Radiochemical Analysis of $^3$H, $^{14}$C, $^{55}$Fe, $^{63}$Ni in Waste and Environmental Samples

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Radionuclides in the nuclear waste

- Gamma radionuclides
  \(^{60}\text{Co}, \, ^{133}\text{Ba}, \, ^{152,154,155}\text{Eu}, \, ^{137}\text{Cs}, \, ^{134}\text{Cs}, \, ^{106}\text{Ru}\)

- Beta Emitter
  \(^{3}\text{H}, \, ^{14}\text{C}, \, ^{63}\text{Ni}, \, ^{55}\text{Fe}, \, ^{36}\text{Cl}, \, ^{41}\text{Ca}, \, ^{90}\text{Sr}, \, ^{99}\text{Tc}, \, ^{129}\text{I}, \, ^{135}\text{Cs}, \, ^{94}\text{Nb}\)

- Alpha emitter (transuranics)
  \(^{238-241}\text{Pu}, \, ^{241}\text{Am}, \, ^{234,244}\text{Cm}, \, ^{237}\text{Np}\)
Waste samples and the relevant critical radionuclides in the decommissioning process:

- **Graphite (reactor)**
  - \(^3\text{H}, ^{14}\text{C}, ^{55}\text{Fe}, ^{63}, ^{69}\text{Ni}, ^{36}\text{Cl}, ^{152,154}\text{Eu}, ^{90}\text{Sr}, ^{137}\text{Cs}, ^{99}\text{Tc}\)

- **Concrete (normal or heavy)**
  - \(^3\text{H}, ^{14}\text{C}, ^{41}\text{Ca}, ^{133}\text{Ba}, ^{36}\text{Cl}, ^{60}\text{Co}, ^{41}\text{Ca}, ^{133}\text{Ba}, ^{134}\text{Cs}, ^{3}\text{H}, ^{14}\text{C}, ^{36}\text{Cl}, ^{60}\text{Co}, ^{55}\text{Fe}, ^{63}, ^{69}\text{Ni}, \text{transuranics}\)

- **Steel/stainless steel**
  - \(^{60}\text{Co}, ^{55}\text{Fe}, ^{63}, ^{69}\text{Ni}, ^{36}\text{Cl}, ^{152,152}\text{Eu}, ^{65}\text{Zn}, ^{151}\text{Sm}\)
  - \(^{60}\text{Co}, ^{55}\text{Fe}, ^{63}, ^{69}\text{Ni}, ^{36}\text{Cl}\)

- **Lead**
  - \(^{133}\text{Ba}, ^{60}\text{Co}, ^{63}\text{Ni}\)

- **Ion exchange resin**
  - \(^{137}\text{Cs}, ^{60}\text{Co}, ^{55}\text{Fe}, ^{63}\text{Ni}, ^{59}\text{Ni}, ^{14}\text{C}, ^{90}\text{Sr}, ^{129}\text{I}, ^{135}\text{Cs}, ^{99}\text{Tc}, \text{transuranics}\)
Tritium and $^{14}$C in the Environment

- **Source:**
  - Nuclear weapons testing in 1960’s
  - Discharge from reprocessing plants
  - Discharge from nuclear power plants

- **Investigation of Tritium and $^{14}$C in the environment**
  - Measurement of the contamination level from nuclear facility
  - $^{14}$C dating

- **Environmental Samples**
  - Water
  - plants (seaweed, grass, lichen, fish.)
  - soil, sediment
55\textit{Fe} and 63\textit{Ni} in the Environment

- Source:
  - Nuclear weapons testing in 1960’s
  - Discharge from reprocessing plants
  - Discharge from nuclear power plants

- Investigation of 63\textit{Ni} and 55\textit{Fe} in the environment
  - Measurement of the contamination level from nuclear facility
  - Using 55\textit{Fe} and 63\textit{Ni} released from nuclear facility as a tracer to study their environmental and chemical behaviours

- Environmental Samples
  - Water
  - plants (seaweed, grass, lichen, fish.)
  - soil, sediment
Content

• Rapid analytical method for the determination of $^3$H and $^{14}$C in graphit and concrete, and other solid samples

