Radioanalytical Chemistry in Decommissioning of Nuclear Facilities

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• Closed nuclear facilities:
  - 100 mines;
  - 90 commercial power reactor;
  - 250 research reactors
  - A number of fuel cycle facilities

A few of them was decommissioned, and most of them is on the way to be decommissioned.
Steps of decommissioning of nuclear facility

- Preparation (investigating the background radioactivity around NPP)
- Plant Cleanout
  - Removal of most radioactive component such as spent fuel elements, reactor internals, reactor vessel, etc. which is transferred for storage and disposal. (high level waste). (Evaluation of radioactivity before transferring)
- Decontamination
  - Removal of contamination from surfaces of facilities or equipment by chemical or mechanical methods, which can reduce the waste volume and active level in the waste. (Measurement of radioactivity to evaluation the decontamination, and estimation of radioactivity in the waste)
- Dismantling
  - Equipments within the facility are dismantled and classified by estimation of the radioactivity
- Demolition and site clearance
  - Buildings demolished and radioactive wastes removed to storage or disposal facilities after estimation of the radioactivity in the waste.
- Release of the site to alternative use (measure the radioactivity level in the released area)
Production of main radionuclides in nuclear reactors

- Long-lived fission products
  \[ ^{137},^{135}\text{Cs}, ^{106}\text{Ru}, ^{90}\text{Sr}, ^{99}\text{Tc}, ^{129}\text{I}, \text{etc.} \]

- Neutron activation products (long-lived)
  \[ ^{58,60}\text{Co}, ^{133}\text{Ba}, ^{134}\text{Cs}, ^{152,154,155}\text{Eu}, ^{3}\text{H}, ^{14}\text{C}, ^{36}\text{Cl}, ^{41}\text{Ca}, ^{63,69}\text{Ni}, ^{94}\text{Nb}, ^{55,59}\text{Fe}, ^{93}\text{Zr}, ^{93}\text{Mo}, ^{54}\text{Mn}, ^{110m}\text{Ag}, ^{238-241}\text{Pu}, ^{241}\text{Am}, ^{243,244}\text{Cm}, ^{237}\text{Np}, \text{etc.} \]
Waste samples and the relevant critical radionuclides for decommissioning

- **Graphite (reactor)**
  - $^3$H, $^{14}$C, $^{55}$Fe, $^{63}$, $^{59}$Ni, $^{60}$Co, $^{152}$Eu

- **Concrete (normal or heavy)**
  - $^{41}$Ca, $^{60}$Co, $^{55}$Fe, $^{63}$, $^{59}$Ni, $^{133}$Ba, $^{152}$Eu

- **Steel/stainless steel**
  - $^{55}$Fe, $^{63}$, $^{59}$Ni, $^{36}$Cl, $^{93}$Zr, $^{93}$Mo, $^{94}$Nb, $^{60}$Co, $^{152}$Eu, transuranics

- **Aluminium**
  - $^{60}$Co, $^{63}$Ni, $^{55}$Fe, $^{36}$Cl

- **Lead**
  - $^{60}$Co, $^{63}$Ni, $^{55}$Fe

- **Water**
  - $^3$H, $^{14}$C, $^{63}$Ni, $^{99}$Tc, $^{129}$I, $^{90}$Sr, $^{60}$Co, $^{137}$Cs, transuranics

- **Ion exchange resin**
  - $^{55}$Fe, $^{63}$, $^{59}$Ni, $^{14}$C, $^{99}$Tc, $^{36}$Cl, $^{93}$Zr, $^{93}$Mo, $^{94}$Nb, $^{90}$Sr, $^{129}$I, $^{137}$Cs, $^{60}$Co, $^{135}$Cs, transuranics
Main Radionuclides in the nuclear waste and used materials in the view of measurement

- **Gamma radionuclides**
  - $^{60}\text{Co}$, $^{133}\text{Ba}$, $^{137}\text{Cs}$, $^{134}\text{Cs}$, $^{106}\text{Ru}$, $^{152,154,155}\text{Eu}$, $^{58}\text{Co}$, $^{54}\text{Mn}$, $^{59}\text{Fe}$, $^{110m}\text{Ag}$, $^{94}\text{Nb}$, etc.
  - Easy to measure, No chemical separation

- **Beta Emitter**
  - $^{3}\text{H}$, $^{14}\text{C}$, $^{36}\text{Cl}$, $^{41}\text{Ca}$, $^{55}\text{Fe}$, $^{63}$, $^{59}\text{Ni}$, $^{90}\text{Sr}$, $^{99}\text{Tc}$, $^{129}\text{I}$, $^{93}\text{Zr}$, $^{93}\text{Mo}$.
  - Difficult to measure, separation of individual radionuclide from matrix and all other radionuclides is needed before measurement.

