Determination of 93Mo (and 94Nb) 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.

- $^3$H, $^{14}$C, $^{36}$Cl, $^{41}$Ca, $^{55}$Fe, $^{59}$Ni, $^{63}$Ni, $^{90}$Sr, $^{93}$Mo, $^{93}$Zr, $^{94}$Nb, $^{99}$Tc, $^{129}$I, $^{210}$Po, $^{210}$Pb, $^{226}$Ra, $^{237}$Np, $^{234}$U, $^{235}$U, $^{236}$U, $^{238}$Pu, $^{239}$Pu, $^{240}$Pu, $^{241}$Pu, $^{241}$Am, $^{244}$Cm; $^{60}$Co, $^{152}$Eu, $^{154}$Eu, $^{134}$Cs, $^{137}$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>
</tr>
</tbody>
</table>
Goal

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

$^{93}$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 $^{nat}$Mo (abundance sensitivity of $^{92}$Mo (15%) and $^{94}$Mo (9%))

$^{94}$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!
  – $^{93}$Mo/$^{60}$Co $\approx 10^{-5} - 10^{-3}$
  – $^{93}$Mo/$^{93m}$Nb $\approx 10^{-5} - 10^2$
  – $^{94}$Nb/$^{60}$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: $^{60}\text{Co}$, $^{94}\text{Nb}$, $^{125}\text{Sb}$; $^{99m}\text{Tc}$
- 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 $c \rightarrow$ 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 stip**: 10 mL 1 M HNO₃

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

<table>
<thead>
<tr>
<th>40 mm column 3 mL fractions</th>
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<tbody>
<tr>
<td>Zr</td>
</tr>
<tr>
<td>---</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>
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</table>
Measurement of $^{94}$Nb using HPGe

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

Counts

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>$^{60}$Co</th>
<th>$^{94}$Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>703 keV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>871 keV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{60}$Co

$< 70$ Bq

$^{94}$Nb

$2 \times 10^2$ Bq

$< 0.2$ Bq

$^{94}$Nb

$10^{-1}$ Bq

$^{60}$Co

$0.2$ Bq

$^{94}$Nb

(MDA = 0.04 Bq)
3. column: Alumina (Al₂O₃).

Purification of Mo

• Widely applied for $^{99m}$Tc/$^{99}$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
  \[ \text{H}_2\text{O} \]
  \[ 0.01 \text{ M NH}_3 \]
- Mo strip: 1:1 NH₃

Other metals pass mainly through

- Load & rinse: $\leq$0.1 M HF
- Wash:
  \[ \text{H}_2\text{O} \]
  \[ 0.01 \text{ M NH}_3 \]
- Mo strip: 1:1 NH₃

Other metals are retained

• In general, results are similar
• Higher c of NH₃ $\rightarrow$ 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)](image1.png)

**Problem:** self-absorption

![LSC spectrum](image2.png)

**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>Separation of Mo</th>
<th>Element</th>
<th>Cation exchange</th>
<th>TEVA Mo fr.</th>
<th>Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>≥ 10^3</td>
<td>10^3</td>
<td>≥ 4*10^2</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>≈ 2</td>
<td>500</td>
<td>≥ 8*10^3</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>10^3</td>
<td>10^4</td>
<td>≥ 10^2</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>10^3</td>
<td>10^4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>10^3</td>
<td>10^4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>1</td>
<td>5*10^2</td>
<td>≥ 2*10^4</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>1</td>
<td>≥ 10</td>
<td>≥ 7*10^2</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>1</td>
<td>3*10^2</td>
<td>4*10^2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Separation of Nb</th>
<th>Element</th>
<th>Cation exchange</th>
<th>TEVA Nb fr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>≥ 10^3</td>
<td>10^5</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>≈ 2</td>
<td>10^3</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>10^3</td>
<td>10^4</td>
<td></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>Mo</td>
<td>1</td>
<td>10^2</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>1</td>
<td>≥ 10</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>1</td>
<td>10^3</td>
<td></td>
</tr>
</tbody>
</table>
Summary. Conclusions and perspectives

• A method for determination of $^{93}\text{Mo}$ (and $^{94}\text{Nb}$) - 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)
  – $^{125}\text{Sb}$: need for an extra step?

• Validation by “standard addition” method

• Gamma-spectrometric measurement of $^{94}\text{Nb}$ before chemical separation (in the presence of lots of $^{60}\text{Co}$) 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 $^{93}$Mo

Reference: Bombard (2005)
PhD Thesis, Nantes University, France (pp 139)

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

Reference: Ermakov et al. (2005)
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