly from the samples and there is no need for radiochemical separations
- However...
- The beta spectra are continuous with energies from zero to E_{\max} . Thus they overlap and if a radionuclide is a pure beta emitter without gamma emissions, it needs to be separated



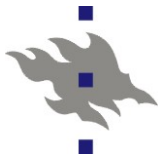


REASONS FOR RADIOCHEMICAL SEPARATIONS

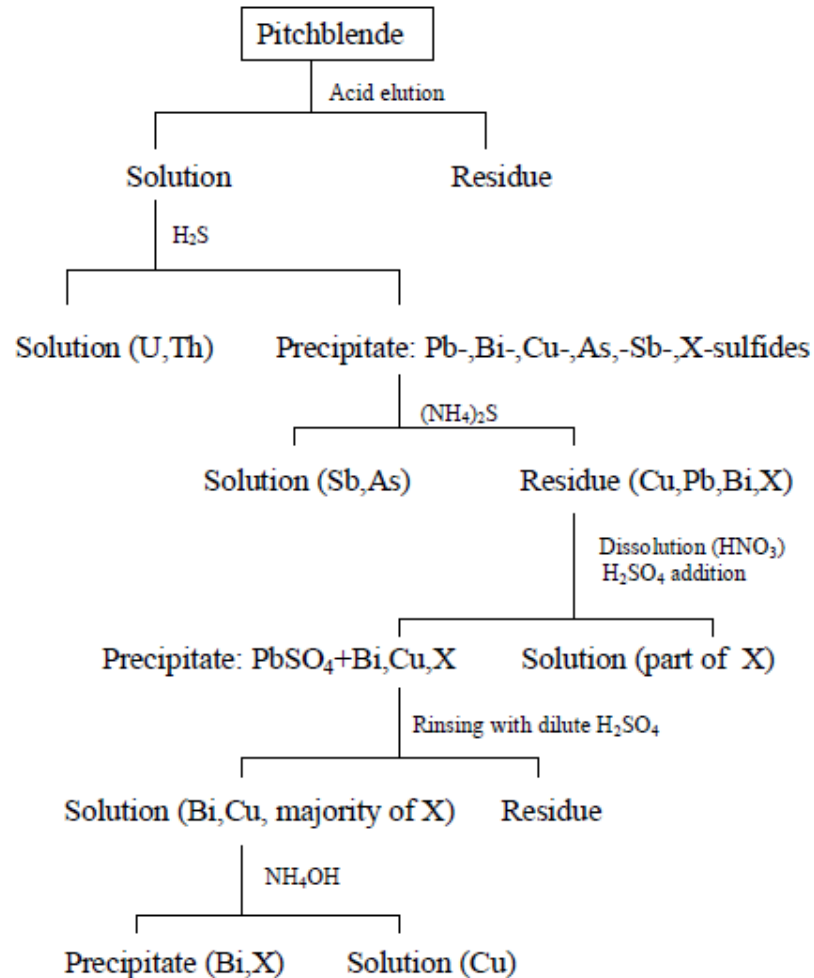
- Radionuclides decaying by electron capture (EC) do not emit any observable radiation in the primary decay process. Secondary X-rays and Auger electrons have low energies and for their detection the nuclide needs to be separated.
- An alpha emitting radionuclide must be separated from other alpha nuclides with similar overlapping alpha energies, and from stable elements to minimize the mass of the counting source.

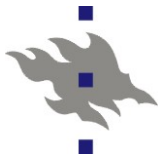
MOST IMPORTANT RADIONUCLIDES NEEDING SEPARATION

<i>Nuclide</i>	<i>Decay mode</i>	<i>Half-life (a)</i>		<i>Nuclide</i>	<i>Decay mode</i>	<i>Half-life (a)</i>
³ H	beta	12.3		⁹⁹ Tc	beta	213000
¹⁴ C	beta	5730		¹²⁶ Sn	beta	100000
³⁶ Cl	beta	301000		¹²⁹ I	beta	15700000
⁴¹ Ca	EC	103000		¹³⁵ Cs	beta	2300000
⁵⁵ Fe	EC	2.7		²¹⁰ Pb	beta (gamma)	22
⁶³ Ni	beta	96		²¹⁰ Po	alfa	0.38
⁵⁹ Ni	EC	76000		²²⁶ Ra	alfa	1600
⁷⁹ Se	beta	1130000		^{234,235,238} U	alfa	$2.5 \times 10^5 - 4.5 \times 10^9$
⁹⁰ Sr	beta	29		²³⁷ Np	alfa	2000000
⁹³ Zr	beta	1530000		^{238,239,240} Pu (²⁴¹ Pu)	alfa (beta)	14-24000
⁹⁴ Nb	beta	20300		²⁴¹ Am	alfa (gamma)	433
⁹³ Mo	EC	4000		²⁴² Cm	alfa	0.44



