Determination of Cl-36 and I-129 by LSC after separation on an extraction chromatographic resin

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Outline

- Scope
- Resin characterization
- Method development
- Spiked samples
- Summary
Scope

- Interest: monitoring of nuclear facilities for long-lived radionuclides
- Cl-36 (and I-129) frequently determined by LSC
  - Cl-36 (3.01 $\times$ 10^4 y, $E_{\beta_{\text{max}}} =$ 708.6 keV),
  - I-129 (1.61 $\times$ 10^7 y, $E_{\beta_{\text{max}}} =$ 151.2 keV)
- Existing separation methods often complicated and time-consuming

Aim:
- Development and characterization of a suited resin
- Development of a simple and quick method for separation of Cl-36 and I-129 from environmental and decommissioning samples
- Cl and I retained as chloride and iodide
  - Oxidation state adjustment might be necessary (e.g. Sn(II))
Resin characterization – Cl resin

- **Determination of** $D_w$ **values**
  - For practical reasons in sulfuric acid

<table>
<thead>
<tr>
<th>Analyte</th>
<th>$D_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Zn</td>
<td>25</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ce</td>
<td>4</td>
</tr>
<tr>
<td>Pd</td>
<td>87000</td>
</tr>
</tbody>
</table>

- $D_w$ values, selected elements, 1M H$_2$SO$_4$, Cl resin

- Selective for Pd and Ag
- $D_w(Ag)$ slightly decreases with increasing pH
  - remains $>3E+5$ at pH 5

- $D_w(Ag)$:
  - 1M H$_2$SO$_4$: $6.5E+05$
  - H$_2$SO$_4$ (pH 3): $6.0E+05$
  - H$_2$SO$_4$ (pH 5): $3.5E+05$

- Ag uptake:
  - 17 – 20 mg Ag$^+$ per 2 mL column
  - extraction equilibrium reached > 30 min
Preparation of Ag loaded Cl resin

- 10 g Cl resin weighed and transferred into 250 mL PE flask
- 650 mg AgNO₃ dissolved in 100 mL 1M H₂SO₄
- AgNO₃ - solution added to Cl resin, flask capped and shaken for 2 hours at a medium speed
- Resin filtered and rinsed twice with 1M H₂SO₄
- Dried

- Alternative: on-column loading
Resin characterization – Ag loaded Cl resin

• Maximum Cl and I uptake evaluated via column experiments (2 mL column loaded with 13 mg Ag⁺)
  ➢ I: 16.3±1.6mg; Cl: 4.3 ±0.2mg
  ➢ Can be increased by longer resin / Ag⁺ contact times and higher Ag⁺ amounts

• $D_w$ values of chloride and iodide
  ➢ Extraction conditions: 1M $\text{H}_2\text{SO}_4$
  ➢ Elution conditions:
    • Chloride: 0.01 – 0.2M KSCN
    • Iodide: 0.01 – 0.2M KSCN; 0.04 – 0.35M $\text{Na}_2\text{S}$

• Batch experiments
Resin characterization – Ag loaded Cl resin

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$D_w$ retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-36</td>
<td>1600</td>
</tr>
<tr>
<td>I-129</td>
<td>1980</td>
</tr>
</tbody>
</table>

- High uptake of chloride and iodide onto Ag$^+$ loaded Cl-resin in 1M $\text{H}_2\text{SO}_4$

Retention of $^{36}\text{Cl}$ and $^{129}\text{I}$ in 1M $\text{H}_2\text{SO}_4$

- $^{36}\text{Cl}$: very low $D_w$ at all tested KSCN concentrations
- $^{129}\text{I}$: high $D_w$ at all tested KSCN concentrations, low $D_w$ at elevated $\text{Na}_2\text{S}$ concentrations
Elution study

- 2 mL column Ag loaded Cl resin
- $^{36}\text{Cl}$ spiked NaCl solution
  - Load from 1M $\text{H}_2\text{SO}_4$
  - Rinse 3 x 5 mL 0.1M KSCN
- $^{129}\text{I}$ spiked NaI solution
  - Load from 1M $\text{H}_2\text{SO}_4$
  - Rinse 2 x 5 mL 0.1M KSCN
  - Rinse 10 mL $\text{H}_2\text{O}$
  - Rinse 2 x 5 mL 0.35M Na$_2$S
- Eluates analyzed by LSC
Elution study

