METHOD ADAPTATION FOR THE ANALYSIS OF SAMPLE MATRICES ENCOUNTERED DURING THE EVALUATION OF POTENTIALLY CONTAMINATED SITES IN AUSTRIA

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History of uranium ore in Europe

• Discovery of radioactivity → uranium ore/pitchblende
• Austria: Joachimsthal mine

• Marie Sklodowska Curie: discovery of radium and polonium in the tailings of the uranium colour production in Joachimsthal

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Carl Auer von Welsbach

• inventor of the incandescent light mantle
  – also called the ‘Welsbach mantle’
Standardised Screening Procedure for potentially contaminated sites

- Dose rate/contamination monitor measurements to locate hotspots (on-site)
- Soil samples/wipe tests (on-site)
- Sample Analysis:
  1. Gamma spectroscopy
  2. Radiochemical analysis using LSC and ICP-MS → lower LLD (lower limit of detection) than gamma spectroscopy → classification of radiological waste
- Determination of a nuclide vector for the site
- Prediction of an exposure scenario
Analysis of Soil Samples

• Radium + daughters Pb-210 and Po-210

• Established method: determination of Ra-226+228 and Pb/Po-210 in water
  → no digestion necessary

• New matrix: soil

• SAMPLES: ~1 g, soil sample, air dried, B1-B5
Empirical approach

• Compare different digestion methods:
  - Microwave digestion
  - Hotplate digestion in a beaker

• Check impact of ashing

• Compare use of different acids for digestion:
  - Standard: HNO₃
  - Sequential digestion: HCl and Aqua Regia

→ are the radionuclides extracted with these acids negligible after prior digestion with HNO₃?
Experimental

Soil Sample → (Ashing) → Microwave → Hotplate → Sequential Acid Digestion

1. HNO₃ + H₂O₂
2. HCl
3. Aqua Regia

ICP-MS measurement
U-238

Radiochemical Analysis
Ra-226 + Ra-228
Pb-210 + Po-210
Radiochemical Procedure:
Po-210, Pb-210, Ra-226, Ra-228

Precipitation
(Na₂S)

- Supernatant ➔ Ra-226/228
- Precipitate ➔ Pb/ Po-210
  - Precipitate washed with 1% HNO₃ ➔ U-238

Co-precipitation
(Ba + H₂SO₄)

- Dissolution in H₃PO₄
  - ICP-MS measurement

Dissolution in EDTA

- Extraction of Bi and Po with POLEX cocktail

LSC measurement
Filtrate after Na$_2$S precipitation (Radium fraction)

(1) HNO$_3$  (2) HCl  (3) Aqua regia

(Fractions resulting from sequential digestion)
Preliminary Results: chemical yield

Determined through ICP-MS measurement

Carriers: Pb-208, Ba-137/138
Preliminary Results: 
HNO$_3$ (1st) fraction

HPGe: 48 ± 18 Bq/kg
Preliminary Results:
HNO₃ (1st) fraction

**HPGe:**
53 ± 3 Bq/kg (Ac-228)
Preliminary Results:
HNO₃ (1st) fraction

HPGe: 78 ± 27 Bq/kg
Preliminary Results: HNO₃ (1st) fraction

- Po-210:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activity Concentr. [Bq/ kg]</th>
<th>Error [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>37.9</td>
<td>16</td>
</tr>
<tr>
<td>B2</td>
<td>29.3</td>
<td>17</td>
</tr>
<tr>
<td>B3</td>
<td>37.2</td>
<td>16</td>
</tr>
<tr>
<td>B4</td>
<td>21.2</td>
<td>19</td>
</tr>
<tr>
<td>B5</td>
<td>31.1</td>
<td>19</td>
</tr>
</tbody>
</table>
Preliminary Results: HCl (2nd) fraction

Activity concentration [Bq/kg]

<table>
<thead>
<tr>
<th></th>
<th>HNO₃+H₂O₂ (1)</th>
<th>HCl (2)</th>
<th>Aqua Regia (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-238 (directly after digestion)</td>
<td>45 ± 5</td>
<td>5 ± 1</td>
<td>1 ± 1</td>
</tr>
<tr>
<td>U-238 (1% HNO₃ solution)</td>
<td>45 ± 5</td>
<td>5 ± 1</td>
<td>1 ± 1</td>
</tr>
</tbody>
</table>
Preliminary Results:
U-238 (ICP-MS)

Activity concentration [Bq/kg]

- HNO₃+H₂O₂ (1)
- HCl (2)
- Aqua Regia (3)

Sample No (pre-treatment) B4 (hotplate, ashing) B5 (hotplate, no ashing)
Preliminary Results:
Aqua Regia (3rd) fraction

• All measurements below LLD
• **Chemical Yield:**
  - Needs to be improved and stabilised for Ra-226 and Ra-228

• **HNO₃ digestion:** sufficient for determination of Ra-226/228, Pb-210 and Po-210
  → no digestion with HCl/Aqua regia needed

• **HCl digestion:** option for uranium determination
Summary + Conclusions

• Wet digestion with **hotplate** gave us better results than microwave digestion – also: bigger sample mass possible

• **Po-210 measurement:** precipitate containing Pb/Po needs to be washed with 1% HNO3 multiple times to remove uranium
Next Steps

• Stabilise and improve chemical yield

• Achieve better LLD through use of higher sample mass

• Test method using samples with higher activities and reference materials
Acknowledgements

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Questions?