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

Osváth, Szabolcs; Hou, Xiaolin; Roos, Per; Qiao, Jixin; Markovic, Nikola

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

Szabolcs Osváth, Xiaolin Hou, Per Roos, Jixin Qiao, Nikola Marković

Technical University of Denmark, Center for Nuclear Technologies (DTU Nutech)

DTU Risø Campus, Frederiksbergvej 399, 4000 Roskilde, Denmark

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, $^{238}$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: $^{60}$Co ($\approx$ 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 $^{93}\text{Mo}$ 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: $^{60}\text{Co}$, $^{94}\text{Nb}$, $^{125}\text{Sb}$; $^{99m}\text{Tc}$
- 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 → higher DF)

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

Pass through: anions
$^{93}\text{Zr}$: $\text{ZrF}_6^{2-}$
$^{125}\text{Sb}$: $\text{SbF}_6^{-}$
$^{99}\text{Tc}$: $\text{TcO}_4^{-}$
$^{93m}\text{Nb}$ and $^{94}\text{Nb}$: $\text{NbF}_6^{-}$, $\text{NbOF}_5^{2-}$
$^{93}\text{Mo}$: $\text{MoO}_2\text{F}_3^{-}$, $[\text{MoO}_2\text{F}_4]^{2-}$, $\text{MoF}_7^{-}$, $\text{MoOF}_5^{-}$
$\text{CrO}_4^{2-}$ (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
Measurement of $^{94}\text{Nb}$ using HPGe

- Dissolution
- Cation exch.
- TEVA
- Zr
- Mo
- Nb
- Alumina
- LSC

Counts

Energy (keV)

$^{60}\text{Co}$

$^{94}\text{Nb}$

$703\text{ keV}$

$871\text{ keV}$

$10^5\text{ Bq}$

$<70\text{ Bq}$

$^{60}\text{Co}$

$2\times10^2\text{ Bq}$

$<0.2\text{ Bq}$

$^{94}\text{Nb}$

$10^{-1}\text{ Bq}$

$0.2\text{ Bq}$

$^{94}\text{Nb}$

(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
  - H₂O
  - 0.01 M NH₃
- Mo strip: 1:1 NH₃

Other metals pass mainly through

- Load & rinse: \(\leq 0.1\) 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 \(\rightarrow\) more effective elution of Mo (no contaminants were found)

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

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

![X-ray spectrum (HPGe)](image1)

Problem: self-absorption

![LSC spectrum](image2)

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>
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</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>
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</tr>
<tr>
<td>Nb</td>
<td>1</td>
<td>10^2</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>1</td>
<td>≥ 10^2</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)  
In: Chalupnik, Schönhofer, Noakes (eds):  
LSC 2005, Advances in Liquid Scintillation Spectrometry (pp 89–98)
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