Validation of radiochemical methods for the determination of difficult-to-measure nuclides using LSC

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ISOTOPTECH Zrt., Debrecen, 4026 Hungary

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DTM nuclides
Method validation principles
Examples for method validation:
  $^{90}\text{Sr}$
  $^{93}\text{Zr}$
Major issues in validation of $^{63}\text{Ni}$ and $^{59}\text{Ni}$
**Difficult-to-measure (DTM) nuclides**

**Properties:**

- long half-life - long-term effect, small specific activity
- low amounts/activities
- \( \alpha \) particles, electrons (\( \beta, \) Auger), X-rays – absorption, self-absorption

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Decay</th>
<th>( \beta_{\text{Max}} )</th>
<th>Specific activity</th>
<th>Occurrence/field of application</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{90}\text{Sr})</td>
<td>29.1 y</td>
<td>( \gamma )</td>
<td>( \beta^- )</td>
<td>546</td>
<td>5.04E+12 DN WD EM, MT</td>
</tr>
<tr>
<td>(^{93}\text{Zr})</td>
<td>1.53 ( \times 10^6 ) y</td>
<td>( \gamma )</td>
<td>( \beta^- )</td>
<td>90</td>
<td>9.27E+07 DN WD</td>
</tr>
<tr>
<td>(^{59}\text{Ni})</td>
<td>76400 y</td>
<td>( \gamma )</td>
<td>EC, ( \beta^+ ) (X: 6.9)</td>
<td>2.94E+09</td>
<td>WD</td>
</tr>
<tr>
<td>(^{63}\text{Ni})</td>
<td>100 y</td>
<td>( \gamma )</td>
<td>( \beta^- )</td>
<td>67</td>
<td>2.09E+12 DN WD</td>
</tr>
</tbody>
</table>

DN=decommissioning of nuclear facilities
WD=waste depository
EM=environmental monitoring
MT=medical tracer
**β** spectrometry by LSC

- High detection efficiency (close to 100 %)
- No absorption/self-absorption

Quench effect – quench correction possibilities

- Poor energy resolution (around 10 %)
- Continuous nature of β decay/spectra

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**LSC spectrum of a processed waste sample**

- **ANALYTE**
- **BACKGROUND**

**Which analyte?**

- $^3$H – 18 keV
- $^{63}$Ni – 67 keV
- $^{151}$Sm – 77 keV
- $^{93}$Zr – 90 keV
- $^{85}$Sr, $^{59}$Ni, $^{55}$Fe ...
LSC measurement

Chemical separation procedure
High selectivity - to remove interfering nuclides

LSC spectrum of a processed waste sample

Which analyte?
- $^3$H – 18 keV
- $^{63}$Ni – 67 keV
- $^{151}$Sm – 77 keV
- $^{93}$Zr – 90 keV
- $^{85}$Sr, $^{59}$Ni, $^{55}$Fe ...
Method validation

by either or the combination of any the following techniques
1. calibration using reference standards or reference materials,
2. inter-laboratory comparisons, e.g. PT
3. systematic assessment of the factors influencing the result,
4. assessment (of the uncertainty of the results) based on scientific understanding of the theoretical principles of the method and practical experience,
5. comparison of results achieved with other methods

ISO/IEC 17025 (2005): General requirements for the competence of testing and calibration laboratories
**90Sr determination**

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Decay mode</th>
<th>$\beta_{\text{Max}}$</th>
<th>Specific activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>keV</td>
<td>Bq/g</td>
</tr>
<tr>
<td>$^{90}\text{Sr}$</td>
<td>29.1 y</td>
<td>$\gamma$</td>
<td>546</td>
<td>5.04E+12</td>
</tr>
<tr>
<td>$^{90}\text{Y}$</td>
<td>64 h</td>
<td>$\beta^-$</td>
<td>2280</td>
<td>2.01E+16</td>
</tr>
</tbody>
</table>

**Standard validation techniques:**
1. Use of **CRM**,
2. Participation in **PTs**
3. Systematic assessment of the factors influencing the result - fish bone
4. Assessment based on scientific understanding

