Radiochemical Analysis of 63Ni, 55Fe, and radiostronium in waste and environmental samples

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Radiochemical Analysis of $^{63}$Ni, $^{55}$Fe, and radiostronium in waste and environmental samples

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Production of $^{63}\text{Ni}$ and $^{55}\text{Fe}$ in Nuclear Reactor (neutron activation)

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

- **$^{55}\text{Fe}$:**
  - $^{54}\text{Fe}(n, \gamma)^{55}\text{Fe}$ ($\sigma=2.3$ b; $\eta_{54\text{Fe}}=5.85\%$)
  - $^{56}\text{Fe}(n, 2n)^{55}\text{Fe}$, ( $\eta_{56\text{Fe}}=91.75\%$)
Type of waste samples 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,$^{55}$Fe, $^{99}$Tc, $^{129}$I, $^{60}$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
55Fe and 63Ni in the Environment

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

• Investigation of 63Ni and 55Fe in the environment
  – Measurement of the contamination level from nuclear facility
  – Using 55Fe and 63Ni released from nuclear facility as a tracer to study their environmental and chemical behaviours

• Environmental Samples
  – Water
  – plants (seaweed, grass, lichen, fish.)
  – soil, sediment
Decay of $^{63}$Ni and $^{55}$Fe

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

- X ray (5.89 keV, 25.4%)
- No gamma ray

$^{55}$Mn (stable)

$^{63}$Ni (100.1y)

- $\beta^-$ (66.95 keV, 100%)
- No gamma ray

$^{63}$Cu (stable)
### Aneutron 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><strong>58</strong>Ni</td>
<td>68.3</td>
<td>4.64</td>
<td><strong>59</strong>Ni</td>
<td>7.6x10⁴ y</td>
<td>EC (Kx=6.9 keV)</td>
</tr>
<tr>
<td><strong>60</strong>Ni</td>
<td>26.1</td>
<td>2.82</td>
<td><strong>61</strong>Ni</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td><strong>61</strong>Ni</td>
<td>1.13</td>
<td>2.51</td>
<td><strong>62</strong>Ni</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td><strong>62</strong>Ni</td>
<td>3.59</td>
<td>14.25</td>
<td><strong>63</strong>Ni</td>
<td>100 y</td>
<td>β-, 66.9 keV</td>
</tr>
<tr>
<td><strong>54</strong>Fe</td>
<td>5.85</td>
<td>2.3</td>
<td><strong>55</strong>Fe</td>
<td>2.73 y</td>
<td>EC</td>
</tr>
<tr>
<td><strong>56</strong>Fe</td>
<td>91.75</td>
<td>2.6</td>
<td><strong>57</strong>Fe</td>
<td>stable</td>
<td></td>
</tr>
<tr>
<td><strong>58</strong>Fe</td>
<td>0.28</td>
<td>1.31</td>
<td><strong>59</strong>Fe</td>
<td>44.5 d</td>
<td>β-, γ</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:** $^{59}\text{Ni}$,
  - $^{58}\text{Ni}(n, \gamma)^{59}\text{Ni}$; $^{60}\text{Ni}(n, 2n)^{59}\text{Ni}$

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

No $\gamma$

X rays, 6.9 keV (30%)

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

- 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.

**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.

**Measurement methods**

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

$^{63}\text{Ni}$: gass flow counting (anti-coincidence, <10-50%)
- Ion implanted silicon detector (1-6%)
- LSC (60-80%)
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 (HNO₃+HClO₄+H₂SO₄) (it takes 3-4 hours)
Decomposition of graphite by ashing for determination of $^{63}\text{Ni}$ and $^{55}\text{Fe}$

