Challenges in assaying beta-emitting radionuclides in wastes

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Commissariat à l’Energie Atomique

Governmental institution in charge of implementing R&D in military and civilian nuclear fields, ~15 000 people

15000 staff

Department of Physico-Chemistry

~190 staff, 50% research engineers, 50% technicians
~20 PhD / Post-doc
Missions:

- Experimental analysis and modelling of elementary mechanisms and of physico-chemical processes involved in the evolution of materials and in the behaviour of radionuclides in their environment.

- Development and implementation of analytical methods in the solid, liquid and gas phase.

Within:

- Industrial media
- Natural media
- Biological media
LANIE : Laboratory of Nuclear, Elementary and Isotopic Analyses

Development and implementation of high performance chemical specific separations and measurement technics for trace level analyses

✎ Expert lab. for the isotopic analyses of spent fuel
Analysis FP/actinides at few ‰ (ID), support to EdF and AREVA NC for the qualification of neutronic codes, development of new fuels, increase of burnup rates, etc.

✎ Characterization of liquid/solid nuclear wastes:
Support to the teams in charge of managing nuclear wastes in Saclay, Expert lab for the analyses of chemical hazards and LLRN at trace levels in LILW. Support to ANDRA, EdF (UNGG dismantling), etc.
LIL Nuclear Wastes Characterization

LILW are coming from:

✓ NPPs, recycling plants or nuclear research centers (clothing, gloves, rags, papers, filters, tooling, seals...)
✓ Medical centers (syringes, bottles...)
✓ Research laboratories (bottles, contaminated objects...)
✓ Industry (spent sources, etc.)

✓ Radiological waste characterization:
Detecting the presence of individual radionuclides and quantifying their inventories in the waste in view of their Waste Acceptance Criteria (WAC) for their handling, transportation, storage, processing and/or disposal service.
Measurement Goals

原有的内容已经标注了相应的自然语言解析。
**Analytical scheme**

**Complex Matrice LILW (A_{total} \sim \text{MBq.g}^{-1})**

*Effluents, Solid Wastes (Resins, Concrete…)*

*Technological Wastes (gloves, filters, plastic, papers, lab materials…)*

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**Preparation**
- Fractionning
- Grinding
- Drying
- Dilution
- Medium Change
- Spiker/Carrier addition

**Mineralization**
- Pyrolysis
- Alcalin Fusion
- Nitric Atac
- Mineralisation under micro-wave flux
- Parr Bomb Combustion

**Separation/Extraction**
- Co-precipitation
- Specific column Chromatography
- HPLC
- Specific molecules spiking
- liquid/liquid extraction

**Measurement**
- Ionic Chromatography
- AAS, ICP-AES
- ICP-MS
- Gravimetry
- Alpha, beta counting
- Alpha, gamma spectrometry
- Liquid Scintillation Counting

**Radionuclides (A \sim 100\text{mBq.g}^{-1})**

- RN : $^3$H, $^{14}$C, $^{59}$Ni, $^{90}$Sr, $^{241}$Pu, $^{238}$et $^{240}$Pu, $^{239}$Pu, $^{108m}$Ag, $^{243}$Am, $^{241}$Am, $^{232}$U, $^{234}$U, $^{235}$U, $^{238}$U,
- $^{10}$Be, $^{36}$Cl, $^{41}$Ca, $^{55}$Fe, $^{63}$Ni, $^{99}$Mo, $^{93}$Zr, $^{94}$Nb, $^{129}$I, $^{79}$Se, $^{107}$Pd, $^{126}$Sn, $^{151}$Sm…
How does it work?