- $^{36}$Cl eluted with 5ml of 0.1M KSCN
- As expected from batch experiments $^{129}$I not affected by KSCN
- $^{129}$I eluted with 5ml 0.35M Na$_2$S, elution not quantitative
Optimisation of I\textsuperscript{-} elution

- Test of various rinsing steps upfront to I\textsuperscript{-} elution

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Influence of the rinsing step upfront to the I-129 elution with Na\textsubscript{2}S: Rinsing with various volumes of dest. water; 10ml 0.01M NaHSO\textsubscript{3} (a), 10ml 0.1M NaHSO\textsubscript{3} (b), 10ml 1M NaHSO\textsubscript{3} (c), 10ml 1M NaNO\textsubscript{2} (d) 10ml 30% H\textsubscript{2}O\textsubscript{2} (e), 10ml 1%NH\textsubscript{3} (f) and 10ml 1% NaOH (g)}
\end{figure}

- Best results achieved with NH\textsubscript{3} and NaOH:
  - 1\% NH\textsubscript{3} : 97.3±0.9\%
  - 1\% NaOH: 93.7±1.4\%

- NaOH preferred
  - Ag bleeding with NH\textsubscript{3}
  - Interference in LSC
Scheme – Optimized method

- Load sample in 1M H₂SO₄
  - Addition of reducing agent if necessary (e.g. Sn(II))
- Rinse with 10ml of MilliQ
- Elute ³⁶Cl with 5ml of 0.1M SCN⁻
- Wash with 10ml of 1% NaOH
- Elute ¹²⁹I with 5ml of 0.35M Na₂S
Elution study

- Method applied to $^{36}\text{Cl}$ and $^{129}\text{I}$ containing solution

Combined Cl/I elution study with optimized method

- Clean $^{36}\text{Cl} / ^{129}\text{I}$ separation
Decontamination factors (Df)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Df in Cl fraction</th>
<th>Df in I fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>&gt;29</td>
<td>&gt;430</td>
</tr>
<tr>
<td>Mn</td>
<td>&gt;210</td>
<td>&gt;370</td>
</tr>
<tr>
<td>Co</td>
<td>&gt;170</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>Ni</td>
<td>&gt;170</td>
<td>&gt;320</td>
</tr>
<tr>
<td>Cu</td>
<td>&gt;210</td>
<td>&gt;190</td>
</tr>
<tr>
<td>Zn</td>
<td>&gt;32</td>
<td>&gt;11</td>
</tr>
<tr>
<td>Rb</td>
<td>&gt;16</td>
<td>&gt;2300</td>
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<tr>
<td>Sr</td>
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<tr>
<td>Ba</td>
<td>&gt;1000</td>
<td>&gt;600</td>
</tr>
<tr>
<td>Pb</td>
<td>&gt;300</td>
<td>&gt;720</td>
</tr>
<tr>
<td>U</td>
<td>&gt;1900</td>
<td>&gt;200</td>
</tr>
<tr>
<td>Cs-137</td>
<td>&gt;150</td>
<td>&gt;150</td>
</tr>
<tr>
<td>Co-60</td>
<td>&gt;320</td>
<td>&gt;320</td>
</tr>
<tr>
<td>Sr/Y-90</td>
<td>&gt;180</td>
<td>&gt;160</td>
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<tr>
<td>Cl-36</td>
<td>NA</td>
<td>&gt;160</td>
</tr>
<tr>
<td>I-129</td>
<td>&gt;420</td>
<td>NA</td>
</tr>
</tbody>
</table>

- Method applied to multi-element solutions
  - ICP-MS
- Cs-137, Co-60, Sr-90, Cl-36 or I-129 containing solutions
  - LSC
- Good decontamination factors in SCN⁻ and Na₂S fractions
- Clean I / Cl separation
Spiked samples I - water

