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)

DTU Nutech

Center for Nukleare Teknologier

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

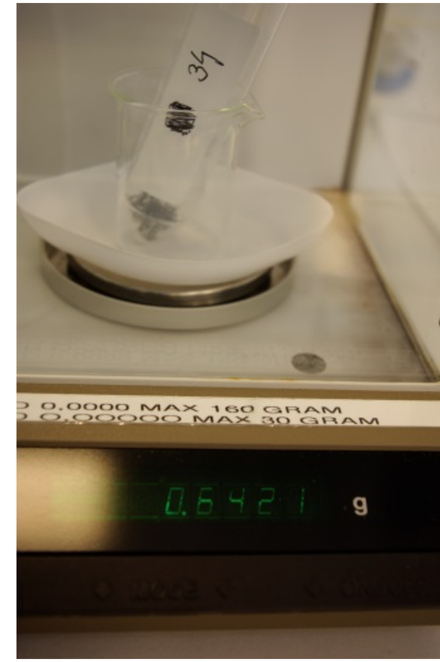
- Metals from a NPP (under decommissioning)
  Main radioactive components: ^{60}Co (≈ kBq-MBq) + ^{55}Fe

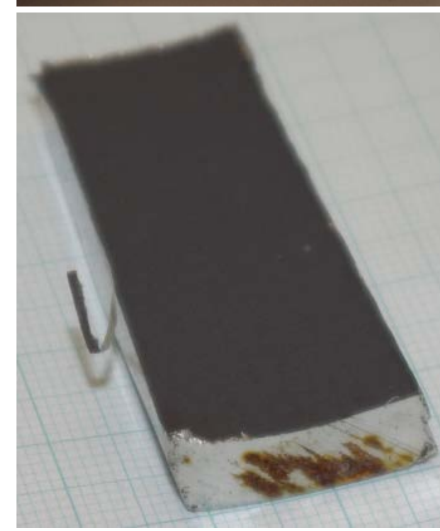
  – Induced activity samples
    Small pieces, irradiated by neutrons
    Activation products

  – 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)

Metal	m / m %
Fe	the rest (68.52%)
Cr	17.40%
Ni	11.34%
Mn	1.75%
Nb	0.65%
Mo	0.22%
Co	0.12%





Goal

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

^{93}Mo

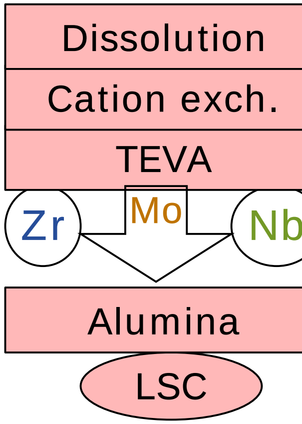
- $t_{1/2}$ = $(4.0 \pm 0.8) \times 10^3$ years
- Electron capture
- Possibilities for detection:
  - X-ray spectrometry: 16.5 keV (62%) and 18.6 keV (9%) – K_α and K_β lines of Nb
  - LSC: Auger-electrons
  - MS: presence of ^{nat}Mo (abundance sensitivity of ^{92}Mo (15%) and ^{94}Mo (9%))

^{94}Nb

- $t_{1/2}$ = 2.0×10^4 years
- β^-–γ 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 ≈ 10^{-5} – 10^{-3}
  - ^{93}Mo/^{93m}Nb ≈ 10^{-5} - 10^{2}
  - ^{94}Nb/^{60}Co ≈ 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 (H_3BO_3)