**STEP 1 : Measurement Protocol Development**
- Chemistry, Radiochemistry….
- Stable and radioactive isotopes of the same element have the same chemical properties

**STEP 2 : Validation Methodology**
- Statistics, Standards….
- Certified Reference Materials

**STEP 3 : ‘Routine’ analysis**
- Skills, traceability
- Audit, PT, Training, Intercomparisons
Validation problems

Find solutions for specific validation methods demonstrating:

- Decontamination yield
- Separation ability
- Extraction yield
- Reproducibility
- Accuracy

\{ Synthetic/Real samples \}

\{ Radioactive Spiker/Stable element \}

CRMs and standards

- No adequate CRMs
- No CRM at all
  - Use liquid standards to implement solid materials
- No Liquid standards
  - Use real samples
  - Implement and qualify our own purified spikers
  - …..
Beta-emitting radionuclides by LSC

 Advised Measurement conditions:

- Impurities control
- Chemical composition control

 Advised Scintillation cocktail:

- Miscibility and stability with time
  - Adaptation of the scintillation cocktail
  - Adaptation of the solution removed after the radiochemistry

- Proportions to optimise the counting efficiency

- Standard quenched correction curve
  - quenching agent
  - liquid standard

Never forget that it will be considered as a waste and that we will have to manage these wastes!
R&D fields on LLRn and Challenges

<table>
<thead>
<tr>
<th>Measurement protocol development</th>
<th>Validation methodology development</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Radiochemistry</td>
<td>129mI (Spec X)</td>
</tr>
<tr>
<td>- Solution chemistry</td>
<td>93Zr (ICP-MS)</td>
</tr>
<tr>
<td>- Nuclear measurements</td>
<td>99mTc (ICP-MS)</td>
</tr>
<tr>
<td>- Mass Spectrometry</td>
<td>94Nb (Spec γ)</td>
</tr>
<tr>
<td>- Analytical Chemistry</td>
<td>14C (SL)</td>
</tr>
<tr>
<td>- Creativity</td>
<td>93Mo (Spec X)</td>
</tr>
<tr>
<td></td>
<td>63Ni (SL)</td>
</tr>
</tbody>
</table>

- Technological monitoring
- Communication
- Knowledge/Skills transfer

- Chemometrics
- Statistics
- Uncertainty
- Standards
- Programming

**T1/2 (ans)**

30

10^-7

10^-6

10^-5

10^-4

10^-3

10^-2

10^-1

10^0

10^1

10^2

10^3

10^4

10^5

10^6

10^7
Examples:

- $^{36}$Cl
- $^{79}$Se
- $^{126}$Sn

Life is like a box of chocolates. You never know what you're gonna get.


**Implementation of an Home-made reference sample**

- Good chlorine trap
- Homogen
- Fractionnable in very low quantity (~100mg)
- Stable for storage and easily handled
- Preparation traceability

**Classical anion exchangers :** resin AG1-X4 type + $^{36}$Cl spiker

**Methodology of validation : comparison between 3 measurement protocols**

- **Solid Sample**
  - **Aliquot ~300mg**
    - Liquid Scintillation
      - Count yield ~99%
      - DL = 1 Bq.g$^{-1}$
  - **Aliquot ~150mg**
    - Parr Bomb
      - Combustion
      - Yield ~100%
  - **Aliquot ~200mg**
    - Pyrolysis or HP µ-wave
      - Radchem
        - 50%<yield<100%
      - Liquid Scintillation
        - DL = 50 Bq.g$^{-1}$
        - 9<DL<5 Bq.g$^{-1}$
**36Cl : No CRM but liquid standard**

Methodology of validation: comparison between 3 measurement protocols

\[ \text{RHA}_{\text{ref}} = 2992 \pm 180 \text{ Bq.g}^{-1} \]

\[ \text{RLA}_{\text{ref}} = 39.4 \pm 2.5 \text{ Bq.g}^{-1} \]

Life is like a box of chocolates. You never know what you're gonna get.
**79Se**

**STEP 1: Measurement Protocol Development**
- Chemistry, Radiochemistry…
  - Few previous studies
    - $^{79}\text{Se}$ in FP solutions
    - Se in environment
  - Measurement methods:
    - LSC (interference: any other $\beta$-$\gamma$ Emitter)
    - ICP-MS (interference: $^{79}\text{Br}$)
  - No consensus on the $T_{1/2}$... Getting stabilised