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Ashing time</th>
<th>Carrier,mg</th>
<th>Digestion</th>
<th>Recovery, %</th>
<th>$^{55}\text{Fe}$</th>
<th>$^{63}\text{Ni}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe</td>
<td>Ni</td>
<td></td>
<td></td>
<td></td>
</tr>
<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 °C)
  - 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 °C
  - 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>$^{3}$H</td>
<td>12.33 y</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>$^{58}$Co</td>
<td>70.86 d</td>
<td>$\beta^+,\gamma$</td>
<td>$^{14}$C</td>
<td>5730 y</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>13.54 y</td>
<td>$\varepsilon,\beta^-,\gamma$</td>
<td>$^{133}$Ba</td>
<td>10.51 y</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>8.59 y</td>
<td>$\beta^-,\gamma$</td>
<td>$^{41}$Ca</td>
<td>1.03E5 y</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>$^{51}$Cr</td>
<td>27.7 d</td>
<td>$\varepsilon,\gamma$</td>
<td>$^{36}$Cl</td>
<td>3.01E5 y</td>
<td>$\beta^-,\varepsilon$</td>
</tr>
<tr>
<td>$^{65}$Zn</td>
<td>244.3 d</td>
<td>$\varepsilon,\beta^+,\gamma$</td>
<td>$^{137}$Cs</td>
<td>30.7 y</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>312.3 d</td>
<td>$\varepsilon,\beta^+,\gamma$</td>
<td>$^{134}$Cs</td>
<td>2.06 y</td>
<td>$\beta^-,\varepsilon$</td>
</tr>
<tr>
<td>$^{151}$Sm</td>
<td>90 y</td>
<td>$\beta^-$</td>
<td>$^{90}$Y</td>
<td>64 h</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>$^{90}$Sr</td>
<td>28.79 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.
Fe and Ni are transite metals
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></td>
<td>NaOH (pH9)</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>&gt;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.
Many metals can form a anion complex with Cl- in HCl solution (MCl$_x^-$), so can adsorbed on anion exchange column.
Separation of Fe, Ni, Co, Cu, 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, 0-40ml:9M HCl, 40-70ml:4M HCl, 70-90ml, 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>Ni fraction</th>
<th>Fe fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>&lt;0.001</td>
<td>&gt;98.5</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>&gt;99.5</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>&lt;0.01</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>&lt;7.5</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>&gt;99.8</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>&gt;99.5</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>&gt;99.5</td>
<td>&lt;0.001</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 Ni²⁺
- 2mg Ni²⁺ + 2mg Co²⁺
- 2mg Ni²⁺ + 2mg Cu²⁺
- 2mg Ni²⁺ + 8mg Fe³⁺
**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
- Triisooctylamine (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 formylsalic 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

**Fe(OH)$_3$, Ni(OH)$_2$, M(OH)$_x$**
- Dissolved 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 NH$_4$Citr, NH$_4$OH to pH9, loading
- Washing with 0.2 M NH$_4$Citr
- Eluting with 3 M HNO$_3$

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

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

**Elute, Fe-55**
- Evaporate, dissolve to 6 M HCl, loading
- Wash with 6 M HCl
- Elut with H$_2$O

**Fe-column**
- ICP-AES for Fe
- LSC for $^{55}\text{Fe}$
The recovery of Fe and Ni and decontamination factors for main interfering radionuclides

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

For all interfering radionuclides, the decontamination factors higher than 10$^5$. 
Measurement of $^{63}\text{Ni}$ and $^{55}\text{Fe}$ by LSC

- In LSC, the radionuclide is mixed with a cocktail, the decay energy will be transferred to the cocktail, and converted to photons, by counting the photons using a PMT (photomultiplier tube), the activity of radionuclides is measured.

- A single photon striking the photocathode has at most a 30% probability of producing an electrical pulse. There are always losses associated with the full light generation process. The factors which effect the energy transfer process is called quench.

**Chemical Quenching**

Any compound that does not have an aromatic structure will produce some quenching effect.

**Physical Quenching**

It occurs when a barrier impairs contact between the radioactive particle and the scintillator solution, or when the photons of light generated are absorbed by some solid within the vial.