- **Alpha emitter (actinides)**
  - $^{238-241}\text{Pu}$, $^{241}\text{Am}$, $^{243,244}\text{Cm}$, $^{237}\text{Np}$, etc.
  - High toxicity, difficult to measure, separation of individual radionuclide from matrix and all other radionuclides is needed.
Radioanalytical Chemistry of important radionucleides for decommissioning

- $^3\text{H}$ and $^{14}\text{C}$
- $^{41}\text{Ca}$ and $^{90}\text{Sr}$
- $^{36}\text{Cl}$ and $^{129}\text{I}$
- $^{99}\text{Tc}$
- $^{55}\text{Fe}$ and $^{63}\text{Ni}$
- Transuranics (Pu isotopes, $^{237}\text{Np}$)
Determination of $^3$H and $^{14}$C in graphite, concrete, and other solid materials

- **Production of $^3$H in reactor**
  - $^2$H (n, $\gamma$)$^3$H
  - $^6$Li(n, $\alpha$)$^3$H
  - $^3$He(n, p)$^3$H

- **Production of $^{14}$C in reactor**
  - $^{13}$C(n, $\gamma$)$^{14}$C
  - $^{14}$N(n, p)$^{14}$C
  - $^{17}$O(n, $\alpha$)$^{14}$C
Properties of C-14 and H-3

<table>
<thead>
<tr>
<th>Nuclides</th>
<th>Half life</th>
<th>Decay</th>
<th>Energy, keV</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H</td>
<td>12.35 y</td>
<td>β</td>
<td>18.6</td>
<td>LSC</td>
</tr>
<tr>
<td>$^{14}$C</td>
<td>5736 y</td>
<td>β</td>
<td>156</td>
<td>LSC</td>
</tr>
</tbody>
</table>

Measurement of C-14 and H-3

- Low energy
  
  Liquid Scintillation Counter

- Continuous spectrum
  
  Separation before measurement
Separation of $^3$H, $^{14}$C by combustion

- Flask 1: $^3$H, $^{129}$I, $^{99}$Tc
- Flask 2,3: $^{14}$C, $^{129}$I

- Time consuming: (2-4 hours is needed for decomposition of sample.
- Large volume of absorption solution worsen the detection limit.
Rapid separation of $^3$H and $^{14}$C waste samples by combustion using Packard Oxidizer
**3H and 14C in concrete and graphite**

No other impurity nuclides were seen in the H-3 and C-14 spectrum.

**3H and 14C in graphite and their stability**

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>code</th>
<th>15-01-2003 (first measurement)</th>
<th>Room temperature 4 months</th>
<th>110 °C for 5 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average</td>
<td>SD %</td>
<td>Average</td>
</tr>
<tr>
<td>C-14</td>
<td>TK5.5 Yi</td>
<td>2,12E+02</td>
<td>4,50</td>
<td>2,08E+02</td>
</tr>
<tr>
<td>C-14</td>
<td>TK7.5 Yi</td>
<td>2,67E+04</td>
<td>2,19</td>
<td>2,54E+04</td>
</tr>
<tr>
<td>H-3</td>
<td>TK5.5 Yi</td>
<td>4,70E+03</td>
<td>17,33</td>
<td>4,72E+03</td>
</tr>
<tr>
<td>H-3</td>
<td>TK7.5 Yi</td>
<td>1,11E+06</td>
<td>3,39</td>
<td>1,05E+06</td>
</tr>
</tbody>
</table>
### $^{41}$Ca in concrete

Activation products of calcium isotopes

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Target isotope Abundance %</th>
<th>Reaction</th>
<th>Cross section, bar</th>
<th>Half life</th>
<th>Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{41}$Ca</td>
<td>96.94</td>
<td>$^{40}$Ca(n, $\gamma$)$^{41}$Ca</td>
<td>0.41</td>
<td>$1.03 \times 10^5$ y</td>
<td>EC</td>
</tr>
<tr>
<td>$^{45}$Ca</td>
<td>2.086</td>
<td>$^{44}$Ca(n, $\gamma$)$^{45}$Ca</td>
<td>0.84</td>
<td>162.7 d</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>$^{47}$Ca</td>
<td>0.004</td>
<td>$^{46}$Ca(n, $\gamma$)$^{47}$Ca</td>
<td>0.7</td>
<td>4.54 d</td>
<td>$\beta, \gamma$</td>
</tr>
<tr>
<td>$^{49}$Ca</td>
<td>0.187</td>
<td>$^{48}$Ca(n, $\gamma$)$^{49}$Ca</td>
<td>1.0</td>
<td>8.72 min.</td>
<td>$\beta, \gamma$</td>
</tr>
</tbody>
</table>

$^{41}$Ca (21.03x10$^5$y)

$^{41}$Ca (21.03x10$^5$y)

EC (421.4 keV, 100%)

$^{41}$K (stable)