**STEP 2: Validation Methodology**
- Statistics, Standards...
  - Certified Reference Materials ➔ MISSING

**STEP 3: "Routine" analysis**
- Skills, traceability
  - Audit, PT, Training, Intercomparisons
79Se – Radiochemistry development on non active samples

**Phase 1: Development on synthetic stable solutions**

- Addition of HNO₃ or NO₃+HF
  - Micro-wave heating
- Addition of 75Se spike
- Evaporation on hot plate
- Cationic exchange resin
  - Halides precipitation
  - Centrifugation
- Anionic exchange resin
- ICP-MS and AAS stable Se measurement

**Conclusions Phase 1:**
- Quantitative extraction of Se
- Salt charge elimination
- Elimination of Br (main interferent in ICP-MS)
$^{79}$Se – Phase 2 : Preliminary tests on real samples

**Phase 2a : Real sample a : effluent spiked with $^{75}$Se**

<table>
<thead>
<tr>
<th>RN</th>
<th>Initial activities (Bq.g$^{-1}$)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{75}$Se</td>
<td>3555 ± 390</td>
<td>70,6</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>4425 ± 100</td>
<td>&lt;0,2</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>38150 ± 765</td>
<td>0,2</td>
</tr>
<tr>
<td>$^{110m}$Ag</td>
<td>1530 ± 45</td>
<td>&lt;0,7</td>
</tr>
<tr>
<td>$^{125}$Sb</td>
<td>1030 ± 45</td>
<td>2,4</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>1900 ± 50</td>
<td>&lt;0,5</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>905 ± 20</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

**Conclusion Phase 2a :**

Improvements needed on the step on the resins in order to :

- Improve the yield of Se removal
- Minimize the removal of co-eluted elements
79Se – Phase 2 : Preliminary tests on real samples

Phase 2b : Real sample b : Sludges spiked with 75Se

Mass 79 free of interferent

<table>
<thead>
<tr>
<th>RN</th>
<th>Activités initiales (Bq.g⁻¹)</th>
<th>Rendement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75Se</td>
<td>52100 ± 2100</td>
<td>60</td>
</tr>
<tr>
<td>54Mn</td>
<td>20100 ± 800</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>60Co</td>
<td>2071000 ± 39000</td>
<td>&lt;5.10⁻³</td>
</tr>
<tr>
<td>65Zn</td>
<td>32100 ± 1800</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>125Sb</td>
<td>7300 ± 1200</td>
<td>7</td>
</tr>
<tr>
<td>133Ba</td>
<td>4400 ± 500</td>
<td>&lt;2.5</td>
</tr>
<tr>
<td>134Cs</td>
<td>24500 ± 900</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>137Cs</td>
<td>3196000 ± 74000</td>
<td>&lt;3,4.10⁻³</td>
</tr>
<tr>
<td>152Eu</td>
<td>42600 ± 1900</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>154Eu</td>
<td>39500 ± 1500</td>
<td>&lt;0.7</td>
</tr>
<tr>
<td>155Eu</td>
<td>6000 ± 700</td>
<td>&lt;5.83</td>
</tr>
<tr>
<td>241Am</td>
<td>291000 ± 1900</td>
<td>&lt;4,4.10⁻²</td>
</tr>
</tbody>
</table>

$F_d$(60Co) ~ 11000
Bad Decontamination in 125Sb

ICP-MS

LSC
$^{79}$Se – Phase 3 : Improvement

Phase 3a : Make the radiochemistry more selective

- Add $\text{HNO}_3$ or $\text{NO}_3^+$ and HF
- Micro-wave heating
- Addition of $^{75}$Se spike
- Evaporation on hot plate
- Cationic exchange resin
- Réduction en Se(IV) dans HCl 6M
- Ethylation / Extraction
- Réextraction dans HNO$_3$ c
- Anionic exchange resin
- ICP-MS and LSC measurements

