Chemical Separation and Source Preparation for α-Spectrometry

J. Eikenberg

Radioanalytical Laboratory

Paul Scherrer Institute, CH-5232 Villigen

Areal graph of PSI + ZWILAG

Activities of the radioanalytical laboratory at PSI

- Analysis of radioactive materials for immission, emission and incorporation measurements (routine program)
- Performance of R & D projects (i.e. dating Quaternary materials via C-14 and U-series, applying in-situ γ-spectrometry in underground rock laboratories for radionuclide migration experiments, developing rapid separation methods for determination of pure α- or β-emitters in various matrices, e.g. ^{63}Ni, ^{90}Sr, actinides)

origin of radioactive sources

type of source	**radioisotopes**
primordial terrestrial	U/Th-Series, ^{40}K, ^{87}Rb
production from cosmic radiation	(spallation, activation) ^{7}Be, ^{3}H, ^{14}C, …
man-made artificial (anthropogenic)	^{3}H, ^{14}C, ^{60}Co, ^{90}Sr, ^{137}Cs, ^{238}Pu, ^{239}Pu, ^{241}Am, ^{244}Cm

example immission surveillance: sample material and relevant α-emitting radioisotopes

samples	**isotopes**
air filters	^{210}Po, ^{239,240}Pu, ^{241}Am
rain-, river-, ground-water	^{226}Ra , ^{210}Po, ^{234}U, ^{238}U
biological (grass, tree leaves, milk etc.)	^{226}Ra , ^{239,240}Pu, ^{241}Am ...
soil, sediments	^{238}U, ^{232}Th with decay series isotopes, ^{239,240}Pu, ^{241}Am

types of spectrometers for radioisotope specific determination

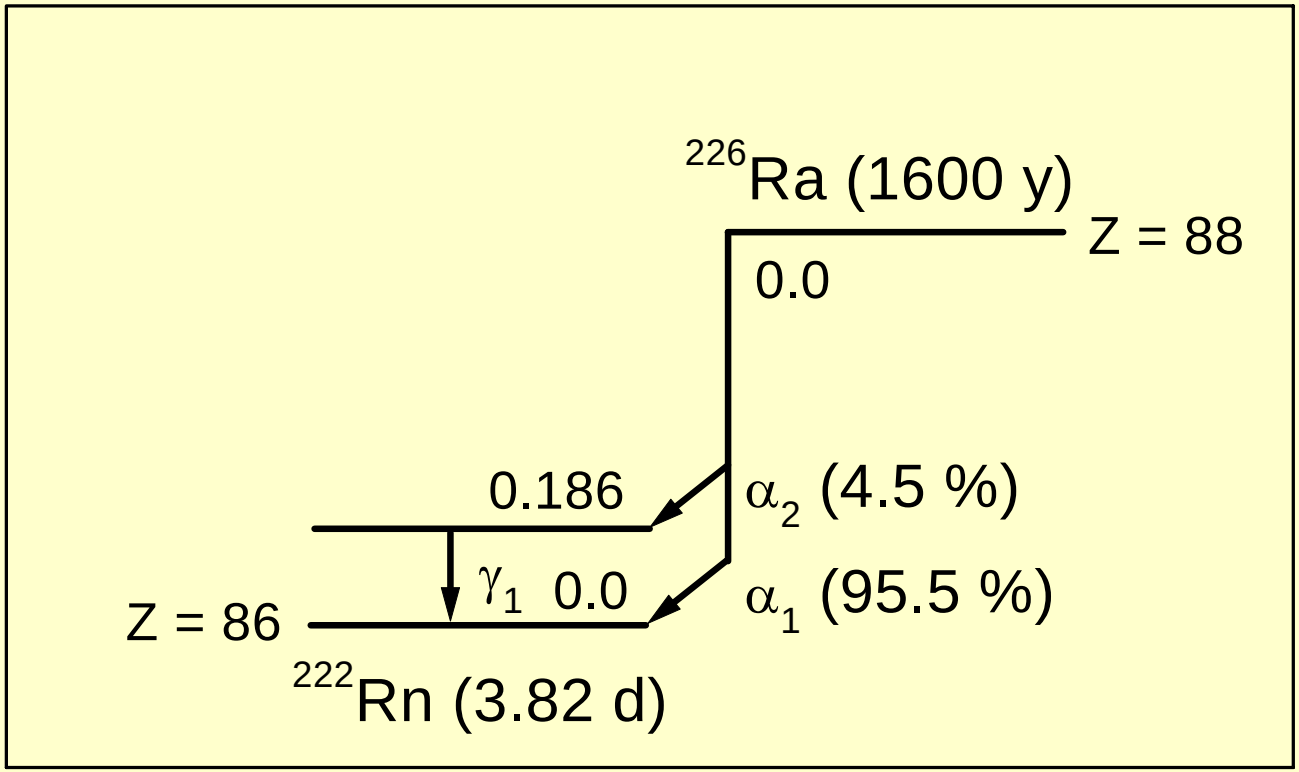
counting technique	**radioisotopes**
gamma-spectrometry	^{7}Be, ^{60}Co, ^{131}I, ^{137}Cs,...
liquid scintillation spectrometry (LSC)	all β-emitters ^{3}H, ^{14}C, ^{90}Sr, ^{241}Pu
alpha-spectrometry	^{238}Pu, ^{239}Pu, ^{241}Am, ^{244}Cm

types of radiation and typical penetration length through material

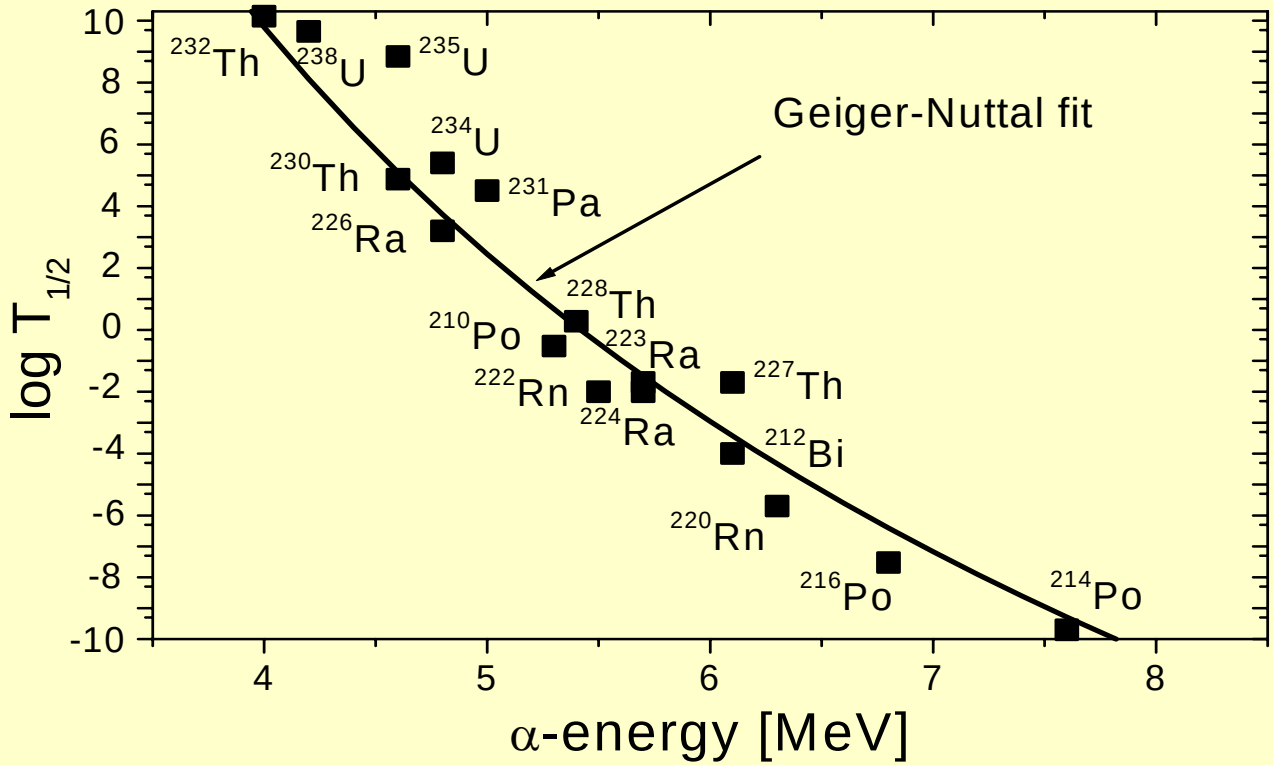
type of radiation	**characteristics**
γ, X-ray (photons)	high penetration length (water: m, air: km)
α-radiation (particles)	very weak penetration length (water: μm, air: cm)
β-radiation (particles)	weak penetration length (water: mm, air: m)

Example: decay scheme of α-emitting ^{226}Ra

$$ {}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}X + {}^{4}_{2}He + decay\ energy $$