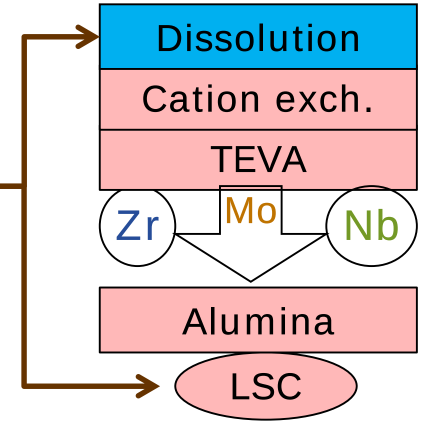
Dissolution

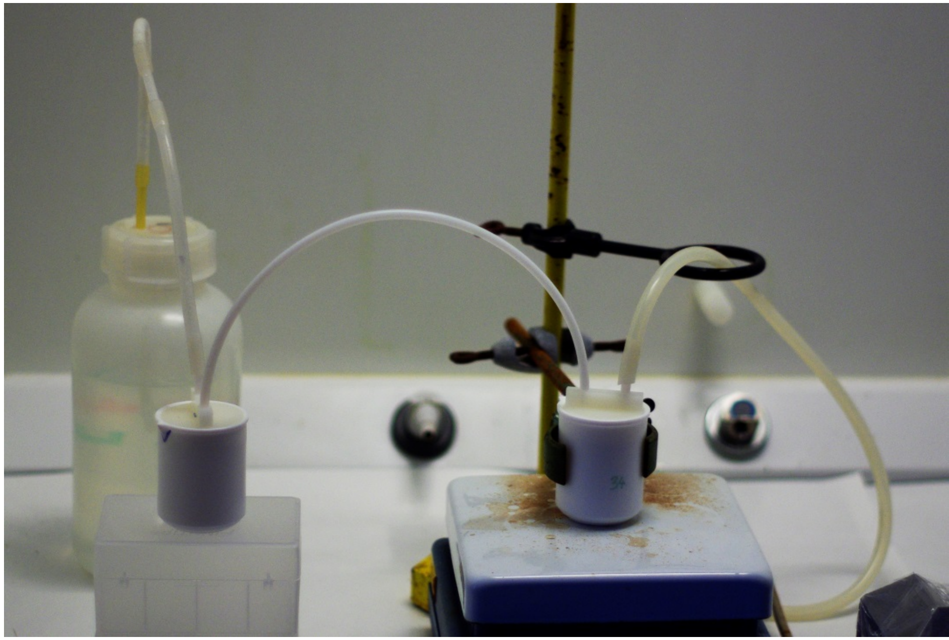
- Surface samples: “leaching” of the activity from the surface
- Induced samples: direct dissolution

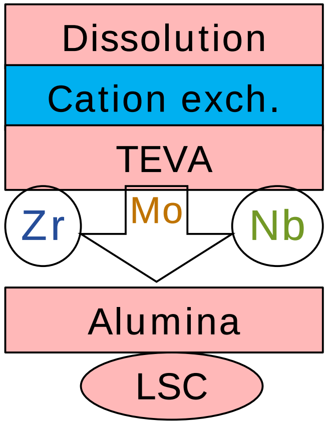
- Addition of carriers (stable Mo and Nb)
  - ICP-OEC measurement of aliquots taken before and after separation → Recovery

- 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+}, Ni^{2+}

- Dissolution in 0.1 M HF
- Dilution until 0.02 M HF





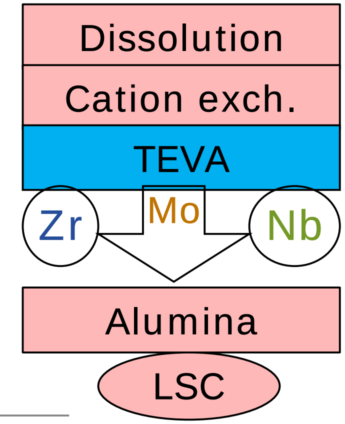


1. column: Cation exchange resin. Getting rid of the matrix

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+}

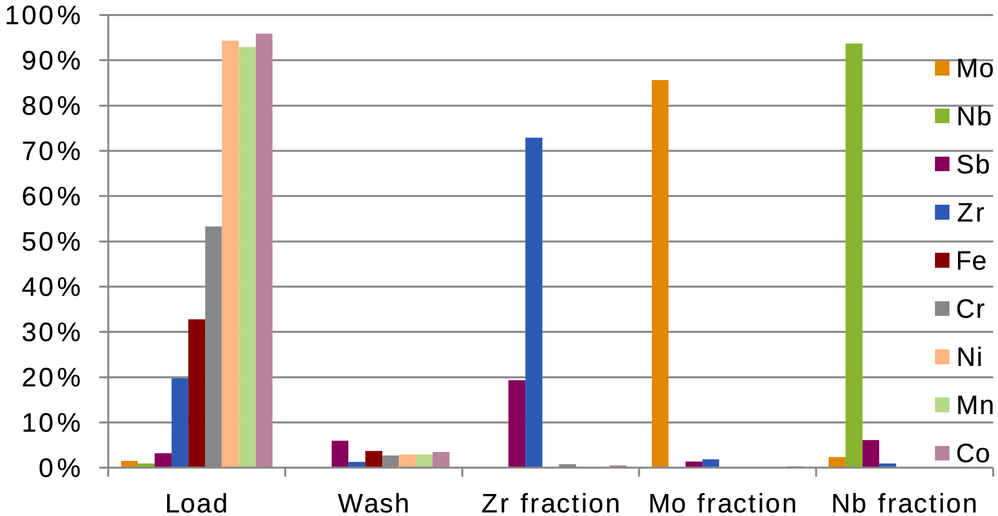
Pass through: anions
^{93}Zr: ZrF_6^{2-}
^{125}Sb: SbF_6^-
^{99}Tc: TcO_4^-
^{93m}Nb and ^{94}Nb: NbF_6^-, $NbOF_5^{2-}$
^{93}Mo: $MoO_2F_3^-$, $[MoO_2F_4]^{2-}$, MoF_7^-, $MoOF_5^-$
CrO_4^{2-} (When applying reducing agents, the Mo recovery is reduced as well.)



