Low level determination of Pb-210, Ra-226, Ra-228 in ground and mineral water using HIDEX 300SL LS-spectrometer with TDCR efficiency tracing and optimized $\alpha/\beta$ discrimination

Jost Eikenberg, Heide Beer
Division for radiation protection and safety
Paul Scherrer Institut, CH-5232 Villigen
Overview / Topics

- Short presentation of the Paul Scherrer Research Institute and the Radioanalytical Laboratory
- Radiochemical method for simultaneous determination of Pb-210 and Ra-226+Ra-228
- Comparison of classical two photomultiplier vs three photomultiplier LS-spectrometry
Areal graph of the Paul Scherrer Institute
Proton beam line: injector II, acceleration of protons to 220000 km/s (70% of the speed of light)
Schematic view of the proton and neutron beam line at PSI
The Synchrotron Light Source (SLS) Switzerland
Beamlines of SLS
microtomography

- Blood circulation in a brain of a mouse with Alzheimer disease
Radionuclide immission surveillance and measurements of dietary products

- Gamma spectrometric measurements of solid samples (mushrooms, milk powder etc)
- Performance of radiochemical separation methods for low level determination of pure $\alpha$- and $\beta$-emitters in aqueous samples (drinking, ground and mineral water)
Terrestrial radioisotopes:

- $^{238}\text{U}$-series
- $^{235}\text{U}$-series
- $^{232}\text{Th}$-series,
- $^{40}\text{K}$, $^{87}\text{Rb}$ etc.
The sun: responsible for the production of cosmogenic isotopes (e.g. radiocarbon, $^{14}$C, $^7$Be)
The high-energy cosmic-ray particle produces a large amount of secondary particles.
Release and deposition of anthropogenic radio-contaminants
environmental monitoring around PSI and the adjacent nuclear power plant at Beznau: locations for sampling and on-line dose rate recording
Locations of on-line dose rate measurements in Switzerland
example immission surveillance: sample material and important radioisotopes

<table>
<thead>
<tr>
<th>samples</th>
<th>isotopes</th>
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<tbody>
<tr>
<td>air filters</td>
<td>$^7$Be, $^{210}$Pb, $^{212}$Pb, $^{131}$I, $^{134}$Cs, $^{137}$Cs, $^{239,240}$Pu, $^{241}$Am</td>
</tr>
<tr>
<td>rain-, river-, ground-water</td>
<td>$^3$H, $^{224}$Ra, $^{226}$Ra, $^{228}$Ra, $^{210}$Po, $^{234}$U, $^{238}$U</td>
</tr>
<tr>
<td>biological (grass, tree leaves, milk etc.)</td>
<td>$^{14}$C, $^{137}$Cs, $^{40}$K, $^{226}$Ra, $^{90}$Sr, $^{239,240}$Pu, $^{241}$Am ...</td>
</tr>
<tr>
<td>soil, rocks, sediments</td>
<td>$^{238}$U, $^{232}$Th with decay series, $^{90}$Sr, $^{239,240}$Pu, $^{241}$Am + $^{244}$Cm</td>
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</table>
• *immission surveillance at PSI: rain water sampler*
immission surveillance at PSI: aerosol collecting unit
types of spectrometers for radioisotope specific determination

<table>
<thead>
<tr>
<th>counting technique</th>
<th>radioisotopes</th>
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<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</td>
<td>all $\beta$-emitters</td>
</tr>
<tr>
<td>spectrometry (LSC)</td>
<td>$^3\text{H}$, $^{14}\text{C}$, $^{90}\text{Sr}$, $^{241}\text{Pu}$</td>
</tr>
<tr>
<td>alpha-spectrometry</td>
<td>$^{238}\text{Pu}$, $^{239}\text{Pu}$, $^{241}\text{Am}$, $^{244}\text{Cm}$</td>
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Wipe test taken from a freight container at the Zurich airport: gamma spectrum analysis
LSC, Perkin Elmer Model TriCarb 3100 TR/SL
LSC with BGO detector guard
HIDEX Model SL 300 with guard detector
Carbon-14 for dating archaeological samples or for monitoring anthropogenic input

LSC: spectrum of $^{14}\text{C}$ und $^{3}\text{H}$

- $^{3}\text{H}$ intensity (not to scale)
- $^{14}\text{C}$ intensity (not to scale)
- $E_{\text{max}}^{^{14}\text{C}} = 18.6\ \text{keV}$
- $E_{\text{max}}^{^{3}\text{H}} = 156\ \text{keV}$

Graph: $^{14}\text{C}/^{12}\text{C}$ specific activity [mBq / g C]
- NBS oxalic acid 1977
- PSI Saphir reactor 1994
- PSI internal sugar standard 1981
- Berne beech standard 1994
- Berne beech standard 2001

Results University of Berne
Results PSI
R&D projects of the radioanalytical laboratory

- Development and implementation of radiochemical separation techniques
- Research projects with universities: dating of Pleistocene samples with applications in volcanology, paleo earth quake dating, ice core samples (global warming)
Decay / Ingrowth relationships: U-Th-series disequilibrium

\[ A_y(t) = A_x(0) \cdot \frac{\lambda_y}{\lambda_y - \lambda_x} \cdot (e^{-\lambda_x t} - e^{-\lambda_y t}) + A_y(0) \cdot e^{-\lambda_y t} \]