Geiger-Nuttal relationship: $T_{1/2}$ vs. energy

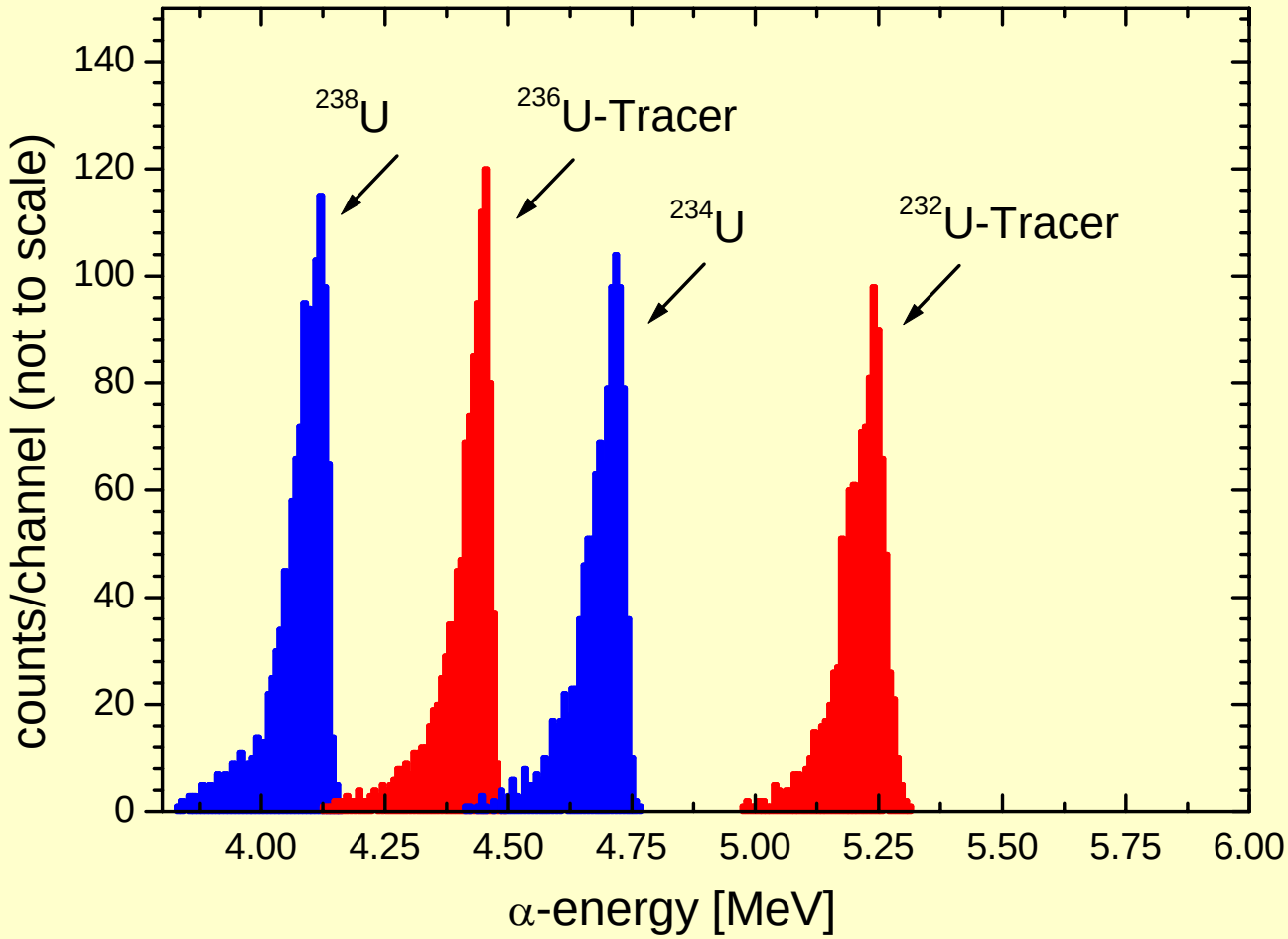


Conclusion: α-emitters have comparable energies (4-8 MeV). Chemical separation procedures and source deposition methods yielding high resolution a-spectra are therefore required.

α-spectrometry using intrinsic Si-Detectors

Double chamber α-spectrometer

α-spectrum of natural uranium



Isotope Spiking

$$A_{238(s)} = \frac{I_{238(s)} - I_{238(bg)}}{t \cdot Y_U \cdot \varepsilon \cdot \eta}$$

$$A_{232(sp)} = \frac{I_{232(sp)} - I_{232(bg)}}{t \cdot Y_U \cdot \varepsilon \cdot \eta}$$

$$A_{238(s)} = \frac{I_{238(s)}}{I_{232(sp)}} \cdot A_{232(sp)}$$

(radio)chemical separation methods

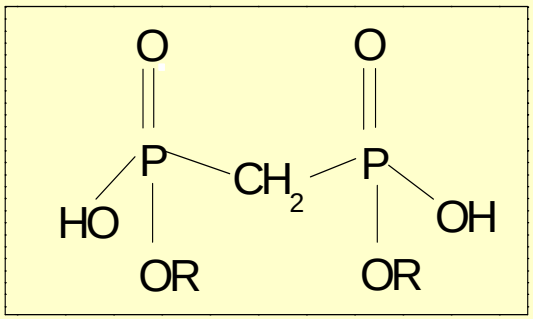
- co-precipitation (pre-concentration)
- solvent extraction (liquid-liquid)
- chromatographic Methods

1. **ion exchange and extraction chromatography (column extraction)**
2. further methods: (HPLC, GC, thin layer chromatography)

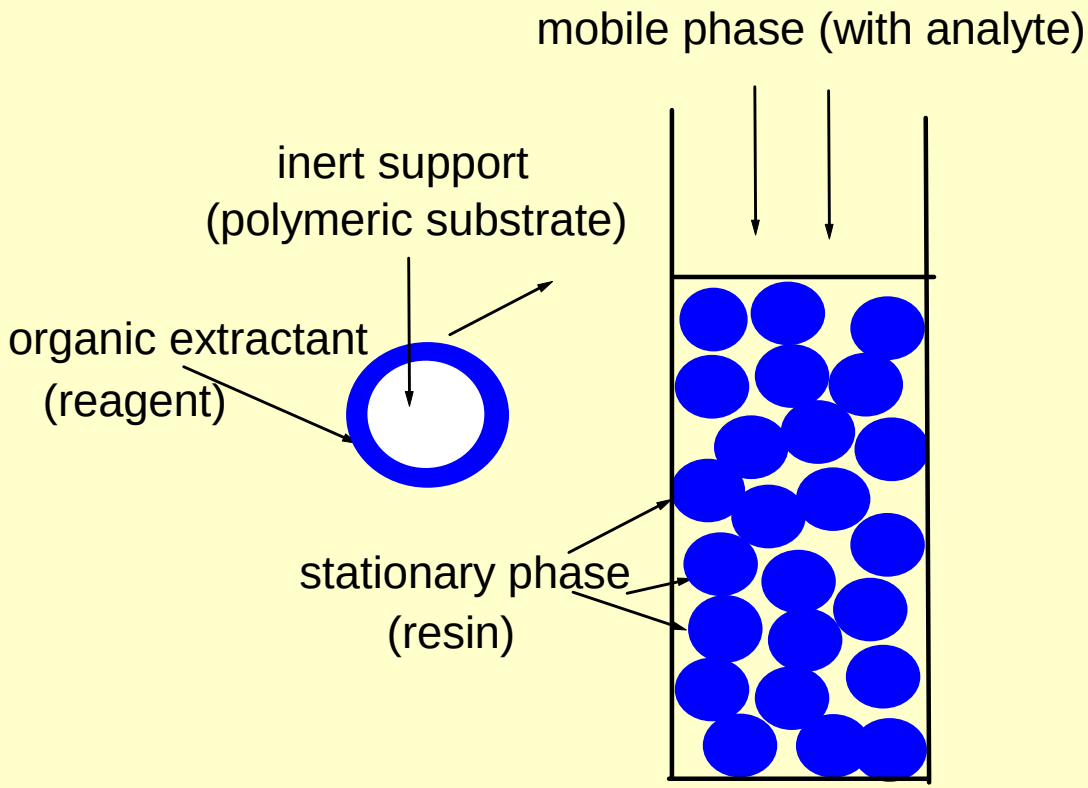
- volatilization / distillation
- electrophoresis / electro-deposition

Chromos = color, graphein = to write

(introduced by Tswett, 1906, who separated chlorophyll from plants into its different colors)



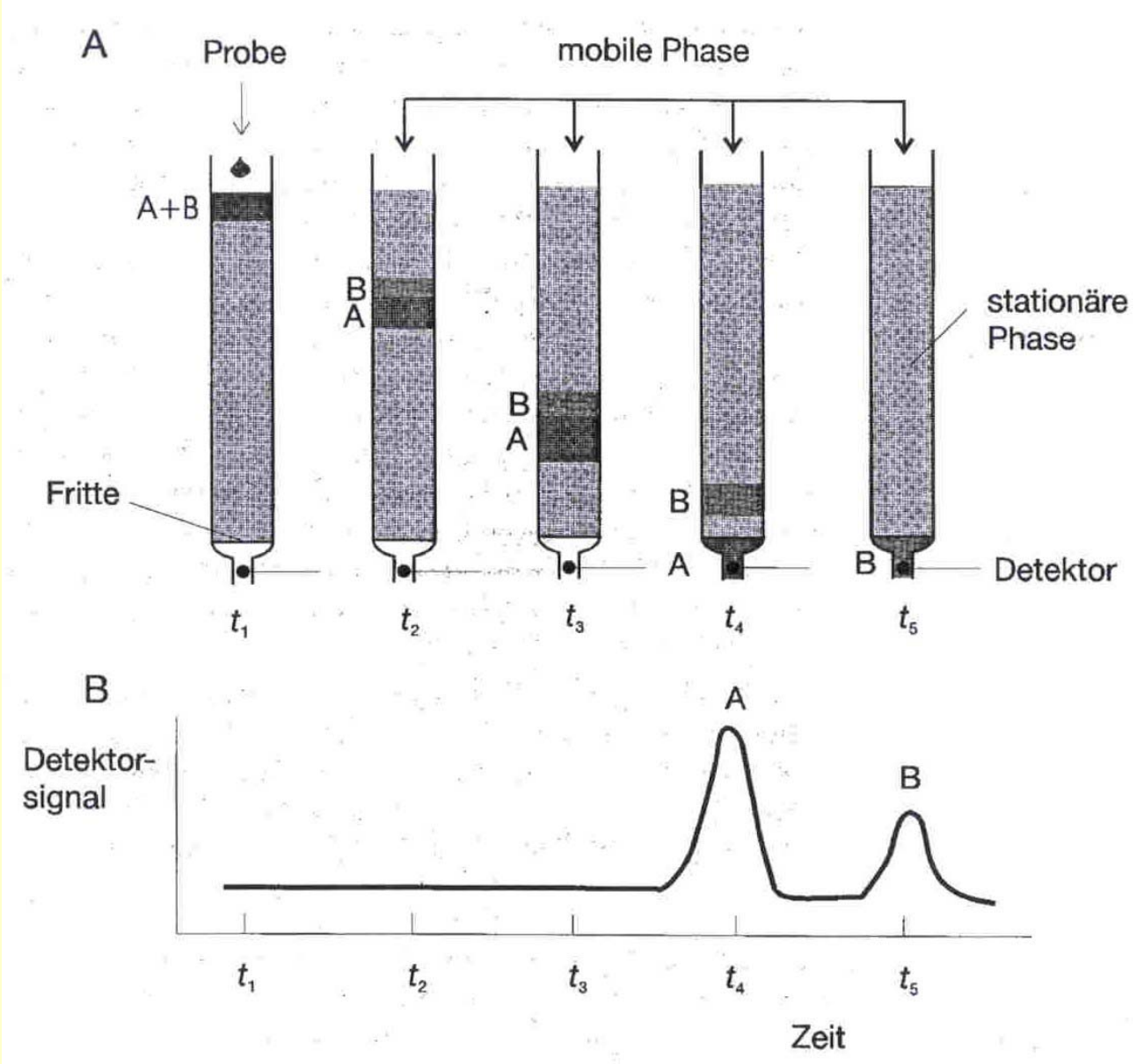
Structure of EiChrom's
Actinide Resin^{tm}