Energy of X-rays and Auger electrons: 0.3-3.6 keV

Determination: X-ray spectrometry (<0.08%)

LSC (10-20%)
Ca, Sr and Ba: Alkline earth element
**Determination $^{41}$Ca in concrete**

- **Separation from matrix**
  - Decomposition of heavy concrete by alkali fussion
  - Leaching Ca by acids

- **Separation from active metals such as $^{60}$Co, $^{152}$Eu, $^{55}$Fe, $^{63}$Ni, $^{65}$Zn, $^{54}$Mn, $^{51}$Cr, etc.**
  - Precipitation with Fe(OH)$_3$ by hydroxides at pH 9

- **Separation from other alkaline metals, such as $^{133}$Ba, $^{226}$Ra and $^{90}$Sr.**
  - BaCrO$_4$ and SrCrO$_4$ precipitation
  - BaCl$_2$ and SrCl$_2$ precipitation in HCl solution
  - Ca(OH)$_2$ precipitation in NaOH solution

Concrete in the reactor
- Ordinary concrete
- Heavy concrete (50-70% BaSO$_4$ was added)
 Decomposition of concrete for $^{41}$Ca and other radionuclides

- For Ordinary concrete, silicates of calcium does not easily be decomposed by acids.

- For heavy concrete, some calcium exists as CaSO$_4$, which does not dissolve by acid.

- Alkaline fusion have to be used for the decomposition of concrete for the determination of calcium isotopes.

**Flowchart:**

1. Concrete
   - Add Na$_2$CO$_3$/NaOH, fuse at 700 °C for 2-3 hours
2. Fused sample
   - Leaching with water, filter through a filter paper and wash with water
   - Precipitate, CaCO$_3$, BaCO$_3$
   - Dissolve with HCl
   - Solution, CaCl$_2$
   - Separation procedure
   - Fitrate, Na, K, Mg, Al, SO$_4^{2-}$ etc.
Separation of Ca and Sr from other metals by hydroxides precipitation

<table>
<thead>
<tr>
<th>Element</th>
<th>Recovery, %</th>
<th>Element</th>
<th>Decontamination factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>97.7±3.9</td>
<td>$^{137}\text{Cs}$</td>
<td>(4.5±0.3)×10^5</td>
</tr>
<tr>
<td>$^{85}\text{Sr}$</td>
<td>97.9±2.1</td>
<td>$^{60}\text{Co}$</td>
<td>(1.2±0.4)×10^5</td>
</tr>
<tr>
<td>$^{133}\text{Ba}$</td>
<td>97.3±2.8</td>
<td>$^{152}\text{Eu}$</td>
<td>(8.5±0.5)×10^5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{59}\text{Fe}$</td>
<td>(2.5±0.1)×10^5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{63}\text{Ni}$</td>
<td>(2.5±0.2)×10^5</td>
</tr>
</tbody>
</table>
The new method for the separation of Ca from Sr and Ba

- Separation of Sr from Ca by Ca(OH)$_2$ precipitation
  - Ca(OH)$_2$: insoluble, $K_{sp} = 5.2 \times 10^{-6}$
  - Sr(OH)$_2$ and Ba(OH)$_2$: Soluble in alkine solution

Precipitate Ca as Ca(OH)$_2$ at 0.5 – 0.8 mol/l NaOH, repeat 3 times, 85% Ca can be recovered, and the decontamination factor for Sr and Ba are higher than $5 \times 10^4$
Separation of Ca from Sr and Ba by 3 repeated steps of Ca(OH)$_2$ precipitations at different NaOH concentrations

<table>
<thead>
<tr>
<th>[NaOH] (mol/l)</th>
<th>Decontamination factor, 3 precipitations</th>
<th>Recovery of Ca, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ba</td>
<td>Sr</td>
</tr>
<tr>
<td>0.10</td>
<td>$6.54 \times 10^4$</td>
<td>$6.54 \times 10^4$</td>
</tr>
<tr>
<td>0.15</td>
<td>$6.33 \times 10^4$</td>
<td>$5.17 \times 10^4$</td>
</tr>
<tr>
<td>0.20</td>
<td>$5.37 \times 10^4$</td>
<td>$4.97 \times 10^4$</td>
</tr>
<tr>
<td>0.30</td>
<td>$5.01 \times 10^4$</td>
<td>$4.57 \times 10^4$</td>
</tr>
<tr>
<td>0.40</td>
<td>$4.62 \times 10^4$</td>
<td>$4.47 \times 10^4$</td>
</tr>
<tr>
<td>0.50</td>
<td>$4.71 \times 10^4$</td>
<td>$4.42 \times 10^4$</td>
</tr>
<tr>
<td>0.60</td>
<td>$4.71 \times 10^4$</td>
<td>$4.37 \times 10^4$</td>
</tr>
<tr>
<td>0.80</td>
<td>$4.51 \times 10^4$</td>
<td>$4.10 \times 10^4$</td>
</tr>
<tr>
<td>1.50</td>
<td>$4.19 \times 10^4$</td>
<td>$3.77 \times 10^4$</td>
</tr>
<tr>
<td>2.00</td>
<td>$3.81 \times 10^4$</td>
<td>$3.18 \times 10^4$</td>
</tr>
</tbody>
</table>
Procedure for simultaneous Fe, Ni, Sr and determination of $^{41}$Ca

