TrisKem International

News TKI

vUGM 2021

Steffen Happel
24/11/2021

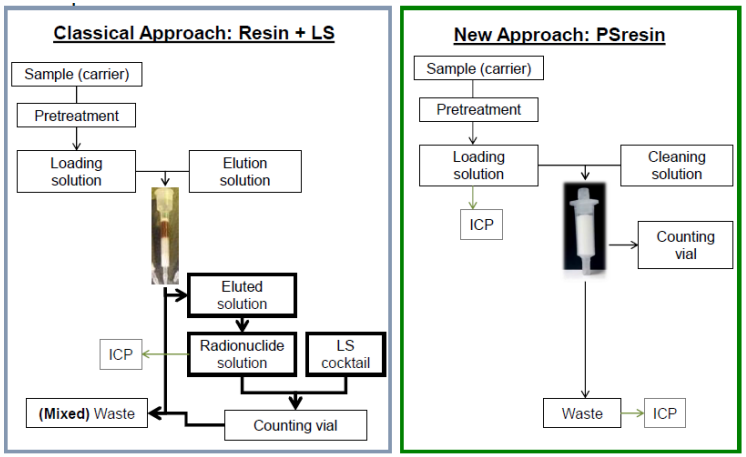
TRISKEM
Expertise in Separation Chemistry

Overview

- New Resins
  - TK-TcScint
  - TK202
- Updates (Methods/applications)
- Upcoming/under development
  - Extractive membranes et al.
  - TK300
  - TK102
  - TK222
  - ‘Industrial’ resins
- LabCom TESMARAC
- Other ongoing projects

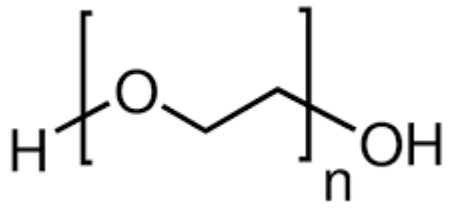
TK-TcScint

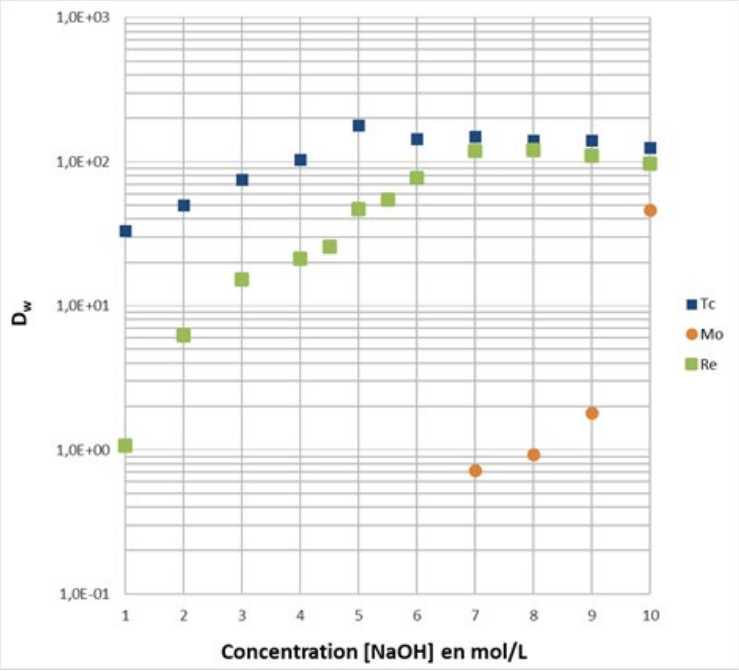
- Plastic scintillator beads impregnated with selective extractants
- Developped at Uni Barcelona
  - García, Tarancón, Bagán
- « TK-ElScint » range of products
- First: « TK-TcScint »
  - Aliquat336 based (selectivity similar to TEVA)
  - Environmental/decommissioning monitoring => Tc-99 by LSC
  - Further of interest: SR, TK101, AC,…
  - Potential applications in RadPharm QC? E.g. Sr-90 via Sr Resin equivalent
- Direct measurement of cartridges after loading on LS counter
  - No elution/evaporation/aliquoting => facile automatisation
- Chemical yield via Re/ICP-MS in effluents



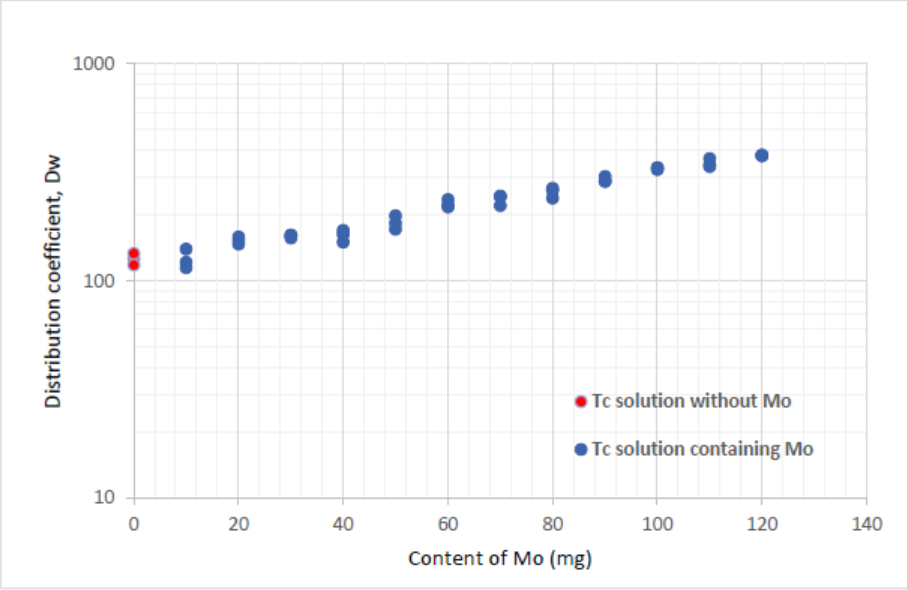
TK202 Resin

- Based on Polyethylene Glycol (PEG) grafted on inert support
- Aqueous Biphasic System (ABS)
- Retention of chaotrophic anions like TcO_4^- in presence of kosmotrophic anions (SO_4^{2-}, CO_3^{2-}, OH^-, MoO_4^{2-},…)
- For high Mo samples: Tc rec. > 90% for 6 – 8g Mo per g TK202





Dw values for Tc, Re and Mo on TK202 Resin, at varying NaOH concentrations. Tc data taken from Cieszykowska et al.

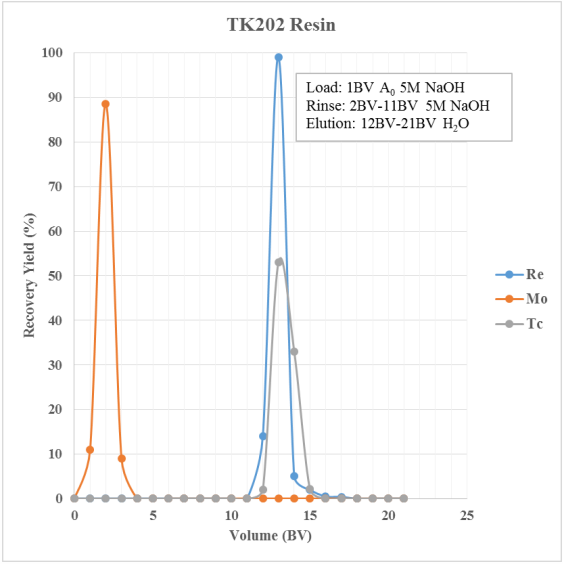


Dw values for Tc in 5M NaOH using 40 mg TK202 Resin, increasing amounts of Mo. Data taken from Cieszykowska et al.

