Determination of $^{36}\text{Cl}$ in decommissioning samples using a Pyrolyser furnace and extraction chromatographic separations

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Origin of $^{36}\text{Cl}$

- $^{36}\text{Cl}$ is predominantly produced via neutron activation of naturally occurring $^{35}\text{Cl}$.

- $^{36}\text{Cl}$ is a long lived ($3.02 \times 10^5$ y) beta emitting radionuclide ($E_{\text{max}} = 709.6$ keV).

- $^{36}\text{Cl}$ is present in nuclear graphite, concretes, ion exchange resins & desiccants.

- Characterisation of $^{36}\text{Cl}$ in nuclear wastes is important due to its mobility in the geosphere and high soil – plant transfer factor.
Current approaches

• Alkaline digestion followed by chemical separation.

• Acid digestion and volatilisation of $^{36}$Cl.

• Thermal decomposition of the sample (with or without modifiers) and liberation of Cl species as HCl or Cl$_2$.

• Final measurement of $^{36}$Cl by liquid scintillation counting (high counting efficiency).

• Potential interferences from $^3$H, $^{14}$C, $^{35}$S, $^{129}$I.
Proposed separation

- Thermal decomposition of the sample and desorption of Cl species.

- Samples heated to 900°C in a tube furnace using a controlled heating cycle (10°C/min to 900°C and held for 60 minutes – total time 2 hrs).

- Moist air used to flush system. Sample moistened with 1ml water.

- Combustion products trapped in an alkaline trap. Bubbler connected to furnace tube using ground glass joints.

- $^{36}$Cl isolated from other radionuclides using Triskem ‘Cl resin’ conditioned with AgNO$_3$

- Total volume of eluent mixed with scintillation cocktail for liquid scintillation analysis.
Thermal desorption of $^{36}\text{Cl}$

Chlorine-36 standard as NaCl

Bubbler (20ml 6mM Na$_2$CO$_3$) changed at 100°C intervals
Recovery of standards

Results for replicate standard analyses

Mean recovery = 86%
(all in 1st bubbler)

Blanks run between samples
Carry over between samples < 0.1%
Residual activity in sample boat ~ 0.3%
Trapping of Cl species

- $^{36}\text{Cl}$ liberated as either $\text{Cl}_2$ or HCl.
- Trapped in 20ml 6 mM Na$_2$CO$_3$ (bubblers 1+2) or 1M NaOH (bubbler 3)
- Air flow rate 200 ml/min
# Characterisation of the Cl resin

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

<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>

$D_w$ values for different KSCN concentrations

<table>
<thead>
<tr>
<th>KSCN conc.</th>
<th>$D_w$ elution</th>
<th>$D_w$ elution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01M</td>
<td>1.7</td>
<td>12000</td>
</tr>
<tr>
<td>0.05M</td>
<td>0.4</td>
<td>15000</td>
</tr>
<tr>
<td>0.1M</td>
<td>0.7</td>
<td>4000</td>
</tr>
<tr>
<td>0.2M</td>
<td>0.4</td>
<td>9000</td>
</tr>
</tbody>
</table>

$D_w$ values for different Na$_2$S concentrations

<table>
<thead>
<tr>
<th>Na$_2$S conc</th>
<th>Mean $D_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04M</td>
<td>40</td>
</tr>
<tr>
<td>0.09M</td>
<td>15</td>
</tr>
<tr>
<td>0.18M</td>
<td>0.7</td>
</tr>
<tr>
<td>0.35M</td>
<td>0.8</td>
</tr>
</tbody>
</table>

- quantative uptake of both isotopes by silver loaded Cl-resin
- $^{36}\text{Cl}$ is eluted quantatively at any KSCN concentration
- $^{129}\text{I}$ remains on the resin at any KSCN concentration
- $^{129}\text{I}$ is eluted at elevated Na$_2$S concentrations
Chloride loading capacity

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Theoretical value</th>
<th>Experimental value</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-</td>
<td>14.9mg</td>
<td>16.3±1.6mg</td>
</tr>
<tr>
<td>Cl-</td>
<td>4.2mg</td>
<td>4.3 ±0.2mg</td>
</tr>
</tbody>
</table>

Loadings are dependent on the quantity of Ag initially loaded onto the resin. Above values are based on 13mg Ag loading.