\( X = \text{parent} \)
\( Y = \text{daughter} \)

Ingrowth term

decay term

- \( 238\text{U}, 234\text{U} \)
- \( 228\text{Th} \)
- \( 228\text{Ra} \)

Relative activity (not to scale)

time after separation [y]

0 2 4 6 8 10 12 14 16 18 20
0.0 0.2 0.4 0.6 0.8 1.0

0 50 100 150 200 250 300
0.0 0.2 0.4 0.6 0.8 1.0
Dating volcanic rock eruption events

$\frac{^{226}\text{Ra}(t)}{^{230}\text{Th}(0)}$ vs time since eruption [ky]

- Excess $^{226}$Ra decay curve
- Secular equilibrium situation

Points M-056, M-137, M-167, M-392, M-142
Study objects: island arc volcanic rocks from the Sunda-Banda subduction zone
Method implementation: low level determination of Pb-210, Ra-226+Ra-228 in drinking water

• Filtration of the sample (2 liter) through 3 Empore RadDisc (Mn-oxide impregnated) membrane filters
• Elution of Pb with Diammonium Hydrogen Citrate
• Elution of Ra with alkaline Na-EDTA solution
• Measuring via LSC with optimized α/β-discrimination
The image shows a diagram representing the decay chains of the uranium-238 (238U) and uranium-235 (235U) series. The diagram includes isotopes and their decay modes, half-lives, and energy levels. The 238U series includes isotopes such as U-238, Pa-234, Th-230, and Po-210, while the 235U series includes isotopes such as U-235, Pa-231, Th-227, and Po-210. The decay modes are denoted by α or β, and the energies are expressed in MeV. Half-lives are given in years or days. The diagram is part of a presentation on radiochemistry, as indicated by the title and the conference information.
Continental water: relevant isotopes

- Alpha-emitter: U-238, U-234
- Beta-emitter: Ra-228 (with fast ingrowing Ac-228)
- Alpha-emitter: Ra-226 (with Rn-222 progentes)
- Beta-emitter: Pb-210 (with ingrowing Bi-210)
- Alpha-emitter: Po-210
relevant isotopes in continental water and their measurement methods at PSI

<table>
<thead>
<tr>
<th>radionuclide</th>
<th>analytical technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}\text{U}$, ($^{235}\text{U}$), $^{238}\text{U}$</td>
<td>U/TEVA separation, electro-deposition, $\alpha$-spectrometry</td>
</tr>
<tr>
<td>$^{226}\text{Ra}$, $^{228}\text{Ra}$, $^{210}\text{Pb}$</td>
<td>filtration (RadDisc), OptiPhase Hisafe3 cocktail, LSC</td>
</tr>
<tr>
<td>$^{210}\text{Po}$</td>
<td>spontaneous deposition on silver disc, $\alpha$-spectrometry</td>
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Schematic view of radioactive transformation

\[ ^{226}\text{Ra} \rightarrow ^{222}\text{Rn} + ^{4}\text{He} + 4.78\text{MeV} \]
Perals Alpha LS-Spectrometer

Ra-226 ENERGY SPECTRUM (MeV)

Ra-226

Rn-222

Po-218

Po-214
Pulse shape $\alpha/\beta$ discrimination

![Graph showing pulse shape discrimination between alpha and beta pulses](graph.png)
Spill-over $\alpha/\beta$ determination

![Graph showing spill-over in $\alpha$ and $\beta$ over discriminator setting in ns. The graph illustrates the crossover point where $\beta$ in $\alpha$ and $\alpha$ in $\beta$.](image-url)
Pulse Length Index (PLI) discrimination with HIDEX SL 300
Classical two photomultiplier LS electronic set-up
The triple coincidence to double coincidence ratio (TDCR) counting technique
The first approximation linear relationship between the counting efficiency and the TDCR
Efficiency tracing: extrapolating hypothetical count rates to 100% efficiency

\[ y = 73144x - 1E-10 \]

\[ R^2 = 1 \]
Typical $\alpha/\beta$ emission spectrum obtained with a TriCarb LS-spectometer
α-spectrum of Ra-226 with ingrowing daughters 2 h and 8 h after separation using HIDEX 300 SL LSC
β-spectrum of Ra-228 with ingrowing Ac-228 1 h and 8 h after separation using HIDEX 300 SL LSC
\[ A^* = k_{1-\alpha} \cdot \frac{1}{\varepsilon \cdot \nu \cdot P_i \cdot R_i} \cdot \sqrt{2} \cdot \sqrt{\frac{r_0}{t_m}} \]
LSC detection limits, 2 l aliquot, quantitative adsorption on RadDisc filter, counting time 6 h

- Ra-226: 3 mBq/liter
- Ra-228: 15 mBq/liter
- Pb-210: 20 mBq/liter
Conclusions

• LSC with optimized alpha/beta separation is a powerful tool to determine almost pure $\alpha$-emitting Ra-226 besides weak $\beta$-emitting Ra-228.

• The RadDisc adsorption procedure allows furthermore simultaneous determination of weak $\beta$-emitting Pb-210
Thank you for your attention