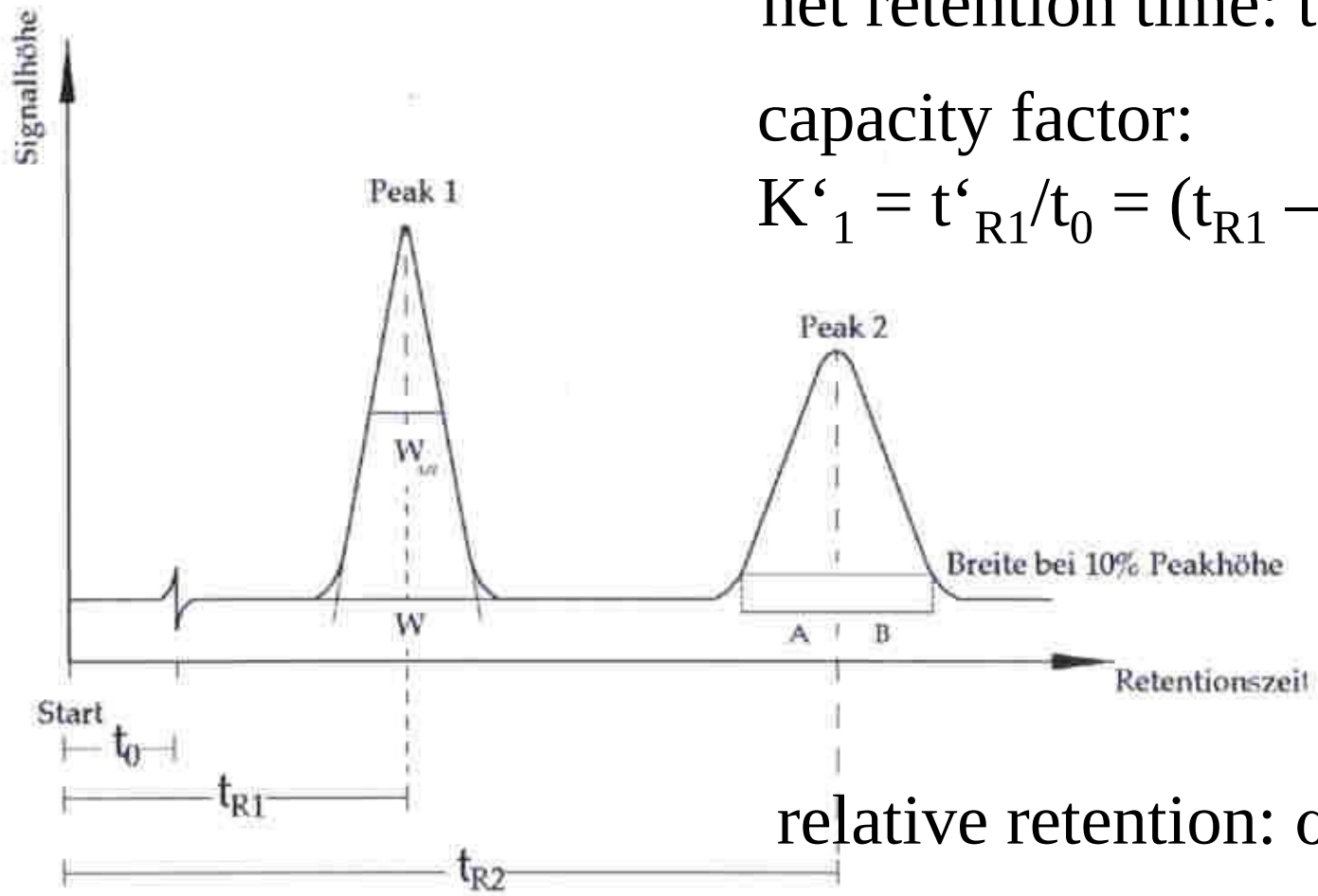
Properties of extraction chromatographic resins

inert support	**extraction substance**
chemically inert	high chemical purity
mechanically stable	high selectivity for analyte
large specific surface	low solubility into the mobile phase
uniform particle size	rapid reaction kinetics

schematic development of a chromatogram of two species (A+B) that were initially mixed homogeneously in the mobile phase



significant parameters of a chromatogram



net retention time: $t'_{R1} = t_{R1} - t_0$

capacity factor:

$K'_1 = t'_{R1}/t_0 = (t_{R1} - t_0)/t_0$

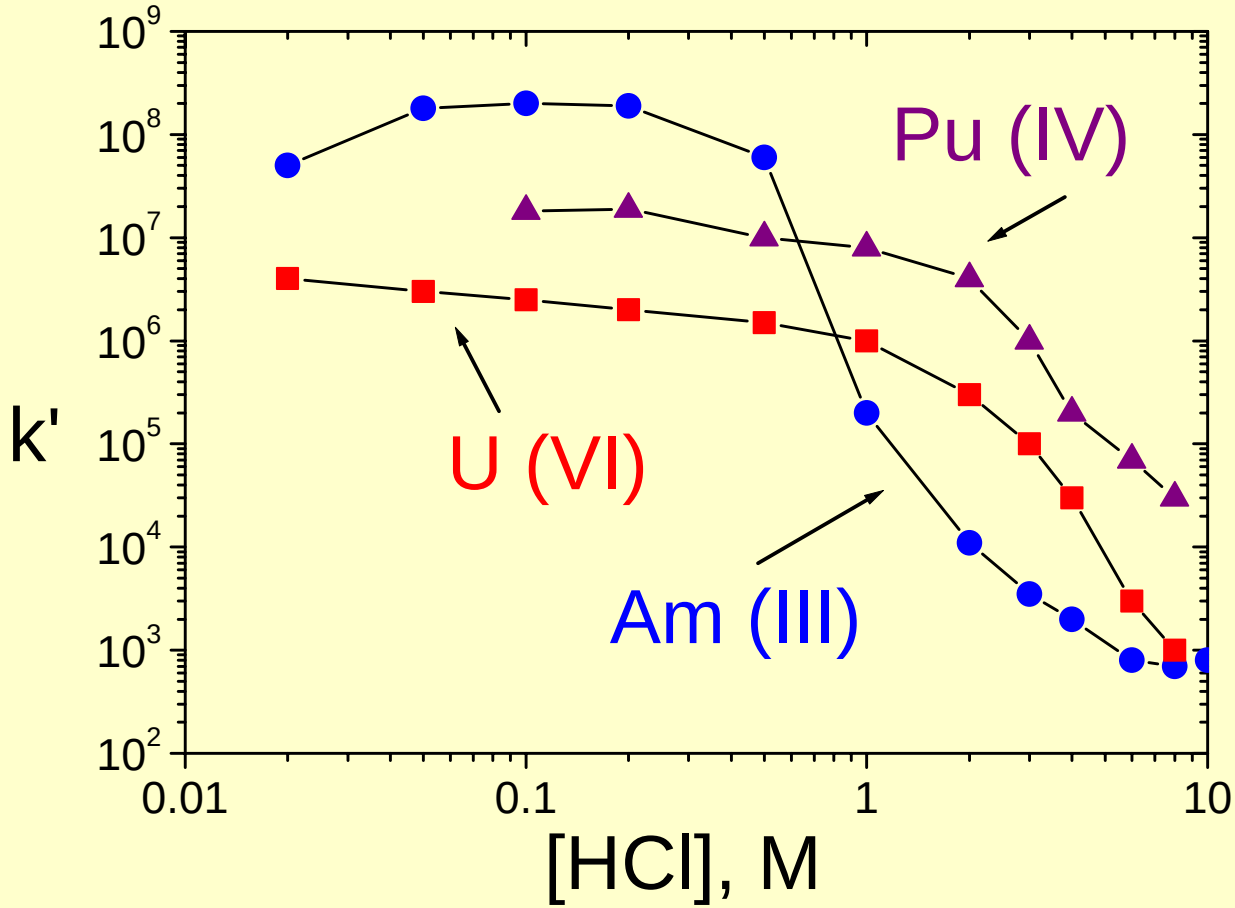
relative retention: $\alpha = K'_1/K'_2$

Important organic extractants for radiochemical application:

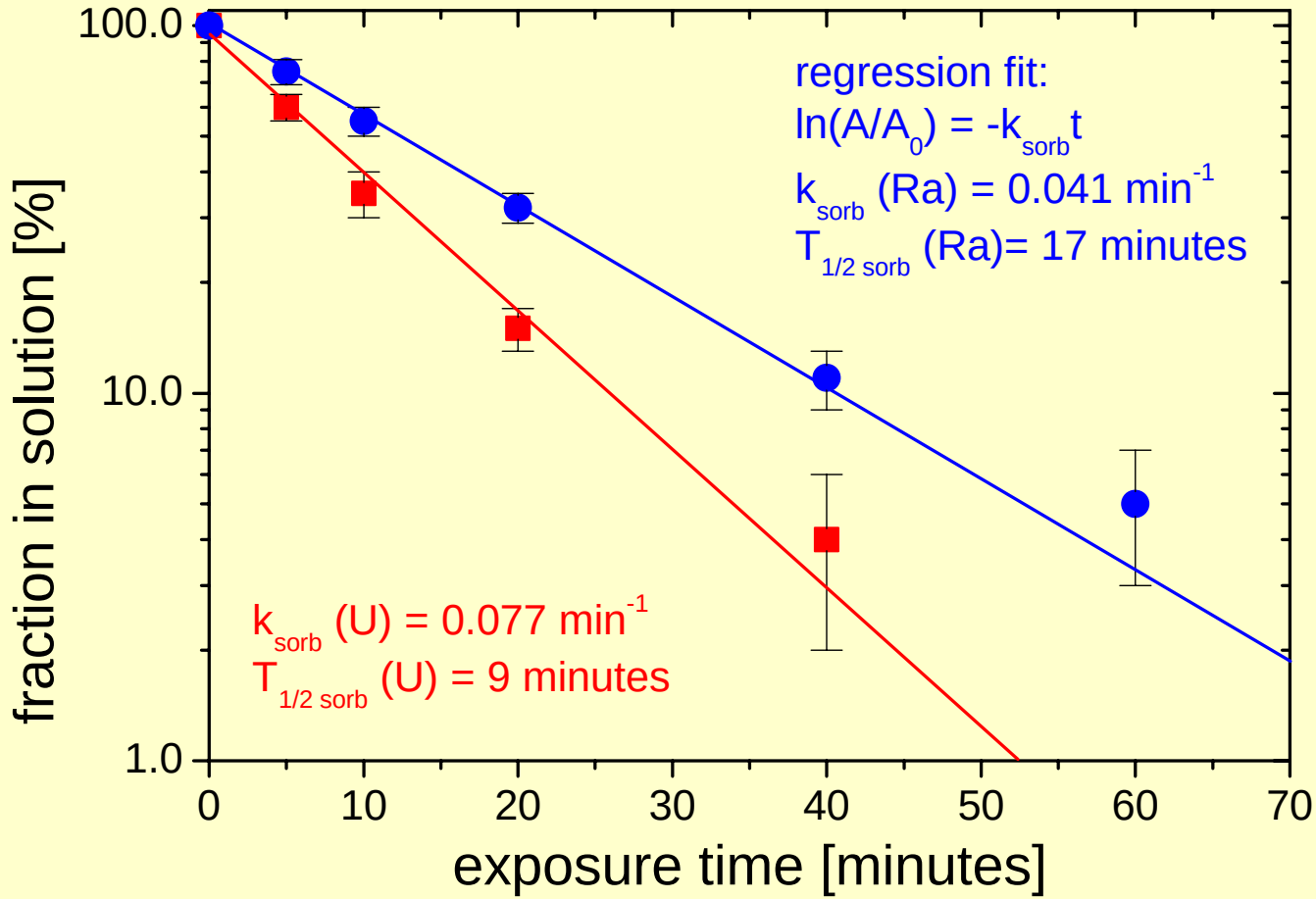
Chemical substance	*product name*
(Ethylhexyl)di-phosphonic acid	*Actinide Resin Eichrom*
(Diamyl)phosphonate	*U/TEVA Resin Eichrom*
CMPO / Tributyl-phosphate (TBP)	*TRU Resin Eichrom*
Anion exchange resin	*BIORAD AG 1-X2*