PRECIPITATION – OLDEST RADIOCHEMICAL SEPARATION METHOD



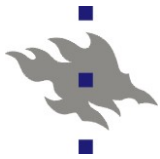


SOLUBILITY PRODUCT (K_s)

For a compound A_xM_y $K_s = [A]^x \cdot [M]^y$

Masses corresponding to 1 Bq activity

<i>Radionuclide</i>	<i>Half-life (a)</i>	<i>Number of atoms</i>	<i>Mass (g)</i>	<i>Concentration in one litre (mol/l)</i>
^{238}U	4.5×10^9	2×10^{17}	8×10^{-5}	3×10^{-7}
^{226}Ra	1600	7×10^{10}	3×10^{-11}	1×10^{-13}
^{210}Po	0.38	2×10^7	6×10^{-15}	3×10^{-17}



TO EXCEED THE SOLUBILITY PRODUCT

CARRIER – ADDITION

- ISOTOPIC CARRIER: stable cobalt (^{59}Co) for ^{60}Co

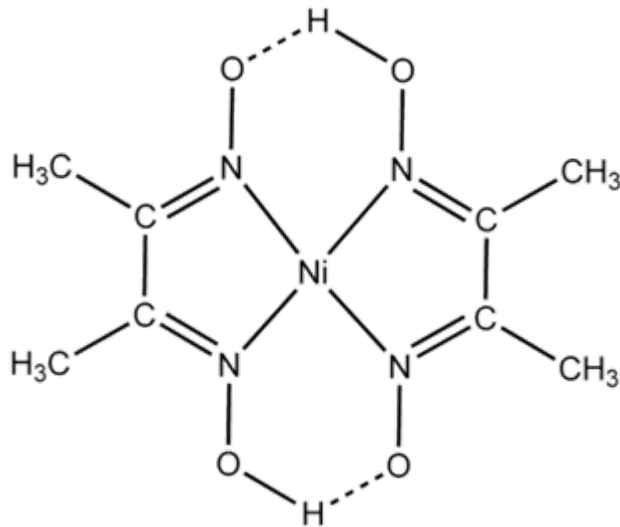
- NON-ISOTOPIC CARRIERS FOR NUCLIDES HAVING NO STABLE ISOTOPES:
 - Stable barium for ^{226}Ra
 - Stable rhenium for ^{99}Tc

- PRECIPITATIONS WITH NONISOTOPIC CARRIERS CALLED COPRECIPITATIONS



GOALS IN PRECIPITATION

- Specific precipitations:
 - ^{63}Ni precipitation with dimethylglyoxime



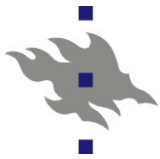


GOALS OF PRECIPITATION - continues

- Preconcentration = enrichment of target nuclide
 - Plutonium preconcentration from natural waters with $\text{Fe}(\text{OH})_3$ precipitation

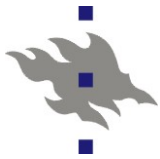
- Removal of interfering radionuclides and stable elements

- Preparation of counting sources for alpha and beta measurements



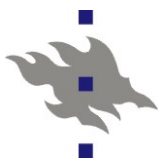
REMOVAL OF INTERFERING ELEMENTS

PRECIPITATION	REMOVED (STAY IN SOLUTION)
hydroxide precipitation ($\text{Fe}(\text{OH})_3$)	<ul style="list-style-type: none">• alkali metals• alkaline earth metals• anionic components
carbonate precipitation	<ul style="list-style-type: none">• alkali metals• anionic components
oxalate precipitation	<ul style="list-style-type: none">• alkali metals• anionic components• iron as Fe(III)



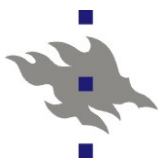
Most typical precipitations

<i>Radionuclide</i>	<i>Precipitation</i>	<i>Purpose of the precipitation</i>
^{14}C	<ul style="list-style-type: none"> • CaCO_3 precipitation of $^{14}\text{CO}_2$ formed in sample combustion and trapped in NaOH solution 	<ul style="list-style-type: none"> • precipitate $^{14}\text{CO}_3^-$ as CaCO_3
^{41}Ca	<ul style="list-style-type: none"> • $\text{Fe}(\text{OH})_3$ coprecipitation • carbonate precipitation 	<ul style="list-style-type: none"> • removal of transition metals • Ca separation from alkali metals
^{55}Fe	<ul style="list-style-type: none"> • $\text{Fe}(\text{OH})_3$ precipitations 	<ul style="list-style-type: none"> • enrichment, separation of interfering components
^{63}Ni	<ul style="list-style-type: none"> • carbonate or hydroxide coprecipitation • dimethylglyoxime precipitation 	<ul style="list-style-type: none"> • separation of interfering components • selective separation of ^{63}Ni
^{90}Sr	<ul style="list-style-type: none"> • nitrate precipitation in 70% HNO_3 • BaCrO_4 precipitation • carbonate precipitations • $\text{Y}(\text{C}_2\text{O}_4)_3$ precipitation 	<ul style="list-style-type: none"> • separation of strontium from calcium • separation of strontium from barium • concentration, separation of interfering components • separation of ^{90}Y from ^{90}Sr