Concrete

- Leaching with HCl + HNO$_3$ at heating, filter

Residue, Silicate, BaSO$_4$

- Filtrate, (metals, Ca, Sr, etc)

Precipitate, M(OH)$_x$

For $^{55}$Fe and $^{63}$Ni

- Add Fe carrier, Add NaOH to pH9, centrifuge

Filtrate, Cs, K

- Add Na$_2$CO$_3$, centrifuge

Precipitate, Ca, Sr, Ba

Supernatant, Sr, Ba, Ra

- Add NaOH to 0.5 mol/l, centrifuge

Supernatant, Sr, Ba

- Dissolve with HCl, add Fe$^{3+}$, and NaOH to pH9, centrifuge

Precipitate, Co, Eu, Fe

Supernatant Ca, Sr, Ba

- Add NaOH to 0.5 M, centrifuge, repeat

Precipitate $^{41}$Ca

- Add HCl to dissolve

$^{41}$Ca solution

LSC measurement

For $^{90}$Sr and $^{89}$Sr

Supernatant, Sr, Ba

- Add NaOH to 0.5 M, centrifuge, repeat

Precipitate Ca(OH)$_2$

- Add Na$_2$CO$_3$, centrifuge

Filtrate, Cs, K

- Add NaOH to pH9, centrifuge

Precipitate, Ca, Sr, Ba

Supernatant, Sr, Ba

- Add NaOH to 0.5 M, centrifuge

Precipitate M(OH)$_x$

- Add Na$_2$CO$_3$, centrifuge

Filtrate, Sr, Ba

- Add NaOH to pH9, centrifuge

Precipitate, Ca, Sr, Ba

Supernatant $^{41}$Ca

- Add HCl to dissolve
**41Ca in heavy concrete from DR-2**

**Sample Spectrum**

**Features of Method for 41Ca**

- A separation of 41Ca from concrete is **easy to operate**
- Good decontamination from interfering radionuclides (>10⁴)
- The **chemical yields** of the separation procedures for 41Ca is **80-90%**.
- The detection limits for 41Ca is **0.020 Bq**.

_Hou X.L., Radiochim Acta, 2005_
36Cl is long-lived radionuclides ($3 \times 10^5$ yrs)

36Cl decays mainly by pure beta emission of $E_{\text{max}} = 708.6$ keV.

36Cl measurement is normally carried out by LSC and AMS
Determination of $^{129}$I

- Liquid scintillation: $10^{12}$ (1 mBq)
- $\gamma$-spectrometry: $10^{14}$ (0.1 Bq)
- ICP-MS: $5 \times 10^{11}$
- Radiochemical neutron activation analysis: $10^8$
- Accelerator mass spectrometry (AMS): $10^6$

$^{129}$I (1.57x$10^7$ y)

$\beta^-$, 196 keV, 100%

$^{129m}$Xe, 8.88d

IC, 96.6%

$\gamma$, 39.6 keV, 3.4%

$^{129}$Xe (stable)
Analytical procedure of $^{36}$Cl and $^{129}$I

- Decomposition of sample to release Chlorine and iodine
- Separation of iodine from solution
- Purification of Cl from other radionuclides
- Measurement of $^{36}$Cl and $^{129}$I by LSC or other methods
Determination of $^{36}$Cl and $^{129}$I in graphite

--- Sample decomposition

- Ashing at 900°C: iodine and part of Cl are lost.
- Decomposition at 900°C with O$_2$ and trapping iodine in NaOH solution: good recovery for iodine, but not good for chlorine.
- Leaching with acid (HNO$_3$) at heating: not complete remove iodine and Cl from graphite, and loss of the leached iodine.
- Digestion with HNO$_3$ and trapping iodine and chlorine with NaOH: Not complete removal of iodine and chlorine.