**Colour Quenching**

light absorbing compounds interpose and lessen the number of photons leaving the scintillation vial. Fluorescence emission takes place in the blue region of the spectrum, therefore the order of severity of colour quenching is: Red > orange > yellow > green > blue
Quench correction for Ni-63

Sample Spectrum

Quench curve of Ni-63

Graphite sample with 2 mg Ni carrier

\[ y = -9E-07x^3 + 0.0015x^2 - 0.6991x + 95.98 \]
Quench correction for Fe-55

Sample Spectrum

Quench curve of Fe-55
Graphite sample with 2 mg Fe carry
**Preparation of separated $^{63}$Ni for LSC**

- $^{63}$Ni was separated in 10-15 ml of 3 mol/l HNO$_3$ eluate, it cannot be used for LSC, due to large volume and high acid concentration. Because:
  - 20 ml counting vial with high capacity scintillation cocktail can only mix with less than 1.5 ml of 3 mol/l HNO$_3$ eluate.
  - Acid solution is a high quench regent, it seriously reduce the counting efficiency of LSC. In 1.5 ml HNO$_3$ eluate, the counting efficiency for $^{63}$Ni is only 10%.
  - The Energy of beta particle emitted from $^{63}$Ni is low (66.95 keV).
- The eluate can be evaporated to small volumn (<0.2 ml) at low temperature (<150 °C) and transfer to counting vial with 0.5 ml water. In this case, the counting efficiency for $^{63}$Ni can be increased to 70%.
- It is very important, do not evaporate eluate to dryness.
  - Low boiling point of Ni(NO$_3$)$_2$ (137 °C) makes >95% loss of $^{63}$Ni when evaporating sample to dryness.
  - Burned Ni-DMG complex is difficult to be decomposed to obtain a clear solution.
Preparation of separated $^{55}\text{Fe}$ for LSC

- 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 oxidized 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 $^{63}\text{Ni}$ 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 15%.
**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>
Sampling of concrete and graphite from Danish reactor, DR-2
Results of $^{55}\text{Fe}$, $^{63}\text{Ni}$ in concrete from Danish reactor, DR-2

**$^{55}\text{Fe}$ in concrete core**

![Graph for $^{55}\text{Fe}$](image)

**$^{63}\text{Ni}$ in concrete core**

![Graph for $^{63}\text{Ni}$](image)
55Fe and 63Ni in the environment surrounding Ignalina NPP

Surface deposition density levels of radionuclides

<table>
<thead>
<tr>
<th>Moss sample code</th>
<th>137Cs</th>
<th>60Co</th>
<th>40K</th>
<th>55Fe</th>
<th>63Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>86</td>
<td>31 ± 3</td>
<td>1.4 ± 0.2</td>
<td>47 ± 4</td>
<td>36 ± 6</td>
<td>–</td>
</tr>
<tr>
<td>87</td>
<td>46 ± 4</td>
<td>5.2 ± 0.4</td>
<td>76 ± 6</td>
<td>17.3 ± 2.6</td>
<td>–</td>
</tr>
<tr>
<td>88</td>
<td>4.7 ± 0.4</td>
<td>2.5 ± 0.2</td>
<td>114 ± 9</td>
<td>70 ± 11</td>
<td>–</td>
</tr>
<tr>
<td>89</td>
<td>8.6 ± 0.7</td>
<td>0.9 ± 0.1</td>
<td>44 ± 4</td>
<td>13.5 ± 2.1</td>
<td>–</td>
</tr>
<tr>
<td>90</td>
<td>13.6 ± 1.1</td>
<td>3.4 ± 0.3</td>
<td>77 ± 6</td>
<td>106 ± 16</td>
<td>2.0 ± 0.3</td>
</tr>
<tr>
<td>91</td>
<td>1.6 ± 0.2</td>
<td>0.8 ± 0.1</td>
<td>55 ± 4</td>
<td>110 ± 17</td>
<td>–</td>
</tr>
<tr>
<td>92</td>
<td>1.9 ± 0.2</td>
<td>0.7 ± 0.1</td>
<td>47 ± 4</td>
<td>222 ± 34</td>
<td>–</td>
</tr>
<tr>
<td>93</td>
<td>1.7 ± 0.2</td>
<td>43 ± 4</td>
<td>53 ± 5</td>
<td>940 ± 140</td>
<td>–</td>
</tr>
<tr>
<td>95</td>
<td>13.4 ± 1.1</td>
<td>0.7 ± 0.1</td>
<td>80 ± 7</td>
<td>200 ± 30</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>20.8 ± 1.3</td>
<td>–</td>
<td>55 ± 4</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
90Sr Analysis