Data from Alexander Zulauf, Philipps Universitat, Marburg
Separation of $^{36}\text{Cl}$ and $^{129}\text{I}$ from 1M NaOH
Separation from 6 mM Na$_2$CO$_3$

Water wash
Load (6mM Na$_2$CO$_3$)
Water wash
1M NaOH wash

Elute 0.1M NH$_4$SCN
Elute 0.35M Na$_2$S

Cl recovery 98%
Decontamination factors (I)

The graph shows the percentage recovery of 
$^{14}$C and $^3$H, with the following steps:

- **Load**
- **H$_2$O wash**
- **Cl elute**
- **NaOH wash**
- **I elute**

Each step is represented by bars, with the height indicating the percentage recovery. The x-axis represents the fraction, with values ranging from 1 to 10 (5ml each). The y-axis represents the percentage recovery, ranging from 0 to 30.

The colors used for the recovery are:
- Light blue for $^{14}$C
- Maroon for $^3$H
Decontamination factors (II)

Additional 0.1M H$_2$SO$_4$ wash stage added to remove $^{14}$C
## Decontamination factors

<table>
<thead>
<tr>
<th></th>
<th>$^{36}\text{Cl}$ fraction</th>
<th>$^{129}\text{I}$ fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\text{HTO}$</td>
<td>&gt; 500</td>
<td>&gt; 2000</td>
</tr>
<tr>
<td>$^{14}\text{CO}_3$</td>
<td>7</td>
<td>5000</td>
</tr>
<tr>
<td>$^{14}\text{C}$ modified wash</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>$^{35}\text{S}$ modified wash</td>
<td>1500</td>
<td>1000</td>
</tr>
<tr>
<td>$^{36}\text{Cl}$</td>
<td></td>
<td>&gt; 2000</td>
</tr>
<tr>
<td>$^{129}\text{I}$</td>
<td>1300</td>
<td></td>
</tr>
</tbody>
</table>
Liquid scintillation analysis

• 5ml 0.1M NH₄SCN eluent mixed with 15ml Proflow P cocktail.

• Some cocktails contain additives which will reduce any residual Ag compounds co-eluted to elemental Ag resulting in a black solution unsuitable for liquid scintillation counting.

• Proflow P (Meridian) mixes well with the NH₄SCN eluent without reducing residual Ag⁺.

\[ y = 4 \times 10^{-6}x^3 - 0.0098x^2 + 7.6727x - 1903.7 \]
\[ R^2 = 0.9971 \]
## Limit of detection

<table>
<thead>
<tr>
<th>Sample mass (g)</th>
<th>1.0 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery %</td>
<td>86 %</td>
</tr>
<tr>
<td>Background CPM</td>
<td>11 cpm</td>
</tr>
<tr>
<td>Efficiency %</td>
<td>98 %</td>
</tr>
<tr>
<td>Count time (mins)</td>
<td>180 mins</td>
</tr>
<tr>
<td>LOD (Currie)</td>
<td>0.02 Bq/g</td>
</tr>
<tr>
<td>Sample type</td>
<td>Expected value</td>
</tr>
<tr>
<td>------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Ion exchange resin</td>
<td>4.1 kBq</td>
</tr>
</tbody>
</table>
Analysis of decommissioning samples

- Method tested using desiccant from a reactor site.

LSC spectra for bubbler solution (dominantly $^3$H)

LSC spectra for purified bubbler solution ($^{36}$Cl)
Benefits over existing approaches

• Rapid procedure with analysis requiring 1 day for 6 samples.

• The total bubbler volume is used in the final measurement increasing sensitivity.

• Applicable to decommissioning samples containing other volatile radionuclides.

• Potential for sequential separation and quantification of other volatile radionuclides.
Summary

• Initial studies indicate that $^{36}\text{Cl}$ is effectively liberated from solid matrices using thermal desorption.

• Other volatile radionuclides co-trapped with $^{36}\text{Cl}$ can be efficiently separated using Cl-resin. The resin will also isolate $^{129}\text{I}$.

• The combination of combustion and isolation of Cl using Cl-columns provides a rapid approach for the separation and purification of $^{36}\text{Cl}$ from solid matrices avoiding the need for time-consuming digestion procedures.

• The Cl and I fractions arising from the separation are readily miscible with commercially available liquid scintillation cocktails.

• Further studies are required to validate the technique and confirm that $^{36}\text{Cl}$ can be quantitatively extracted from the range of materials routinely analysed for $^{36}\text{Cl}$. 