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Determination of $^{93}$Mo (and $^{94}$Nb) in nuclear decommissioning waste from a nuclear reactor

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RAS academic meeting (23 April 2018)
Nutech meeting (26 April 2018)
18th Radiochemical Conference (13-18 May 2018, Mariánské Lázně)
NKS RadWorkshop (8-12 October 2018, Risø)
A short introduction

- DTU Nutech (Technical University of Denmark, Center for Nuclear Technologies) is the Danish competence center for nuclear technologies.
- The 3 former Danish research reactors were on the campus.
- DTU Nutech (1956-2006 called Risø) has long-term experience on radiochemical analyses of (among others) nuclear waste, especially decommissioning waste.
- \( ^3\text{H}, \ ^{14}\text{C}, \ ^{36}\text{Cl}, \ ^{41}\text{Ca}, \ ^{55}\text{Fe}, \ ^{59}\text{Ni}, \ ^{63}\text{Ni}, \ ^{90}\text{Sr}, \ ^{93}\text{Mo}, \ ^{93}\text{Zr}, \ ^{94}\text{Nb}, \ ^{99}\text{Tc}, \ ^{129}\text{I}, \ ^{210}\text{Po}, \ ^{210}\text{Pb}, \ ^{226}\text{Ra}, \ ^{237}\text{Np}, \ ^{234}\text{U}, \ ^{235}\text{U}, \ ^{236}\text{U}, \ ^{238}\text{U}, \ ^{238}\text{Pu}, \ ^{239}\text{Pu}, \ ^{240}\text{Pu}, \ ^{241}\text{Pu}, \ ^{241}\text{Am}, \ ^{244}\text{Cm}; \ ^{60}\text{Co}, \ ^{152}\text{Eu}, \ ^{154}\text{Eu}, \ ^{134}\text{Cs}, \ ^{137}\text{Cs}. \)
Samples

- Metals from a NPP (under decommissioning)
  Main radioactive component: $^{60}\text{Co} \ (\approx \text{kBq-MBq})$
  
  - Induced activity samples
    Small pieces, irradiated by neutrons
    Activation products
  
  - Surface layer activity samples
    Big pieces, contacted with primary water
    Corrosion products

- Model sample (for method development):
  NIST Standard Reference Material 123c
  (Cr-Ni-Nb Stainless Steel; AISI 348)

<table>
<thead>
<tr>
<th>Metal</th>
<th>m/m %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>the rest (68.52%)</td>
</tr>
<tr>
<td>Cr</td>
<td>17.40%</td>
</tr>
<tr>
<td>Ni</td>
<td>11.34%</td>
</tr>
<tr>
<td>Mn</td>
<td>1.75%</td>
</tr>
<tr>
<td>Nb</td>
<td>0.65%</td>
</tr>
<tr>
<td>Mo</td>
<td>0.22%</td>
</tr>
<tr>
<td>Co</td>
<td>0.12%</td>
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</table>
Goal

• To develop a new method for determination of $^{93}\text{Mo}$ and $^{94}\text{Nb}$ in nuclear power plant decommissioning wastes

$^{93}\text{Mo}$
• $t_{1/2} = (4.0 \pm 0.8) \times 10^3$ years
• Electron capture
• Possibilities for detection:
  - X-ray spectrometry: 16.5 keV (62%) and 18.6 keV (9%) – $K_{\alpha}$ and $K_{\beta}$ lines of Nb
  - LSC: Auger-electrons
  - MS: presence of natMo (abundance sensitivity of $^{92}\text{Mo}$ (15%) and $^{94}\text{Mo}$ (9%))

$^{94}\text{Nb}$
• $t_{1/2} = 2.0 \times 10^4$ years
• $\beta^{-}\gamma$ emitter ($E_{\beta,\text{max}} = 470$ keV)
• Detection by gamma-spectrometry:
  - 703 keV (98%) and 871 keV (100%)

• Radiochemical separation is needed before measurement!
  - $^{93}\text{Mo}/^{60}\text{Co} \approx 10^{-5} - 10^{-3}$
  - $^{93}\text{Mo}/^{93m}\text{Nb} \approx 10^{-5} - 10^2$
  - $^{94}\text{Nb}/^{60}\text{Co} \approx 10^{-5} - 10^{-3}$

(activity ratios in our samples)
Overview of our method

• Dissolution
• Combined chromatographic separation
  – Cation exchange
  – TEVA
  – Alumina
• Measurements