**Validation issue**
5. No good independent method for validation
### 90Sr determination

<table>
<thead>
<tr>
<th>Fuming nitric acid (Sr)</th>
<th>TBP or HDEHP (Y)</th>
<th>Crown ether (Sr)</th>
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</thead>
<tbody>
<tr>
<td><strong>Sample Carriers/tracers</strong></td>
<td><strong>Sample Carriers/tracers</strong></td>
<td><strong>Sample Carriers/tracers</strong></td>
</tr>
<tr>
<td>Destruction</td>
<td>Destruction</td>
<td>Destruction</td>
</tr>
<tr>
<td>Separation of alkaline metals, Ca</td>
<td>Separation of Y by extraction</td>
<td>Separation of alkaline metals</td>
</tr>
<tr>
<td>Separation of Ba, Ra and Pb</td>
<td>time of separation of Y from Sr</td>
<td>Separation of Sr by extraction</td>
</tr>
<tr>
<td>Separation of fission products, Y</td>
<td>Y back-extraction</td>
<td>time of separation of Y from Sr</td>
</tr>
<tr>
<td>time of separation of Y from Sr</td>
<td>Y purification, source preparation</td>
<td>Sr purification, source preparation</td>
</tr>
<tr>
<td>Sr purification, source preparation</td>
<td>Proportional/LSC</td>
<td>LSC</td>
</tr>
<tr>
<td>Proportional/LSC</td>
<td>90Y/90Sr</td>
<td>90Sr (91Y)</td>
</tr>
</tbody>
</table>

### After Chernobyl:
- failure due to 89Sr
- failure due to 91Y
- possible failure due to 89Sr

**Methods validated under normal conditions can fail during accidents!**
Analytes and possible interferences in radiostrontium analysis:

$^{\text{90}}\text{Sr} \rightarrow ^{\text{90}}\text{Y} \rightarrow ^{\text{90}}\text{Zr}$ (stable)

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life (yr)</th>
<th>Decay mode</th>
<th>$\beta_{\text{Max}}$ (keV)</th>
<th>Specific activity (Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{\text{89}}\text{Sr}$</td>
<td>50.6</td>
<td>d</td>
<td>$\beta^-$</td>
<td>1501</td>
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<tr>
<td>$^{\text{90}}\text{Sr}$</td>
<td>29.1</td>
<td>γ</td>
<td>$\beta^-$</td>
<td>546</td>
</tr>
<tr>
<td>$^{\text{90}}\text{Y}$</td>
<td>64</td>
<td>h</td>
<td>$\beta^-$</td>
<td>2280</td>
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<tr>
<td>$^{\text{91}}\text{Y}$</td>
<td>59</td>
<td>d</td>
<td>$\beta^-$</td>
<td>1544</td>
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<tr>
<td>$^{\text{91}}\text{Sr}$</td>
<td>9.7</td>
<td>h</td>
<td>$\beta^-, \gamma$</td>
<td>2700</td>
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<tr>
<td>$^{\text{92}}\text{Sr}$</td>
<td>2.6</td>
<td>h</td>
<td>$\beta^-, \gamma$</td>
<td>568</td>
</tr>
</tbody>
</table>

Environment

After accident

Fresh fuel
Radiostrontium determination using Sr crown ether in nuclear samples

- separation after 2-5 days of cooling
- repeated counting after 2 weeks
- checking the shape of LS spectra
- calculations described in IAEA-AQ-27_web

<table>
<thead>
<tr>
<th></th>
<th>act.conc.</th>
<th>unc</th>
<th>LD</th>
<th>Remark</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Bq/l</td>
<td>%</td>
<td>Bq/l</td>
<td></td>
</tr>
<tr>
<td>Sr-90</td>
<td>2.98E+04</td>
<td>7</td>
<td></td>
<td>supposing no Sr-89</td>
</tr>
<tr>
<td>Sr-89</td>
<td></td>
<td></td>
<td>1.08E+03</td>
<td>supposing Sr-89</td>
</tr>
<tr>
<td>Sr-90</td>
<td>2.84E+04</td>
<td>±</td>
<td>26</td>
<td>1.87E+02</td>
</tr>
</tbody>
</table>

90Sr LSC spectrum of H16-3 waste sample

89Sr, 90Sr LSC spectrum of 10TV20 primary coolant sample

Old waste

Fresh coolant
Validation of the method for Radiostrontium determination

Conclusions

$^{90}$Sr results can be validated by measurement of reference materials, by participation in inter-laboratory comparisons.