- One of main fission products (Y=5.8%)
- Beta emitter, measured by GM detector or LSC.
- It has to be separated from other radionuclides before measurement.
- For some waste, it may contain 89Sr (50.5 d), it can be also measured by LSC with 90Sr.
89Sr properties

- 89Sr: fission product, Y=4.73%, Beta emitter

Gammas from 89Sr (50.53 d)

<table>
<thead>
<tr>
<th>Eγ (keV)</th>
<th>Iγ (%)</th>
<th>Decay mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>908.96</td>
<td>0.010</td>
<td>β⁻</td>
</tr>
</tbody>
</table>
Analytical Procedure for $^{90}\text{Sr}$ and $^{89}\text{Sr}$

1. **Sample**
   - Carbonate precipitate from water
   - Ash and Acid leaching from solid sample

2. **Decomposed sample or Coprecipitate**

3. **Separation of Sr from Ca, Cs, metals and transuranics**

4. **Separation of Sr from Ra and Ba**

5. **Measurement of $^{89}\text{Sr} + ^{90}\text{Sr}$**

6. **Measure $^{89}\text{Sr}$ by Cherenkov radiation**
Decomposition of solid sample

Graphite, resin
  Ashing at 700-800 °C
      residue
          solution
              Separation procedure

Concetre
Add Na₂CO₃/NaOH, fuse at 700 °C for 2-3 hours

Fused sample
Leaching with water, filter through a filter paper and wash with water

Precipitate, SrCO₃, BaCO₃
Dissolve with HCl
Solution, CaCl₂
Separation procedure

Fitrate, Na, K, Mg, Al, SO₄²⁻ etc.
Methods for the Separation of Sr

- Solvent extraction
- Liquid membrane extraction
- Extraction chromatography (Sr-Spec resin)
- Ion-exchange chromatography
- Strontium rhodizonate precipitation
- \( \text{Sr(NO}_3\text{)}_2 \) precipitation in 70% HNO₃

Note: These procedures cannot be used for separation of Sr from a large amount of Ca)
### Solubilities of Ca, Sr, Y, Ba and Ra compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$</td>
<td>insoluble, $K_{sp} = 5.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Sr(OH)$_2$</td>
<td>Soluble in alkine solution</td>
</tr>
<tr>
<td>SrCl$_2$, BaCl$_2$</td>
<td>soluble in water</td>
</tr>
<tr>
<td>SrCl$_2$</td>
<td>soluble in HCl &lt; 9.5 mol/L solution</td>
</tr>
<tr>
<td>BaCl$_2$ and RaCl$_2$</td>
<td>insoluble in HCl &gt; 9 mol/l solution</td>
</tr>
<tr>
<td>Y$_2$(SO$_4$)$_3$</td>
<td>soluble in water</td>
</tr>
<tr>
<td>Sr(Ba, Ra)SO$_4$</td>
<td>insoluble in water</td>
</tr>
</tbody>
</table>
A new method for the separation of Sr

Separation of Sr from Ca:
Ca(OH)$_2$ precipitation

Separation of Sr from Ba and Ra:
Ba(Ra)Cl$_2$ precipitation in concentrated HCl solution

Separation of $^{90}$Y from Sr, Ra and Ba:
Sr(Ra, Ba)SO$_4$ precipitation
**Separation of Sr from Ca by Ca(OH)$_2$**

<table>
<thead>
<tr>
<th>Sr$^{85}$ added (Bq)</th>
<th>Ca added (g)</th>
<th>Sr$^{85}$ (Bq)</th>
<th>Recovery of Sr (%)</th>
<th>Ca in supernatant (g)</th>
<th>Ca decontamination (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1050</td>
<td>50.00</td>
<td>31.6</td>
<td>1058.4</td>
<td>97.0</td>
<td>0.18</td>
</tr>
<tr>
<td>1050</td>
<td>31.00</td>
<td>38.1</td>
<td>1037.7</td>
<td>96.4</td>
<td>0.14</td>
</tr>
<tr>
<td>1050</td>
<td>10.00</td>
<td>30.6</td>
<td>1029.6</td>
<td>97.1</td>
<td>0.07</td>
</tr>
</tbody>
</table>