Detection techniques used in method development:

• Gamma-spectrometry: $^{60}$Co, $^{94}$Nb, $^{125}$Sb; $^{99m}$Tc

• ICP-OES: stable elements (Fe, Cr, Ni, Mn, Mo, Nb, Zr)
  – Interferences
  – Extra problem: elimination of HF by dilution, evaporation or complexation ($\text{H}_3\text{BO}_3$)
Dissolution

- Surface samples: “leaching” of the activity from the surface
- Induced samples: direct dissolution

- Addition of carriers (stable Mo and Nb)
  - ICP-OEC measurement of aliquots taken before and after separation → Recovery

- Dissolution and repeated evaporation using aqua regia (68% HNO₃ + 36% HCl) and 40% HF
  - Oxidation to MoO₄²⁻ (+VI, crucial)
  - Green solution: Cr³⁺

- Dissolution in 0.1 M HF
- Dilution until 0.02 M HF
1. column: Cation exchange resin. Getting rid of the matrix

Load & rinse: 0.02 M HF (lower c → higher DF)

Retained: cations (majority of the activity)
- $^{54}$Mn$^{n+}$, $^{55}$Fe$^{3+}$, $^{60}$Co$^{2+}$,
- $^{59}$Ni$^{2+}$, $^{63}$Ni$^{2+}$, $^{65}$Zn$^{2+}$, Cr$^{3+}$

Pass through: anions
- $^{93}$Zr: ZrF$_6^{2-}$
- $^{125}$Sb: SbF$_6^{-}$
- $^{99}$Tc: TcO$_4^{-}$
- $^{93m}$Nb and $^{94}$Nb: NbF$_6^{-}$, NbOF$_5^{2-}$
- $^{93}$Mo: MoO$_2$F$_3^{-}$, [MoO$_2$F$_4$]$^2-$, MoF$_7^{-}$, MoOF$_5^{-}$, CrO$_4^{2-}$ (When applying reducing agents, the Mo recovery is reduced as well.)
2. column: TEVA® resin. Separation of anions

- Based on a quaternary ammonium salt
  (Triskem product, very similar to anion exchangers)

- Load & rinse: 0.02 M HF
- **Zr strip**: 5 mL 7 M HCl/0.5 M HF
- **Mo strip**: 12 mL 4 M HF
- **Nb strip**: 10 mL 1 M HNO₃

Reference:
Shimada & Kameo (2016)
J Radioanal Nucl Chem 310:1317-1323

Dissolution
Cation exch.
TEVA
Zr  Mo  Nb
Alumina
LSC

<table>
<thead>
<tr>
<th>40 mm column 3 mL fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
</tr>
<tr>
<td>1.</td>
</tr>
<tr>
<td>2.</td>
</tr>
<tr>
<td>3.</td>
</tr>
<tr>
<td>4.</td>
</tr>
<tr>
<td>5.</td>
</tr>
</tbody>
</table>

Reference:
Shimada & Kameo (2016)
J Radioanal Nucl Chem 310:1317-1323
04.12.2018
Measurement of $^{94}$Nb using HPGe

- Original sample
- After cation exchange column
- After TEVA column (Nb fraction)

- $^{60}$Co
- $^{94}$Nb

Counts vs. Energy (keV)

- $^{94}$Nb: $2 \times 10^2$ Bq
- $^{60}$Co: $< 0.2$ Bq
- MDA = 0.04 Bq

- Dissolution
- Cation exch.
- TEVA
- Alumina

- $^{60}$Co: $< 70$ Bq
- $^{94}$Nb: $10^5$ Bq
3. column: Alumina (Al₂O₃). Purification of Mo

- Widely applied for \(^{99m}\text{Tc}/^{99}\text{Mo}\) separation in "technogenerator"s (using HNO₃ media)
- But practically no information is available about usage of HF media

- Load & rinse: 1 M HNO₃
- Wash: 0.1 M HNO₃
  - H₂O
  - 0.01 M NH₃
- Mo strip: 1:1 NH₃

Other metals pass mainly through

- Load & rinse: ≤0.1 M HF
- Wash:
  - H₂O
  - 0.01 M NH₃
- Mo strip: 1:1 NH₃

Other metals are retained

- In general, results are similar
- Higher \(c\) of NH₃ → more effective elution of Mo (no contaminants were found)