Most typical precipitations - continues

<i>Radionuclide</i>	<i>Precipitation</i>	<i>Purpose of the precipitation</i>
^{99}Tc	<ul style="list-style-type: none"> • $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$ coprecipitations 	<ul style="list-style-type: none"> • preconcentration of Tc from natural waters
^{36}Cl	<ul style="list-style-type: none"> • AgCl precipitation 	<ul style="list-style-type: none"> • ^{36}Cl separation/purification
^{129}I	<ul style="list-style-type: none"> • AgI precipitation 	<ul style="list-style-type: none"> • ^{129}I separation/purification
^{210}Pb	<ul style="list-style-type: none"> • PbSO_4 and PbS precipitations 	<ul style="list-style-type: none"> • ^{210}Pb separation/purification
^{226}Ra	<ul style="list-style-type: none"> • BaSO_4 coprecipitation 	<ul style="list-style-type: none"> • separation of ^{226}Ra
Th isotopes $^{234,235,238}\text{U}$ ^{237}Np $^{238,239,240,241}\text{Pu}$ ^{241}Am ^{242}Cm	<ul style="list-style-type: none"> • $\text{Fe}(\text{OH})_3$ coprecipitation • oxalate coprecipitation • CeF_3 or NdF_3 coprecipitation 	<ul style="list-style-type: none"> • preconcentration, separation of interfering components • preconcentration, separation of interfering components • source preparations for activity measurement, determination of oxidation states



ION EXCHANGE RESINS

DVB-PS = polystyrene crosslinked with divinylbenzene

PMMA = polymethyl metacrylic acid

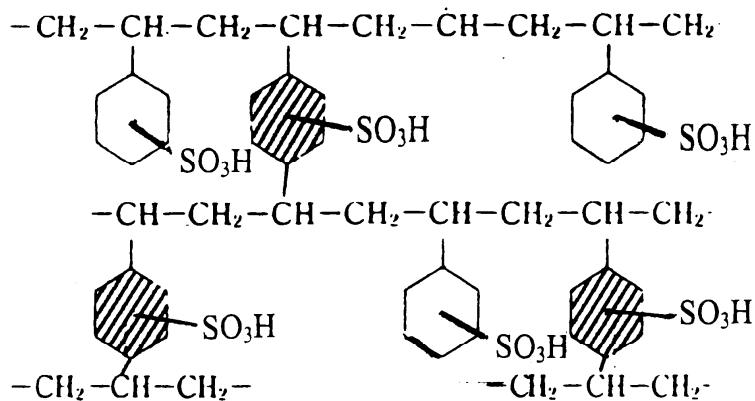
Resin type	Matrix	Functional group
Strongly acidic cation resin	DVB-PS	Sulphonate $-\text{SO}_3^-$
Weakly acidic cation resin	PMMA	Carboxylate $-\text{CO}_2^-$
Strongly basic anion resin	DVB-PS	Quaternary ammonium ion $-\text{N}(\text{CH}_3)_3^+$
Weakly basic anion resin	DVB-PS	Tertiary amino $-\text{N}(\text{CH}_3)_2$
Chelating resin (an example)	DVB-PS	Aminophosphonate $-\text{CH}_2-\text{NH}-\text{PO}_2^{2-}$