- 50ml tap water adjusted to 1M $\text{H}_2\text{SO}_4$
- Spiked with known activities of Cl-36 and I-129
- Each 0.5 mg NaCl and NaI
- Addition of 17Bq of each Co-60, Sr-90 and Cs-137
- Three 10ml aliquots analyzed following optimized method
- Chemical yields obtained in reproducibility test applied
- LSC measurement of Cl- and I-fractions
## Spiked samples I - water

<table>
<thead>
<tr>
<th></th>
<th>determined activities</th>
<th>added activities</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I-129</strong></td>
<td><strong>A(I-129) / Bq</strong></td>
<td><strong>UA(I-129) / Bq</strong></td>
<td><strong>A(I-129) / Bq</strong></td>
<td><strong>UA(I-129) / Bq</strong></td>
<td><strong>Bias / %</strong></td>
<td><strong>E_n</strong></td>
<td></td>
</tr>
<tr>
<td>Repl. 1</td>
<td>8,24</td>
<td>1,98</td>
<td>8,22</td>
<td>1,31</td>
<td>0,3%</td>
<td>0,01</td>
<td></td>
</tr>
<tr>
<td>Repl. 2</td>
<td>8,17</td>
<td>1,97</td>
<td>8,22</td>
<td>1,31</td>
<td>-0,5%</td>
<td>0,02</td>
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<tr>
<td>Repl. 3</td>
<td>7,86</td>
<td>1,89</td>
<td>8,22</td>
<td>1,31</td>
<td>-4,4%</td>
<td>0,16</td>
<td></td>
</tr>
<tr>
<td><strong>Cl-36</strong></td>
<td><strong>A(Cl-36) / Bq</strong></td>
<td><strong>UA(Cl-36) / Bq</strong></td>
<td><strong>A(Cl-36) / Bq</strong></td>
<td><strong>UA(Cl-36) / Bq</strong></td>
<td><strong>Bias / %</strong></td>
<td><strong>E_n</strong></td>
<td></td>
</tr>
<tr>
<td>Repl. 1</td>
<td>8,97</td>
<td>1,05</td>
<td>9,44</td>
<td>0,94</td>
<td>-5,1%</td>
<td>0,34</td>
<td></td>
</tr>
<tr>
<td>Repl. 2</td>
<td>9,11</td>
<td>1,06</td>
<td>9,44</td>
<td>0,94</td>
<td>-3,5%</td>
<td>0,23</td>
<td></td>
</tr>
<tr>
<td>Repl. 3</td>
<td>9,12</td>
<td>1,06</td>
<td>9,44</td>
<td>0,94</td>
<td>-3,5%</td>
<td>0,23</td>
<td></td>
</tr>
</tbody>
</table>

Comparison determined vs. reference activities, water, 3 replicates, bias and $E_n$, $k=2$

- Overall good agreement, slight negative bias for Cl-
Spiked samples II – effluents (Subatech)

- 4 spiked effluent samples
  - Cl 0: Blank sample
  - Cl 1 and Cl2: No I-129, identical Cl-36 activities
  - Cl 3: Cl-36 / I-129 activity ratio 1:1
  - Cl 4: Cl-36 / I-129 activity ratio 1:10

- Preparation loading solutions:
  - 2.5 mL Standard solution (Cl1 – Cl4)
  - 0.5 mL 0.1M NaCl and 0.5 mL 0.1M NaI
  - 6.5 mL 1M H₂SO₄

- Cl fraction collected, 5 mL 0.1M NaSCN added

- 10 mL Cocktail

- LSC (TriCarb 3170TR/SL, 12 – 250 keV, 60min)
Spiked samples II – effluents (Subatech)

Column loading

Cl⁻ elution
### Spiked samples II – effluents (Subatech)

