36Cl measurement in stainless steel by liquid scintillation counting

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OUTLINE

✓ Context of the study

✓ Radioanalytical process

✓ Validation

✓ Conclusion
CONTEXT OF THE STUDY

RADIOANALYTICAL PROCESS

VALIDATION

CONCLUSION
**CONTEXT OF THE STUDY**

- Dismantling of 1\textsuperscript{st} French generation nuclear reactors (UNGG)
  - Large volume of radioactive waste

- \( ^{36}\text{Cl} \) is a long-lived (3.01 \( \times 10^5 \) y) beta-emitting radionuclide produced from neutron activation of naturally occurring \( ^{35}\text{Cl} \)

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Acceptance limit (Bq.g(^{-1})) for surface disposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{3}\text{H} )</td>
<td>( 2 \times 10^5 )</td>
</tr>
<tr>
<td>( ^{60}\text{Co} )</td>
<td>( 1.3 \times 10^8 )</td>
</tr>
<tr>
<td>( ^{137}\text{Cs} )</td>
<td>( 3.3 \times 10^5 )</td>
</tr>
<tr>
<td>( ^{14}\text{C} )</td>
<td>( 9.2 \times 10^4 )</td>
</tr>
<tr>
<td>( ^{36}\text{Cl} )</td>
<td>( 5 )</td>
</tr>
<tr>
<td>( ^{63}\text{Ni} )</td>
<td>( 3.2 \times 10^6 )</td>
</tr>
<tr>
<td>( ^{55}\text{Fe} )</td>
<td>( 6.1 \times 10^9 )</td>
</tr>
<tr>
<td>( \Sigma ) alpha-emitters</td>
<td>( 3.7 \times 10^3 )</td>
</tr>
</tbody>
</table>

**ANDRA**: radioactive waste management agency in France

\( ^{36}\text{Cl} \leq 5\text{Bq/g} \)

1 mg/g \( ^{35}\text{Cl} \) \( \rightarrow \) 0.03 to 91 Bq/g \( ^{36}\text{Cl} \) (depends on neutron flux)
Limitations:

- Activated product Total digestion is required
- Lack of data on stable Cl 200 samples collected to obtain good statistical data
  Minimal experimental time for radiochemistry
- Required limit of detection <5 Bq/g
- Samples can be highly radioactive should be implemented in a glove box
- Pure beta emitters Separation from matrix and interference prior to the measurement
  Radioanalytical process must be developed
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Based on the existing standard method (AFNOR M60-332, May 2010), a protocol has been developed:

1. **Dissolution of steel**
   - Optimisation of the solution composition for complete digestion of steel to minimize the quantity of stable Cl

2. **Chlorine extraction**
   - Optimisation of the trapping solution for preliminary measurements (establishment of a first screening of sample)

3. **Radiochemical separation**

4. **$^{36}$Cl Liquid scintillation measurement**
   - Optimisation of the scintillation cocktail
provide the complete dissolution of the sample by minimizing the amount of stable chlorine

used KCl instead of HCl

optimal solution to dissolve 0.2 g of stainless steel is 8 mL of 69% HNO₃ and 1.8 g of KCl

28 mmol of Cl : high salt concentration
Chlorine extraction and optimisation of the trapping solution

Two constraints:

- The volume of the trapping solution must be minimal to have a good limit of detection.
- The trapping solution must be compatible with scintillation cocktails for preliminary measurements by LSC.

For the trap flask, 2 trapping solutions tested:

- NaOH 3.8 M (10 ml)
- Na₂CO₃ + H₂O₂ + H₂O (30 ml)
Chlorine extraction and optimisation of the trapping solution

NaOH

- nitrous vapor trapped in the trap flask
- progressive coloration of the trapping solution
2 Chlorine extraction and optimisation of the trapping solution

NaOH

- nitrous vapor trapped in the trap flask
- progressive coloration of the trapping solution

quenching

Na₂CO₃ + H₂O₂ + H₂O

- no nitrous vapor in the trap flask
- no quenching
2 Chlorine extraction and optimisation of the trapping solution

- trapping of $^{14}$C: problem of specificity

<table>
<thead>
<tr>
<th>Trapping solution</th>
<th>LS trap bottle (Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>stainless steel 1</td>
<td>NaOH</td>
</tr>
<tr>
<td></td>
<td>18 000</td>
</tr>
</tbody>
</table>
Cl radioanalytical process

2 Chlorine extraction and optimisation of the trapping solution

<table>
<thead>
<tr>
<th>Trapping solution</th>
<th>LS trap bottle after radiochemistry (Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>18 000</td>
</tr>
<tr>
<td>NaOH</td>
<td>6</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>2 300</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>6</td>
</tr>
</tbody>
</table>

Removal of $^{14}$C trapped in the trap flask by acidification
Chlorine extraction and optimisation of the trapping solution

Trapping solution

Trapping solution after $^{14}\text{C}$ removal

Optimal solution: 10 ml Na$_2$CO$_3$ + 5 ml H$_2$O$_2$ + 15 ml H$_2$O
Precipitation of AgCl by addition of AgNO₃