ION EXCHANGE RESINS

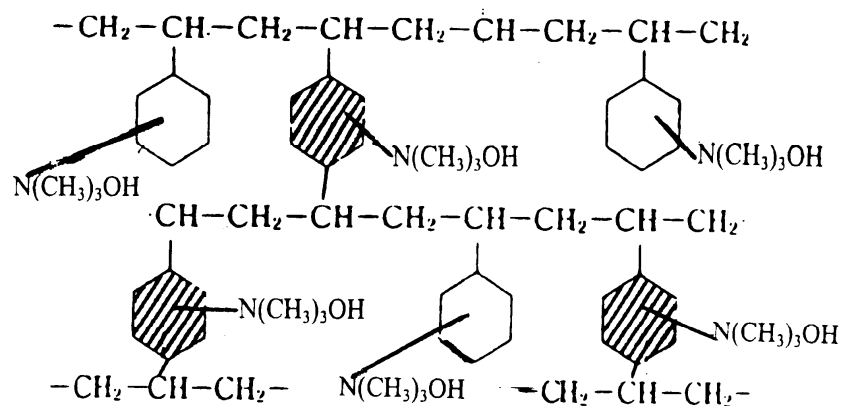
Cation exchange resin

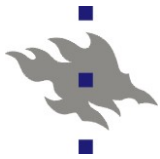
- strongly acidic



Anion exchange resin

- strongly basic

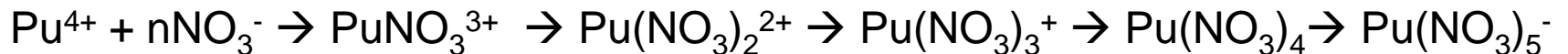




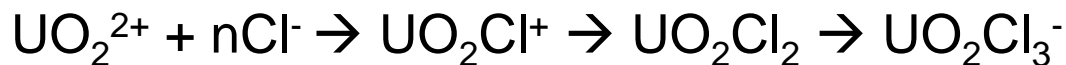
ION EXCHANGE OF METALS BY ANION EXCHANGE RESINS

Formation of anionic complexes in acids:

Nitric acid:



Hydrochloric acid:



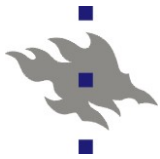
Ion exchange:



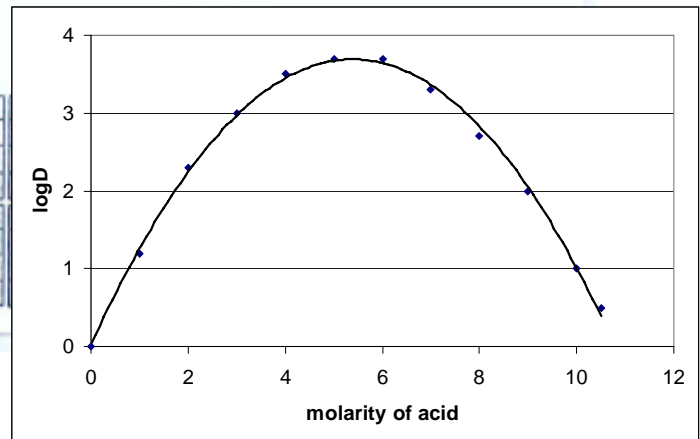
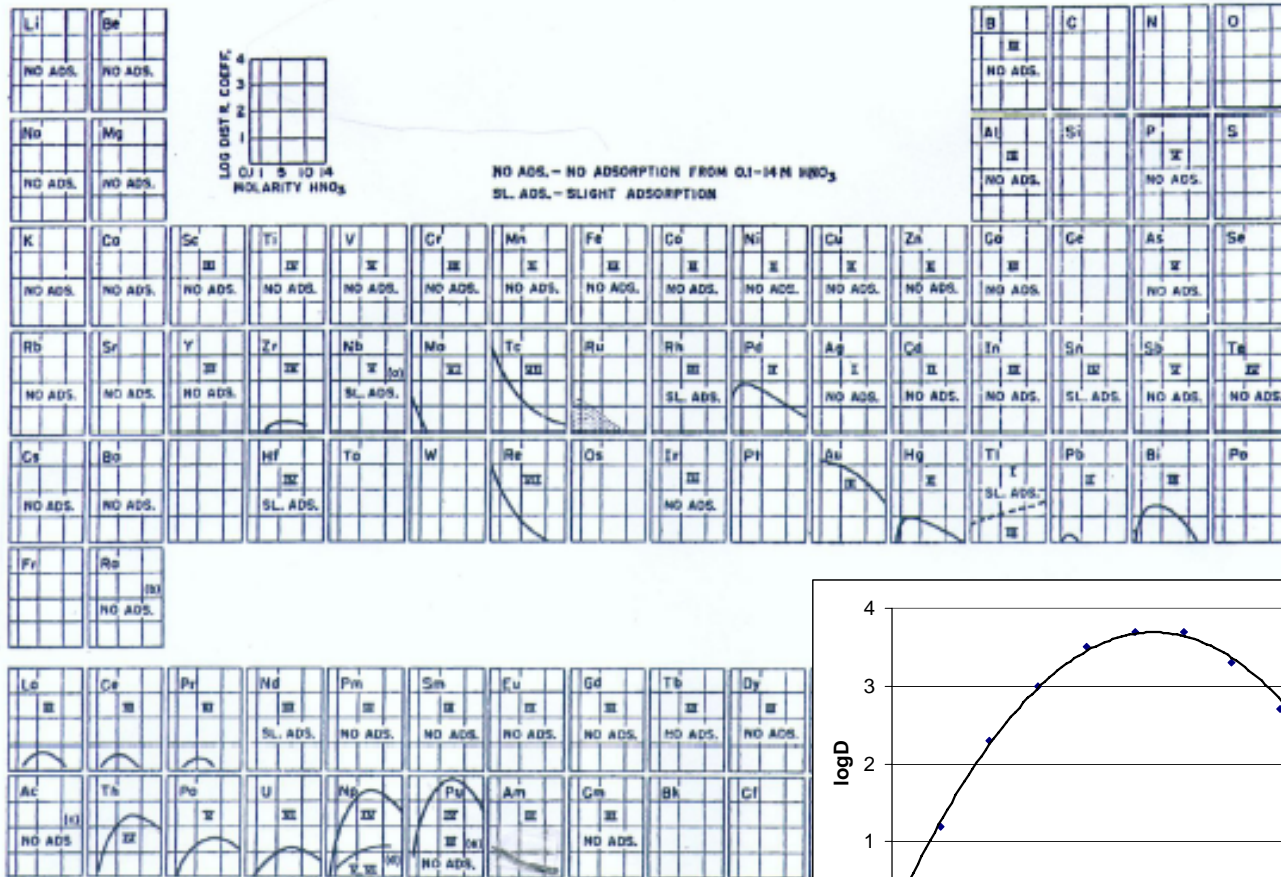