• Analytical method for the determination of $^{63}$Ni, $^{55}$Fe in waste samples (Steel, Al, lead, graphite and concrete) and environmental sample
Determination of $^3\text{H}$ and $^{14}\text{C}$ in graphite and concetre

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

- **Production of $^{14}\text{C}$ in reactor**
  - $^{13}\text{C}(n, \gamma)^{14}\text{C}$
  - $^{14}\text{N}(n, p)^{14}\text{C}$
  - $^{17}\text{O}(n, \alpha)^{14}\text{C}$
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 $^3\text{H}$, $^{14}\text{C}$ from solid waste by combustion method

- Flask 1: $^3\text{H}$, $^{129}\text{I}$, $^{99}\text{Tc}$
- Flask 2,3: $^{14}\text{C}$, $^{129}\text{I}$
Disadvantage of these method for the determination of $^{14}$C and $^3$H

- Time consuming: (3-4 hours is needed for decomposition of sample and 1-2 hours for separation and purification of $^{14}$C and $^3$H in the absorbed solution.)
- Additional purification procedure is needed.
- Worse detection limit, due to large volume of absorption solution
- High quench, due to high concentration acid or alkali solution is used.
- High risk acid (perchloric acid) is used.
Rapid separation of $^3$H and $^{14}$C waste samples by combustion using Packard Oxidizer
Problems?

• Cross contamination

• Efficiency of combustion (recovery)

• Impurity nuclides in separated fractions
### Decomposition of graphite and concrete for release C-14 and H-13 using Oxidizer

<table>
<thead>
<tr>
<th>sample</th>
<th>weight (mg)</th>
<th>$^3$H added (Bq)</th>
<th>$^{14}$C added (Bq)</th>
<th>$^3$H counts (CPM)</th>
<th>$^{14}$C counts (CPM)</th>
<th>Recovery or memory of $^3$H (%)</th>
<th>Recovery or memory of $^{14}$C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphite</td>
<td>106.03</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>12</td>
<td>0.01</td>
<td>94.09</td>
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<tr>
<td>graphite</td>
<td>55.95</td>
<td>0</td>
<td>0</td>
<td>16</td>
<td>13</td>
<td>0.02</td>
<td>105.50</td>
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<tr>
<td>graphite</td>
<td>41.2</td>
<td>0</td>
<td>0.47</td>
<td>11</td>
<td>13925</td>
<td>0.10</td>
<td>98.24</td>
</tr>
<tr>
<td>graphite</td>
<td>30.03</td>
<td>0</td>
<td>1.46</td>
<td>25</td>
<td>60960</td>
<td>0.02</td>
<td>100.42</td>
</tr>
<tr>
<td>graphite</td>
<td>34.76</td>
<td>0.4</td>
<td>0</td>
<td>12083</td>
<td>20</td>
<td>96.21</td>
<td>0.16</td>
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<tr>
<td>graphite</td>
<td>38.27</td>
<td>4.87</td>
<td>0</td>
<td>115038</td>
<td>24</td>
<td>93.07</td>
<td>0.02</td>
</tr>
<tr>
<td>concrete</td>
<td>35.23</td>
<td>0</td>
<td>0.47</td>
<td>16</td>
<td>12292</td>
<td>0.10</td>
<td>97.87</td>
</tr>
<tr>
<td>concrete</td>
<td>41.57</td>
<td>0</td>
<td>2.92</td>
<td>27</td>
<td>119809</td>
<td>0.02</td>
<td>96.93</td>
</tr>
<tr>
<td>concrete</td>
<td>38.35</td>
<td>0.4</td>
<td>0</td>
<td>12338</td>
<td>26</td>
<td>98.24</td>
<td>0.2</td>
</tr>
<tr>
<td>concrete</td>
<td>37.63</td>
<td>4.87</td>
<td>0</td>
<td>124118</td>
<td>28</td>
<td>100.42</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Beta spectrum of $^3$H and $^{14}$C measured by Quantulus Liquid Scintillation Counter

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

- For graphite, 0.1 gram sample can be directly decomposed, the detection limits of $^{14}$C and H-3 can be calculated to be: 0.7 and 0.5 Bq/g.