Example I: actinides in waste water

Distribution coefficients of actinides on *Actinide Resin*^{tm} with varying HCl concentration (from Horwitz et al., 1987)

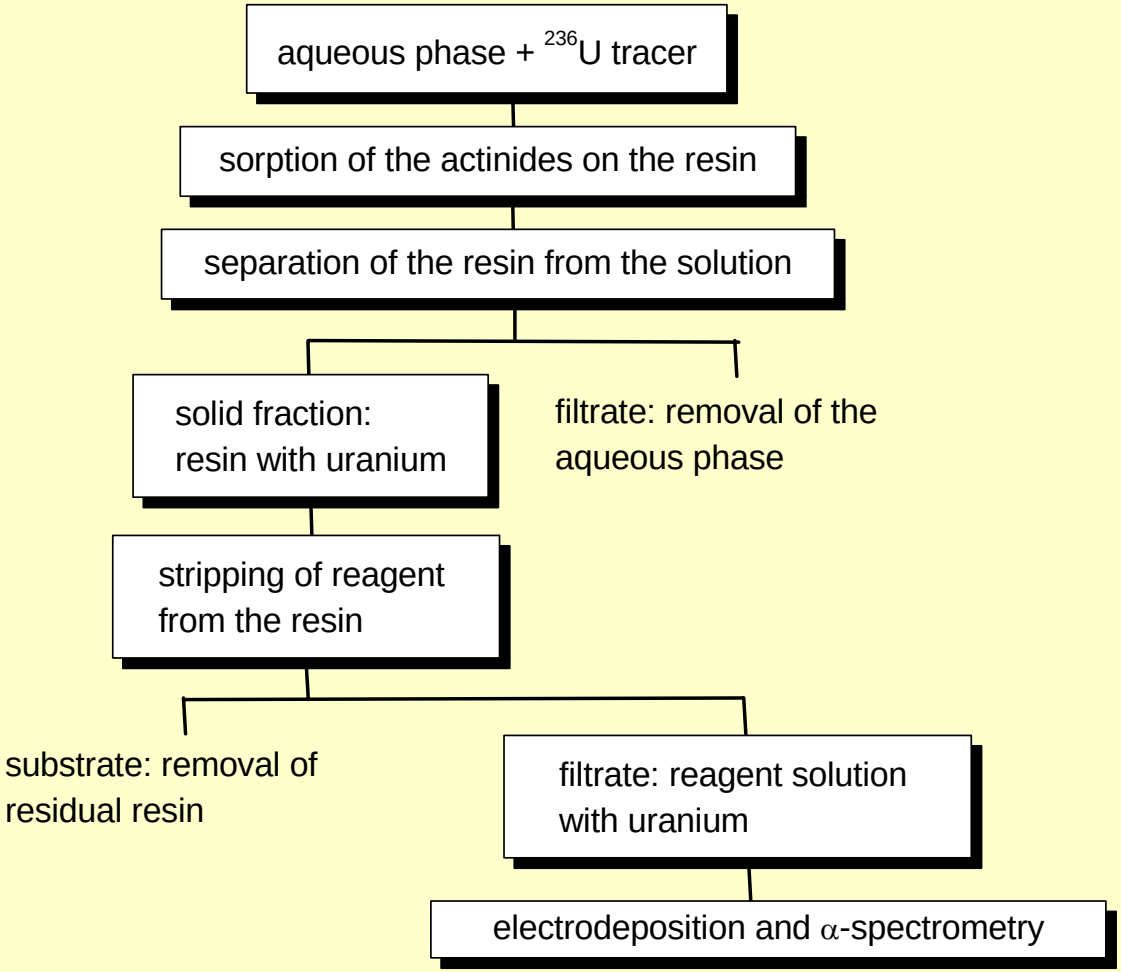


Sorption uptake kinetics

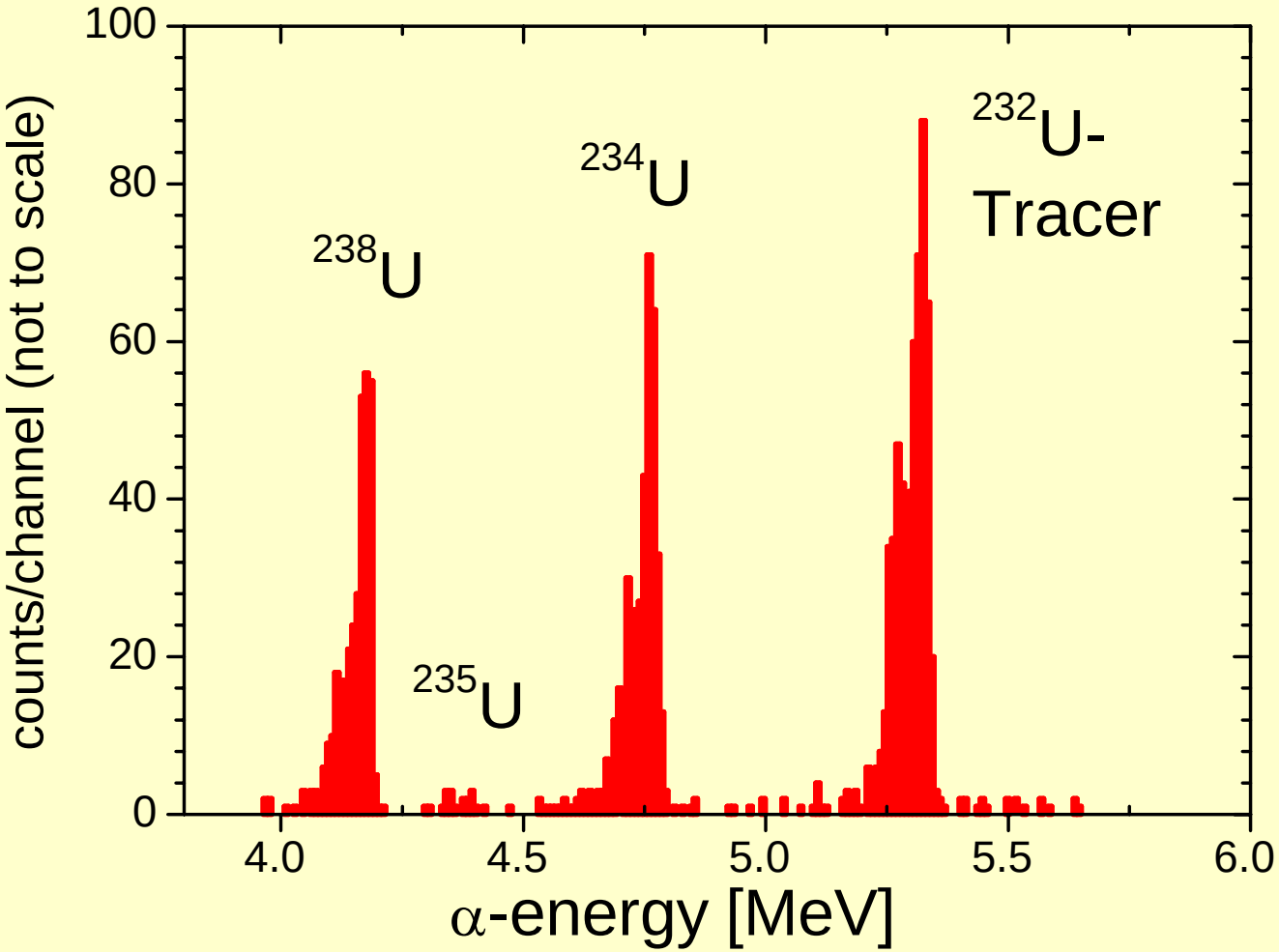


Example I: actinides in waste water

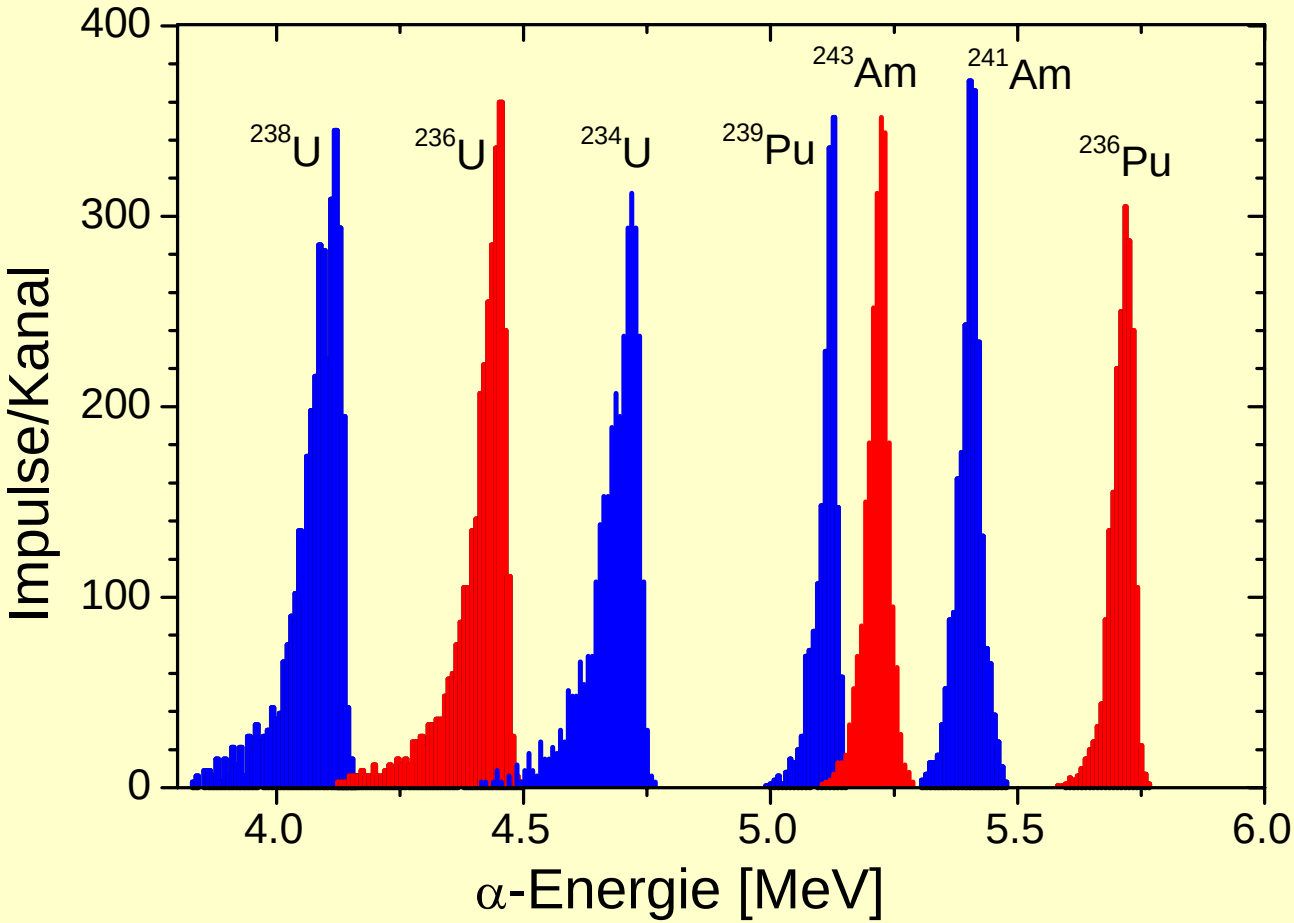
selective actinide separation via *Actinide Resin*^{tm}