* Concentration of NaOH in the solution: 0.5 mol/L
# Separation of Sr from Ba by BaCl₂ and BaCrO₄

<table>
<thead>
<tr>
<th>[HCl], mol/l</th>
<th>Tracers added (Bq)</th>
<th>Supernat. (^{85}\text{Sr}) (Bq) *</th>
<th>Precipitate (^{85}\text{Sr}) (Bq) *</th>
<th>Recovery of Sr, %</th>
<th>Decontam. of Ba, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.5</td>
<td>1050</td>
<td>1510</td>
<td>918.8±14.2</td>
<td>2.0±3.4</td>
<td>99.8±0.3</td>
</tr>
<tr>
<td>9.0</td>
<td>1050</td>
<td>1510</td>
<td>484.7±18.4</td>
<td>2.1±2.4</td>
<td>98.8±0.3</td>
</tr>
<tr>
<td>9.5</td>
<td>1050</td>
<td>1510</td>
<td>43.8±9.4</td>
<td>62.4±5.9</td>
<td>94.1±0.6</td>
</tr>
<tr>
<td>10.0</td>
<td>1050</td>
<td>1510</td>
<td>40.5±7.2</td>
<td>331.2±11.1</td>
<td>68.5±1.5</td>
</tr>
<tr>
<td>10.5</td>
<td>1050</td>
<td>1510</td>
<td>28.6±4.2</td>
<td>743.4±18.4</td>
<td>29.5±1.3</td>
</tr>
<tr>
<td>11.0</td>
<td>1050</td>
<td>1510</td>
<td>7.9±4.8</td>
<td>846.3±21.2</td>
<td>21.1±1.1</td>
</tr>
<tr>
<td>BaCrO₄</td>
<td>1050</td>
<td>1510</td>
<td>15.3±5.7</td>
<td>49.0±7.8</td>
<td>95.3±0.7</td>
</tr>
</tbody>
</table>

* Average and standard deviation of two determinations
**Separation of Y from Ra, Sr, and Ba by sulphate precipitation**

<table>
<thead>
<tr>
<th>Tracer</th>
<th>Added</th>
<th>Supernat.</th>
<th>Precipitate</th>
<th>Recovery of Y, %</th>
<th>Decontam.of Sr, Ba, Ra %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y, mg</td>
<td>11.10</td>
<td>10.95±0.22</td>
<td></td>
<td>98.6±2.0</td>
<td></td>
</tr>
<tr>
<td>$^{85}$Sr, Bq</td>
<td>1050</td>
<td>8.7±2.4</td>
<td>1042±38</td>
<td></td>
<td>99.2±0.2</td>
</tr>
<tr>
<td>$^{133}$Ba, Bq</td>
<td>1510</td>
<td>2.2±1.8</td>
<td>1511±21</td>
<td></td>
<td>99.9±0.1</td>
</tr>
<tr>
<td>$^{226}$Ra, Bq</td>
<td>33.0</td>
<td>0.14±0.26</td>
<td>32.87±0.47</td>
<td></td>
<td>99.6±1.4</td>
</tr>
</tbody>
</table>
Separation procedure of $^{90}\text{Sr}$

**Solution**

Add $^{85}\text{Sr}$, SrCl$_2$, pH 8-10, add (NH$_4$)$_2$CO$_3$, stand overnight

- **Supernatant**
- **Precipitate** (SrCO$_3$, Ca, Ra, Ba, transuranics)
  - Add HNO$_3$ to dissolve, Fe$^{3+}$, add NaOH to 0.5 mol/L, centrifuge
  - **Supernatant, Sr**
    - Add HNO$_3$, Y, Sr and Ba, 3 weeks ingrowth of $^{90}\text{Y}$, add H$_2$SO$_4$, centrifuge
  - **Precipitate** (Sr, Ba, Ra)SO$_4$
    - Add H$_2$C$_2$O$_4$, centrifuge

- **Precipitate, Y$_2$(C$_2$O$_4$)$_3$ H$_2$O**
  - $\beta$ Measurement of Y-90, calculation of Sr-90

Sr-Resin

Figures 4 and 5

Acid dependence of $k'$ for various ions at 23-25°C.