Reference:
Bernhard (1994)
J Radioanal Nucl Chem 177(2):321-325
Measurement of $^{93}$Mo using LSC

- Evaporated sample (300-400 μL) + 20 mL Ultima Gold LLT
- $\eta = 52\%$

X-ray spectrum (HPGe)
- Problem: self-absorption

LSC spectrum
- Problem: quench

Calibration
- Sample 34
- Sample 24
Method performance

• Recoveries:
  – Mo: typically over 85%
  – Nb: typically over 75%
  – Zr: typically over 70%

• The procedure was successfully applied for the first 2 real samples

• Decontamination factors:

<table>
<thead>
<tr>
<th>Element</th>
<th>Cation exchange</th>
<th>TEVA Mo fr.</th>
<th>Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>$\geq 10^3$</td>
<td>$10^3$</td>
<td>$\geq 4\times10^2$</td>
</tr>
<tr>
<td>Cr</td>
<td>$\approx 2$</td>
<td>500</td>
<td>$\geq 8\times10^3$</td>
</tr>
<tr>
<td>Co</td>
<td>$10^3$</td>
<td>$10^4$</td>
<td>$\geq 10^2$</td>
</tr>
<tr>
<td>Ni</td>
<td>$10^3$</td>
<td>$10^4$</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>$10^3$</td>
<td>$10^4$</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>1</td>
<td>$5\times10^2$</td>
<td>$\geq 2\times10^4$</td>
</tr>
<tr>
<td>Zr</td>
<td>1</td>
<td>$\geq 10$</td>
<td>$\geq 7\times10^2$</td>
</tr>
<tr>
<td>Sb</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>1</td>
<td>$3\times10^2$</td>
<td>$4\times10^2$</td>
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</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Cation exchange</th>
<th>TEVA Nb fr.</th>
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<tbody>
<tr>
<td>Fe</td>
<td>$\geq 10^3$</td>
<td>$10^5$</td>
</tr>
<tr>
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</tr>
<tr>
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<td>$10^4$</td>
</tr>
<tr>
<td>Ni</td>
<td>$10^3$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Mn</td>
<td>$10^3$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Mo</td>
<td>1</td>
<td>$10^2$</td>
</tr>
<tr>
<td>Zr</td>
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<td>$\geq 10^2$</td>
</tr>
<tr>
<td>Sb</td>
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<td></td>
</tr>
<tr>
<td>Tc</td>
<td>1</td>
<td>$10^3$</td>
</tr>
</tbody>
</table>
Summary. Conclusions and perspectives

• A method for determination of $^{93}$Mo (and $^{94}$Nb) - based on combined chromatographic separation - was successfully developed

• Recoveries and separation factors are satisfying

• Analysis of real samples is in progress
  – Comparison of results with estimated values (based on modelling)
  – $^{125}$Sb: need for an extra step?

• Validation by “standard addition” method

• Gamma-spectrometric measurement of $^{94}$Nb before chemical separation (in the presence of lots of $^{60}$Co) using an anti-coincidence gamma-spectrometer

• Method might be extended for determination of Zr (ICP: recovery, LSC: activity)
Thank you very much for all your help and kind attention.

http://www.nutech.dtu.dk/english
We acquired the 3rd LSC spectrum in the world about $^{93}\text{Mo}$


Contaminated with $^{185}\text{W}$ (433 keV, 100% $\beta^-$)

Calibration of LSC for measurement of $^{93}$Mo

- No certified $^{93}$Mo can be purchased
- “Home-made” solution: Separation of Mo from irradiated Nb
  - Dissolution and repeated evaporation: 40% HF + 68% HNO$_3$
  - Dissolution in 6 M HF
  - First separation step: Precipitation of Nb$_2$O$_5$ and co-precipitation on Fe(OH)$_3$ (using NH$_3$)
    
    *Based on “the lost method” from Patricia Puech (1998): Détermination des radionucléides zirconium 93 et molybdène 93 dans des effluents de retraitement des combustibles irradiés. Thesis, Univ. Paris XI, 211, France*

  - Repeated evaporation: 36% HCl + 68% HNO$_3$
  - Repeated evaporation: 40% HF
  - Dissolution in 0.1 M HF
  - Dilution until 0.05 M HF
  - Second separation step: purification on Alumina column

- Performance of separation: Recovery of Mo $\approx 60$
  - DF of Nb $\geq 10^6$

- Measurement by calibrated X-ray spectrometer
- Measurement by LSC