- For Concrete, 0.3 gram sample can be decomposed, the detection limits of C-14 and H-3 are 0.23 and 0.18 Bq/g.
Sampling of concrete and graphite from Danish reactor, DR-2
### Analytical Results of $^3$H and $^{14}$C in 9 graphite samples

<table>
<thead>
<tr>
<th>Code</th>
<th>$^3$H, Bq/g</th>
<th></th>
<th>$^{14}$C, Bq/g</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>SD %</td>
<td>Average</td>
<td>SD %</td>
</tr>
<tr>
<td>TK5.5 Yi</td>
<td>2.12E+02</td>
<td>4.50</td>
<td>4.70E+03</td>
<td>17.33</td>
</tr>
<tr>
<td>TK5.5 Yy</td>
<td>7.55E+03</td>
<td>2.85</td>
<td>1.97E+05</td>
<td>11.48</td>
</tr>
<tr>
<td>TK5.5 Ii</td>
<td>1.96E+04</td>
<td>2.43</td>
<td>1.04E+06</td>
<td>10.36</td>
</tr>
<tr>
<td>TK5.5 Iy</td>
<td>9.04E+03</td>
<td>3.01</td>
<td>4.31E+05</td>
<td>0.93</td>
</tr>
<tr>
<td>TK7.5 Yi</td>
<td>2.67E+04</td>
<td>2.19</td>
<td>1.11E+06</td>
<td>3.39</td>
</tr>
<tr>
<td>TK7.5 Yy</td>
<td>1.08E+04</td>
<td>1.74</td>
<td>3.67E+05</td>
<td>7.88</td>
</tr>
<tr>
<td>TK7.5 Ii</td>
<td>1.46E+04</td>
<td>2.76</td>
<td>9.31E+05</td>
<td>5.53</td>
</tr>
<tr>
<td>TK7.5 Iy</td>
<td>6.77E+03</td>
<td>1.61</td>
<td>3.44E+05</td>
<td>9.66</td>
</tr>
<tr>
<td>Sample-G</td>
<td>3.21E+03</td>
<td>1.25</td>
<td>7.16E+04</td>
<td>11.73</td>
</tr>
</tbody>
</table>
$^3$H and $^{14}$C in heavy concrete in Danish reactor DR2

![Graphs showing concentration of $^{14}$C and $^3$H vs. distance to the core, cm.](image)
Production of $^{63}$Ni and $^{55}$Fe in Nuclear Reactor (neutron activation)

- $^{63}$Ni:
  - $^{62}$Ni(n, $\gamma$)$^{63}$Ni, ($\sigma=14.5$ b; $\eta_{62\text{Ni}}=3.63\%$)
  - $^{63}$Cu(n, p)$^{63}$Ni, ($\eta_{63\text{Cu}}=69.17\%$)

- $^{55}$Fe:
  - $^{54}$Fe(n, $\gamma$)$^{55}$Fe, ($\sigma=2.3$ b; $\eta_{54\text{Fe}}=5.85\%$)
  - $^{56}$Fe(n, 2n)$^{55}$Fe, ($\eta_{56\text{Fe}}=91.75\%$)
Decay of $^{63}$Ni and $^{55}$Fe

$^{55}$Fe (2.73 y)
- EC (232 keV, 100%)
- No gamma ray
- $^{55}$Mn (stable)

$^{63}$Ni (100.1 y)
- $\beta^-$ (66.95 keV, 100%)
- No gamma ray
- $^{63}$Cu (stable)

$^{55}$Fe decays by electron capture emitting X-rays, conversion electrons and Auger electrons (5 - 6 keV)
- X ray (5.89 keV, 25.4%)
- Fe-55

$^{63}$Ni decays by $\beta^-$ emission (66.95 keV, 100%) without emitting gamma rays.

$^{55}$Fe decays to $^{55}$Mn (stable) without emitting gamma rays.