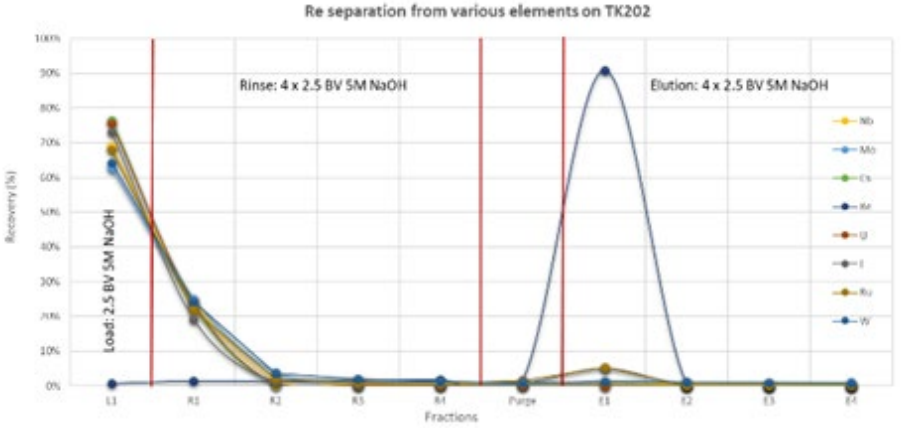
TK202 Resin

- Tc retention from high NaOH (5 - 7M)
  - alkaline fusion e.g. decommissioning samples
  - Dissolved Mo targets
  - Clean separation from other elements tested

  => attn. to other chaotrophic anions (e.g. I^-)
- Re may serve as internal standard
- Elution in small volume of water
  - Eluate will still be quite alkaline
  - Pass through CEX for 'neutralisation' and Na^+ removal and through
  - aluminium oxide for trace Mo removal and recovery as 0.9% NaCl solution

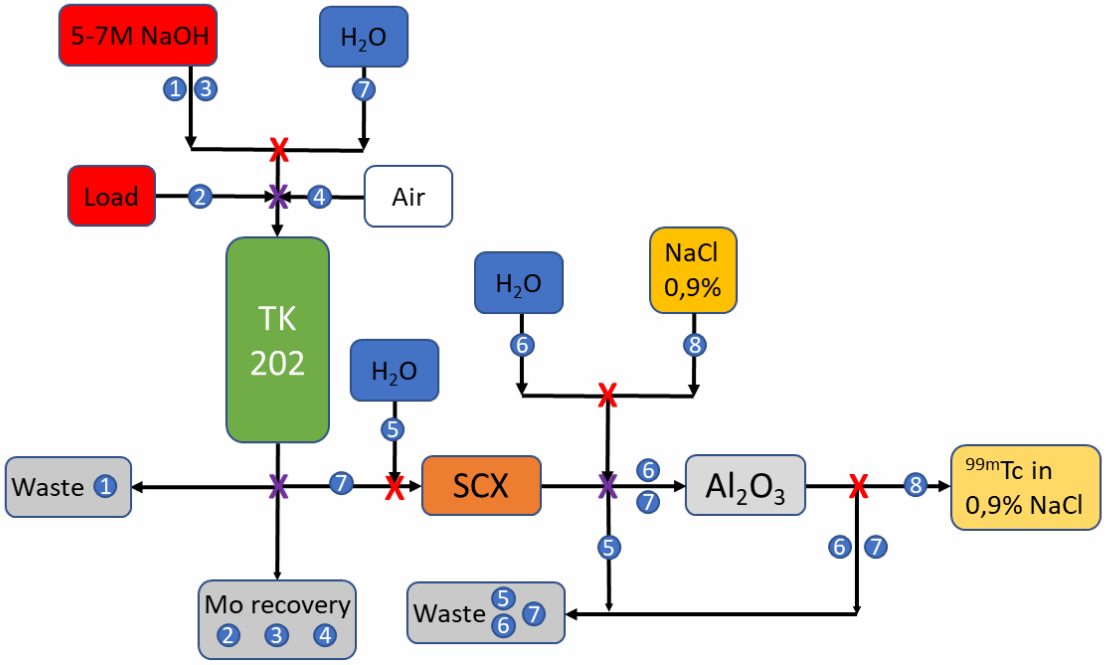


Re/Tc separation from Mo on TK202 Resin



Re separation from selected elements on 2 mL TK202 Resin cartridge, load and rinse at 1 BV/min, elution at 0.25 BV/min.

Tc-99m separation from Mo targets – suggested scheme (similar to Zeisler et al.)



1. Pre-cond. TK202 – 5-7M NaOH → alkaline waste
2. Load Mo/Tc on TK202 → Mo recovery
3. Rinse TK202 – 5-7M NaOH → Mo recovery
4. Purge TK202 – Air → Mo recovery
5. Pre-cond. SCX – HCl then H_2O → Aq. waste
6. Pre-cond. Al_2O_3 – H_2O → Aq. waste
7. Elute Tc from TK202 on SCX and load on Al_2O_3 – H_2O
8. Elute Tc from Al_2O_3 – NaCl 0,9% → Tc recovery

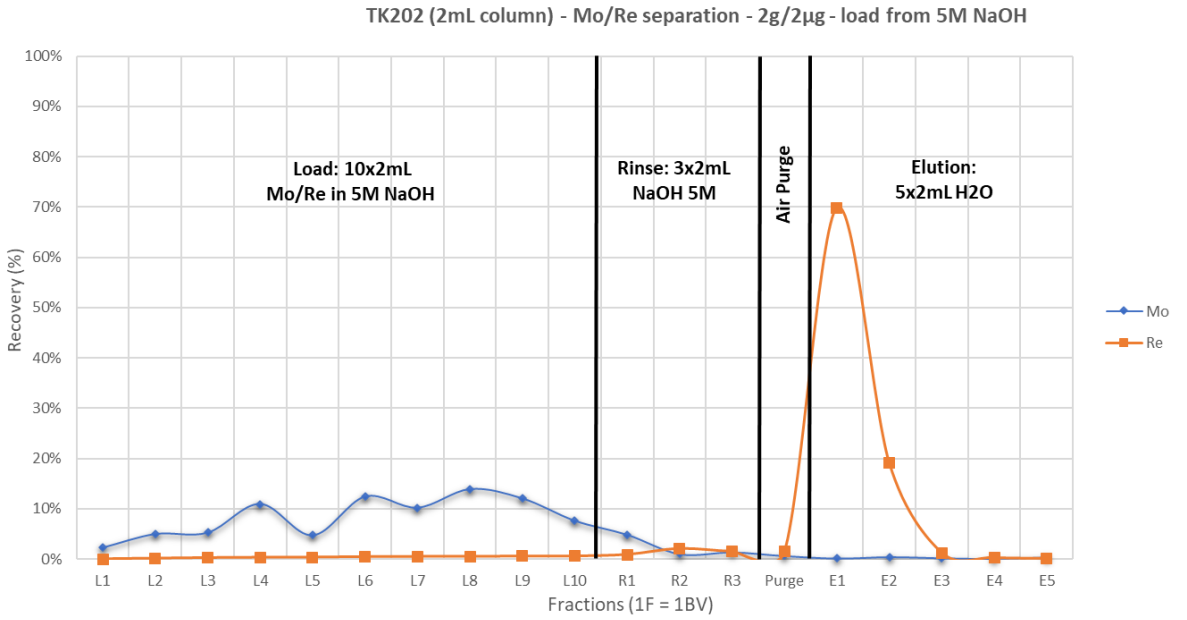
TK202 : 35-75 or 75-150µm
X : 3-ways valve
X : 4-ways valve
SCX : Strong Cation Exchange
Al_2O_3 : Acidic Alumina

Developed with ReO_4^- as TcO_4^- surrogate

Re recovered on saline solution from alkaline

Separation with 2g Mo → From 20mL to 2mL
Separation with 200g Mo → From 3L to 20mL