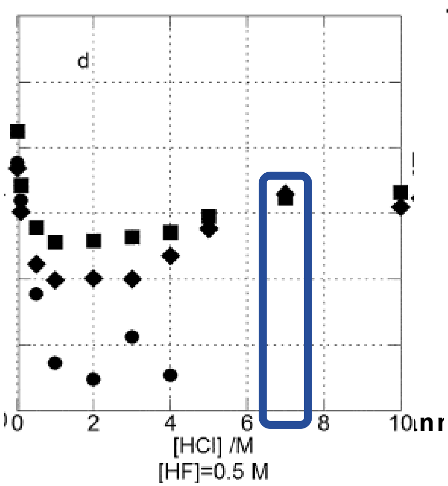
2. column: TEVA® resin. Separation of anions

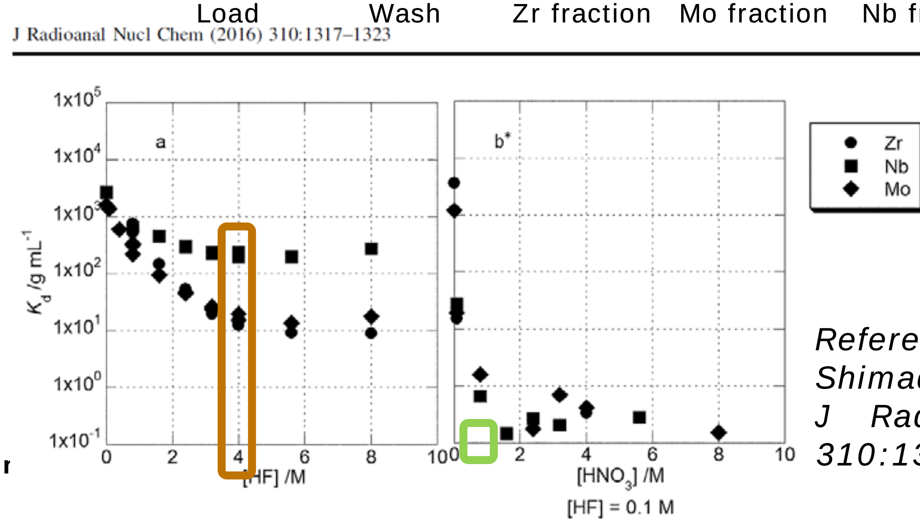
- Based on a quaternary ammonium salt
  (TrisKem product, very similar to anion exchangers)

- Load & rinse: 0.02 M HF
- **Zr strip**: + **Sb**
  5 mL 7 M HCl/0.5 M HF
- **Mo strip**: 12 mL 4 M HF
  + **Sb** contamination
- **Nb stip**: 10 mL 1 M HNO_3



40 mm column 3 mL fractions			
	Zr	Mo	Nb
1.	104%	59%	91%
2.	2%	7%	0.2%
3.	0%	2%	0.1%
4.	0%	1%	-
5.	0% + 1% Nb	1% + 1% Nb	-





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

12.10.2018

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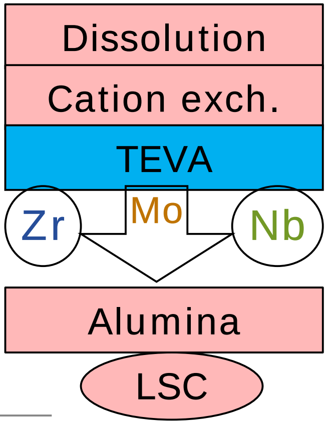