<table>
<thead>
<tr>
<th>Sample</th>
<th>CI-36 Theoretical activity</th>
<th>I-129 Theoretical activity</th>
<th>Perkin Elmer TriCarb 3190TR/SL</th>
<th>Comparison of CI-36 activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (Bq.L⁻¹)</td>
<td>Uₐ (Bq.L⁻¹)</td>
<td>A (Bq.L⁻¹)</td>
<td>Uₐ (Bq.L⁻¹)</td>
</tr>
<tr>
<td>CI0</td>
<td>Blank</td>
<td>-</td>
<td>Blank</td>
<td>-</td>
</tr>
<tr>
<td>CI1</td>
<td>1.873E+04</td>
<td>6.556E+02</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>CI2</td>
<td>1.873E+04</td>
<td>6.556E+02</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>CI3</td>
<td>1.873E+04</td>
<td>6.556E+02</td>
<td>1.889E+04</td>
<td>5.100E+02</td>
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<td>CI4</td>
<td>1.873E+03</td>
<td>6.556E+01</td>
<td>1.897E+04</td>
<td>5.121E+02</td>
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</tbody>
</table>

Comparison determined vs. reference activities, effluents, bias and zeta test values

- Very good agreement between theoretical and obtained activity
- Repeatability CI1/CI2: 3.7% (N = 2, k = 1)
- Clean Cl/I separation
Spiked samples III – filter

- Filter samples (250 mg)
- Spiked with known activities of Cl-36 and I-129
- Extracted with 1M NaOH at 70°C for 4h
- Centrifugation, residue rinsed with 2 mL water
- Supernatants combined, adjusted to 1M H$_2$SO$_4$ and filled up to 50 mL
- Analysis of three 10 mL aliquots
- Average extraction and separation yields used for result calculation
Spiked samples III – filter

<table>
<thead>
<tr>
<th>Determined activities</th>
<th>Reference activities</th>
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<tr>
<td>$^{129}\text{I}$</td>
<td>$^{129}\text{I}$</td>
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<td>$A_{0}^{(129}\text{I}), \text{ Bq}$</td>
<td>$A_{0}^{(129}\text{I}), \text{ Bq}$</td>
</tr>
<tr>
<td>$U_{A(129}\text{I}), \text{ Bq}$</td>
<td>$U_{A(129}\text{I}), \text{ Bq}$</td>
</tr>
<tr>
<td>Bias, %</td>
<td>$E_{n}$</td>
</tr>
<tr>
<td>Repl. 1</td>
<td>7.89</td>
</tr>
<tr>
<td>Repl. 2</td>
<td>8.28</td>
</tr>
<tr>
<td>Repl. 3</td>
<td>7.58</td>
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<table>
<thead>
<tr>
<th>$^{36}\text{Cl}$</th>
<th>$^{36}\text{Cl}$</th>
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<tbody>
<tr>
<td>$A_{0}^{(36}\text{Cl}), \text{ Bq}$</td>
<td>$A_{0}^{(36}\text{Cl}), \text{ Bq}$</td>
</tr>
<tr>
<td>$U_{A(36}\text{Cl}), \text{ Bq}$</td>
<td>$U_{A(36}\text{Cl}), \text{ Bq}$</td>
</tr>
<tr>
<td>Bias, %</td>
<td>$E_{n}$</td>
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<tr>
<td>Repl. 1</td>
<td>9.58</td>
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<td>Repl. 2</td>
<td>9.20</td>
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<tr>
<td>Repl. 3</td>
<td>9.70</td>
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</tbody>
</table>

Comparison determined vs. reference activities, filter, 3 replicates, bias and $E_{n}$, k=2

- Overall good agreement, slight negative bias for $^{129}\text{I}$.
On-going work

- Combined use of Raddec Pyrolyser and Cl resin
  - Co-operation with Raddec (UK)
  - Presentation P. Warwick at 11th ERA next week

- Analysis of real samples and comparison with other methods
  - Co-operation with Subatech (France)

- ‘Beta testing‘ by different labs
  - If you are interested in participating please contact us!
Summary

- Cl-resin selective for Pd and Ag (Pt, Hg and Au)
  - Method robust against potential interferences

- Method for the separation of $^{36}\text{Cl}$ and $^{129}\text{I}$ presented
  - Applies to chloride and iodide
  - Reduction with Sn(II)

- Clean Cl$^-$ / I$^-$ separation

- Analysis of spiked samples showed overall good agreement
Thank you for your attention!