Dissolution of AgCl into NH₄OH

Elimination of Ag by reduction of Ag⁺ with N₂H₅⁺, HSO₄⁻

Elimination of sulphate by BaSO₄ precipitation

Volume reduction by evaporation from 150mL to 10mL

Yield: 90%

AgCl

Ag, NH₄⁺, Cl⁻

NH₄⁺, Cl⁻, SO₄²⁻

NH₄⁺, Cl⁻, NO₃⁻

NaNO₃ 2.3 M
NaCl 1.3 M
Liquid scintillation measurement

Choice of LSC cocktail

At the end of the radioanalytical process: NaNO₃ + NaCl 2 mol/L

LSC Cocktail tested in the laboratory: Ultimagold LLT® / Ultimagold XR®
§\textsuperscript{36}Cl Liquid scintillation measurement

- 15 ml Ultimagold XR ®
  - 5 ml of (NaNO\textsubscript{3} 2.3 M + NaCl 1.3M)

- Establishment of the quenching curve
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Application of the French AFNOR NF T90-210 standard

norme française

NF T 90-210
Mai 2009

Indice de classement : T 90-210
ICS : 03.120.30 ; 13.060.50 ; 13.060.60

Qualité de l'eau

Protocole d'évaluation initiale des performances d'une méthode dans un laboratoire

E : Water quality — Protocol for the initial method performance assessment in a laboratory

“B test” : method to check whether a presupposed Limit of Quantification can be acceptable
1. Presuppose a limit of quantification LOQ

2. Choice of a representative sample without $^{36}\text{Cl}$:

3. Spike the sample with LOQ presupposed:

4. Protocol repeated to be in intermediate fidelity conditions.
1. Presuppose a limit of quantification LOQ

\[
LOQ_{\text{detection}} \approx 3LD \approx 3 \times 4 \times \sqrt{\frac{2 \times \text{CPM}_{\text{MP}} \times T}{60 \times T \times \text{Eff}}} 
\]

\[
LOQ_{\text{méthode}} \approx \text{yield} \times LOQ_{\text{detection}}
\]

LOQ \approx 0.35 \text{ Bq}

2. Choice of a representative sample without $^{36}\text{Cl}$ :

3. Spike the sample with LOQ presupposed :

4. Protocol repeated four times and the measurement has been performed on two distinct scintillation counter
1. Presuppose a limit of quantification LOQ

\[ \text{LOQ}_{\text{detection}} \approx 3LD \approx 3 \times 4 \times \frac{\sqrt{2 \times CPM_{MP} \times T}}{60 \times T \times \text{Eff}} \]

\[ \text{LOQ}_{\text{methode}} \approx \text{yield} \times \text{LOQ}_{\text{detection}} \]

\[ \text{LOQ} \approx 0.35 \text{ Bq} \]

2. Choice of a representative sample without \(^{36}\text{Cl} \):

**stainless steel 316, 200 mg**

3. Spike the sample with LOQ presupposed:

4. Protocol repeated four times and the measurement has been performed on two distinct scintillation counters.
1. Presuppose a limit of quantification LOQ

\[ \text{LOQ}_{\text{detection}} \approx 3 \times 4 \times \frac{\sqrt{2 \times CPM_{MP} \times T}}{60 \times T \times \text{Eff}} \]

\[ \text{LOQ}_{\text{methode}} \approx \text{yield} \times \text{LOQ}_{\text{detection}} \]

\[ \text{LOQ} \approx 0.35 \text{ Bq} \]

2. Choice of a representative sample without \(^{36}\text{Cl}\) :

**stainless steel 316, 200 mg**

3. Spike the sample with LOQ presupposed :

**labeled KCl \(^{36}\text{Cl}\)**

4. Protocol repeated four times and the measurement has been perform on two distinct scintillation counters
The presupposed LOQ is valid if:

$$z_{LOQ} - 2 \times s_{LOQ} > LOQ - 60\% \times LOQ$$
$$z_{LOQ} + 2 \times s_{LOQ} < LOQ + 60\% \times LOQ$$
the presupposed LOQ 0.35Bq is valid (1.75 Bq/g)

$$\text{LOD} = \frac{\text{LOQ}}{3} = 0.6 \text{ Bq/g} \quad \llll 5 \text{ Bq/g}$$
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Measurement of $^{36}$Cl in steel sample with a validated procedure

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weigh (g)</th>
<th>Activity (Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>0,9</td>
<td>&lt;0,4</td>
</tr>
<tr>
<td>Sample 2</td>
<td>0,2</td>
<td>&lt;1,8</td>
</tr>
<tr>
<td>Sample 3</td>
<td>0,09</td>
<td>4 (23%)</td>
</tr>
<tr>
<td>Sample 4</td>
<td>0,05</td>
<td>6 (33%)</td>
</tr>
</tbody>
</table>

Improvement of the limit of detection for steel materials:
- alternative dissolution with less stable chlorine (HBr)
- alternative detection: measurement by AMS
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