Tc-99m via cyclotron route

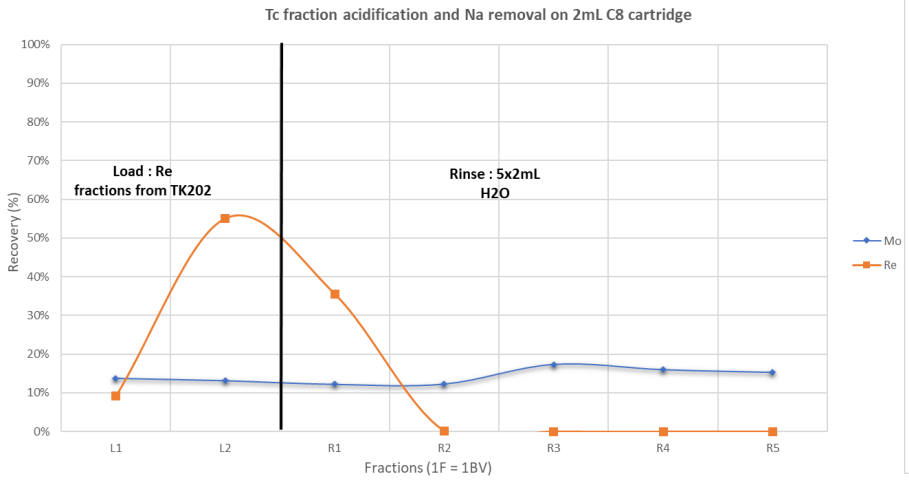


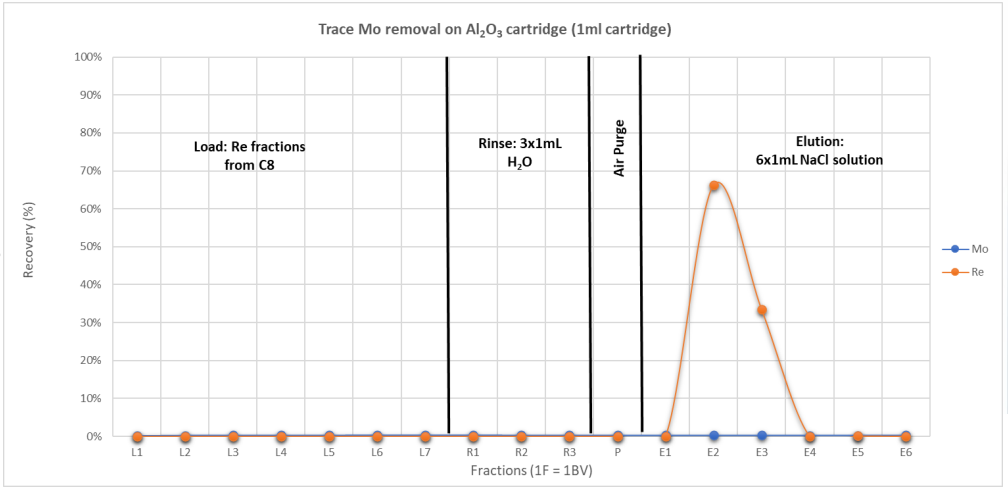
Tests performed cold with 2g Mo and 2 µg Re

- 2 mL TK202 cartridge
- 2 mL C8 cartridge
- 1 mL AlOxA cartridge

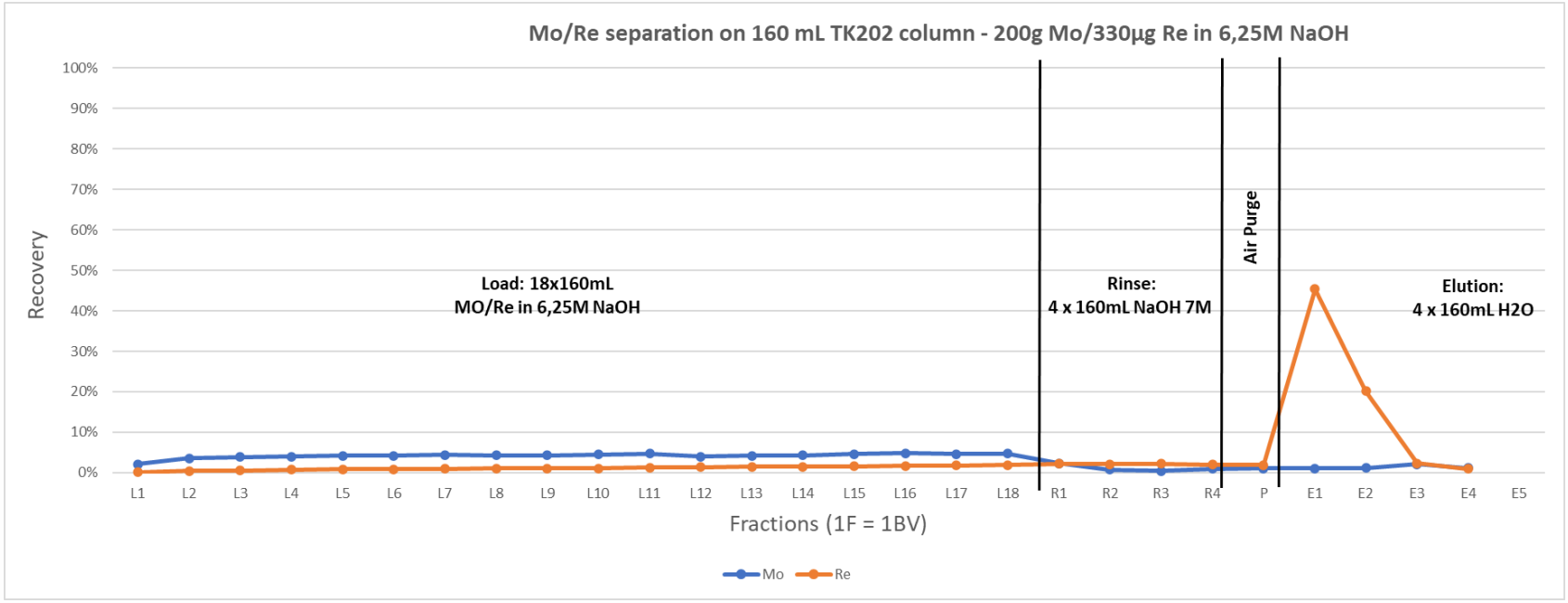
Method similar to Zeisler et al.

High Re yield (~90%) in 2 – 3 mL 0.9% NaCl solution

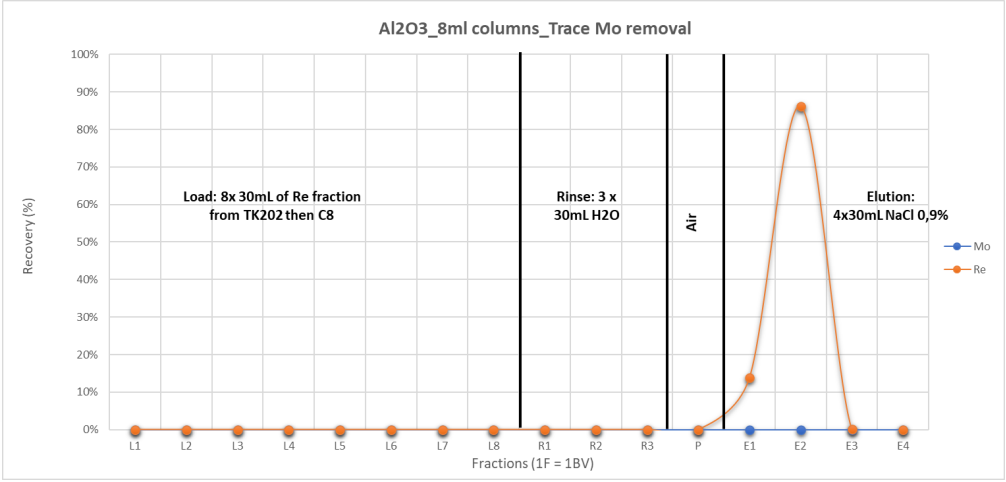




On-going :Tc-99m from large Mo targets



- On-going work on 200g Mo
- ~160 mL TK202 column
- Load from 6 - 7M NaOH - elution in water
- Pass through C8 cartridge for acidification and Na removal
- Final concentration/conversion to 0.9% NaCl on 8 mL AlOxA cartridge