$^{63}$Cu (stable)
### Neutron activation products of Fe and Ni

<table>
<thead>
<tr>
<th>Target nuclide</th>
<th>Abundance %</th>
<th>(n, γ) cross section</th>
<th>Activation product</th>
<th>Half life</th>
<th>Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{58}\text{Ni}$</td>
<td>68.3</td>
<td>4.64</td>
<td>$^{59}\text{Ni}$</td>
<td>$7.6\times10^4$ y</td>
<td>EC (Kx=6.9 keV)</td>
</tr>
<tr>
<td>$^{60}\text{Ni}$</td>
<td>26.1</td>
<td>2.82</td>
<td>$^{61}\text{Ni}$</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td>$^{61}\text{Ni}$</td>
<td>1.13</td>
<td>2.51</td>
<td>$^{62}\text{Ni}$</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td>$^{62}\text{Ni}$</td>
<td>3.59</td>
<td>14.25</td>
<td>$^{63}\text{Ni}$</td>
<td>100 y</td>
<td>$\beta$, 66.9 keV</td>
</tr>
<tr>
<td>$^{54}\text{Fe}$</td>
<td>5.85</td>
<td>2.3</td>
<td>$^{55}\text{Fe}$</td>
<td>2.73 y</td>
<td>EC</td>
</tr>
<tr>
<td>$^{56}\text{Fe}$</td>
<td>91.75</td>
<td>2.6</td>
<td>$^{57}\text{Fe}$</td>
<td>stable</td>
<td></td>
</tr>
<tr>
<td>$^{58}\text{Fe}$</td>
<td>0.28</td>
<td>1.31</td>
<td>$^{59}\text{Fe}$</td>
<td>44.5 d</td>
<td>$\beta$, $\gamma$</td>
</tr>
</tbody>
</table>

Atomic ratio: $^{59}\text{Ni}/^{63}\text{Ni}=6.5:1$

Activity ratio: $^{59}\text{Ni}/^{63}\text{Ni}=1:133$
Other isotopes of Ni and Fe produced in Nuclear reactor

- Ni isotopes: $^{59}$Ni,
  - $^{58}$Ni(n, $\gamma$)$^{59}$Ni;
  - $^{60}$Ni(n,2n)$^{59}$Ni

- Fe isotopes: $^{59}$Fe
  - $^{58}$Fe(n, $\gamma$)$^{59}$Fe; $^{59}$Co(n, p)$^{59}$Fe

No $\gamma$

X rays, 6.9 keV (30%)

$^{59}$Co

Can be measured by $\gamma$-rays
Analytical method for $^{63}$Ni and $^{55}$Fe

- Due to their low energy of beta particle and measurable electrons, LSC is the most suitable method for their measurement.
- Due to their pure beta and EC decay, they have to be separated from matrix elements and all other radionuclides.

Measurement methods

$^{55}$Fe: X-ray spectrometry (<1%); LSC (30-45%)

$^{63}$Ni: gas flow counting (anti-coincidence, <10-50%)
- Ion implanted silicon detector (1-6%)
- LSC (60-80%)

Analytical procedure:

- Decomposition of sample
- Separation of Ni or Fe from matrix elements and all other radionuclides
- Preparation of a suitable solution for LSC measurement.
Decomposition of samples

- Metals (steel, Ni-Cr-X alloy, Copper, Lead, Al alloy)
  - Acid digestion
- Concrete, soil, sediment
  - Alkali fusion followed by water leaching
  - Acid digestion
- Plants, organic materials, resin
  - Ashing followed by acid digestion
- Graphite
  - Ashing (800 °C) followed by acid leaching
  - Digestion with mixed acids (HNO$_3$+HClO$_4$+H$_2$SO$_4$) (it takes 3-4 hours)
### Decomposition of graphite by ashing for determination of $^{63}$Ni and $^{55}$Fe

<table>
<thead>
<tr>
<th>Temp  oC</th>
<th>Ashing time</th>
<th>Carrier, mg</th>
<th>Digestion</th>
<th>Recovery, %</th>
<th>55Fe</th>
<th>63Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>3 min.</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>45%</td>
</tr>
<tr>
<td>800</td>
<td>2-3 h</td>
<td>…</td>
<td>…</td>
<td>HCl</td>
<td>96-98%</td>
<td>97-99%</td>
</tr>
<tr>
<td>800</td>
<td>2-3 h</td>
<td>10</td>
<td>…</td>
<td>HCl</td>
<td>95-98%</td>
<td>90-95%</td>
</tr>
<tr>
<td>800</td>
<td>2-3 h</td>
<td>…</td>
<td>10</td>
<td>HCl</td>
<td>90-95%</td>
<td>95-98%</td>
</tr>
<tr>
<td>800</td>
<td>3 h</td>
<td>4</td>
<td>2</td>
<td>HCl</td>
<td>40-75%</td>
<td>30-65%</td>
</tr>
<tr>
<td>800</td>
<td>24 h</td>
<td>4</td>
<td>2</td>
<td>HCl + HClO$_4$</td>
<td>30-45%</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>6 h</td>
<td>…</td>
<td>2</td>
<td>HCl + HClO$_4$</td>
<td>80-85%</td>
<td>75-80%</td>
</tr>
<tr>
<td>800</td>
<td>3.5 h</td>
<td>4</td>
<td>2</td>
<td>HCl + HClO$_4$</td>
<td>92-95%</td>
<td>90-95%</td>
</tr>
<tr>
<td>800</td>
<td>3</td>
<td>10</td>
<td>5</td>
<td>HCl + HClO$_4$</td>
<td>91-95%</td>
<td>90-95%</td>
</tr>
</tbody>
</table>

