Chemical Separation and Source Preparation for α-Spectrometry

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Radioanalytical Laboratory

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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 $\gamma$-spectrometry in underground rock laboratories for radionuclide migration experiments, developing rapid separation methods for determination of pure $\alpha$- or $\beta$-emitters in various matrices, e.g. $^{63}$Ni, $^{90}$Sr, actinides)
# origin of radioactive sources

<table>
<thead>
<tr>
<th>type of source</th>
<th>radioisotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>primordial terrestrial</td>
<td>U/Th-Series, $^{40}$K, $^{87}$Rb</td>
</tr>
<tr>
<td>production from cosmic radiation</td>
<td>(spallation, activation) $^{7}$Be, $^{3}$H, $^{14}$C, …</td>
</tr>
<tr>
<td>man-made artificial (anthropogenic)</td>
<td>$^{3}$H, $^{14}$C, $^{60}$Co, $^{90}$Sr, $^{137}$Cs, $^{238}$Pu, $^{239}$Pu, $^{241}$Am, $^{244}$Cm</td>
</tr>
</tbody>
</table>
example immission surveillance: sample material and relevant $\alpha$-emitting radioisotopes

<table>
<thead>
<tr>
<th>samples</th>
<th>isotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>air filters</td>
<td>$^{210}\text{Po}$, $^{239,240}\text{Pu}$, $^{241}\text{Am}$</td>
</tr>
<tr>
<td>rain-, river-, ground-water</td>
<td>$^{226}\text{Ra}$, $^{210}\text{Po}$, $^{234}\text{U}$, $^{238}\text{U}$</td>
</tr>
<tr>
<td>biological (grass, tree leaves, milk etc.)</td>
<td>$^{226}\text{Ra}$, $^{239,240}\text{Pu}$, $^{241}\text{Am}$ ...</td>
</tr>
<tr>
<td>soil, sediments</td>
<td>$^{238}\text{U}$, $^{232}\text{Th}$ with decay series isotopes, $^{239,240}\text{Pu}$, $^{241}\text{Am}$</td>
</tr>
</tbody>
</table>
## types of spectrometers for radioisotope specific determination

<table>
<thead>
<tr>
<th>Counting Technique</th>
<th>Radioisotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamma-spectrometry</td>
<td>$^7\text{Be}$, $^{60}\text{Co}$, $^{131}\text{I}$, $^{137}\text{Cs}$, ...</td>
</tr>
<tr>
<td>Liquid scintillation spectrometry (LSC)</td>
<td>all $\beta$-emitters $^3\text{H}$, $^{14}\text{C}$, $^{90}\text{Sr}$, $^{241}\text{Pu}$</td>
</tr>
<tr>
<td>Alpha-spectrometry</td>
<td>$^{238}\text{Pu}$, $^{239}\text{Pu}$, $^{241}\text{Am}$, $^{244}\text{Cm}$</td>
</tr>
</tbody>
</table>
types of radiation and typical penetration length through material

<table>
<thead>
<tr>
<th>type of radiation</th>
<th>characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$, X-ray (photons)</td>
<td>high penetration length</td>
</tr>
<tr>
<td></td>
<td>(water: m, air: km)</td>
</tr>
<tr>
<td>$\alpha$-radiation (particles)</td>
<td>very weak penetration length</td>
</tr>
<tr>
<td></td>
<td>(water: $\mu$m, air: cm)</td>
</tr>
<tr>
<td>$\beta$-radiation (particles)</td>
<td>weak penetration length</td>
</tr>
<tr>
<td></td>
<td>(water: mm, air: m)</td>
</tr>
</tbody>
</table>
Example: decay scheme of $\alpha$-emitting $^{226}$Ra

\[ \frac{A}{Z} X \rightarrow \frac{A-4}{Z-2} X + ^{4}\text{He} + \text{decay energy} \]

$^{226}$Ra (1600 y) → $Z = 88$

0.0

$Z = 86$
0.186

$^{222}$Rn (3.82 d)

$\alpha_1$ (95.5 %)

$\gamma_1$ 0.0

$\alpha_2$ (4.5 %)
Conclusion: $\alpha$-emitters have comparable energies (4-8 MeV). Chemical separation procedures and source deposition methods yielding high resolution $\alpha$-spectra are therefore required.
α-spectrometry using intrinsic Si-Detectors
Double chamber $\alpha$-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™

mobile phase (with analyte)
inert support (polymeric substrate)
organic extractant (reagent)
stationary phase (resin)
## Properties of extraction chromatographic resins

<table>
<thead>
<tr>
<th>Inert Support</th>
<th>Extraction Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemically inert</td>
<td>High chemical purity</td>
</tr>
<tr>
<td>Mechanically stable</td>
<td>High selectivity for analyte</td>
</tr>
<tr>
<td>Large specific surface</td>
<td>Low solubility into the mobile phase</td>
</tr>
<tr>
<td>Uniform particle size</td>
<td>Rapid reaction kinetics</td>
</tr>
</tbody>
</table>
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:
$K'_{1} = \frac{t'_{R1}}{t_0} = \frac{(t_{R1} - t_0)}{t_0}$

relative retention: $\alpha = \frac{K'_{1}}{K'_{2}}$
# Important organic extractants for radiochemical application:

<table>
<thead>
<tr>
<th>Chemical substance</th>
<th>product name</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ethylhexyl)di-phosphonic acid</td>
<td><em>Actinide Resin</em> Eichrom</td>
</tr>
<tr>
<td>(Diamyl)phosphonate</td>
<td><em>U/TEVA Resin</em> Eichrom</td>
</tr>
<tr>
<td>CMPO / Tributyl-phosphate (TBP)</td>
<td><em>TRU Resin</em> Eichrom</td>
</tr>
<tr>
<td>Anion exchange resin</td>
<td><em>BIORAD AG 1-X2</em></td>
</tr>
</tbody>
</table>
Example I: actinides in waste water
Distribution coefficients of actinides on Actinide Resin™ with varying HCl concentration (from Horwitz et al., 1987)
Sorption uptake kinetics

regression fit:
\[ \ln\left(\frac{A}{A_0}\right) = -k_{sorb} t \]

\( k_{sorb\ (Ra)} = 0.041 \text{ min}^{-1} \)
\( T_{1/2\ sorb\ (Ra)} = 17 \text{ minutes} \)

\( k_{sorb\ (U)} = 0.077 \text{ min}^{-1} \)
\( T_{1/2\ sorb\ (U)} = 9 \text{ minutes} \)
Example I: actinides in waste water
selective actinide separation via Actinide Resin™

- aqueous phase + $^{236}$U tracer
- sorption of the actinides on the resin
- separation of the resin from the solution
  - solid fraction: resin with uranium
  - filtrate: removal of the aqueous phase
- stripping of reagent from the resin
  - substrate: removal of residual resin
  - filtrate: reagent solution with uranium
- electrodeposition and $\alpha$-spectrometry
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)

Sample solution
3 M HNO₃ + 0.5 M Al(NO₃)₃
+ $^{232}$U/$^{228}$Th tracer

5 M HCl (Th)

NaHSO₄/H₂SO₄ buffer solution, evaporation

Th-fraction

Electrolysis

$^{228}$Th, $^{230}$Th, $^{232}$Th

$\alpha$-spectrometry

0.02 M HCl (U)

NaHSO₄/H₂SO₄ buffer solution, evaporation

U-fraction

Electrolysis

$^{234}$U, $^{235}$U, $^{238}$U

$\alpha$-spectrometry
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

\[
\begin{align*}
\text{NO}_2^- + 2H^+ + e^- &= NO + H_2O \\
\text{Pu}^{3+} &= \text{Pu}^{4+} + e^- \\
2\text{M HNO}_3 + \text{NaNO}_2 &\quad [\text{Pu}^{4+}] \\
\text{TRU-Spec} &\quad \text{Pu, Am, Cm} \\
2\text{M HNO}_3 &\quad \text{discard} \\
2\text{M HNO}_3 + \text{NaNO}_2 [\text{Pu}^{4+}] &\quad \text{discard} \\
0.5\text{M HNO}_3 &\quad \text{discard} \\
9\text{M HCl} &\quad \text{discard} \\
4\text{M HCl} &\quad \text{discard} \\
0.1\text{M NH}_4\text{HC}_2\text{O}_4 &\quad \text{Pu (IV)} \\
3\text{M HNO}_3 &\quad \text{discard} \\
\text{U/TEVA-Spec} &\quad \text{Thorium} \\
3\text{M HNO}_3 &\quad \text{discard} \\
9\text{M HCl} &\quad \text{discard} \\
5\text{M HCl} &\quad \text{discard} \\
0.01\text{M HCl} &\quad \text{discarded} \\
\text{TRU-Spec} &\quad \text{Plutonium} \\
0.1\text{M NH}_4\text{HC}_2\text{O}_4 &\quad \text{Americium, Curium} \\
2\text{M HNO}_3 &\quad \text{discard} \\
2\text{M HNO}_3 + \text{NaNO}_2 [\text{Pu}^{4+}] &\quad \text{discard} \\
0.5\text{M HNO}_3 &\quad \text{discard} \\
9\text{M HCl} &\quad \text{discard} \\
4\text{M HCl} &\quad \text{discard} \\
\end{align*}
\]
Methods for preparation of planar counting sources for $\alpha$-spectrometry

- micro-precipitation (e.g. La-fluoride etc.)
- electrolysis / electro-deposition
- spontaneous deposition
Schematic illustration of the electrodeposition 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

\[ Cl^- > OH^- > NO_3^- > SO_4^{2-} \]

\[ 2OH^- \rightarrow H_2O + 1/2O_2 + 2e^- \]

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 NaHSO₄/Na₂SO₄ buffer in 0.6 m total sulfate conc.

Advantages:
(1) relative high concentration of the electrolyte,
(2) fixed pH at the pK of NaHSO₄ (i.e. 1.8)
pH of NaHSO₄/Na₂SO₄ buffer solutions

NaHSO₄ + Na₂SO₄:

- 0.32 M
- 0.63 M
- 1.00 M

molar ratio NaHSO₄ / (NaHSO₄ + Na₂SO₄)

pH
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 $\alpha$-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 $\alpha$-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

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

Sorption time: 45 hours
Sorption temperature: 20°C
Minimum detectable activities for $^{226}$Ra in water with counting time for three different analytical methods

- **method (i) Rn-emanation**
- **method (ii) $\gamma$-spectrometry**
- **method (iii) $\alpha$-spectrometry**
$\alpha$-spectrum of Radium

Counts/channel (not to scale)

$\alpha$-energy [MeV]
α-spectrum of Polonium

\[ \begin{align*}
\text{counts/channel (not to scale)} \\
\text{α-energy [MeV]} \\
\text{α-energy [MeV]} \\
\end{align*} \]

\( ^{209}\text{Po-Tracer} \)

\( ^{210}\text{Po} \)
Concluding Remarks

• Application of extraction chromatographic procedures is highly useful for separation (isolation) of pure $\alpha$- and $\beta$-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 $\alpha$-spectrometry (yields excellent $\alpha$-peak resolution).