Cu-64 separation on TK201/CU Resin

Svedjehed et al. EJNMMI Radiopharmacy and Chemistry (2020) 5:21
https://doi.org/10.1186/s41181-020-00108-7

EJNMMI Radiopharmacy and Chemistry

RESEARCH ARTICLE Open Access

Automated, cassette-based isolation and formulation of high-purity [^{61}Cu]$CuCl_2$ from solid Ni targets

Johan Svedjehed[1], Christopher J. Kutyreff[2], Jonathan W. Engle[2,3] and Katherine Gagnon[1*]

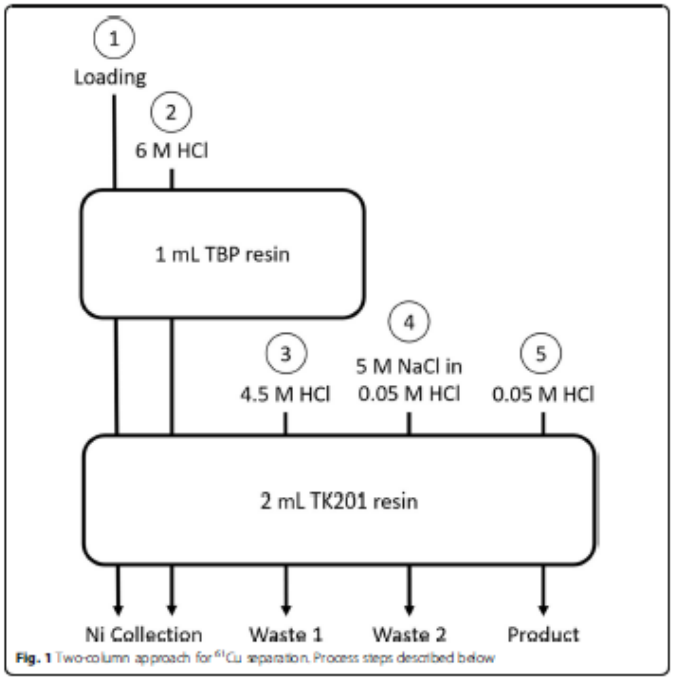


Fig. 1 Two-column approach for ^{61}Cu separation. Process steps described below

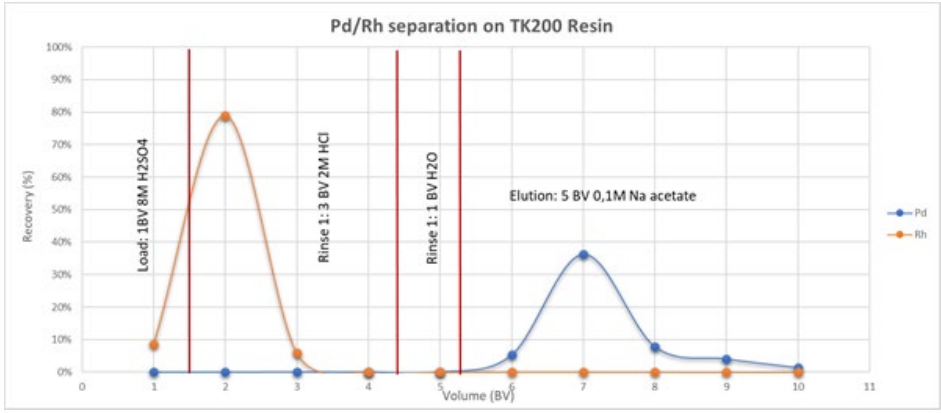
- Use of modified rinse on TK201 allows for Cu elution at defined pH

- Finally, combined TK201/CU Resin method?
- Use of 2 mL TK201 for Cu 'conversion' and matrix removal at 6M HCl
  - Ni passes through.
  - No TBP needed (Fe/Ga removal on CU Resin)
  - Cu eluted in acetate buffer
  - Modified TK201 rinse (HCl/NaCl) is key!
- TK201 eluate directly be loaded onto 1 mL CU Resin cartridge for further purification
  - Zn, Fe, Ga, Ni,… removal
- Cu Elution with 6M HCl onto 0.3 mL TK201 for conversion and concentration
- Proof of principle OK, now further volume optimization on-going!

Other examples for separations

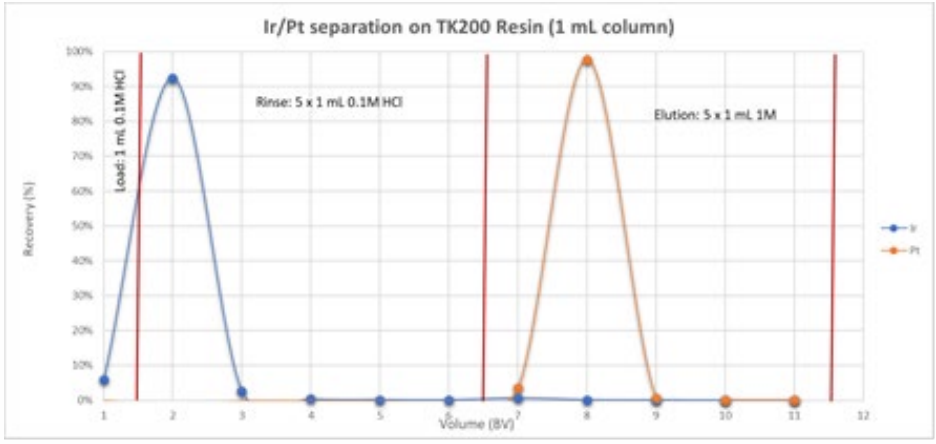
- Pd separation form Rh targets
- Main challenge: target dissolution
- Request: Pd separation from high H_2SO_4
- Removal of H_2SO_4 necessary
  - Rinse with 2M HCl
- Elution in acetate possible
  - To be optimized
- Separation on TK200 possible

• Pd separation from Rh



- Pd/Rh separation. Elution study, ICP-MS measurement

• Pt separation from Ir

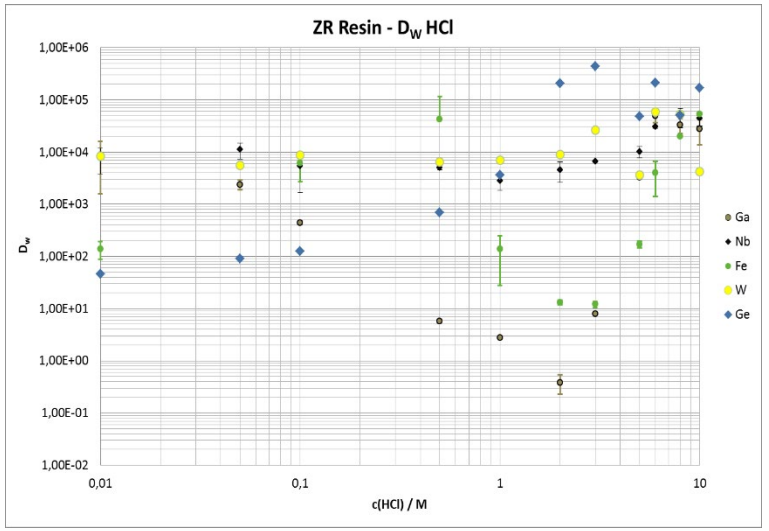


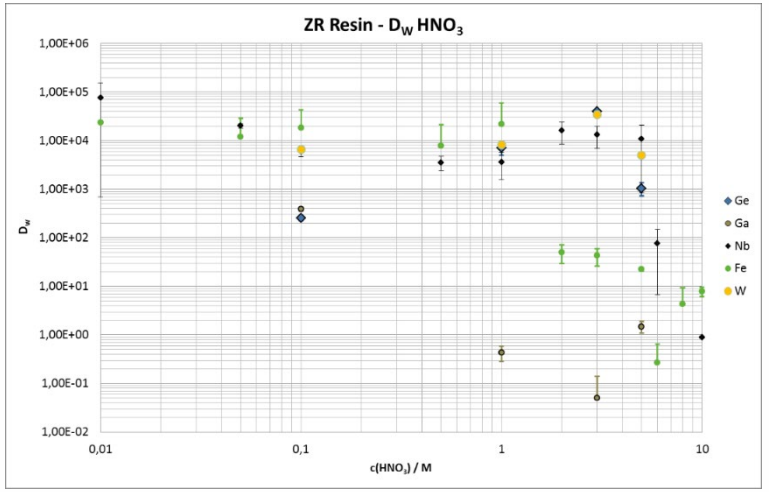
- Pt/Ir separation. Elution study, ICP-MS measurement