- How to Do?
Determination of $^{36}$Cl and $^{129}$I in graphite
--- Sample decomposition

• Graphite can be completely dissolved in a mixture of acids: HNO$_3$+H$_2$SO$_4$ +HClO$_4$

• The optimal ratio of mixture is:
  $$\text{H}_2\text{SO}_4:\text{HNO}_3:\text{HClO}_4 = 15:4.1$$

• A closed dissolution system is used for dissolve graphite in heating, Cl on the condenser tube and trap solution, while iodine mainly in the trap solution.
Decomposition of sample to release chlorine and iodine

- Acid digestion (graphite, steel, Al, Pb,)
  - Graphite (H$_2$SO$_4$:HNO$_3$:HClO$_4$=15:4:1)
  - Steel, aluminum (8 mol/l H$_2$SO$_4$)
  - Lead (8 mol/l HNO$_3$)

Flask 9: $^3$H, $^{129}$I, $^{99}$Tc, $^{36}$Cl
Flask 10, 11: $^{14}$C, $^{129}$I,
Sample flask: non-volatile elements, Ca, Ni, Fe, Cs, Co, Ba, tritium, Cl, Tc, transuranics, etc.
Determination of $^{36}\text{Cl}$ and $^{129}\text{I}$ in concrete

--- Sample decomposition

- Leaching with acid (HNO$_3$) at heating: --- not complete remove iodine and Cl from graphite, and loss of the leached iodine.

- Digestion with HNO$_3$ and trapping iodine and chlorine with NaOH: ---- Not complete removal of iodine and chlorine

- Alkalinal fussion using NaOH and Na$_2$CO$_3$, dissolution of fused cake in water, the supernatant is used for $^{129}\text{I}$ and $^{36}\text{Cl}$: ---- sample is completely decomposed and iodine and Cl are released. Iodine and Cl are not lost in alkaline medium.
Determination of $^{36}\text{Cl}$ and $^{129}\text{I}$ in stainless steel
--- Sample decomposition

- Stainless steel is normally dissolved with HCl or HCl+HNO$_3$: --- could not be used for $^{36}\text{Cl}$ because of too much Cl in HCl is introduced.

- Single acid, HNO$_3$, could not dissolve stainless steel.

- 10M H$_2$SO$_4$ with H$_3$PO$_4$ is sucessfully used for dissolve stainless steel for$^{129}\text{I}$ and $^{36}\text{Cl}$: ---- sample is completely decomposed and iodine and Cl are released.
Separation procedure of iodine

Solid samples
- decompose sample by combustion, acid digestion, or alkali fusion

solution
- Extracting with CCl₄,
- Back-extracting with H₂SO₃, repeat

Iodide separated
- convert to MgI₂ or AgI

Iodine Sample

Measurement by LSC
- Gamma measurement
- AMS
Separation of Chlorine and iodine from matrices and other radionuclides

- Specific precipitation of Cl\(^{-}\) with Ag\(^{+}\) (AgCl) can be used to selectively separation of Cl from matrix and other radionuclides (except iodine and bromine).

- Iodine (\(^{129}\)I) should be first separated from the solution before AgCl precipitation.

- \(^{129}\)I can be separated by solvent extraction using CHCl\(_3\)

- No need to separate Br, since no long-lived radioisotopes of Br in the waste and environmental samples.

- The separated AgCl can be dissolved in NH\(_4\)OH and mixed with scintillation cocktail for LSC: But less AgCl can be used and high quench effect. How to improve?
Separation of Ag⁺ and Cl⁻ in anion exchange chromatography

100mg Cl, 0.2 M NH₄NO₃-0.6 M NH₄OH eluting
200mg Cl 0.2 M NH₄NO₃-0.6 M NH₄OH eluting
50 mg Cl, 0.1 M NH₄NO₃-0.6 M NH₄OH eluting
100 mg Cl, 0.1 M NH₄NO₃-0.6 M NH₄OH eluting
Combined Analytical procedure for $^{36}$Cl and $^{129}$I

**Graphite, steel**
- Add stable Cl and I carriers, dissolve with acids, combine the absorption solutions and dissolved solution
- AG 1×4 column
- Wash with NH$_3$
- Eluting with 0.1 M NH$_4$NO$_3$-0.6 M NH$_4$OH
- Washing, Ag$^+$ etc.
- Evaporate, dissolved with H$_2$O
- ICP-MS for Cl

**Heavy Concrete**
- Add stable Cl and I carriers and NaOH and Na$_2$CO$_3$, fuse at 500 °C, leaching with H$_2$O, centrifuge to separate the supernatant
- Add NaHSO$_3$, transfer to a separation funnels, add CCl$_4$, HNO$_3$, and NaNO$_2$ to extract, repeat the extraction
- Sodium phase, $^{129}$I
- Washing, Ag$^+$ etc.
- Evaporate, dissolved with H$_2$O
- ICP-MS for Cl