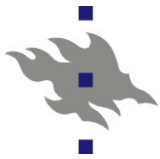
SELECTIVITY – DISTRIBUTION COEFFICIENT

$$K_D, D, K_d = \frac{\text{ion concentration in the exchanger (meq/g)}}{\text{ion concentration in the solution (meq/ml)}}$$



DISTRIBUTION COEFFICIENTS ON STRONGLY BASIC ANION EXCHANGE RESIN AS A FUNCTION OF NITRIC ACID CONCENTRATION

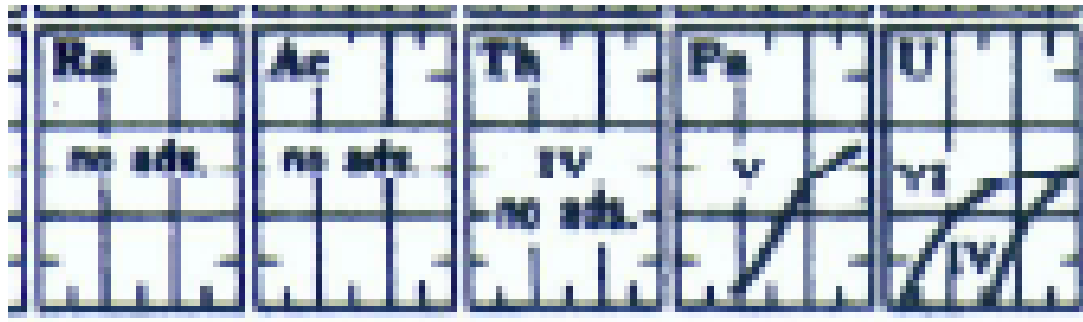




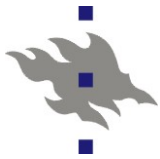
EXAMPLE 1: Separation of U, Th and Ra by anion exchange chromatography

Anion exchange in packed bed (column) in 9M HCl:

- uranium: retains as UO_2Cl_3^-
- thorium and radium: no retention, eluted out

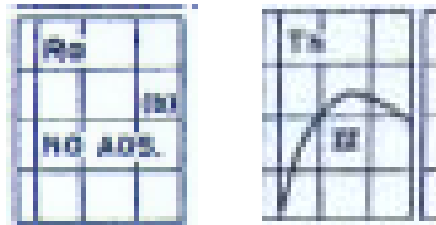


- uranium eluted out of the column with dilute acid

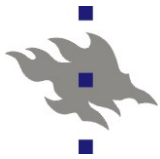


continues

- Effluent evaporated to dryness and dissolved in 8M HNO₃

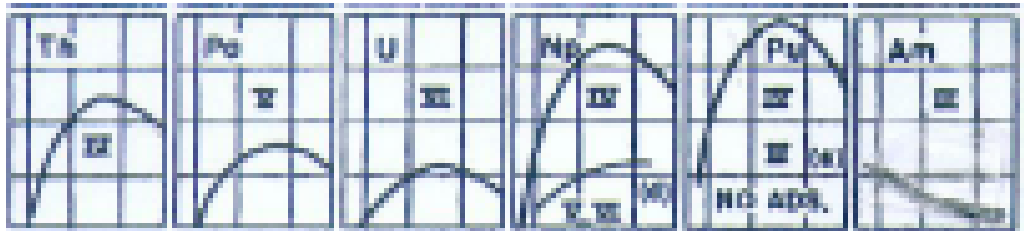


- Thorium: retains in the column as $\text{Th}(\text{NO}_3)_5^-$
- Radium: no retention, elutes out
- Thorium eluted out with dilute acid

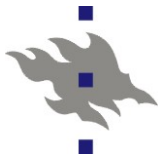


EXAMPLE 2: Separation of U, Th, Pu and Am by anion exchange chromatography

- Pu⁴⁺ reduced to Pu³⁺
- Anion exchange in 8M HNO₃:
 - Uranium (VI) and thorium (IV) retained as anionic nitrate complexes
 - Pu³⁺ and Am³⁺ not retained, elute out