- **Ni and Fe is lost during ashing at:**
  - Higher ashing temperature (>900 oC)
  - Longer ashing time
  - Add both Fe and Ni carrier and leaching just with HCl (this is due to a Fe-Ni compound formed which is difficult to be dissolved by HCl)

- **Optimal ashing conditions:**
  - 750-850 oC
  - Less than 3.5 hours
  - Leaching with HCl + HClO$_4$ or add Fe and Ni carrier individually or after ashing.
## Interfering Radionuclides

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Decay</th>
<th>Nuclide</th>
<th>Half-life</th>
<th>Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{60}$Co</td>
<td>5.27 y</td>
<td>$\beta^-, \gamma$</td>
<td>$^{133}$Ba</td>
<td>10.51 y</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>$^{58}$Co</td>
<td>70.86 d</td>
<td>$\beta^+, \gamma$</td>
<td>$^{41}$Ca</td>
<td>1.03E5 y</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>13.54 y</td>
<td>$\varepsilon, \beta^-, \gamma$</td>
<td>$^{36}$Cl</td>
<td>3.01E5 y</td>
<td>$\beta^-, \varepsilon$</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>8.59 y</td>
<td>$\beta^-, \gamma$</td>
<td>$^{137}$Cs</td>
<td>30.7 y</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>$^{51}$Cr</td>
<td>27.7 d</td>
<td>$\varepsilon, \gamma$</td>
<td>$^{134}$Cs</td>
<td>2.06 y</td>
<td>$\beta^-, \varepsilon$</td>
</tr>
<tr>
<td>$^{65}$Zn</td>
<td>244.3 d</td>
<td>$\varepsilon, \beta^+, \gamma$</td>
<td>$^{90}$Sr</td>
<td>28.79 y</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>312.3 d</td>
<td>$\varepsilon, \beta^+, \gamma$</td>
<td>$^{90}$Y</td>
<td>64 h</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>$^{151}$Sm</td>
<td>90 y</td>
<td>$\beta^-$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chemical Separation of Ni

1. From main matrix elements
2. From Ba, Cl, Cs, Ca, Sr, etc.
3. From actinides
4. From Fe, Co, Cu, Mn, Zn etc.
5. From Cr, Eu, Cu, Co.
Chemical Separation of Fe

1. From main matrix elements
2. From Ba, Cl, Cs, Ca, Sr, etc.
3. From actinides
4. from Ni, Co, Cu, Mn, Zn, Cr, Eu, etc.
Traditional methods for separation of Ni

- Precipitation as Ni(OH)$_2$, separation from Sr, Cs, $^3$H, $^{14}$C, Ba, Ca, Cl.

- Precipitation by ammonium, separate Ni from Fe, Mn, Eu, Pb, Al, Cr.
  - Low recovery of Ni in this method (Ni can be also partly precipitate in ammonium solution)
  - Cannot separate Cu, Co, etc.

- Ion exchange to separate Ni from Co, Cu, Zn, Fe, and transuranics.