- Pt separation from Ir targets
- Challenge oxidation state control
- Separation possible on TK200
- Alternative: use of TBP => Obata et al.
- [$^{188, 189,191}$Pt]cisplatin
- TBP and AIX based method
  - 3x 2 mL TBP cartridges followed by QMA cartridge

Ge-68 separation from GaNi or GaCo

- Loading from HNO_3, HCl or H_2SO_4 possible
  - Target dissolution in H_2SO_4
- Cold tests on >5g GaNi
- First cycle on ZR (**2 mL ZR Resin cartridge**):
  - Load/rinse from 5M H_2SO_4
  - High Ge retention/purification from Ga, Ni & Co
  - Elution: 0.1M citric acid (pH 3)
- Second cycle on ZR (**1 mL ZR cartridge**):
  - Adjustment of eluate to 5M H_2SO_4
  - Load/rinse from 5M H_2SO_4
  - Elution with 0.1M citric acid (pH 3)
- Conversion step (**2 mL Guard Resin cartridge**):
  - Acidification to 9M HCl, load onto Guard Resin
  - Ge/Ga selectivity => further purification
  - Rinse with 9M HCl
  - Elution with to 0.05M HCl => pH!





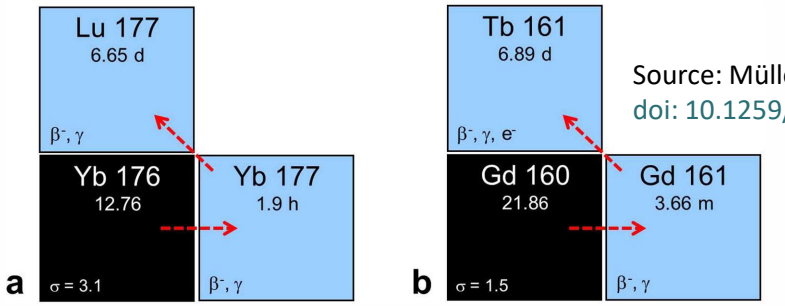
Important for high amounts of Ge: pre-rinse of GR with EtOH, then water necessary!

Other Germanium work

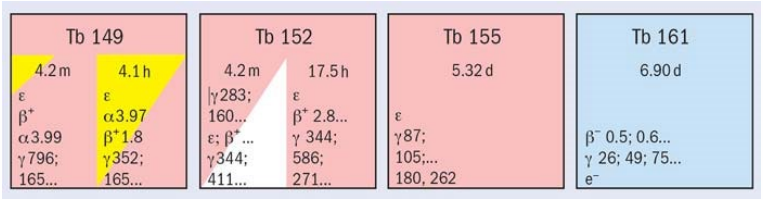
- Ge removal using CeO_2-PAN ("TK-GeRem")
  - Extracts Ge from dilute acid, seawater…
    - Decontamination of waste
    - Ge-68 breakthrough elimination from generator effluents?
- Combination of several Ge-68 generator eluents
  - Load Ga-68 onto ZR followed by TK200 or
  - Acidification of Ga-68 and load onto TK200
  - Elution in dilute HCl
- Ge-68 recycling
  - Evaluation of possibility to elute Ge from 'spent' generators using 9M HCl => quantitative elution, metallic impurities,…
  - Use of two subsequent Guard Resins cartridges to collect and purify Ge => Ge-68 method

Lu-177/Tb-161

- nca Lu-177 still more frequently used but Tb-161 getting strong interest
  - Part of the 'Swiss knife of nuclear medicine' => Tb isotopes
- Similar production for both



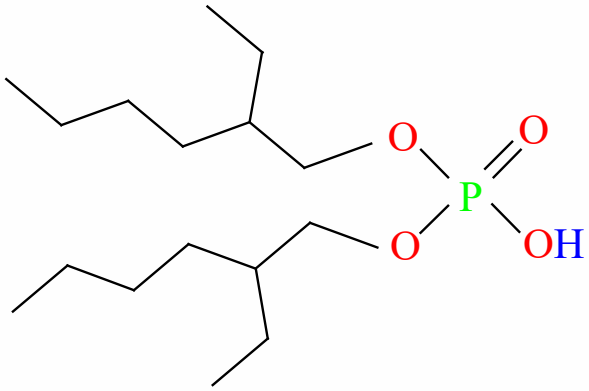
Source: Müller et al. 2018
doi: 10.1259/bjr.20180074



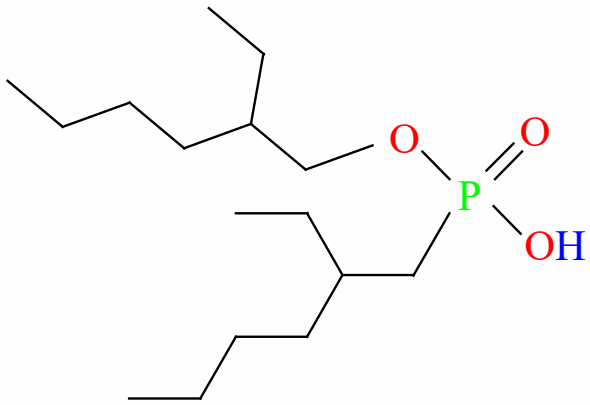
Terbium: a new 'Swiss army knife' for nuclear medicine
Source: https://cerncourier.com/a/terbium-a-new-swiss-army-knife-for-nuclear-medicine/

  - Irradiation of several hundreds of mg or more
  - Upscale on-going (incl. recycling) => typically 1g
- Prepacked PP columns now starting to be available
  - 4cm x 30cm (375 mL), 2.5cm x 30cm,
    1.5cm x 30cm & 1.1cm x 30cm
  - Connection: ¼'' 28G, up to ~10bar
  - QC/CoA per column (peak asymmetry) for TK211/2/3
  - TK221 => dry packing

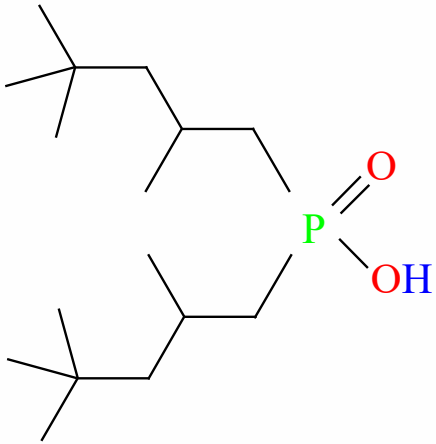
Lanthanide separation on TK211/2/3



HDEHP (LN)