**Organic phase**
- Back-extract with NaHSO$_3$ solution, repeat extraction and back-extraction

**Aqueous phase, $^{129}$I**
- LSC for $^{129}$I

**Aqueous phase**
- AG 1×4 column
- Wash with NH$_3$
- Eluting with 0.1 M NH$_4$NO$_3$-0.6 M NH$_4$OH
<table>
<thead>
<tr>
<th>Element</th>
<th>AgCl precipitation</th>
<th>Anion exchange</th>
<th>Whole procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl (recovery, %)</td>
<td>96.5</td>
<td>98.3</td>
<td>94.7±3.2</td>
</tr>
<tr>
<td>I ($^{125}$I)</td>
<td>1.4 ×10$^3$</td>
<td>1.4 ×10$^3$</td>
<td>8.9 ×10$^5$</td>
</tr>
<tr>
<td>S</td>
<td>1.5 ×10$^3$</td>
<td></td>
<td>5.6 ×10$^5$</td>
</tr>
<tr>
<td>tritium</td>
<td>2.1 ×10$^3$</td>
<td></td>
<td>4.8 ×10$^6$</td>
</tr>
<tr>
<td>$^{14}$C ($CO_3^{2-}$)</td>
<td>1.5 ×10$^3$</td>
<td></td>
<td>2.8 ×10$^6$</td>
</tr>
<tr>
<td>Co ($^{60}$Co)</td>
<td>1.9 ×10$^3$</td>
<td>2.5 ×10$^3$</td>
<td>1.5 ×10$^6$</td>
</tr>
<tr>
<td>Eu ($^{152}$Eu)</td>
<td>4.7 ×10$^3$</td>
<td>6.5 ×10$^3$</td>
<td>8.9 ×10$^6$</td>
</tr>
<tr>
<td>Cs ($^{137}$Cs)</td>
<td>3.8 ×10$^3$</td>
<td>5.1 ×10$^3$</td>
<td>7.9 ×10$^6$</td>
</tr>
<tr>
<td>Ba ($^{133}$Ba)</td>
<td>6.7 ×10$^3$</td>
<td>4.9 ×10$^3$</td>
<td>5.6 ×10$^6$</td>
</tr>
<tr>
<td>Sr ($^{85}$Sr)</td>
<td>4.7 ×10$^3$</td>
<td>3.3 ×10$^3$</td>
<td>6.7 ×10$^6$</td>
</tr>
<tr>
<td>Ni ($^{63}$Ni)</td>
<td>5.9 ×10$^3$</td>
<td>3.8 ×10$^3$</td>
<td>4.8 ×10$^6$</td>
</tr>
<tr>
<td>Fe ($^{55}$Fe)</td>
<td>1.9 ×10$^3$</td>
<td>2.8 ×10$^3$</td>
<td>2.1 ×10$^6$</td>
</tr>
</tbody>
</table>
Recovery of chlorine in the chemical separation procedure measured from stable chlorine and $^{36}$Cl tracer

<table>
<thead>
<tr>
<th>Graphite g</th>
<th>form</th>
<th>Cl mg</th>
<th>measured, mg</th>
<th>Recovery %</th>
<th>Added Bq</th>
<th>measured Bq</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.210</td>
<td>NaCl</td>
<td>50</td>
<td>315.5</td>
<td>87.4</td>
<td>2.50</td>
<td>2.17</td>
<td>86.8</td>
</tr>
<tr>
<td>0.255</td>
<td>NaCl</td>
<td>50</td>
<td>368.9</td>
<td>92.3</td>
<td>2.50</td>
<td>2.13</td>
<td>91.2</td>
</tr>
<tr>
<td>0.195</td>
<td>NaClO$_3$</td>
<td>50</td>
<td>297.2</td>
<td>89.8</td>
<td>2.50</td>
<td>2.18</td>
<td>89.2</td>
</tr>
<tr>
<td>0.301</td>
<td>NaClO$_3$</td>
<td>50</td>
<td>305.7</td>
<td>96.5</td>
<td>2.50</td>
<td>2.20</td>
<td>97.0</td>
</tr>
</tbody>
</table>
Separated $^{36}$Cl from concrete-1

$T_c = 85000 \text{ s}$

$\gamma$-spectrum before separation, $T_c=6000\text{s}$

Fig. Gamma spectra of sample (graphite) before and after chemical separation of $^{36}$Cl
LSC spectrum of $^{129}$I and $^{36}$Cl in waste samples

$^{129}$I in swip from Ignalina NPP

$^{36}$Cl in Steel and graphite from DR-2
Effect of the medium of measurement solution to counting efficiency by LSC

![Graph showing the effect of Cl concentration on counting efficiency.](image1)

![Graph showing the effect of SQP(E) on counting efficiency.](image2)

200 mg Cl in NH₄NO₃
Performance of the procedure for $^{36}$Cl

- Recovery of Cl: $>70\%$
- Decontamination factors for most of radionculides: $>10^6$
- Detection limit using LSC : 14 mBq
- Decommissioning samples, concrete, graphite, stainless steel, aluminum, lead, have been successfully analysed for $^{36}$Cl.