- Based on a quaternary ammonium salt
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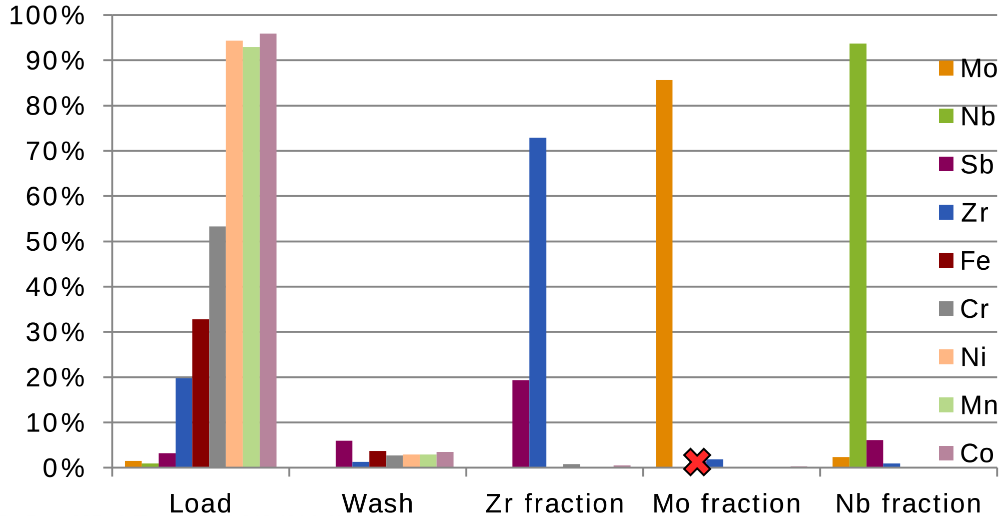
- Load & rinse: 0.02 M HF
- **Zr strip**: + **Sb**
  5 mL 7 M HCl/0.5 M HF
- 3 mL 0.02 M HF
- **Mo strip**: 12 mL 4 M HF
  no **Sb** contamination
- **Nb stip**: 10 mL 1 M HNO_3



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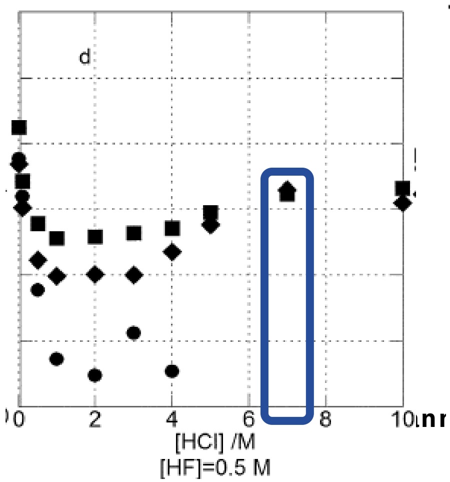
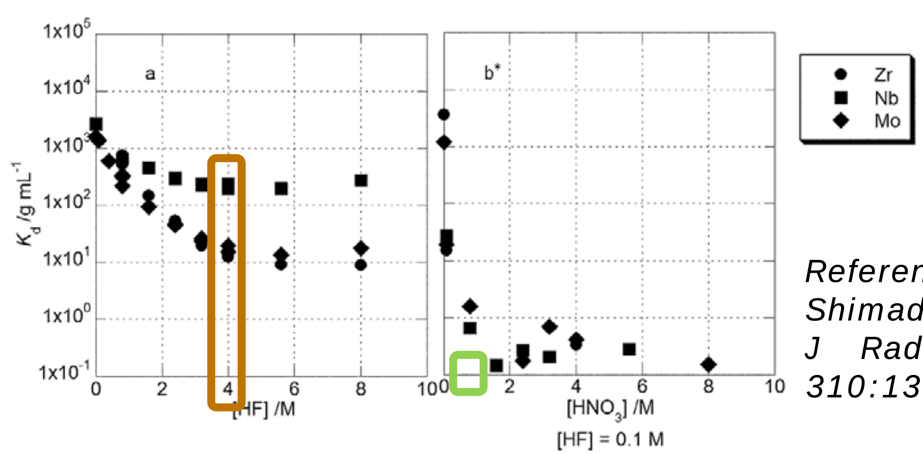