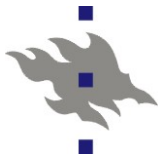


- thorium separated from uranium by anion exchange in 9M HCl
- Pu³⁺ oxidised to Pu⁴⁺ and separated from Am³⁺ by anion exchange in 8M HNO₃



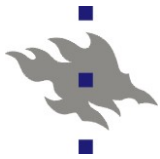
SEPARATION OF AMERICIUM AND CURIUM FROM LANTHANIDES

- Am^{3+} , Cm^{3+} and Ln^{3+} ions as anionic nitrate complexes retained in anion exchange resin in 1 M HNO_3 - 93% methanol
- Column eluted with 0.1 M HCl – 0.5 M NH_4SCN – 80% methanol:
 - Am and Cm form $\text{Am}(\text{SCN})_4^-$ and $\text{Cm}(\text{SCN})_4^-$ complexes and retain in column
 - Lanthanides do not form negative complexes and elute out
 - Am/Cm eluted from the column with dilute HCl



SOLVENT EXTRACTION

- METALS FORM NEUTRAL COMPLEXES WHICH TRANSFER INTO ORGANIC PHASE
- EXTRACTABLE COMPLEXES:
 - Simple molecules and compounds: I_2 or Tc_2O_7
 - Simple coordination complexes with anionic unidentate ligands (halide ions, CN^- , SCN^- , NO_3^-): $Pu(NO_3)_4$
 - Simple coordination complexes with neutral unidentate ligands (R_3N , R_3P , R_3S , in which R is an organic group)
 - Chelates, ring-structured complexes, which form with multidentate ligands.



Solvent extraction agents for actinide separations

■ *HDEHP (bis(2-ethylhexyl) phosphoric acid)*

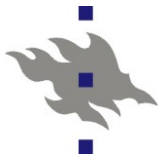
- *Extracts tri- and tetravalent actinides, lanthanides, Fe³⁺, Y³⁺***

■ *TBP (tri-n-butylphosphate)*

- *Extracts tetra- and hexavalent actinides but not tri- and pentavalent***

■ *TTA (thenoyltrifluoroacetone)*

- *At pH 1 extracts only tetravalent actinides***
- *At pH 4-5 extracts tri-, tetra- and hexavalent actinides***

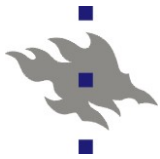


EXTRACTION CHROMATOGRAPHY (SOLID PHASE EXTRACTION)

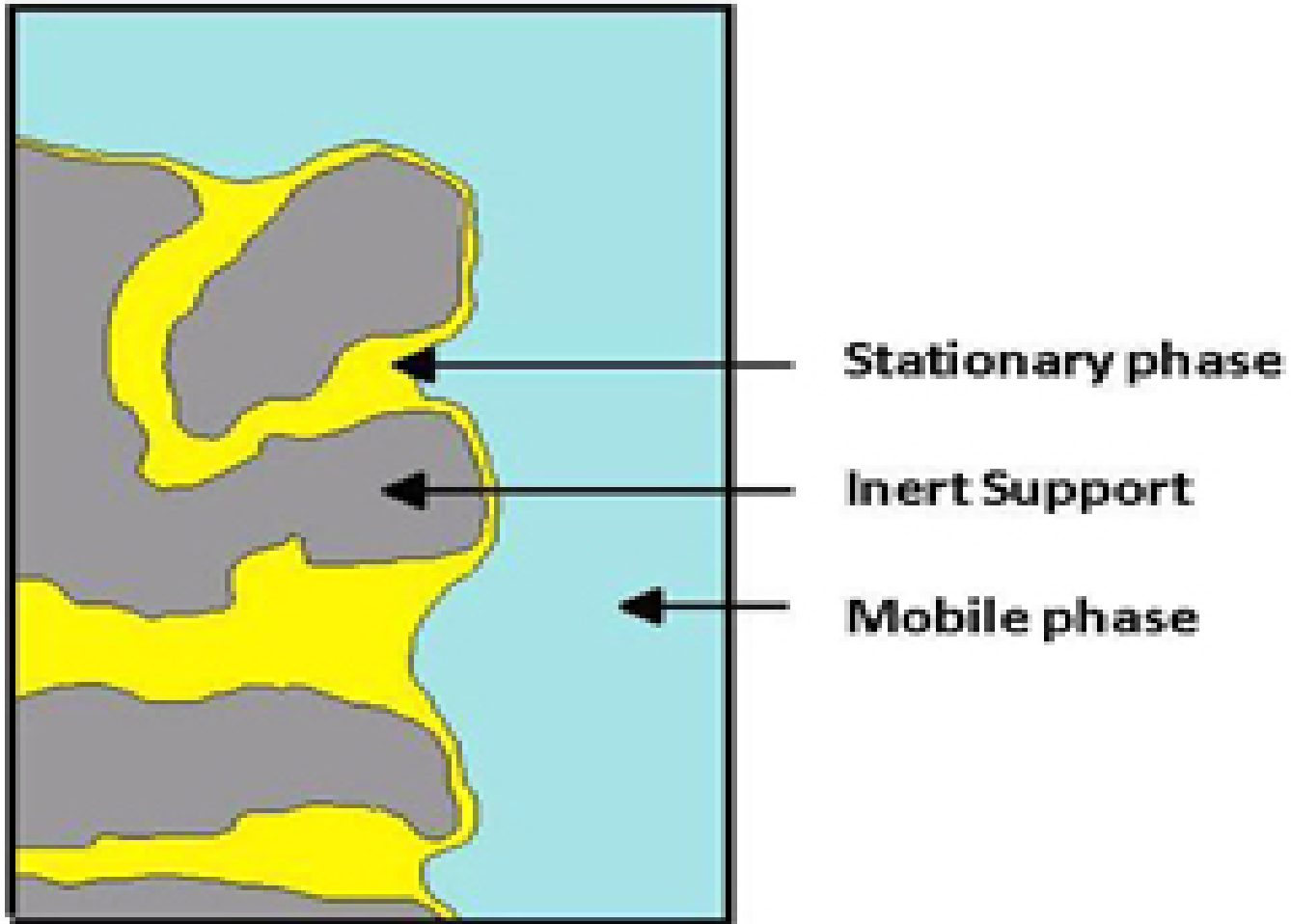
Extraction chromatography combines solvent extraction and column chromatography