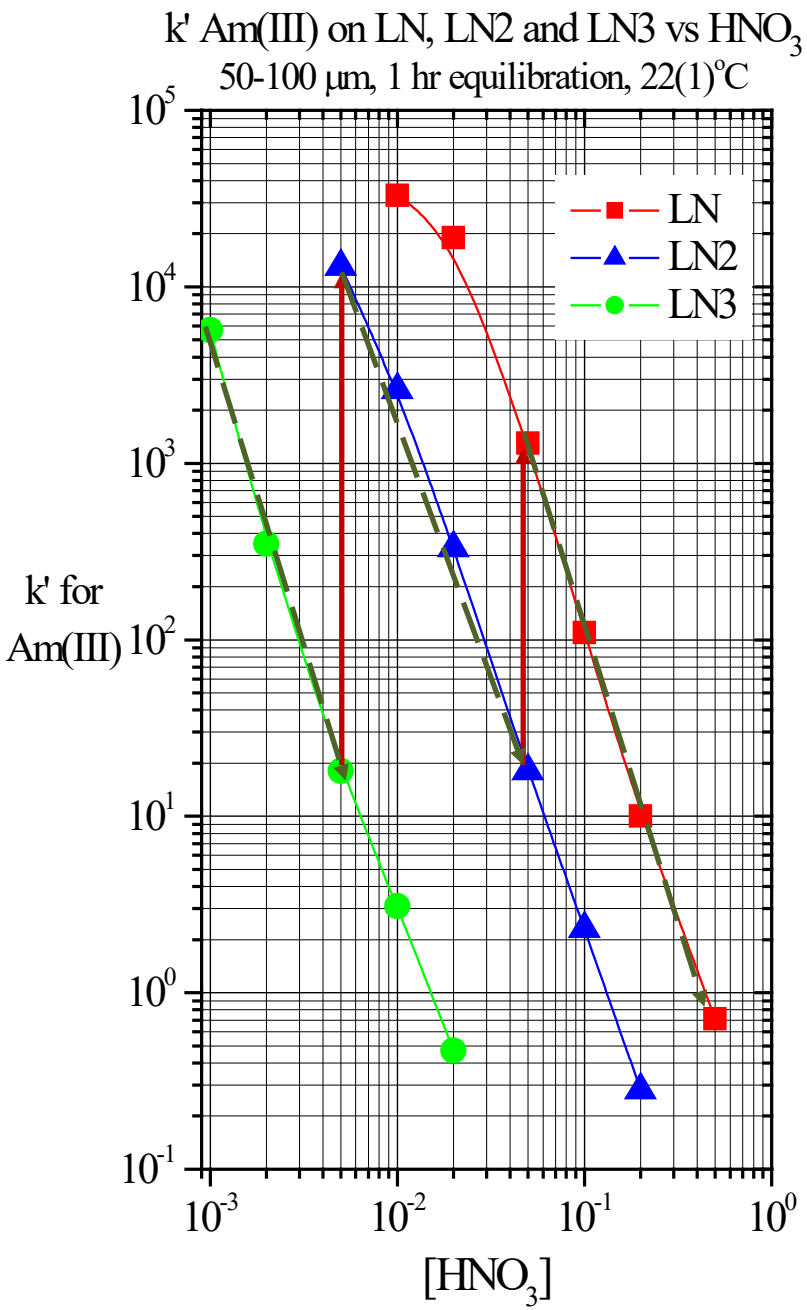
HEH[EHP] (LN2)



H[TMPeP] (LN3)

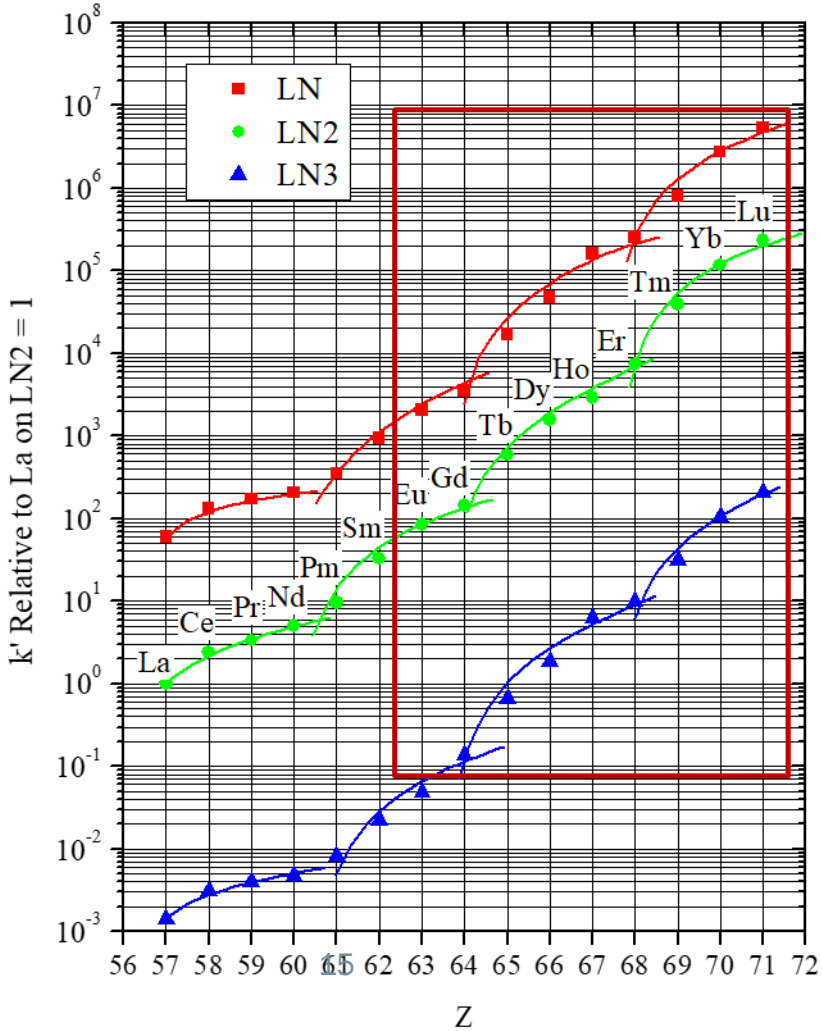
Extractants e.g. employed in **TK211/2/3**