_Hou et al., Anal. Chem., 2007_
Distribution of $^{36}\text{Cl}$ in the concrete core from DR-2 with comparison to $^{55}\text{Fe}$, and $^{63}\text{Ni}$

$^{36}\text{Cl}$ in 2 swip samples from Ignalina NPP

<table>
<thead>
<tr>
<th>Sample</th>
<th>Count rate, CPM</th>
<th>$^{36}\text{Cl}$ measured, Bq</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No.1</td>
<td>No.2</td>
</tr>
<tr>
<td>SWIPE-111-2</td>
<td>117.05</td>
<td>120.83</td>
</tr>
<tr>
<td>SWIPE-111-1</td>
<td>112.20</td>
<td>114.83</td>
</tr>
<tr>
<td>$^{36}\text{Cl}$-SWIPE-2-ST</td>
<td>226.90</td>
<td>227.51</td>
</tr>
<tr>
<td>BK</td>
<td>3.05</td>
<td>2.98</td>
</tr>
</tbody>
</table>
Combined analytical procedure for $^{36}$Cl, $^{129}$I, $^{41}$Ca, $^{90}$Sr, $^{63}$Ni, and $^{55}$Fe

**Aqueous phase,**
- Add $\text{CO}_2$, HNO$_3$ to pH2, add NaNO$_2$ to extract, repeat.
- Add NaHSO$_3$ solution to back-extract iodine
- Add 25% NH$_3$ to dissolve AgCl, add HNO$_3$ to pH2, centrifuge, washing precipitate with H$_2$O, repeat precipitate
- Load to column
  - Eluate $^{36}$Cl
  - Evaporate to 3 ml

**Organic phase,** I
- Add AgNO$_3$, centrifuge
- Supernatant, Cl, I, Cs, K
- Supernatant, Ca, Sr, Ba
- Precipitate M(OH)$_x$
- Add Na$_2$CO$_3$, centrifuge
- Dissolve with HCl, add NaOH to pH9, centrifuge
- Washing with 0.2 M NH$_4$Citr, Eluting with 3 M HNO$_3$
- Wash with 6 M HCl
- Elute with H$_2$O

**Concrete**
- Add Fe, Ni, Ca, Cl and I carriers and hold-back carriers, NaOH, Na$_2$CO$_3$ fuse at 500 ºC, leaching with water, centrifuge, washing precipitate with 0.2 M Na$_2$CO$_3$ for 4 times
- Precipitate (metals, Ca, Sr,)
- Dissolve with HCl, add NaOH to pH9, centrifuge
- Evaporate, dissolved with HCl, add NH$_4$Citr, NH$_2$OH to pH9, loading
- Evaporate; dissolve to 6 M HCl, loading
- Wash with 6 M HCl
- Elute with H$_2$O

**Eluate, $^{63}$Ni**
- Evaporate to dryness, dissolve with H$_3$PO$_4$
- LSC measurement for $^{36}$Cl, $^{129}$I, $^{41}$Ca, $^{63}$Ni, $^{55}$Fe
- ICP-MS or ICP-AES measurement for chemical yield of Cl, I, Ca, Ni, Fe AES
**99Tc analysis**

- Long half-life \((2.1 \times 10^5 \text{ y})\)
- High mobility \((\text{TcO}_4^-)\)
- High fission yield (about 6 %)
- Tc is a volatile element, and easily to be loss at high temperature.
- A pure beta emitter
- Measured by GM counter, LSC, and ICP-MS.
- It has to be separated from other radionuclides before measurement by beta counting, especially \(^{106}\text{Ru}\) and \(^{93}\text{Mo}\)
- Completely Removal of Ru \(^{99}\text{Ru}\) and Mo \((^{1\text{H}}^{98}\text{Mo})\) for ICP-MS.
Loss of $^{99}\text{Tc}$ in Solid sample in dry ashing

(samples ashed at different temperature for 6 h) (seaweed ashed at 700 °C; soil ashed at 550 °C)

- In seaweed, Tc is relatively stable when ashed at 700 °C for ≤ 14 h
- In soil, Tc starts to lost when ashed at > 550 °C
Loss of $^{99}$Tc in Solution evaporation

<table>
<thead>
<tr>
<th>Solution media</th>
<th>Yield of Tc after evaporation at different temperature (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 °C</td>
</tr>
<tr>
<td>25% NH$_3$·H$_2$O</td>
<td>97.0 ± 2.1</td>
</tr>
<tr>
<td>0.1 M NaOH</td>
<td>98.0 ± 0.8</td>
</tr>
<tr>
<td>0.01 M NaOH</td>
<td>98.4 ± 1.6</td>
</tr>
</tbody>
</table>

(The sample solutions were evaporated to dryness and then prepared for measurement)
Tc 的化学分离

- Adjust Tc to TcO$_4^-$ by K$_2$S$_2$O$_8$
- Separate Tc from transition metals, transuranics, Po etc by hydroxides, because TcO$_4^-$ can not be precipitate at high pH.
- TcO$_4^-$ can be tightly absorbed by anion exchange column, washing with NaOH and HNO$_3$ can remove most of interfering nuclides.
- Not satisfactory for removal Ru, and Mo
Two TEVA columns separation