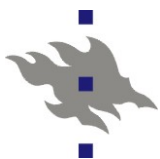
The solvent extraction agents functioning as the stationary phase are impregnated into a porous inert support, either silica gel or an organic polymer.

The space between the beads provide passage for the mobile phase, normally nitric or hydrochloric acid, which contains the radionuclides to be separated



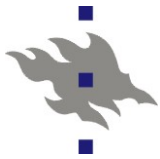
SOLVENT EXTRACTION RESIN





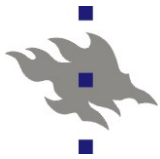
EICHROM AND TRISKEM RESINS

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



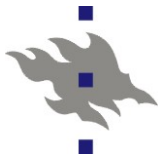
TEVA, TRU AND UTEVA RESINS IN ACTINIDE SEPARATIONS

- TEVA resin binds only tetravalent actinides Th^{4+} , U^{4+} , Np^{4+} , Pu^{4+}
- TRU resin binds 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 binds tetravalent actinides Th^{4+} , U^{4+} , Np^{4+} , Pu^{4+} and hexavalent uranium UO_2^{2+}

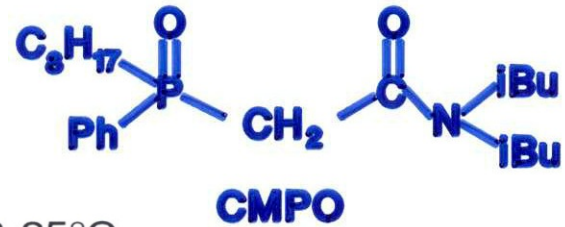


Formation of extractable species in nitric acid



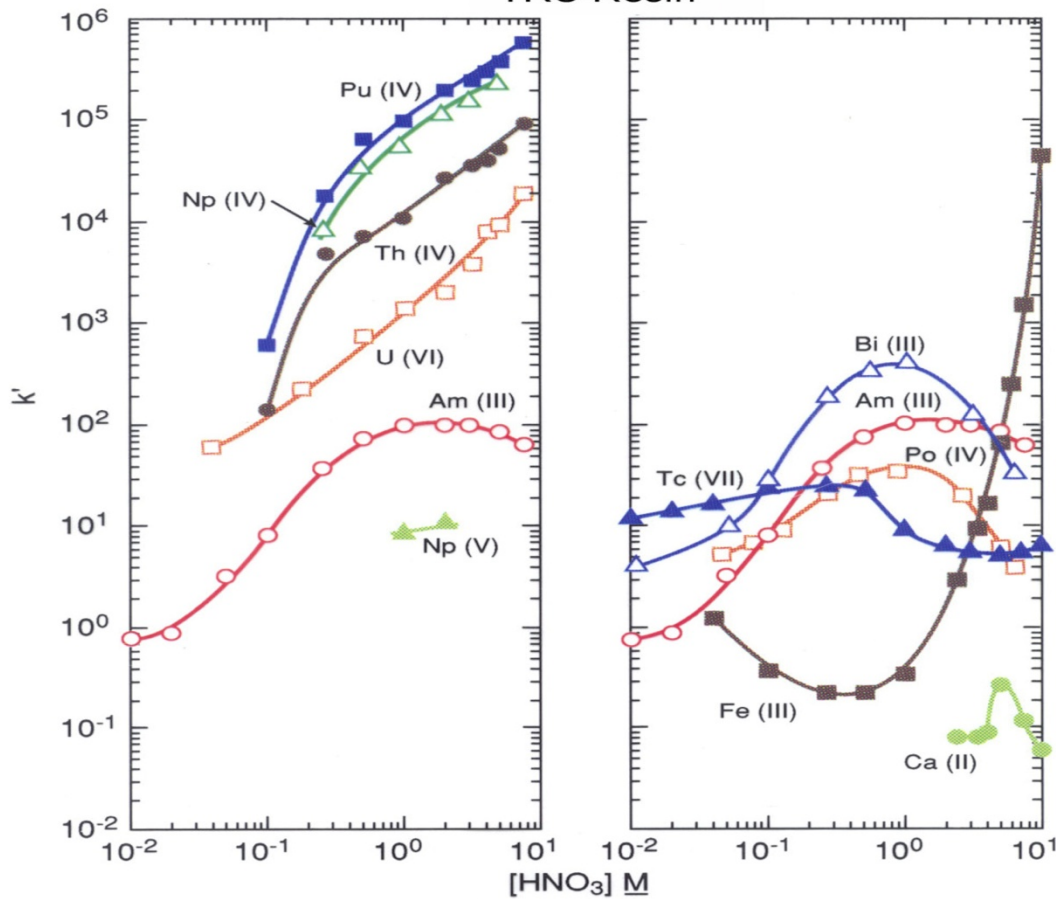


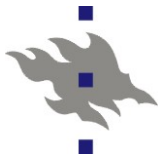
TRU Resin



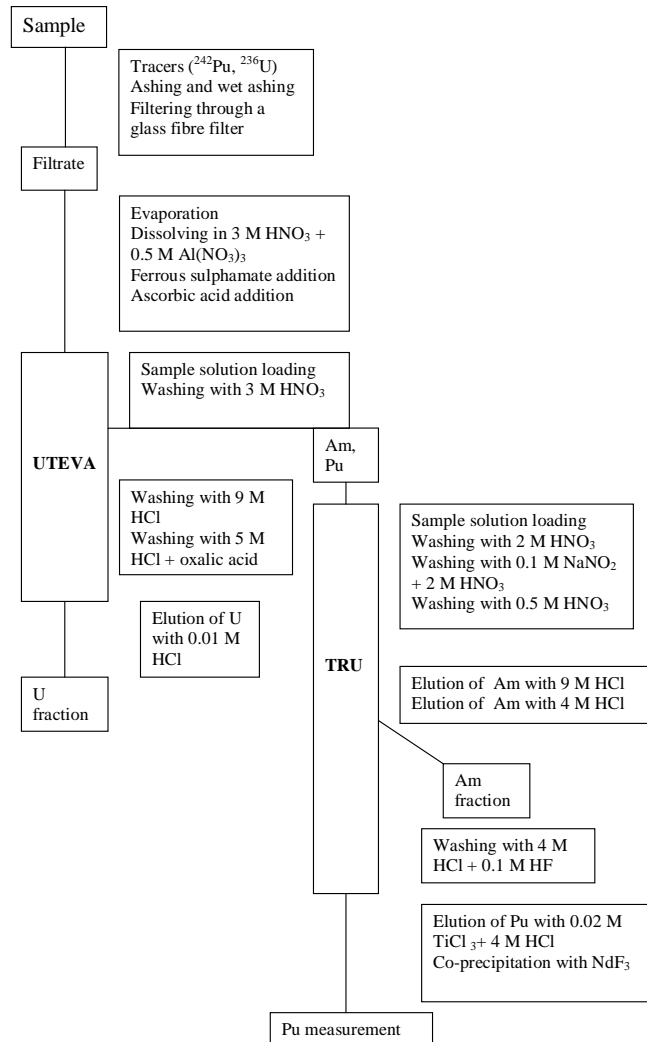
Acid dependency of k' for various ions at 23-25°C.

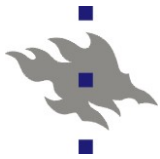
TRU Resin





Separation of U, Pu, Am with UTEVA and TRU





continues

- Pu reduced to Pu^{3+}
- UO_2^{2+} , Pu^{3+} and Am^{3+} introduced into UTEVA column in 3M HNO_3 :
 - UO_2^{2+} retains – eluted out with 0.01M HCl
 - Pu^{3+} and Am^{3+} do not retain but go through
- Pu^{3+} and Am^{3+} introduced into TRU column where they retain
- Pu^{3+} oxidized to Pu^{4+} within the column for stronger retention
- Am^{3+} eluted from TRU column with 4M HCl
- Pu^{4+} reduced to Pu^{3+} within the column and eluted from the column with 4M HCl