- Precipitation or extraction of complex of Ni with dimethylglyoxime (DMG).
  - Co and Cu can also form a complex with DMG and extracted

- Evaporation of Ni(CO)$_6$
### Separation of Fe and Ni by hydroxides precipitation

<table>
<thead>
<tr>
<th>Element</th>
<th>Precipitation, %</th>
<th>Solution, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH (pH9)</td>
<td>NH₄OH</td>
<td>NH₄OH</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>&gt;99.8</td>
<td>&gt;99.8</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>&gt;99.8</td>
<td>≥20</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>&gt;99.5</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>&lt;30.5</td>
<td>&lt;30.0</td>
</tr>
<tr>
<td>Eu³⁺</td>
<td>&gt;99.8</td>
<td>&gt;99.8</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>&lt;37.5</td>
<td>&lt;35.0</td>
</tr>
</tbody>
</table>

- Most of matrix in concrete and environmental samples, such as C, S, Ca, Si, Na will be separated.
- The recovery of Ni is not satisfied using ammonium to separate Ni from other metals by hydroxides precipitation.
- Other metals such as Mn, Cr, V, Al, Pb, and transuranics will also be precipitated by NaOH, and cannot be separated from Ni and Fe.
Separation of Ni, Co, Eu, Ba by anion exchange chromatography

- Loading at 9 mol/l HCl, Ni is not absorbed on column, while others are absorbed.
- Removing Co, Cu by washing with 4 mol/l HCl
- Eluting Fe with 0.5 mol/l HCl

Separation of Eu, Ba, Co by anion exchange chromatography, Bio-Rad AG1x4, 1x15 cm, 0-40 ml: 9M HCl, 40-70 ml: 4M HCl, 70-90 ml: 0.05M HCl
Separation of Ni and Fe by anion exchange chromatography (conclusion)

• Ni can be completely separated from Fe, Co, Cu, Zn, U, Pu, etc.
• Fe can be separated from Ni, Cr, Mn, Th, etc.

• Ni cannot be efficiently separated from Cr, Eu, Sm, Mn, V, Sc, Ti, Zr, Ba, Th, Am. Of them, the radioisotopes of Eu, Sm, Ba, Zr, Mn, Cr and matrix elements of Cr, Mn V in metal and alloy seriously interfere the determination of Ni-63.

• Fe cannot be completely separated from Zn, Co, Cu, Pu, Np, especially when a large amount of Fe (>10 mg) is loaded on the column.

Thus: a further purification for both Ni and Fe is needed.

<table>
<thead>
<tr>
<th>Element</th>
<th>Content, %</th>
<th>Ni fraction</th>
<th>Fe fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe³⁺</td>
<td>&lt;0.001</td>
<td></td>
<td>&gt;98.5</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>&gt;99.5</td>
<td></td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>&lt;0.01</td>
<td></td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>&lt;7.5</td>
<td>&lt;0.001</td>
<td></td>
</tr>
<tr>
<td>Eu³⁺</td>
<td>&gt;99.8</td>
<td>&lt;0.001</td>
<td></td>
</tr>
<tr>
<td>Cs⁺</td>
<td>&gt;99.5</td>
<td>&lt;0.001</td>
<td></td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>&gt;99.5</td>
<td>&lt;0.001</td>
<td></td>
</tr>
</tbody>
</table>
Separation of Ni using Ni-DMG complex

- Ni can form a stable specific complex with dimethylglyoxime. By Ni-DMG precipitation or organic solvent extraction of Ni-DMG complex at low concentration, Ni can be separated from many other elements.

- While, some other metals, such as Co, Cu can also form a complex with DMG and interfering the separation of Ni.
Formation of M-DMG complex

2mg Ni$^{2+}$

2mg Ni$^{2+}$ + 2mg Co$^{2+}$

2mg Ni$^{2+}$ + 2mg Cu$^{2+}$

2mg Ni$^{2+}$ + 8mg Fe$^{3+}$
Purification of Ni by specific Ni-extraction chromatography

The Nickel Resin contains the DMG inside the pores of a polymethacrylate resin. The nickel-DMG precipitate occurs on the resin, where it is held and readily separated from other elements in the supernatant.

1. Loading of solution
2. Washing with 0.2 M ammonium citrate to remove other elements
3. Eluting Ni using HNO3
4. Evaporte eluted Ni-DMG solution to 0.1-0.2 ml for LSC
Purification of Ni by specific Ni-extraction chromatography (conclusion)

<table>
<thead>
<tr>
<th>Element</th>
<th>Recovery or decontamination factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$^{2+}$</td>
<td>&gt; 98.5%</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>$10^3$</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>$10^4$</td>
</tr>
</tbody>
</table>

Ni specific extraction chromatography has a higher decontamination to most of elements, such as Fe, Co, Cu, Cr, Mn, Ba, Eu, transuranics, etc.

