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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.
- $^3$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%) – $K_a$ 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 ($E_{\beta,max} = 470$ 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: $^{60}$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% HNO$_3$ + 36% HCl) and 40% HF
  - Oxidation to MoO$_4^{2-}$ (+VI, crucial)
  - Green solution: Cr$^{3+}$

- 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)
$^{54}\text{Mn}^{2+}$, $^{55}\text{Fe}^{3+}$, $^{60}\text{Co}^{2+}$,
$^{59}\text{Ni}^{2+}$, $^{63}\text{Ni}^{2+}$, $^{65}\text{Zn}^{2+}$, $\text{Cr}^{3+}$

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

Measurement of $^{94}$Nb using HPGe

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

Energy (keV)

Counts

$^{60}$Co
$^{94}$Nb
$^{703}$ keV
$^{871}$ keV

$10^5$ Bq
$< 70$ Bq
$2 \times 10^2$ Bq
$< 0.2$ Bq
$10^{-1}$ Bq
$0.2$ Bq
$^{94}$Nb
(MDA = 0.04 Bq)

$^{60}$Co
3. column: Alumina (Al$_2$O$_3$). Purification of Mo

- Widely applied for $^{99m}$Tc/$^{99}$Mo separation in “technogenerator”s (using HNO$_3$ media)
- But practically no information is available about usage of HF media

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

Other metals pass mainly through

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

Other metals are retained

- In general, results are similar
- Higher $c$ of NH$_3$ $\rightarrow$ 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
- $\eta = 52\%$

**Problem:** self-absorption

**Problem:** quench
**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>
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<td>$\geq 10^3$</td>
<td>$10^3$</td>
<td>$\geq 4 \times 10^2$</td>
</tr>
<tr>
<td>Cr</td>
<td>$\approx 2$</td>
<td>500</td>
<td>$\geq 8 \times 10^3$</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>$5 \times 10^2$</td>
<td>$\geq 2 \times 10^4$</td>
</tr>
<tr>
<td>Zr</td>
<td>1</td>
<td>$\geq 10$</td>
<td>$\geq 7 \times 10^2$</td>
</tr>
<tr>
<td>Sb</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>1</td>
<td>$3 \times 10^2$</td>
<td>$4 \times 10^2$</td>
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</table>

<table>
<thead>
<tr>
<th>Element</th>
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</tr>
</thead>
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<td>Fe</td>
<td>$\geq 10^3$</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Cr</td>
<td>$\approx 2$</td>
<td>$10^3$</td>
</tr>
<tr>
<td>Co</td>
<td>$10^3$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Ni</td>
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<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>
<td>1</td>
<td>$\geq 10^2$</td>
</tr>
<tr>
<td>Sb</td>
<td>1</td>
<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 $^{93}\text{Mo}$ (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