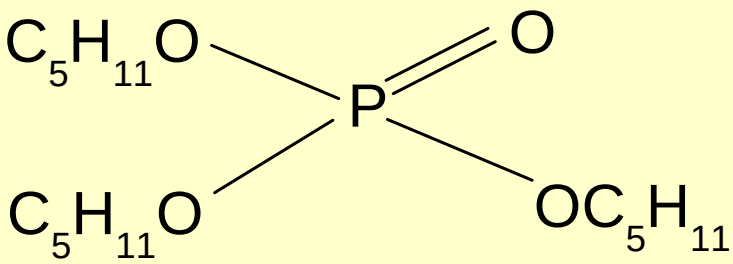
α-spectrum of uranium



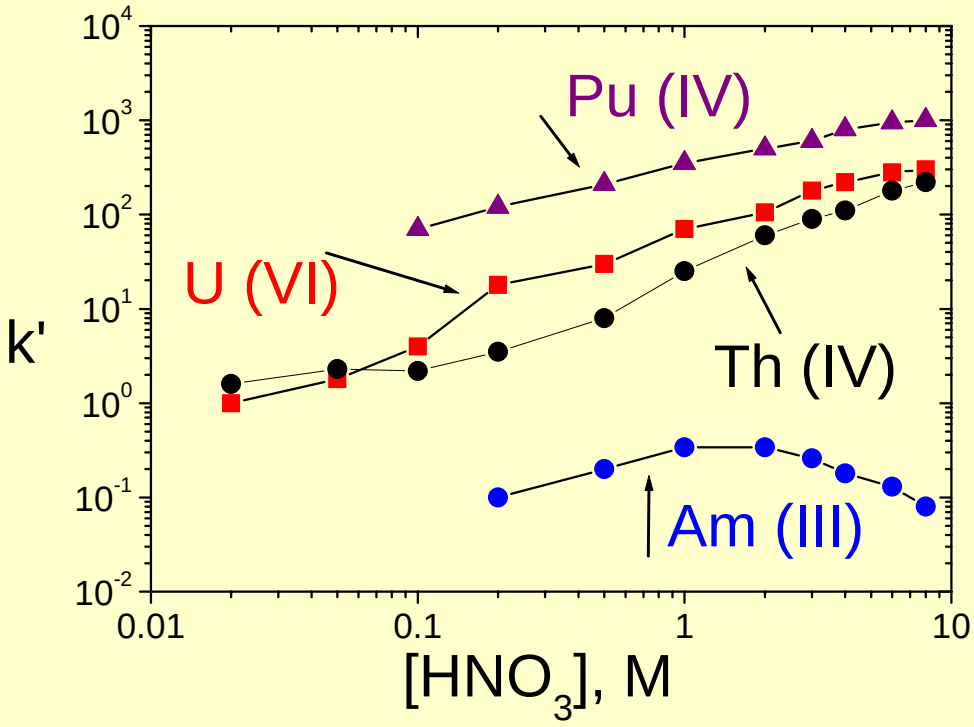
α-spectrum of U, Pu and Am (blue sample isotopes to be analyzed; red added spike isotopes)



Example II: U and Th in geological material



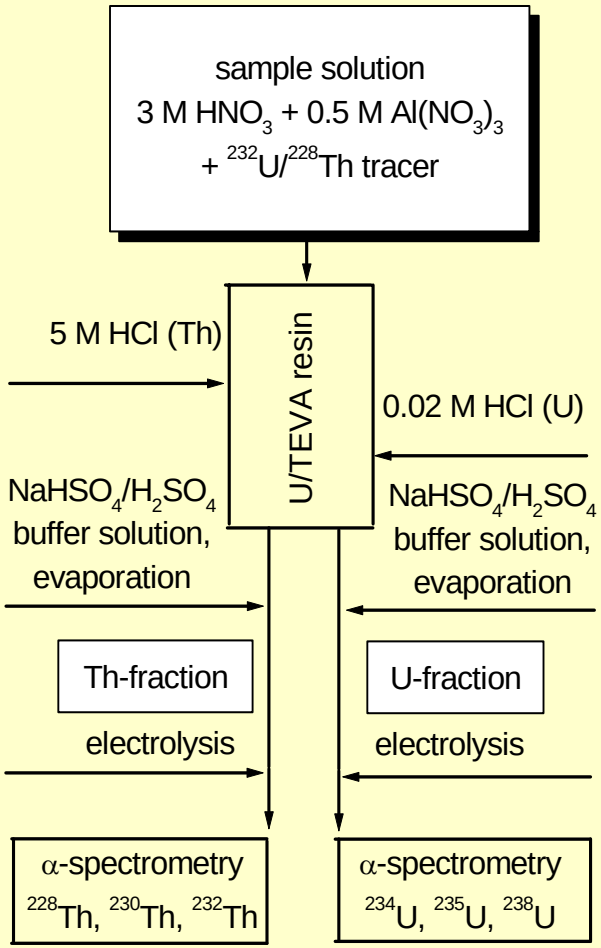
Structural composition of Diamyl-Phosphonate (U/TEVA)



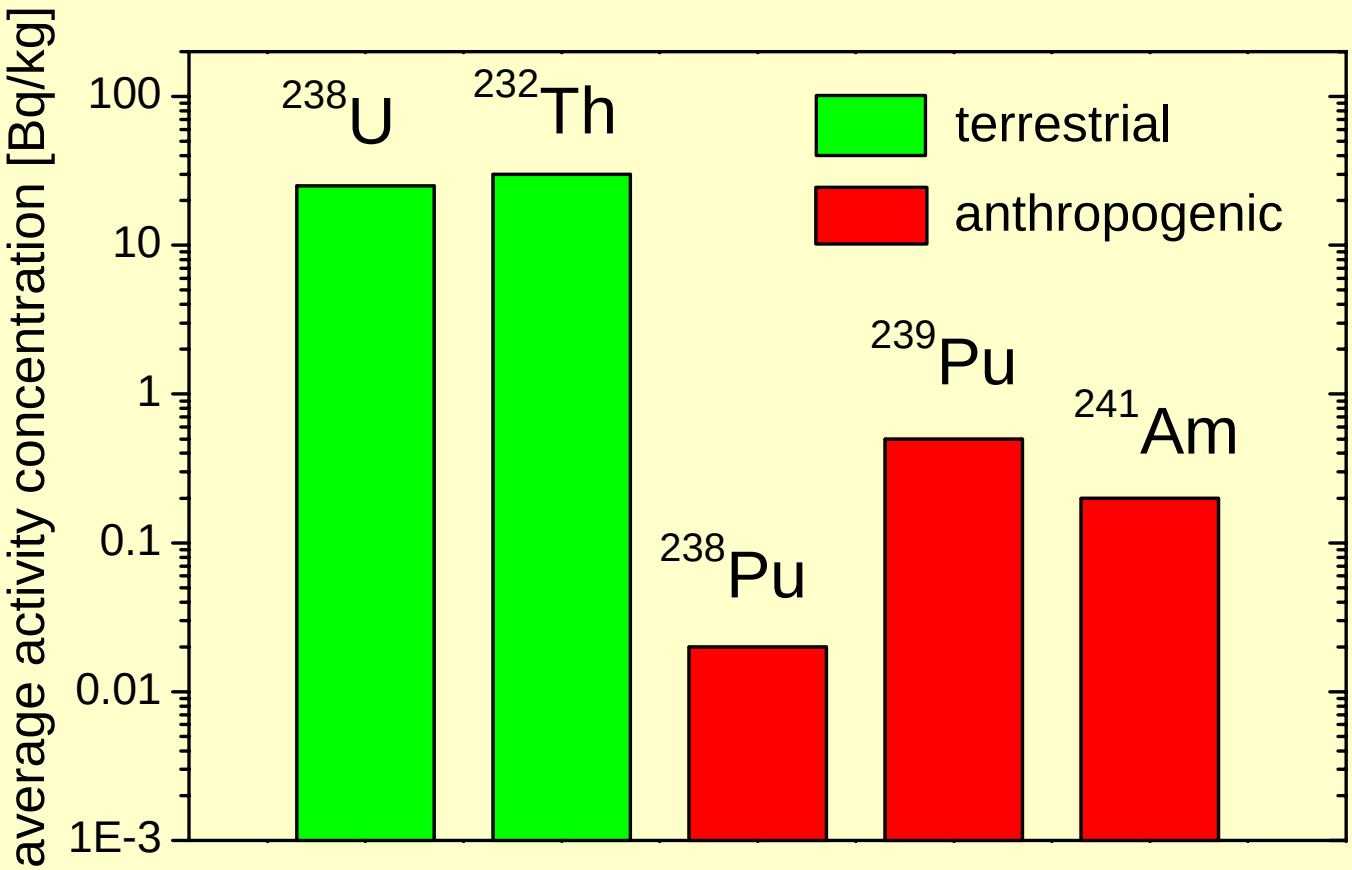
Example II: U and Th in geological material:

consecutive separation of both elements using U/TEVA resin

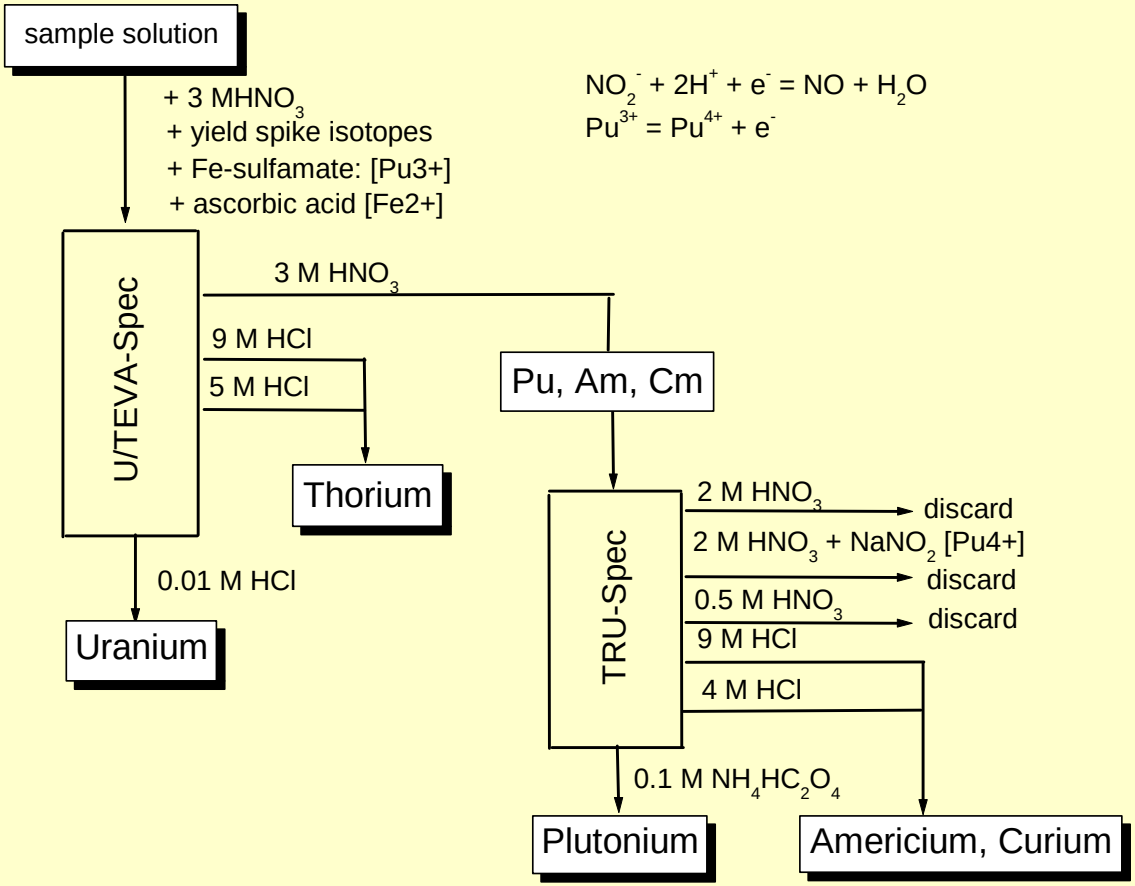
Flow chart showing the procedure used at PSI for the chromatographic separation of U and Th from geological samples (penetration length of α-particles through matter is less than 0.05 mm)

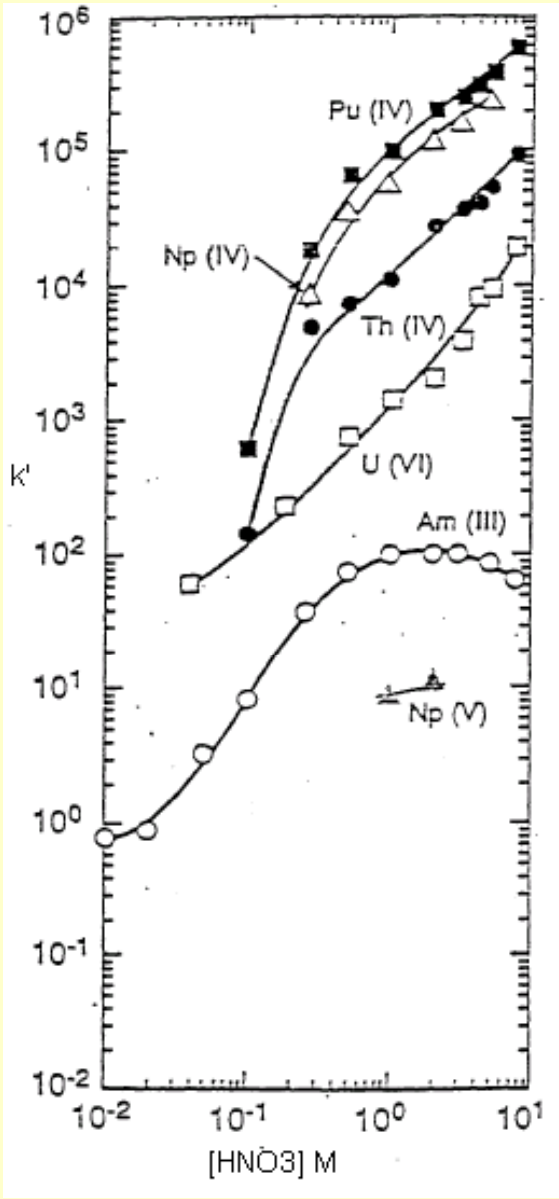


Example III: Pu and Am in environmental samples: bar chart illustrating the average actinide concentrations in soil samples taken from Northern Switzerland



Example III: Pu and Am in environmental samples

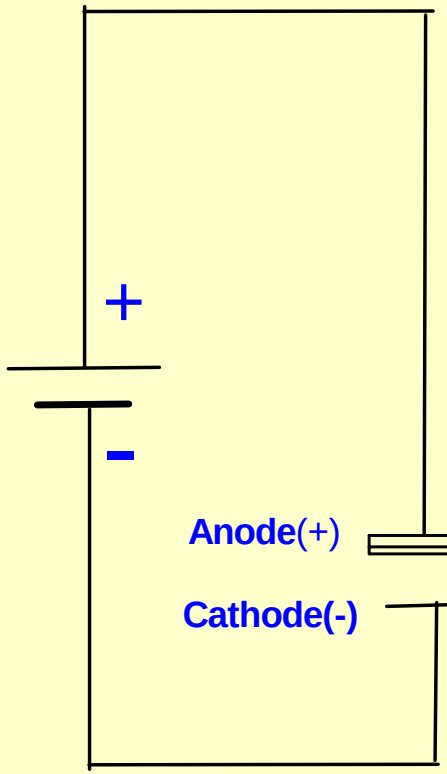




Methods for preparation of planar counting sources for α-spectrometry

- micro-precipitation (e.g. La-fluoride etc.)
- electrolysis / electro-deposition
- spontaneous deposition

Schematic illustration of the electro-deposition process



electrodeposition of actinides:

$$4H^+ + UO_2^{2+} + 2e^- = U^{4+} + 2H_2O$$

$$4OH^- + U^{4+} = U(OH)_4$$

$$2H_2O + UO_2^{2+} + 2e^- = U(OH)_4$$

$NaHSO_4/Na_2SO_4$ buffer can be used as electrolysis solution, because

de-loading affinity: sequence for anions

$$Cl^- > OH^- > NO_3^- > SO_4^{2-}$$

$$2OH^- \rightarrow H_2O + 1/2O_2\uparrow + 2e^-$$

$$2H^+ + e^- \rightarrow H_2\uparrow$$

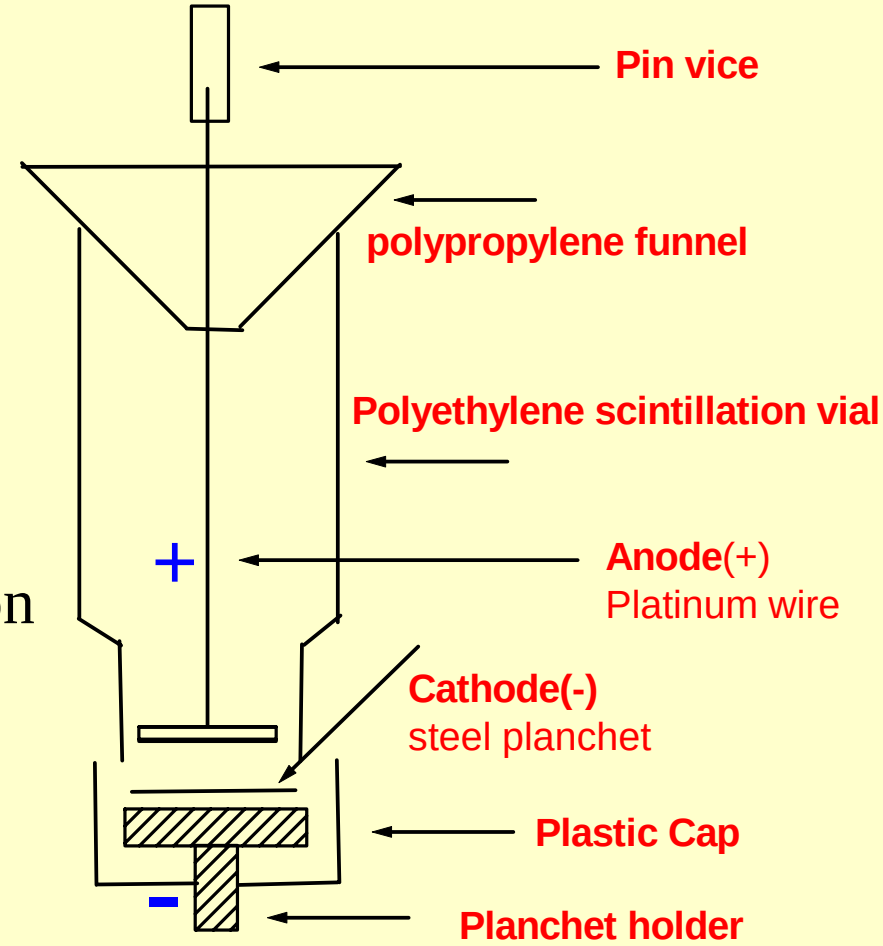
de-loading affinity: sequence for cations