Selective extraction step
**79Se – Phase 3 : Improvement**

**Phase 3b : Real sample c : Sludges spiked with 75Se**

60Co (3,1 MBq l⁻¹), 137Cs (3,7 MBq l⁻¹), 241Am (0,07 MBq l⁻¹)

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**LSC**

75Se pur dans l'échantillon final

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**Spectrometrie gamma**

- Bonne décontamination
- Seul émetteur détecté : 75Se
- Rendement 75Se : 60%
79Se - To be continued…

**STEP 1 : Measurement Protocol Development**
- Chemistry, Radiochemistry….
- OK but could be improved

**STEP 2 : Validation Methodology**
- Statistics, Standards…
- Certified Reference Materials ➔ MISSING
- Certified liquid standards ➔ MISSING

**STEP 3 : Routine analysis**
- Skills, traceability
- Audit, PT, Training, Intercomparisons

References:
- Aguerre S. and Frechou C., "Development of a radiochemical separation for selenium with the aim of measuring its isotope 79 in low and intermediate nuclear wastes by ICP-MS" Talanta (2006), Vol. 69, pp. 565-571
- **Examples:**
  - $^{36}$Cl
  - $^{79}$Se
  - $^{126}$Sn

*Life is like a box of chocolates. You never know what you're gonna get.*
**126Sn**

### STEP 1: Measurement Protocol Development

- **Chemistry, Radiochemistry…**
  - OK tested with different isotopes

### STEP 2: Validation Methodology

- **Statistics, Standards…**
- **Certified Reference Materials** → **MISSING**
- **Certified liquid standards** → **MISSING**
- **Different isotopes** → **OK** (113Sn, 121mSn)
- **Sample containing high amounts of 126Sn** → **OK**

### STEP 3: ‘Routine’ analysis

- **Skills, traceability**
- **Audit, PT, Training, Intercomparisons**
126Sn – STEP 1

Mineralization: 113Sn spiker and stable Sn as carrier

Co-precipitation Al(OH)₃ / Dissolution HCl 8M
⇒ SnCl₄²⁻

Preliminary Purification on AG1X8
⇒ Sn⁴⁺ en HNO₃ 1M

Coo-precipitation with MoS₃ / Dissolution in HNO₃ 69% + HCl
⇒ SnCl₄

Ethylation in acetic acid buffer
⇒ Sn(Et)₄ in isooctane

Back-extraction of Sn via degradation of tetra-ethyl Sn
(HNO₃ 69% + HCl 12M) ⇒ SnCl₄

Final purification on AG1X4 with Ultrex products
⇒ Sn⁴⁺ in HNO₃ 1M + HF (0.01M)

Tests with 113Sn as a spiker

✓ Different real samples (effluents to sludges)
✓ Yields from 55% to 70%
✓ Good decontamination factors

ICP-MS
γ Spec
\[ ^{126}\text{Sn} \] – More informations

- \[ ^{126}\text{Sn} : \beta^- - T = 1.10^5 \text{ a (FP)} \]
  - No liquid standard
  - ICP-MS

- \[ ^{113}\text{Sn} : \gamma (392 \text{ keV}) - T = 115.09 \text{ j (AP)} \]
  - Liquid standard
  - \( \gamma \text{ Spec} \)

- \[ ^{121m}\text{Sn} : \beta^- , X (37.1 \text{ keV}) - T = 55.0 \text{ a (PF+PA)} \]
  - Home-made purified solution from zircaloy sheath
  - \( \gamma \text{ Spec} \)

- Lack of certified liquid standard \( ^{126}\text{Sn} \). Furthermore, it's impossible to bracket the 126 uma to evaluate the mass bias. How qualifying the final measurement?

- Spikers: \( ^{113}\text{Sn} \) or \( ^{121m}\text{Sn} \) (or stable?) : measurement by a different method than the one possible for the \( ^{126}\text{Sn} \). Which one should be used to optimise uncertainty budget?