J Radioanal Nucl Chem (2016) 310:1317–1323



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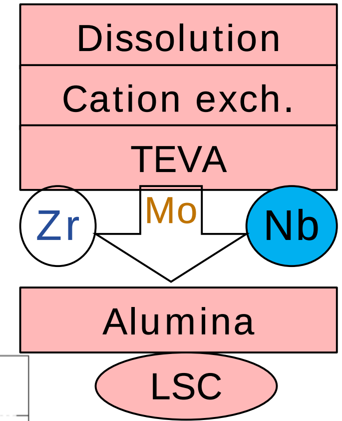
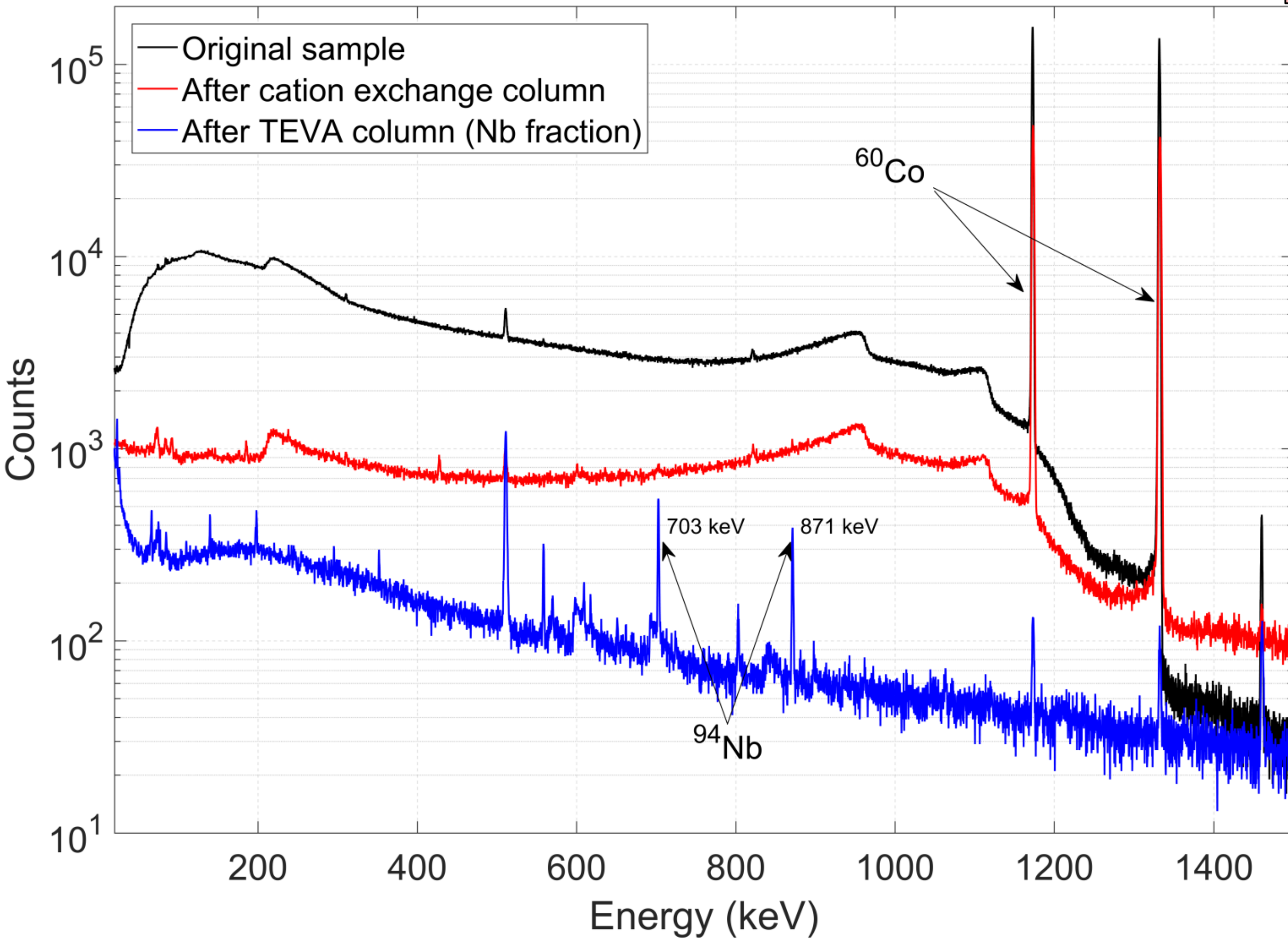
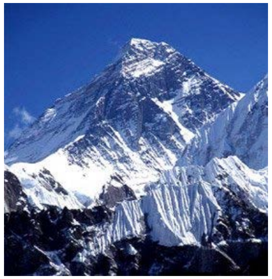