It is important to assess all influencing factors, such as the presence of other Sr and Y isotopes, or other possible contamination (radionuclides of K, Ba, Pb) by performing ingrowth/decay measurements as part of method validation.
### Validation issues:
- No $^{93}$Zr standard
- No reference material
- No intercomparison exercise

### Validation option:
Comparison of independent methods: LSC

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Decay</th>
<th>$\beta_{\text{Max}}$</th>
<th>Specific Occurance/field of application</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{93}$Zr</td>
<td>$1.53 \times 10^6$ y</td>
<td>$\beta^-$</td>
<td>90</td>
<td>9,27E+07</td>
</tr>
</tbody>
</table>
$^{93}$Zr determination

**SAMPLE**: 100 mL waste
- Tracers: $^{95}$Zr, $^{239}$Np

**DESTRUCTION**
- $\text{Fe(OH)}_2 / \text{ZrO(OH)}_2$
- PRECIPITATION

**UTEVA EC**
- $\alpha$ spectrometry
  - $^{239,240}$Pu, $^{238}$Pu
- $\alpha$ spectrometry
  - $^{238,235}$U, $^{234}$U

**UTEVA EC**
- $\gamma$ spectrometry
  - $^{95}$Zr, $^{239}$Np yield
- Cooling for months

**ICP-MS**
- $^{93}$Zr, $^{237}$Np (Th)

**LSC**
- $^{93}$Zr, $^{237}$Np (Th)

**Carrier free tracers by NAA of U**
- Purification on UTEVA
- $\gamma$ spectrometry

**Repeated separation on UTEVA**
- to purify Zr

**Yield**: Zr: 60-90%
- Fluctuating significantly due to Zr adsorption to surfaces.
**ICP-MS** (Agilent Triplequad 8800)

Possible interferences in ICP-MS
- **isobaric interference**: **stable Nb** ($^{93}\text{Nb}$), $^{93m}\text{Nb}$, $^{93}\text{Mo}$
- abundance sensitivity: **stable Zr** ($^{92}\text{Zr}$, $^{94}\text{Zr}$)
- polyatomic interferences, e.g. $^{92}\text{Zr}^{1}\text{H}$

**Countermeasures**
- Nb decontamination DF > $10^3$
- mathematical correction

**LSC** (Perkin Elmer Tricarb 2800)

Possible interferences in LSC
- $^{95}\text{Zr}$-$^{95}\text{Nb}$ tracer
- $\alpha$ emitting nuclides ($^{237}\text{Np}$, $^{232}\text{Th}$, $^{230}\text{Th}$...)
- any contamination ($^{110m}\text{Ag}$... $^{93m}\text{Nb}$)

**Countermeasures**
- cooling, correction
- spectrometric separation
- chemical purification
Measurement of $^{93}$Zr by ICP-MS

- Background correction
- Correction for measurement instability using internal standard (Rh)

\[ I_{net} = (I_{measured} - I_{blank}) \cdot \frac{I_{Rh,ref}}{I_{Rh}} \]

- Correction for abundance sensitivity due to stable Zr ($^{92}$Zr, $^{94}$Zr)

\[ I_{net,cor.} = I_{net} - I_{net,Zr92+94} \cdot f_{1} \]

\[ f_{(93/92+94)}: 4.4 \times 10^{-5} \text{ cps/cps} \]

- Calibration with stable Zr standard solution ($^{92}$Zr)

\[ C_{Zr-93} = \frac{I_{net,cor}}{I_{net,cor,Zr-92\text{ std}}} C_{Zr-92\text{ std}} \]

\[ \text{sensitivity: } 5.6 \times 10^{4} \text{ cps/ppb nuclide} \]