- Purify a solution of \( ^{126}\text{Sn} \)

- Implementation of an home-made reference sample with 3 spikers: \( ^{126}\text{Sn}, ^{121}\text{Sn} \) et \( ^{113}\text{Sn} \)

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<table>
<thead>
<tr>
<th>M</th>
<th>%T/%T ___</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>0.96</td>
</tr>
<tr>
<td>113</td>
<td>115d</td>
</tr>
<tr>
<td>114</td>
<td>0.66</td>
</tr>
<tr>
<td>115</td>
<td>0.35</td>
</tr>
<tr>
<td>116</td>
<td>14.3</td>
</tr>
<tr>
<td>117</td>
<td>7.61</td>
</tr>
<tr>
<td>118</td>
<td>24.03</td>
</tr>
<tr>
<td>119</td>
<td>8.58</td>
</tr>
<tr>
<td>120</td>
<td>32.85</td>
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<tr>
<td>121</td>
<td>1.13d</td>
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<td>122</td>
<td>4.72</td>
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<tr>
<td>123</td>
<td>129.2d</td>
</tr>
<tr>
<td>124</td>
<td>5.94</td>
</tr>
<tr>
<td>125</td>
<td>9.63d</td>
</tr>
<tr>
<td>126</td>
<td>1.10^5a</td>
</tr>
</tbody>
</table>
**126Sn - STEP 2**

**Phase 2a : preparation of a purified 126Sn solution**

- **Solution of irradiated fuel sample : 2 x 0.5mL**
- **Alpha decontamination**
  - TRU SPEC
- **Cs decontamination**
  - + A⁺³ + H₃BO₃ + NH₄OH + Filtration
- **Preparation for transport**
  - Dissolution en HNO₃ 6M (~20mL) et conditionnement
- **Removal**
  - Coprecipitation Al(OH)₃ + dissolution HCl 8M
- **Resine AG1X8 with spec gamma track**
  - Initial : 93000Bq ¹³⁷Cs + 1 autre beta pur?
  - Cleaning n°1 : HCl 1M + hydroxylamine : 300 Bq ¹⁰⁶Ru + 400 Bq ¹²⁵Sb + 35 Bq ¹³⁷Cs
  - Cleaning n°2 : HNO₃ 1M : 13 Bq ¹²⁵Sb
  - Elution HNO₃ 1M : 175Bq ¹²⁵I + 21 Bq ¹²⁵Sb + 53.3Bq ¹⁰⁶Ru
- **Separation protocol**
- **Final purification on AG1X4**
  - Sn⁺⁺⁺ in HNO₃ 1M + HF 0.01M

**2 x 20mL HNO₃ (1M) / HF (0.01M)**
- **Sce1* : ~10,2 Bq (20,0113g)**
- **Sce2* : ~9,9 Bq (20,1181g)**

*Activité spécifique 126Sn : 9,52.10⁻¹⁰ g.Bq⁻¹
28

**126Sn - STEP2**

**Phase 2b : Resin spiking (AG1X8)**

- Resin AG1X8 m. g
- HCl 4M + stable Sn
- 126Sn 121mSn 113Sn

\[ \text{Solution} \]

\[ \text{Gamma Spec For spiking yield evaluation} \]

\[ \text{Resin} \rightarrow \text{Drying 60}^\circ\text{C} \]

\[ \text{Dry resin} \sim A, Bq.g^{-1} \]

- 1,6340 g of resin
- 113Sn / 121mSn / 126Sn
- **Same trapping yields**
- 5 aliquots for radiochemistry

DEN / DPC/SECR
Laboratoire d'Analyses Nucléaires Isotopiques et Elémentaires

NPL LSUF - 14th October 2008
Phase 2c: Tests on the resin spiked with $^{113}\text{Sn}$, $^{121m}\text{Sn}$ and $^{126}\text{Sn}$
Many clues and tracks

- Verify the stability of the solution... (No liquid standard for the 126 isotope)
- Define the measurement uncertainties
- Find a way to measure the activity of the 126Sn solution
- Work on the calibration problem on ICP-MS
Life is like a box of chocolates. You never know what you're gonna get.