Measurement of ^{94}Nb using HPGe





10^5 Bq ^{60}Co

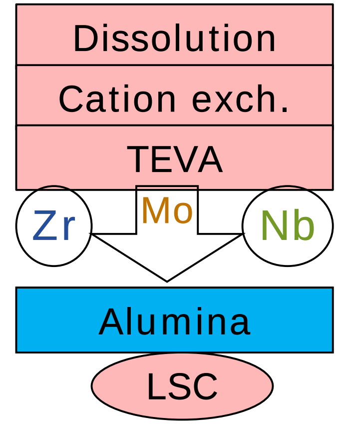
< 70 Bq ^{94}Nb

$2x10^2$ Bq ^{60}Co

< 0.2 Bq ^{94}Nb

10^{-1} Bq ^{60}Co

0.2 Bq ^{94}Nb (MDA = 0.04 Bq)



3. column: Alumina (Al_2O_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
  H_2O
  0.01 M NH_3
- Mo strip: ≥1 M NH_3

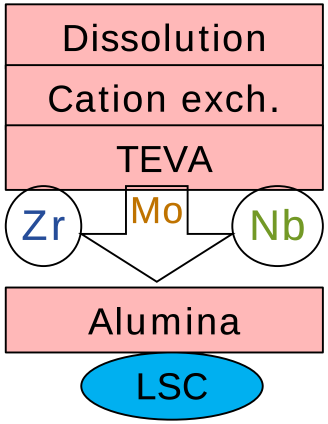
Other metals pass mainly through

- Load & rinse: ≤0.1 M HF
- Wash:
  H_2O
  0.01 M NH_3
- Mo strip: ≥1 M NH_3

Other metals are retained

- In general, results with HNO_3 and HF are similar
- Higher *c* of NH_3 → more effective elution of Mo
- Sb always contaminates the Mo – except when cc. NH_3 is used for elution

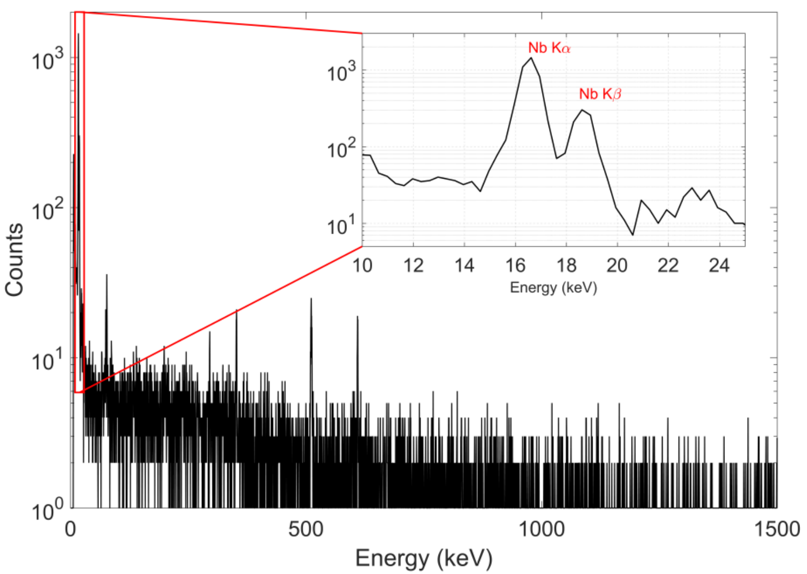
Reference:
Bernhard (1994)
J Radioanal Nucl Chem 177(2):321-325