$$M^{3+} + 3\overline{(HY)_2} \leftrightarrow \overline{M(HY_2)_3} + 3H^+$$



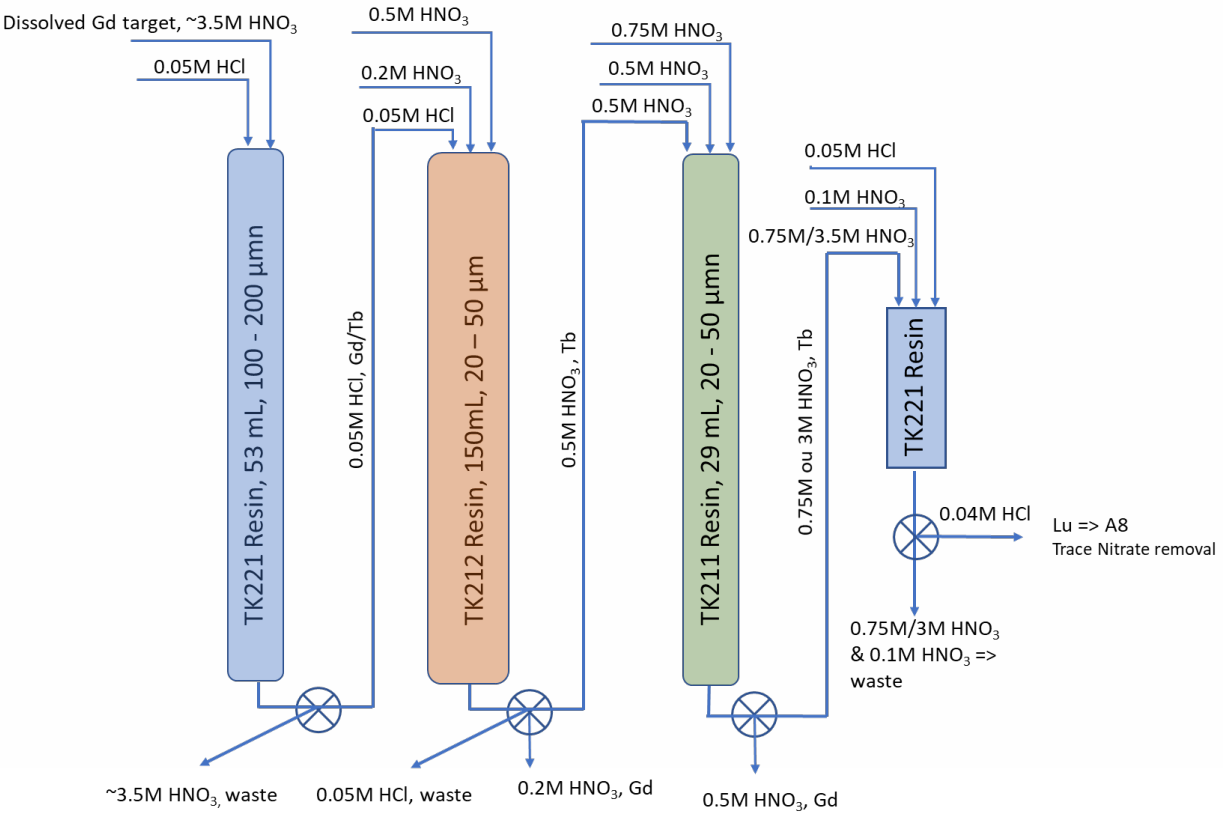
Main difference: acidity

=> Sequential separations…



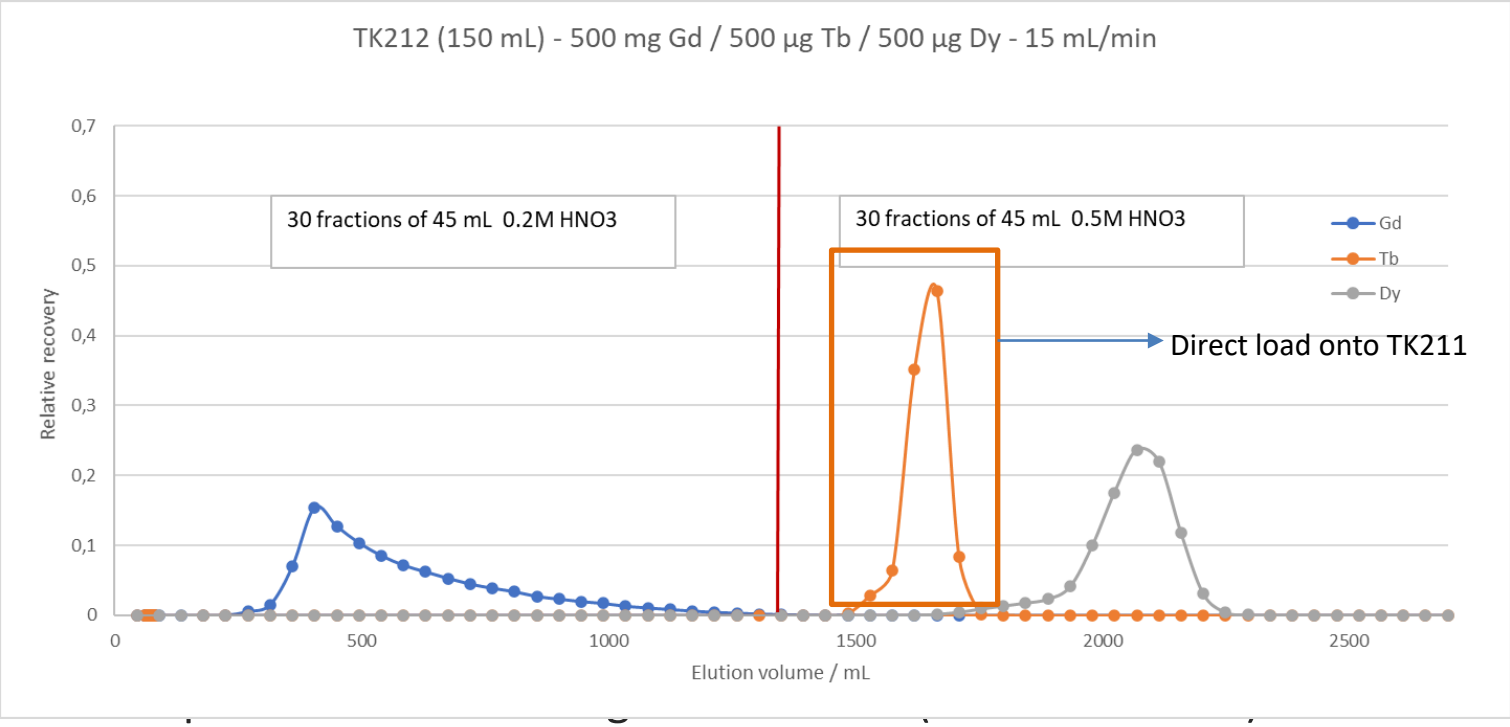
Tb separation from 500 mg Gd targets

- Irradiated target typically oxide => dissolved in >3M HNO_3
  - For separation solution needs to be dilute acid
- Conversion via TK221 Resin
- Sequential separation on TK212/TK211
- Final conversion to dilute HCl on TK221 + trace nitrate removal on AIX

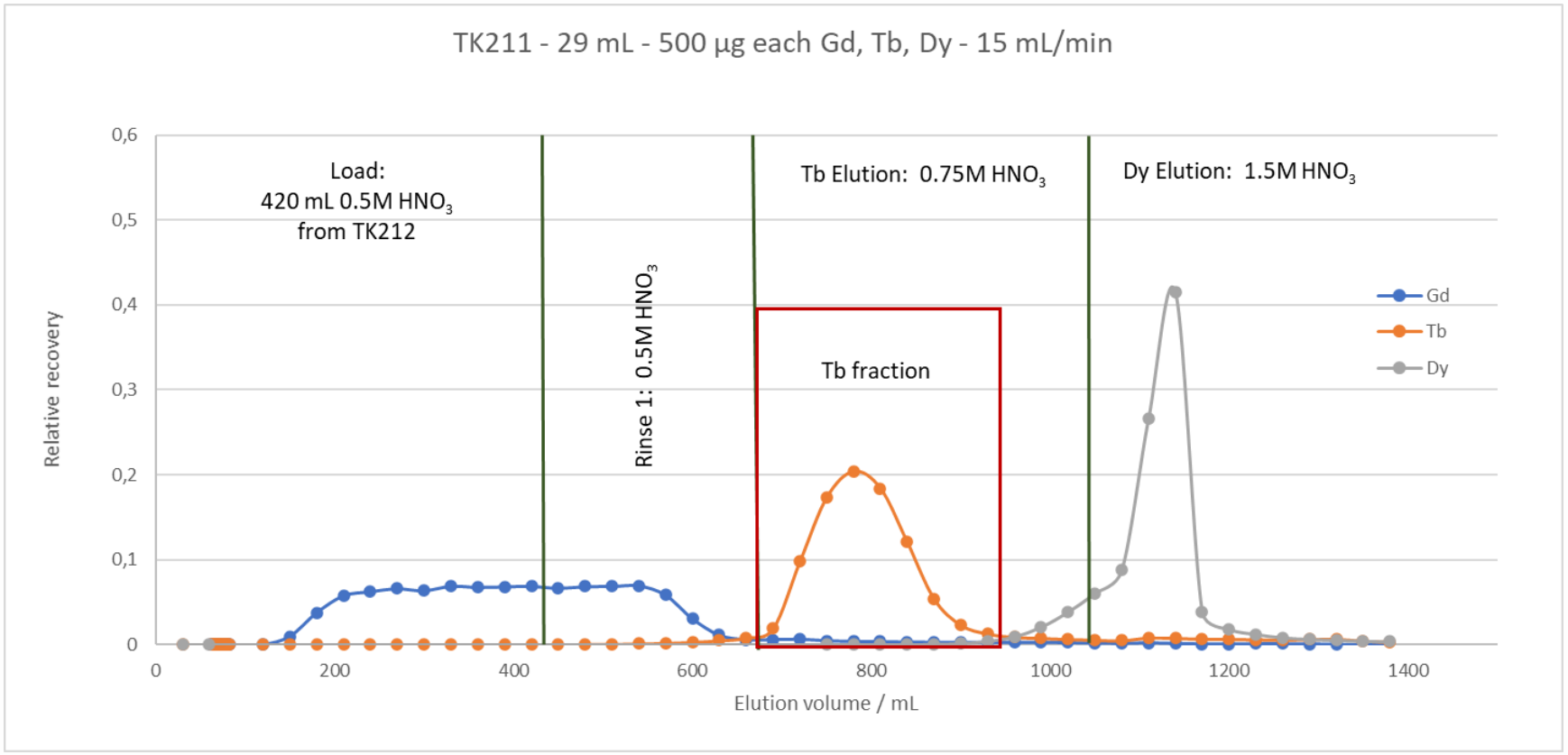


Tb separation from 500 mg Gd targets

- Initial separation on TK212 – 150 mL column (30cm x 2.5cm)
- Large amount of Gd present leads to significant tailing
- Tb separation from Gd and Dy – ideally using online detection
- Fine purification on TK211 (29 mL)