- $K_d$ of TcO$_4^-$ decreased with increase of [HNO$_3$]
- Relatively high $K_d$ of MoO$_4^{2-}$ in low [HNO$_3$] (<1 M)
- RuO$_4^{2-}$ is insensitive with the variation of [HNO$_3$]

Graph showing the relationship between $K_d$ (mL/g) and HNO$_3$ (mol/L).
Decontamination of Mo and Ru

- One column is *not* enough
- Two TEVA columns
  1) High chemical yield of Tc
  2) Sufficient removal of Mo and Ru

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size</th>
<th>Chemical yield %</th>
<th>Mo (x10^4)</th>
<th>Ru (x10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Danish soil</td>
<td>10 g</td>
<td>78-85</td>
<td>(4.4 ± 0.3)</td>
<td>(1.0 ± 0.2)</td>
</tr>
<tr>
<td>Danish soil</td>
<td>100 g</td>
<td>65-75</td>
<td>(2.5 ± 0.2)</td>
<td>(1.1 ± 0.1)</td>
</tr>
<tr>
<td>Danish soil</td>
<td>500 g</td>
<td>60-68</td>
<td>(1.2 ± 0.1)</td>
<td>(5.1 ± 0.3)</td>
</tr>
</tbody>
</table>
**H₂O₂ 对Ru在TEAV柱上吸附的影响**

<table>
<thead>
<tr>
<th>Volume (mL)</th>
<th>Pre-treatment with H₂O₂</th>
<th>No H₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1M NaOH</td>
<td>H₂O</td>
</tr>
<tr>
<td>Sample loading</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.131</td>
<td>0.102</td>
</tr>
<tr>
<td>8</td>
<td>0.197</td>
<td>0.150</td>
</tr>
<tr>
<td>12</td>
<td>0.197</td>
<td>0.159</td>
</tr>
<tr>
<td>16</td>
<td>0.196</td>
<td>0.154</td>
</tr>
<tr>
<td>20</td>
<td>0.195</td>
<td>0.154</td>
</tr>
<tr>
<td>Washing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.067</td>
<td>0.054</td>
</tr>
<tr>
<td>8</td>
<td>&lt; 0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>12</td>
<td>&lt; 0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>16</td>
<td>&lt; 0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>20</td>
<td>&lt; 0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>Removal (%)</td>
<td>98</td>
<td>79</td>
</tr>
</tbody>
</table>

*Washing with 0.1 M HNO₃*
Procedure for solid sample analysis

Environmental solid samples

Seaweed
- Spike with $^{99m}$Tc
- Dry ashing at 700 °C for 3h
  - Leaching with 3 mol/L HCl and H$_2$O$_2$ at 70-90 °C
    - Add 100 mg Fe (FeCl$_3$ solution)
    - Add K$_2$S$_2$O$_3$ to reduce Tc to Tc$^{4+}$; add NaOH to pH 9-10 to coprecipitate TcO$_4$ with Fe(OH)$_3$; dissolve precipitate with HNO$_3$ and oxidize Tc$^{4+}$ to TcO$_4^-$ using H$_2$O$_2$; add NaOH to pH 9-10 to precipitate Fe(OH)$_3$ and separate the solution by centrifuge.

Soil or sediment
- Dry ashing at 550 °C for 3h
  - Leaching with 3 mol/L HCl and H$_2$O$_2$ at 70-90 °C

Sample pretreatment

Tc concentration

Separation and purification

Source preparation

Measurement

Measure $^{99m}$Tc for chemical yield

ICP-MS measurement of $^{99}$Tc
# Achievement

<table>
<thead>
<tr>
<th></th>
<th>Developed methods</th>
<th>Reported methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decontamination factor for Mo</td>
<td>$4 \times 10^4 \sim 1 \times 10^6$</td>
<td>$&lt; 5 \times 10^3$</td>
</tr>
<tr>
<td>Decontamination factor for Ru</td>
<td>$1 \times 10^5 \sim 7 \times 10^6$</td>
<td>$&lt; 1 \times 10^4$</td>
</tr>
<tr>
<td>Analytical time (h)</td>
<td>$&lt; 24$</td>
<td>$&gt; 30$</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>60-95</td>
<td>60-90</td>
</tr>
</tbody>
</table>
Chemistry and Analysis of Radionuclides
—Laboratory Techniques and Methodology

Jukka Lehto & Xiaolin Hou

- The comprehensive guide to radioactive elements, written by chemists for chemists
- Provides practical instructions for the every day work of radiochemists
- Introduces readers to the important laboratory techniques and methodologies in the field
- Includes details on how to determine radionuclides in nuclear waste and in the environment
- Essential reading for Radio and Nuclear Chemists, Geochemists, Masters’ and Doctoral Students