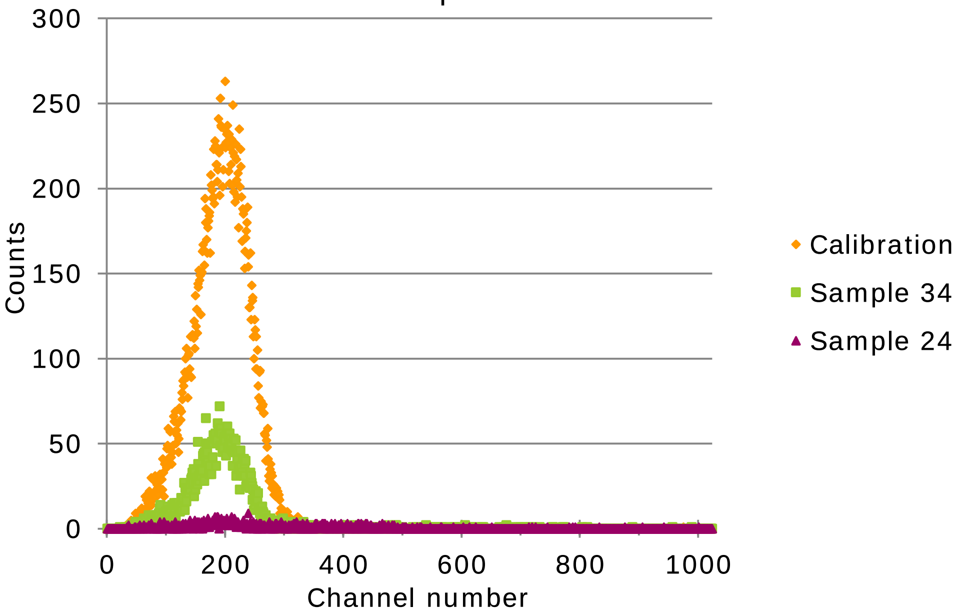
Measurement of ^{93}Mo using LSC

- Evaporated sample (≈450 μL dw) + 20 mL Ultima Gold LLT
- How to calibrate? Remember Per´s presentation
- η = 52%

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



LSC spectrum
Problem: quench



Method performance

- Recoveries (model samples):
  - Mo: typically over 85%
  - Nb: typically over 75%
  - Zr: typically over 70%

- Analysis of real samples is in progress

- Decontamination factors:

Separation of Mo			
Element	Cation exchange	TEVA Mo fr.	Alumina
Fe	≥ 10^3	10^3	≥ $4*10^2$
Cr	≈2	500	≥ $8*10^3$
Co	10^3	10^4	≥ 10^2
Ni	10^3	10^4	
Mn	10^3	10^4	
Nb	1	$5*10^2$	≥ $2*10^4$
Zr	1	≥ 10	≥ $7*10^2$
Sb	1	≥ 10^3	≥ 10^2
Tc	1	$3*10^2$	$4*10^2$

Separation of Nb		
Element	Cation exchange	TEVA Nb fr.
Fe	≥ 10^3	10^5
Cr	≈2	10^3
Co	10^3	10^4
Ni	10^3	10^4
Mn	10^3	10^4
Mo	1	10^2
Zr	1	≥ 10^2
Sb	1	
Tc	1	10^3

Summary. Conclusions and perspectives

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

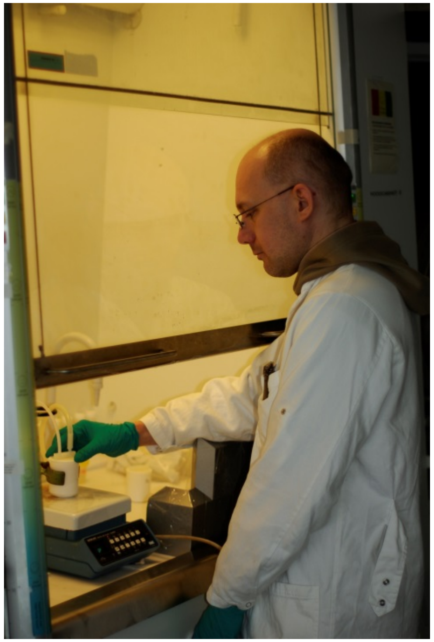
- Model samples: recoveries and separation factors are satisfying

- Real samples: in some cases very low recoveries - maybe Zr saturates the TEVA column? (longer columns should be used)
  - Comparison of results with estimated values (based on modelling)

- 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

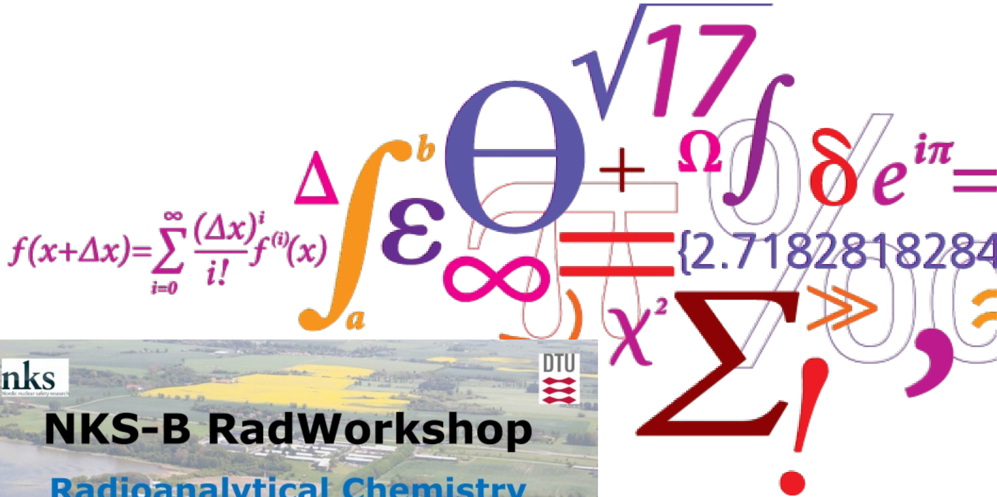
- Method might be extended for determination of Zr (ICP: recovery, LSC: activity)