- No correction for isobaric Nb interference
Measurement of $^{93}$Zr by LSC

LS spectra can reveal radioactive contamination of Zr fraction!
Measurement of $^{93}$Zr by ICP-MS and LSC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zr-93</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>code</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSC</td>
<td>ICPMS</td>
<td></td>
</tr>
<tr>
<td>Bq/L</td>
<td>Bq/L</td>
<td></td>
</tr>
<tr>
<td>H16-10</td>
<td>51,1</td>
<td>20,0</td>
</tr>
<tr>
<td>H16-1</td>
<td>77,9</td>
<td>53,3</td>
</tr>
<tr>
<td>H16-9</td>
<td>57,8</td>
<td>71,0</td>
</tr>
<tr>
<td>H16-8</td>
<td>47,8</td>
<td>108,8</td>
</tr>
<tr>
<td>H16-5</td>
<td>49,6</td>
<td>118,0</td>
</tr>
<tr>
<td>H16-2</td>
<td>76,1</td>
<td>137,4</td>
</tr>
<tr>
<td>H16-4</td>
<td>44,9</td>
<td>327,0</td>
</tr>
<tr>
<td>H16-6</td>
<td>924,8</td>
<td>1196,3</td>
</tr>
<tr>
<td>H16-3</td>
<td>140,3</td>
<td>55,7</td>
</tr>
</tbody>
</table>

Correlation between ICP-MS and LSC results of Zr-93 analyses

- Nb impurity!
- Contamination!
Measurement of $^{93}$Zr by ICP-MS and LSC

Conclusions

ICP-MS is a sensitive technique to determine $^{93}$Zr but small amounts of stable Nb can cause overestimation of the result.

LSC is exposed to the hazards of radioactive contamination. The presence of radioactive Zr tracer reduces the sensitivity.

LSC helps discover deviation from true value.

The method can be validated by the use of two methods.
63Ni and 59Ni determination

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Decay</th>
<th>$\beta_{\text{Max}}$</th>
<th>Specific Occurance/field of application</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{59}\text{Ni}$</td>
<td>76400 y</td>
<td>EC, $\beta^+$ (X: 6,9)</td>
<td>2,94E+09 keV Bq/g</td>
<td>WD</td>
</tr>
<tr>
<td>$^{63}\text{Ni}$</td>
<td>100 y</td>
<td>$\beta^-$</td>
<td>67, 2,09E+12 keV Bq/g</td>
<td>DN WD</td>
</tr>
</tbody>
</table>

Validation issues:
- No $^{59}\text{Ni}$ standard
- No reference material for $^{59}\text{Ni}$ determination
- No intercomparison exercise for $^{59}\text{Ni}$ determination

Validation options:
- $^{63}\text{Ni}$ determination in CRM and in PT
- Comparison of independent methods: LSC for $^{63}\text{Ni}$, X spectrometry for $^{59}\text{Ni}$, ICP-MS for $^{63}\text{Ni}$ ???, $^{59}\text{Ni}$ ???
63Ni and 59Ni determination

**SAMPLE**
Carriers: 6 mg Fe, 6 mg Ni

**DESTRUCTION**
- MIBK EC
  - LSC/X spectrometry
  - 55Fe
- DMG EC
- DMG precipitate
  - X spectrometry
  - 59Ni
  - LSC
  - 63Ni
  (Fe, Ni recovery: AAS)

- Removal of Fe by extraction chromatography
- Selective separation of Ni by extraction chromatography (from Co, Cu)
- Ni purification by precipitation
- Decomposition of DMG
$^{63}\text{Ni}$ and $^{59}\text{Ni}$ determination

**LSC for $^{63}\text{Ni}$** (Perkin Elmer Tricarb 2800)
Possible interferences

$^{59}\text{Ni}$
- correction if necessary
- any contamination ($^{110}\text{mAg}$...$^{60}\text{Co}$)
- chemical purification

**X-ray spectrometry for $^{59}\text{Ni}$** (Si(Li) and MCA)
Possible interferences: none

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LSC spectrum of a Ni source from H16-3 waste

