FAST DETERMINATION OF Po-210 IN URINE BY LSC AS A MEANS TO ESTIMATE DELIBERATE POISONING

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Introduction

Po-210: decay product of U-238, discovered by Marie and Pierre Curie 1898 in Paris, named in honour of Marie’s home country

Half life: 138 days, α-decay to stable Pb-206

Extremely rare in nature – about 0.1mg/t uranium ore

Considerable amounts dissolved in water: drinking water, mineral water
EC Recommandation K(2001): max. conc. 0.1 Bq/L
Present in sea water → accumulates in shellfish and seafood

The dose to large populations in the South Pacific is not due mainly to the French nuclear tests on Mururoa and Fangataufa, but to natural Po-210. The same is true for Cumbria and the Sellafield nuclear installation.

Baltic Sea: Po-210 dose to population from fish consumption similar to that of Cs-137, even after the Chernobyl accident

aboriginal people in the north: Po-210 gives 57-72% of the total annual dose → one particular food chain: lichen – reindeer – humans
Po-210 in tobacco and in cigarette smoke

Dalheimer et al. (2007):
daily urinary excretion median value of 3.5 mBq/d for non-smokers

6.6 mBq/d for smokers
Use of Po-210:

Consumer products: static eliminators, dust removers, spark plugs

Po(Be) neutron sources, isotope batteries, atomic bomb triggers

Production:
neutron activation of Bi-209 (stable), $\beta$-decay of Bi-210 to Po-210, worldwide production estimated to $\sim 100$ g per year
Physiological properties:

extremely radiotoxic if incorporated

50 - 90 % of ingested Po will leave the body in feces, the rest will enter the bloodstream, biological half life ~ 50 d

Target organs: spleen, kidney and liver (appr. 45 %), 10% deposited in bone marrow and the remainder distributed throughout the body, including lymph nodes and the respiratory tract
Poisoning with Po-210

literature:
2 lethal accidents
   a researcher poisoned due to his work with Po-210 (France)
   a worker accidently inhaled a Po-210 aerosol (Russia)

November 2006:
poisoning of Aleksander Litvinenko, „a former KGB spy“
Presumptions:

poisoned with thallium?
    unlikely, because easy to proof within short time

poisoned with radioactive Tl-210?
    $\gamma$-emitter $\rightarrow$ high amount necessary, in urine no $\gamma$-emitters

poisoned by Po-210?
    nobody looked for alphas!
Incorporation and excretion

lethal dose: $1$ to $3$ GBq $\leftrightarrow 6$ to $18$ µg Po-210

$10^5$-$10^6$ Bq Po-210 in daily urine (1.5 L) after ingestion of 1 GBq
$\rightarrow 67$-$670$ Bq/mL in urine
• vice versa an acute intake can be calculated from urine measurements of the victim

• the dose to the individual can be estimated:

dose coefficient (ingestion): 2.4E-07Sv/Bq
- Table 1 shows the calculation of the actual intake detectable in relation to time elapsed between intake and measurement.

<table>
<thead>
<tr>
<th>Intake am Tag d vor der Messung [d]</th>
<th>Ausscheidungsrate am Tag x [Bq.d⁻¹/Bq]</th>
<th>Intake (gerundet) [MBq]</th>
<th>Effektive Folgedosis [Sv]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,9.10⁻⁴</td>
<td>0,11</td>
<td>0,026</td>
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<td>5</td>
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<td>10</td>
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<td>0,06</td>
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<td>100</td>
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<td>500</td>
<td>3,4.10⁻⁸</td>
<td>618</td>
<td>148</td>
</tr>
</tbody>
</table>

1) Ausscheidungsrate nach [1]
2) Effektive Folgedosis: 0,24 Sv/MBq nach [2]
Example: Intake of 0.5 MBq (0.003 microgram) Po-210, causing a dose of appr. 100 mSv (non lethal and not acute detrimental) easily detected still after 120 days.

24 Bq/d excretion $\rightarrow$ 16 mBq/mL (1dpm)

For comparison: 1 to 3 GBq acute intake leads to death within a few weeks intake of Alexander Litvinenko likely to have been in that range, determination of such intakes would be trivial
in an emergency situation very rapid analyses are needed – not extremely accurate ones!

„Rapid“: Very little or no handling of the sample, result latest within a few hours

time consuming: $\alpha$-source preparation for traditional surface barrier counting

much quicker and probably available at a hospital: liquid scintillation counting!
Instrumentation in the lab

- Ultra Low-level Liquid Scintillation Spectrometer Quantulus™1220 (Wallac Oy, now PerkinElmer, Turku, Finland)

- Pulse shape analysis for α/β-separation

- Counting efficiency for α ~100%, independant of quench level

- used for drinking water investigations and other environmental samples
Direct measurement of Po-210 in urine

Very quick estimation of the order of magnitude of Po-210 in urine in the case of a lethal poisoning

1-3 mL of urine diluted 1:1 with water + HiSafe®III
→ 10-100 min counting

background 1.4 cpm ↔ 0.023 Bq per sample
Direct measurement of Po-210 by LSC
0.7 Bq of Po-210 added to 1ml of urine, dilution with 1ml of distilled water, + 18ml of HiSafe III
Identification of the $\alpha$-emitter?

The only thinkable other radionuclide used in (terroristic) attacks is Pu-239.

decay energies of Po-210 (5.30 MeV) and Pu-239 (5.16 MeV) cannot be resolved by LSC – no discrimination possible!

→ 3 methods for Po-separation
1) Po-210 extraction by POLEX®

1 mL urine sample diluted 1:1 with water
Po-210 added
2 mL H$_3$PO$_4$ conc. added
Shake solution with 2 mL Polex®
After 10 min measure aliquot of Polex® phase

Extraction efficiency >95%
Blank value 0.02 cpm $\leftrightarrow$ 0.3 mBq per sample

The same procedure with a sample spiked with Pu-239
$\rightarrow$ Pu is not extracted!
Separation of Po-210 by extraction into Polex™
Extraction efficiency: 95%, blank: 0.02 cpm
Pu is not extracted under these conditions
2) Po-210 extraction with Sr·Spec® resin

Resin soaked in water and 2M HCl
Sample diluted, spiked, acidified to 2M HCl, → column
Po-210 eluted with 8 mL of 6M HNO₃
95% recovery

Sample evaporated to dry
residue taken up into 2 mL of 2 M HNO₃,
mixed with HiSafe® III, LSC measurement

Pu is not retained on the column!
Can be rinsed with 3 mL 2M HCl
3) Po-210 extraction with Sr Rad Disk

Disk rinsed with water and 6M HCl
Diluted and spiked sample acidified to 6M HCl
and sucked through the disk

100% Po extraction
Pu is not extracted!

Po eluted with basic 0.05 M EDTA,
mixed with HiSafe®III
LSC measurement
Conclusions

• Very quick LSC methods for measuring Po-210 available

• Using Polex, Sr·Spec resin or Sr Rad Disk only Po is extracted and measured

• Analysis time for large amounts of Po-210 in urine: 15 min sample preparation time a few min counting time