- A higher recovery of Ni can be obtained in the procedure.
Separation of Fe by solvent extraction

- Di-isopropyl ether (DIPE)
- Methyl-isobutyle (MIBK)
- Ethyl acetate
- Iso-pentanol
- 8-hydroxyquinoline
- Triisoocylamine (TIOA)
- …

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Medium</th>
<th>Distribution factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl acetate</td>
<td>6 mol/l</td>
<td>65</td>
</tr>
<tr>
<td>DIBK</td>
<td>6 mol/l</td>
<td>38</td>
</tr>
<tr>
<td>DIPE</td>
<td>6 mol/l</td>
<td>4</td>
</tr>
</tbody>
</table>
## Purification of Fe by extraction chromatography

<table>
<thead>
<tr>
<th>Column</th>
<th>Capacity</th>
<th>Fe-specific</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRU</td>
<td>3 mg</td>
<td>no</td>
</tr>
<tr>
<td>Silica-immobilised formylosalic acid</td>
<td>54 mg</td>
<td>no</td>
</tr>
<tr>
<td>XAD-7/DIBK</td>
<td>1700 mg</td>
<td>yes</td>
</tr>
</tbody>
</table>
Analytical procedure for $^{63}\text{Ni}$ and $^{55}\text{Fe}$

Sample

- Stable Ni and Fe carrier/tracer, Cu, Co, Eu, Cr, Mn, Zn, Sr hold-back carrier, decompose

Decomposed sample solution

- Adjust pH9 using NaOH, centrifuge
- $\text{Fe(OH)}_3$, $\text{Ni(OH)}_2$, $\text{M(OH)}_x$

Disolved to 9 mol/l HCl, loading to anion exchange column

AG 1x4 column

- Washing with 4 mol/l HCl
- Eluting with 0.5 mol/l HCl

Effluent, Ni-63

- Evaporate, dissolved with 1M HCl, add $\text{NH}_4\text{Citr}$, $\text{NH}_4\text{OH}$ to pH9, loading
- Washing with 0.2 M $\text{NH}_4\text{Citr}$
- Eluting with 3 M HNO3

Ni-column

- ICP-AES for chemical yield by Ni
- LSC for $^{63}\text{Ni}$

Eluate, $^{63}\text{Ni}$

- Washes, Cu, Co, etc.
- discard

Elut, Fe-55

- Evaporate, dissolve to 6 M HCl, loading
- Wash with 6 M HCl
- Elut with H2O

Fe-column

- ICP-AES for Fe

Eluate, $^{55}\text{Fe}$

LSC for $^{55}\text{Fe}$
The recovery of Fe and Ni in the analytical procedure and decontamination factors for main interfering radionuclides and elements

<table>
<thead>
<tr>
<th>Interference</th>
<th>Recovery/decontamination factor</th>
<th>Interference</th>
<th>Recovery/decontamination factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe fraction</td>
<td>Ni fraction</td>
<td>Fe fraction</td>
</tr>
<tr>
<td>$^{55}$Fe</td>
<td>85-95%</td>
<td>&gt;10$^5$</td>
<td>$^{133}$Ba</td>
</tr>
<tr>
<td>$^{63}$Ni</td>
<td>&gt;10$^5$</td>
<td>80-95%</td>
<td>$^{134,137}$Cs</td>
</tr>
<tr>
<td>$^{58,60}$Co</td>
<td>&gt;10$^5$</td>
<td>&gt;10$^5$</td>
<td>$^{89,90}$Sr</td>
</tr>
<tr>
<td>$^{152,154}$Eu</td>
<td>&gt;10$^6$</td>
<td>&gt;10$^5$</td>
<td>$^{41,45}$Ca</td>
</tr>
<tr>
<td>$^{151}$Sm</td>
<td>&gt;10$^6$</td>
<td>&gt;10$^5$</td>
<td>$^{36}$Cl</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>&gt;10$^5$</td>
<td>&gt;10$^6$</td>
<td>$^3$H</td>
</tr>
<tr>
<td>$^{51}$Cr</td>
<td>&gt;10$^6$</td>
<td>&gt;10$^5$</td>
<td>$^{14}$C</td>
</tr>
</tbody>
</table>