X-ray spectrum of a Ni source from H17-4 waste

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63Ni and 59Ni determination

**ICP-MS** (Agilent Triplequad 8800)

Possible interferences in ICP-MS
- isobaric interference of 63Ni: **stable Cu** (63Cu-65Cu)
- isobaric interference of 59Ni: **stable Co** (59Co)
- abundance sensitivity: stable Ni (58Ni, 60Ni, 62Ni)
- polyatomic interferences, e.g. 58NiH, 62NiH

Calculation: similar to the case of 93Zr

**Countermeasures**
- mathematical correction
- chemical purification
- mathematical correction
- collision cell
Validation of $^{63}\text{Ni}$ results

Use of reference materials, participation in PTs

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Measured</th>
<th>Reference value</th>
<th>Precision index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{63}\text{Ni}$ activity unc</td>
<td>$^{63}\text{Ni}$ activity unc</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>concentration Bq/kg</td>
<td>concentration Bq/kg</td>
<td></td>
</tr>
<tr>
<td>MAPEP-06-MaS15</td>
<td>357</td>
<td>329</td>
<td>22</td>
</tr>
</tbody>
</table>

Measurement by ICP-MS

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Net intensity at mass 63 (Ni-63+Cu-65)</th>
<th>Net intensity at mass 65 (Cu-65)</th>
<th>Ni-63 corrected concentration for Cu-63</th>
<th>Ni-63 activity concentration</th>
<th>Ni-63 activity concentration ratio</th>
<th>LSC Ni-63 activity concentration in waste</th>
<th>Cu concentration in waste</th>
<th>Ni concentration in waste</th>
<th>Cu/ppb</th>
<th>Ni/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>H16-3/1</td>
<td>3,34E+07</td>
<td>1,48E+07</td>
<td>LD</td>
<td>LD</td>
<td>LD</td>
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<td>H17-4</td>
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<td>H17-6</td>
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<td>8,55E+04</td>
<td>1,53E+00</td>
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<td>6,42E+05</td>
<td>76</td>
<td>37</td>
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<td></td>
</tr>
</tbody>
</table>

Cu-63/Cu-65 ratio: $2,22$

Ni sensitivity: $5,61E+04$ cps/ppb nuclide

Ni-63 specific activity: $2,09E+03$ Bq/ng

Not waste matrix

The presence of a few ppb Cu causes significant overestimation!

Work in high purity environment
Validation of $^{59}$Ni results

No reference material, no PT

Measurement by ICP-MS

<table>
<thead>
<tr>
<th>Sample code</th>
<th>MP-AES measurement</th>
<th>ICP-MS measurements</th>
<th>XRF measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co concentration</td>
<td>Ni-59 intensity</td>
<td>Ni-59 activity</td>
</tr>
<tr>
<td></td>
<td>by AES ppb</td>
<td>corrected for Co</td>
<td>concentration</td>
</tr>
<tr>
<td></td>
<td>at mass 59 cps</td>
<td>Ni-59 ppb=ng/mL</td>
<td>activity concentration</td>
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<tr>
<td></td>
<td></td>
<td>Bq/mL</td>
<td>Bq/L waste</td>
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<td>1,25E+02</td>
<td>5,10E+06</td>
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<td>1,21E+05</td>
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<tr>
<td></td>
<td></td>
<td>2,15E+00</td>
<td>6,33E+00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5694</td>
<td>1080</td>
</tr>
</tbody>
</table>

Co sensitivity: $5,44E+04$ cps/ppb

Ni sensitivity (isotopic): $5,61E+04$ cps/ppb nuclide

Ni-59 specific activity: $2,94$ Bq/ng

The presence of a 1-2 ppb Co causes significant overestimation!
Conclusions

\(^{63}\text{Ni}\) results obtained by LSC can be validated by the measurement of reference materials, participation in intercomparison exercises.

Techniques for validation of \(^{59}\text{Ni}\) results obtained by X–ray spectrometry are not available.
Conventional techniques of method validation are not always sufficient or available.

The accuracy of $^{90}$Sr results can be confirmed by performing repeated measurements.

$^{93}$Zr results can be validated by comparing LSC and ICP-MS measurements.

Validation of $^{63}$Ni and $^{59}$Ni results by comparing LSC/X-ray spectrometry and ICP-MS measurements has failed due to the presence of a few ppb Cu or Co.