$$Cu^{2+} > Fe^{2+} > H^+ > Na^+$$

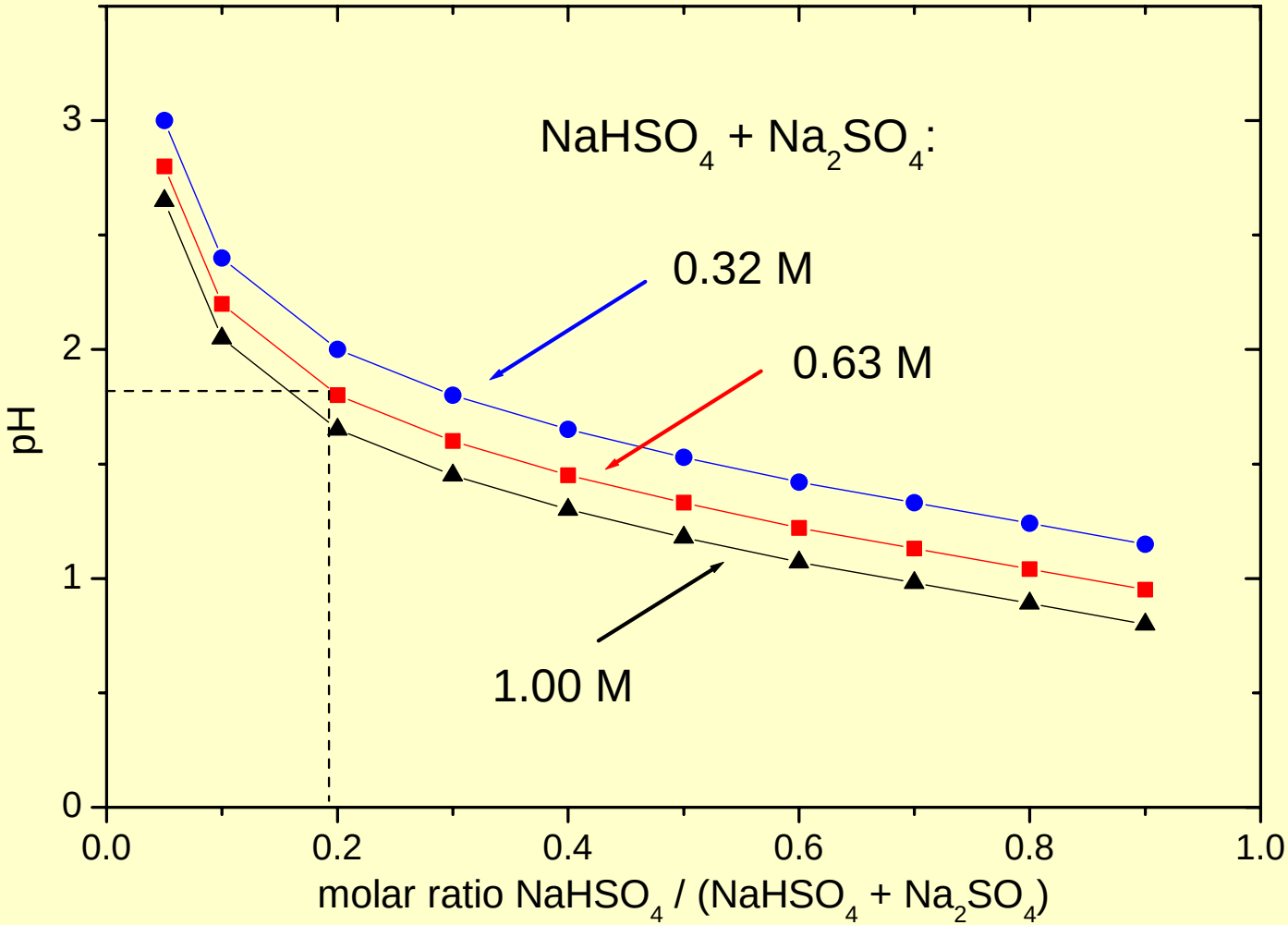
apparatus used at PSI for electro-deposition of actinides

Electrolysis solution:
1/5 molar ratio
$NaHSO_4/Na_2SO_4$ buffer
in 0.6 m total sulfate conc.

Advantages:
(1) relative high concentration of the electrolyte,
(2) fixed pH at the pK of $NaHSO_4$ (i.e. 1.8)