Sr Resin

$k'_{Bi} < 0.4$

$k'_{Y} < 0.4$

Horwitz (HP1999)
Separation of Sr using Sr-resin

Add Sr, Y, Ba, pH 8-10, add Na₂CO₃, heat, cool to room temperature

Add HNO₃ to 8M

Wash with 8M HNO₃

Elute with 0.05M HNO₃

Effluent

Atomic Sr

Solution

Precipitate (SrCO₃), Ra, Ba, transit metals, transuranics

Supernatant

Add Scintillation cocktail

LSC for ⁹⁰Sr (no ⁸⁹Sr)

Measure immediately

LSC for Cherenkov radiation of ⁸⁹Sr

Measure after >10 days for ingrowth of ⁹⁰Y

LSC for Cherenkov radiation of ⁸⁹Sr+⁹⁰Sr/⁹⁰Y
Fig. 1 Beta spectrum of Sr sample separated from DR1 core solution.

Fig. 2 Cherenkov radiation of Sr sample separated from one DR1 core solution sample.

Cherenkov counts of Y-90 after 2.8 days of the separation of Y-90

Cherenkov counts after 7 hour of the separation of Y-90

90Sr in sample
Procedure for simultaneous determination of $^{55}$Fe, $^{63}$Ni, and $^{90}$Sr

Sample
Stable Ni and Fe carrier, and Cu, Co, Eu, Sr, Y, decompose

Decomposed sample solution
Adjust pH9 using NaOH, centrifuge

Fe(OH)$_3$, Ni(OH)$_2$, M(OH)$_x$
Disolved to 9 mol/l HCl, load
Wash with 4 mol/l HCl
Elute with 0.5 mol/l HCl

Effluent, Ni-63
Evaporate, dissolved with 1M HCl, add
NH$_4$Citr, NH$_4$OH to pH9, load
Washing with 0.2 M NH$_4$Citr
Eluting with 3 M HNO$_3$

Eluate, Fe-55
ICP-AES for Fe
LSC for $^{55}$Fe

Ni-resin column
Eluate, $^{63}$Ni
ICP-AES for chemical yield by Ni
LSC for $^{63}$Ni

Supernatant, Ca, Sr, Ba, Cs, K
Add Na$_2$CO$_3$, centrifuge
Precipitate, (Ca, Ba, Sr, Ra)CO$_3$
Dissolve with 8M HNO$_3$, load
Eluting with 8 M HNO$_3$
Eluting with 0.01 M HNO$_3$

Sr-resin column
Eluate, $^{90}$Sr ($^{89}$Sr)
LSC for $^{90}$Sr ($^{89}$Sr)

AG1x4 column
Ni-resin column

$^{90}$Sr ($^{89}$Sr)
Summary

• A analytical method based on radiochemical separation and liquid scintillation counting was developed for the determination of $^{63}\text{Ni}$ and $^{55}\text{Fe}$ in nuclear waste and environmental samples.
• Nickel and iron are separated from matrix and interfering nuclides by a procedure combining hydroxidesprecipitation, anion exchange and extraction chromatography.
• 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 $^{63}\text{Ni}$ and $^{55}\text{Fe}$ are 0.015 Bq and 0.035 Bq respectively.
• Some graphite, concrete and sediment have been analysed for the $^{63}\text{Ni}$ and $^{55}\text{Fe}$.
• By combining with a SrCO$_3$ precipitation and Sr-column extraction chromatographic separation, $^{89}\text{Sr}$ and $^{90}\text{Sr}$ can be also determined using the same sample.