For all interfering radionuclides, the decontamination factors higher than 10$^5$. 
Quench correction for Ni-63

Graphite sample with 2 mg Ni carrier

Quench curve of Ni-63

\[ y = -9 \times 10^{-7}x^3 + 0.0015x^2 - 0.6991x + 95.98 \]
Quench correction for Fe-55

Graphite sample with 2 mg Fe carrier
• Yellow colour Fe$^{3+}$ is a very effective quenching agent
• Reduction of Fe$^{3+}$ to Fe$^{2+}$ using suitable reductant, such as ascorbic acid can reduce the quench, but Fe$^{2+}$ is not stable and can be oxidize to Fe$^{3+}$ again, and Fe$^{2+}$ also has some colour quench.
• Solvent extraction of Fe$^{3+}$ using some organic compounds such as di-2-ethylhexyl phosphoric acid can reduce the Fe$^{3+}$ colour quench, but not effective for large Fe content sample.
• In H$_3$PO$_3$ solution, a stable and colourless Fe-H$_3$PO$_3$ complex can be formed, therefore can significantly reduce the Fe$^{3+}$ colour quench.
• H$_3$PO$_3$ as an acid has less quench and high solubility with scintillation cocktail, therefore can significantly improve the counting efficiency.
• As high as 40% counting efficiency of $^{63}$Ni in 1.5 ml of 2 mol/l H$_3$PO$_3$ solution.
• The separated Fe was evaporated to dryness and then dissolved in 2 M H$_3$PO$_3$ solution in this work, for less than 10 mg Fe, 40% counting efficiency was obtained, and for 200 mg Fe, the efficiency is still as high as 13%.
Spectrum of $^{55}$Fe and $^{63}$Ni separated from samples

No interference was found from other radionuclides in the $^{63}$Ni and $^{55}$Fe spectra, it indicates the decontamination from interference radionuclides is satisfied.
# Determination of $^{63}$Ni and $^{55}$Fe in graphite samples

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Sample and Source</th>
<th>$^{55}$Fe</th>
<th>$^{63}$Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Recovery,%</td>
<td>Bq/g</td>
</tr>
<tr>
<td>DR-3-T</td>
<td>Graphite from DR3</td>
<td>92.2</td>
<td>545000</td>
</tr>
<tr>
<td>Ly7.5</td>
<td>Graphite from DR-2</td>
<td>90.4</td>
<td>0.53</td>
</tr>
<tr>
<td>Ly5.5</td>
<td>Graphite from DR-2</td>
<td>90.6</td>
<td>1.05</td>
</tr>
<tr>
<td>Yi7.5</td>
<td>Graphite from DR-2</td>
<td>92.5</td>
<td>1.92</td>
</tr>
<tr>
<td>Yi5.5</td>
<td>Graphite from DR-2</td>
<td>91.3</td>
<td>9.21</td>
</tr>
<tr>
<td>B-6</td>
<td>Heavy concrete from DR-2</td>
<td>92.3</td>
<td>0.015</td>
</tr>
</tbody>
</table>
$^{63}\text{Ni}$ and $^{55}\text{Fe}$ in heavy concrete from DR-2

![Graphs showing the activity of $^{55}\text{Fe}$ and $^{63}\text{Ni}$ relative to distance from the core.](image)
• The oxidizer method is simple, rapid, accurate method for $^3$H and $^{14}$C in graphite, concrete samples. No significant cross contamination between $^3$H and $^{14}$C was observed. No significant interference from other radionuclides to the determination of $^3$H and $^{14}$C by this method.

• A radiochemical separation procedure using hydroxides precipitation, anion exchange and extraction chromatography was developed for the determination of $^{63}$Ni and $^{55}$Fe in nuclear waste. The recoveries of Fe and Ni are 80-95%. The decontamination factors for most of interfering nuclides are higher than $10^5$. The detection limit for $^{63}$Ni and $^{55}$Fe are 0.015 Bq and 0.035 Bq respectively.

• The method has been successfully used for the analysis of graphite and concrete from Danish reactors.