pH of $NaHSO_4/Na_2SO_4$ buffer solutions

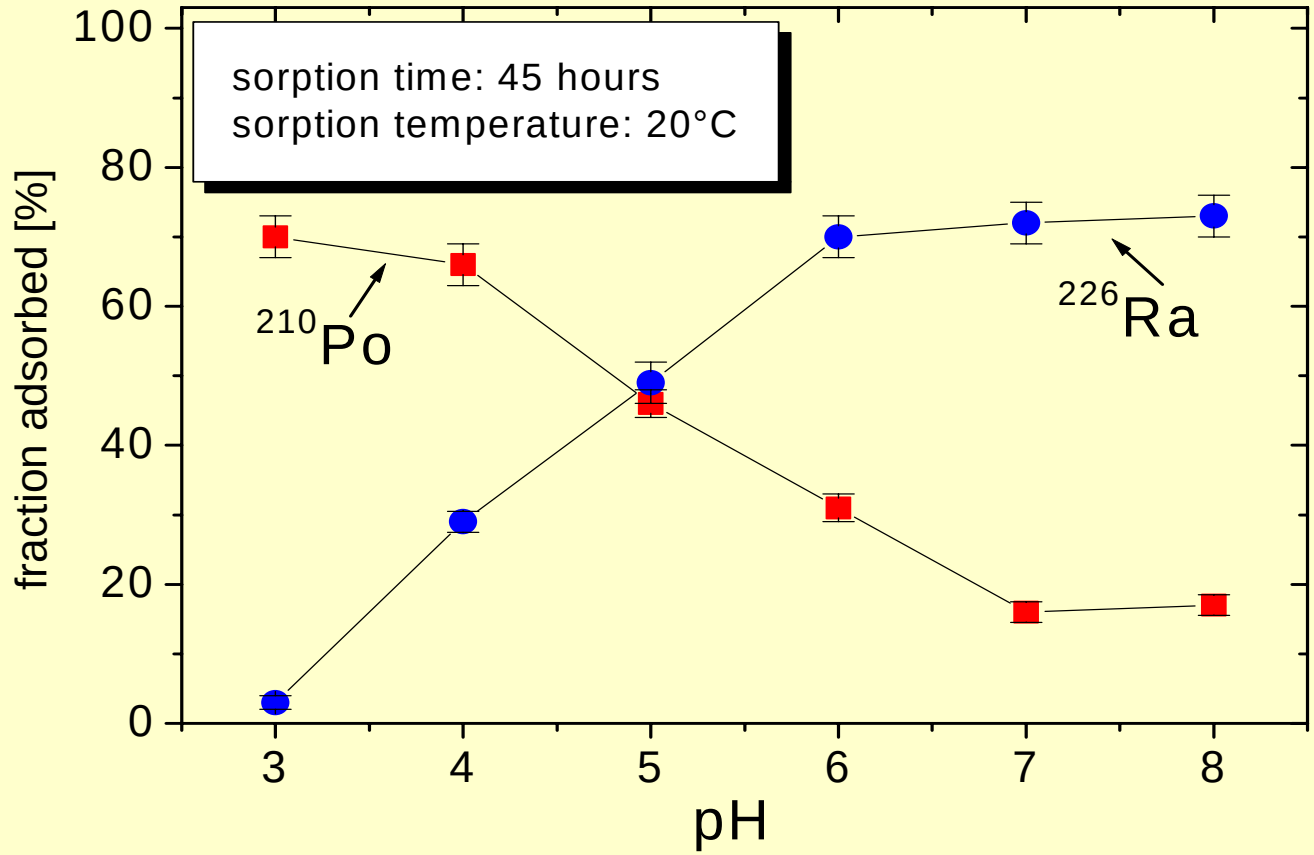


Spontaneous deposition methods

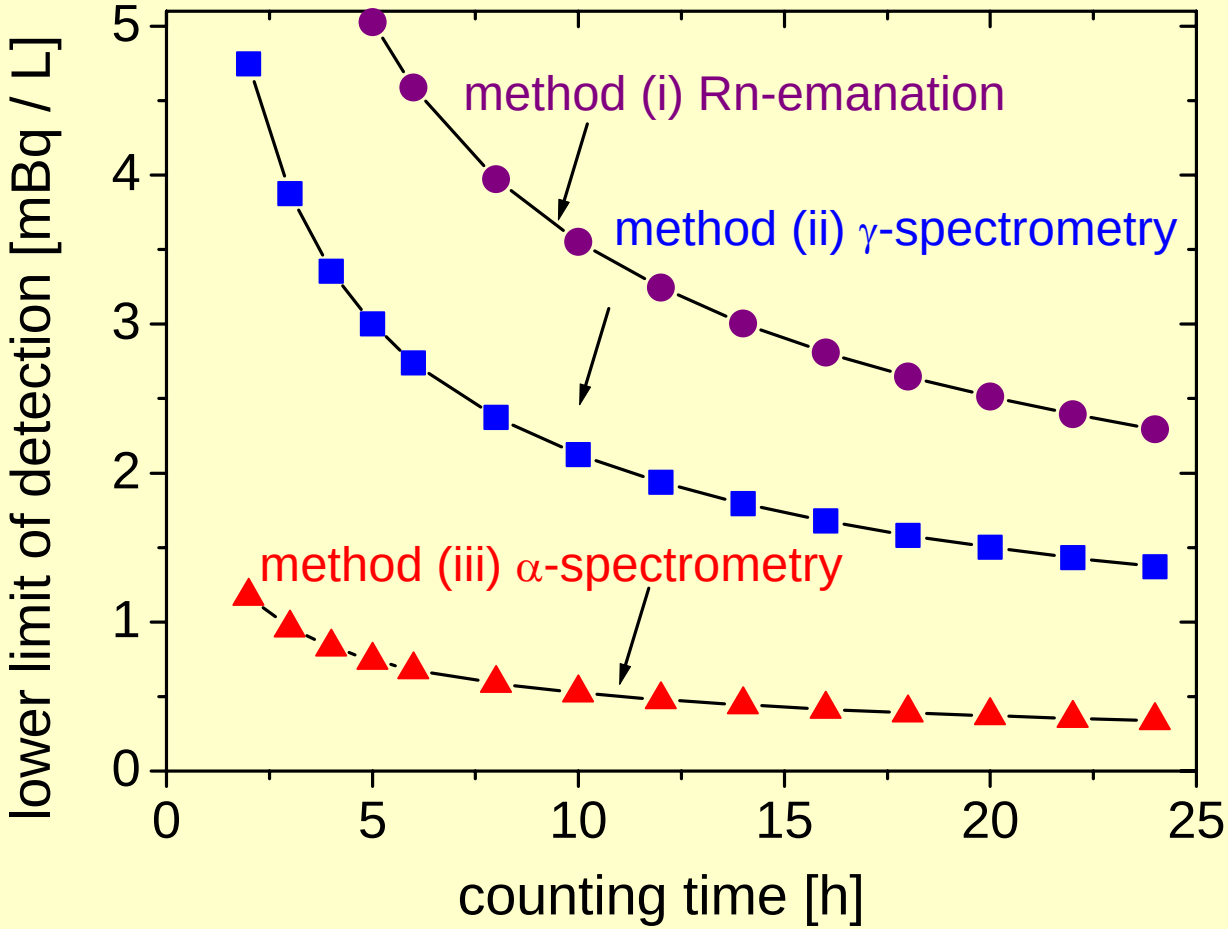
1. **Determination of ^{226}Ra: ^{224}Ra or ^{223}Ra addition to a 500 ml sample, direct sorption onto MnO_2-coated plastic discs, subsequent α-spectrometric measurement (MDA for 1 day counting time: 0.5 mBq/l)**
2. **Determination of ^{210}Po: ^{209}Po addition to a 200 ml sample, spontaneous deposition of Po isotopes onto a silver disc and subsequent α-spectrometric measurement (MDA for 1 day counting time: 1 mBq/l)**

Effect of pH on the adsorption yield of Ra^{2+} and PoO_3^{2-} on MnO_2 coated discs

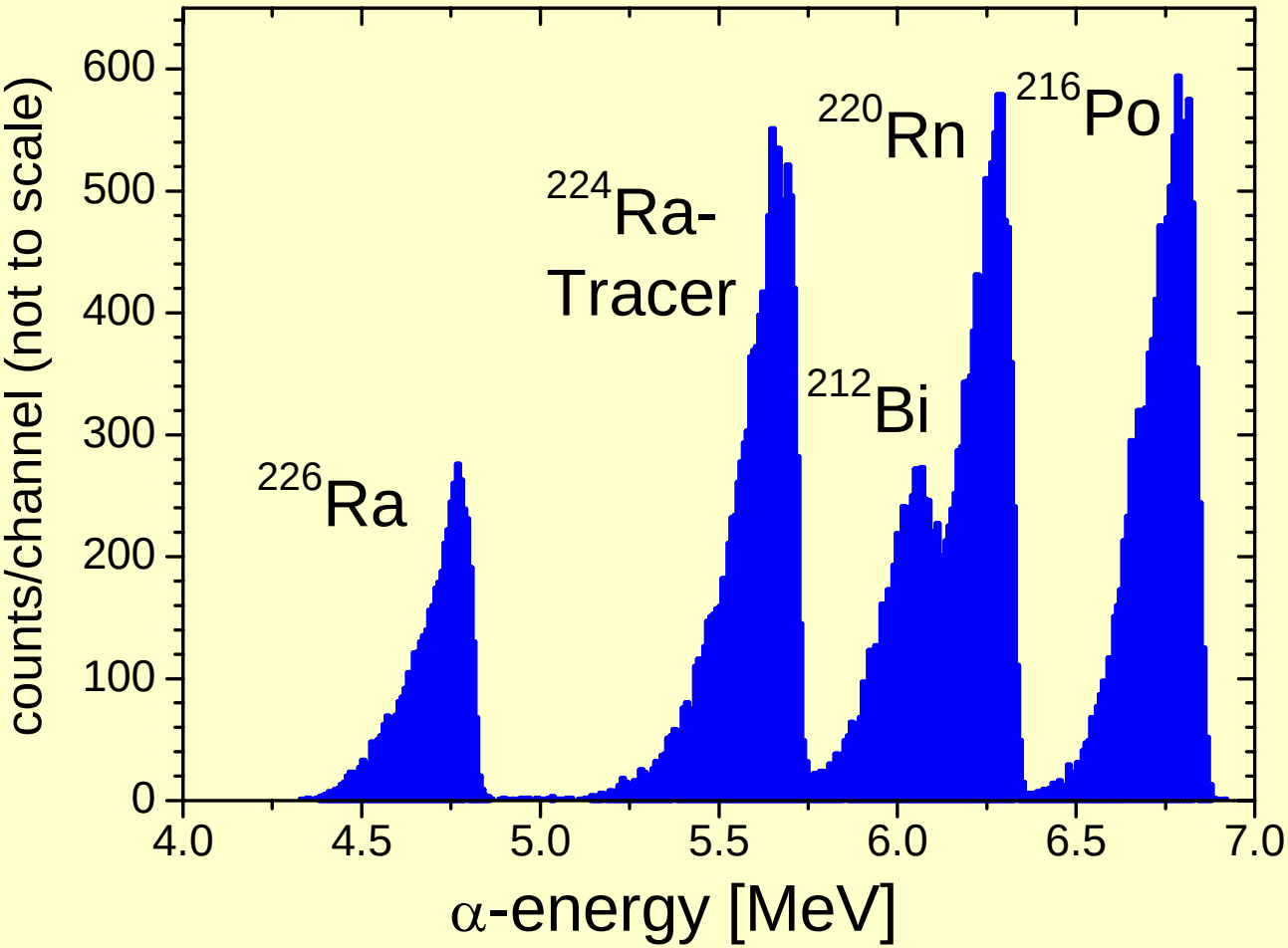
$$2S(OH)^- + Ra^{2+} \leftrightarrow (SOH)_2 Ra \qquad 2S(H)^+ + PoO_3^{2-} \leftrightarrow (SO)_2 Po + H_2O$$



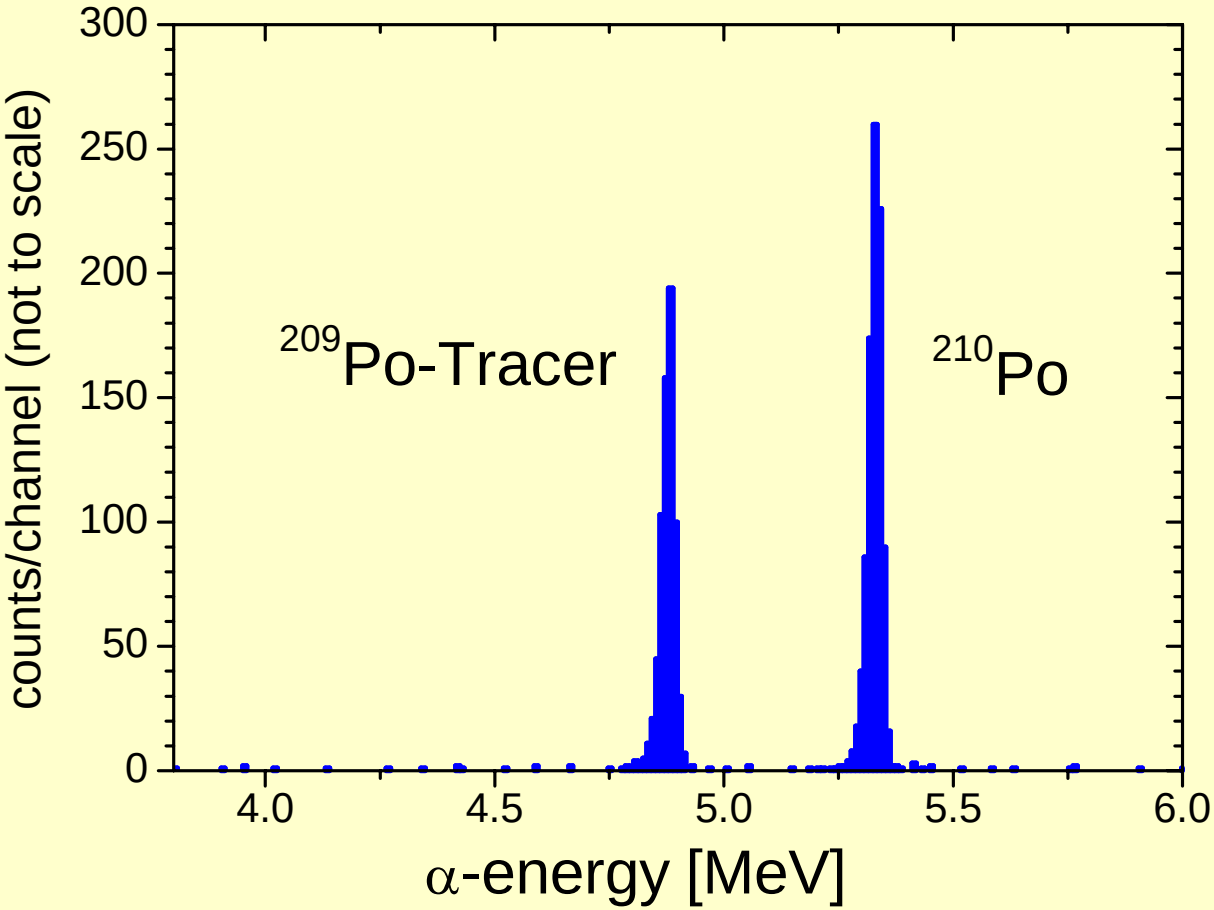
Minimum detectable activities for ^{226}Ra in water with counting time for three different analytical methods



α-spectrum of Radium



α-spectrum of Polonium



Concluding Remarks

- Application of extraction chromatographic procedures is highly useful for separation (isolation) of pure α- and β-particle emitting isotopes particularly from samples with complex chemical matrix and complex radioisotope composition (i.e. soil, waste water, rock samples...)
- Electro-deposition following extraction chromatographic methods is furthermore highly recommended for precise α-spectrometry (yields excellent α-peak resolution).