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}Mo

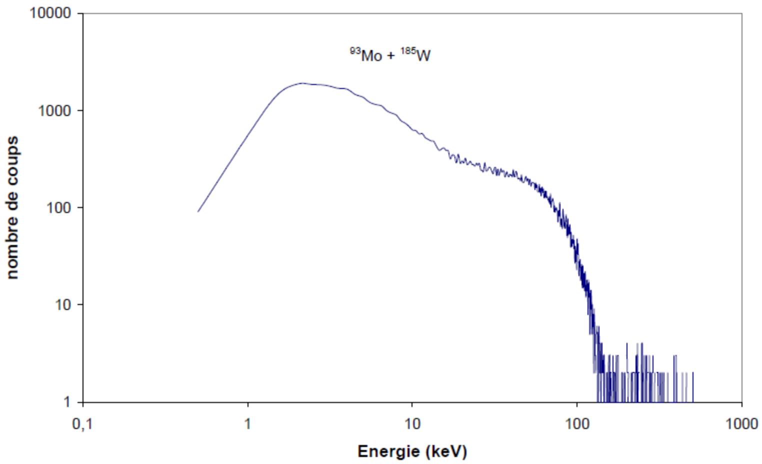
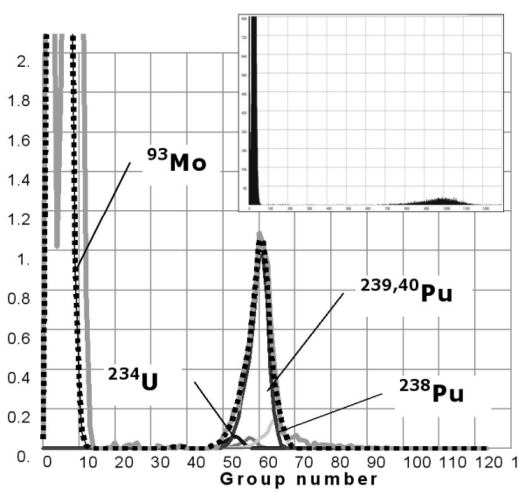


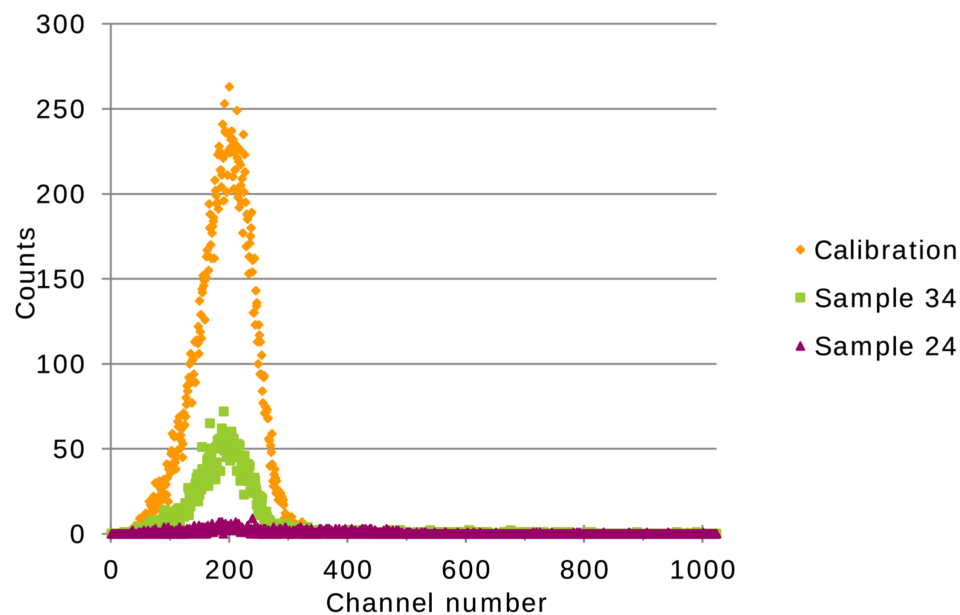
Figure 62 : Spectres de scintillation liquide de la fraction 202ME_M (temps de comptage = 600 minutes).

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

Contaminated with ^{185}W (433 keV, 100% β^-)



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_2O_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 ≈ 60%

  DF of Nb $\geq 10^6$
- Measurement by calibrated X-ray spectrometer
- Measurement by LSC