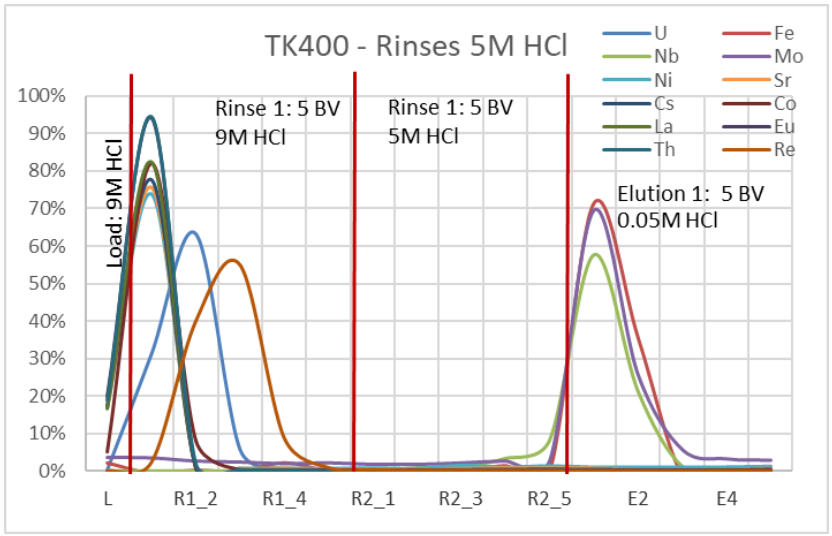
Tb purification on TK211

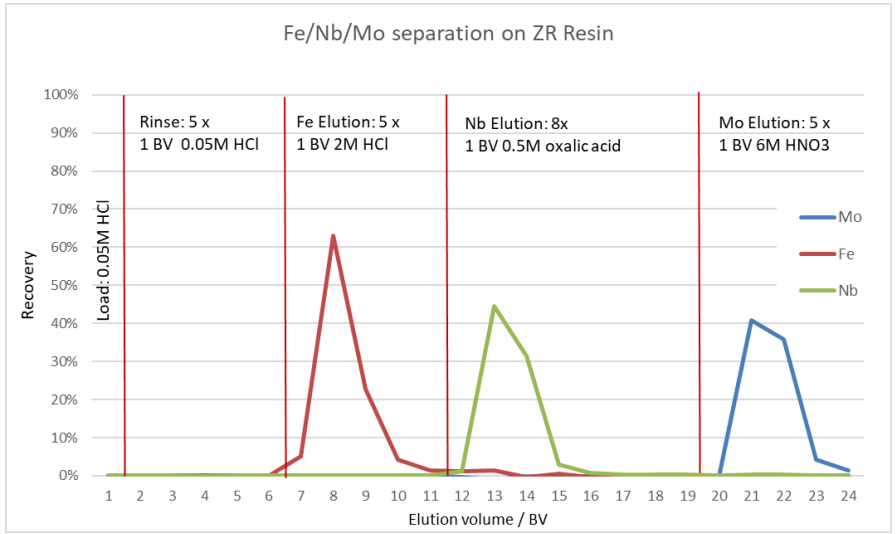


- Direct load of Tb fraction from TK212 onto TK211 (29 mL – 30cm x 1.1cm)
- Gd breakthrough during load & rinse with 0.5M HNO_3 (alternatively HCl)
- Tb elution: 2 options => 0.75M or 3.5M HNO_3 (3.5M HNO_3 preferable)
- Conversion to dilute HCl via TK221, A8 for nitrate removal

TK400 Resin

- Recovery of Fe/Nb/Mo from high HCl on TK400
  - Majority of other elements removed during load and rinses (9M and 5M HCl)
  - Fe/Nb/Mo eluted in dilute HCl => separation e.g. on ZR Resin

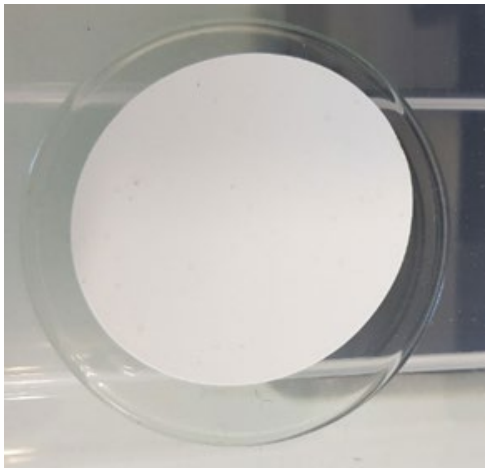




- TK400 also used to remove Nb (and Fe) from Zr or Pu-241
  - Zr-93 in decommissioning samples => method under development (with UTEVA)
  - Zr-89 separation from Y targets (with TBP)
- TK400 use in Ga-68 separation from solid Zn targets
  - e.g. Tieu et al. 2019 & Svedjehed et al. 2021 (+A8 and TK200)

Upcoming

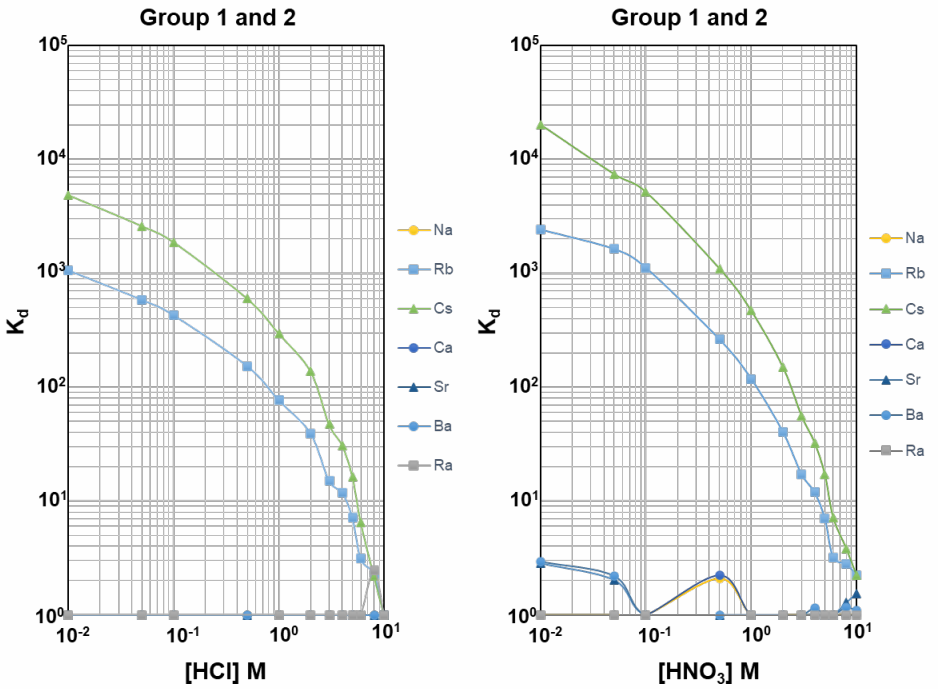
- New product line: **impregnated membrane filters (MF)**
  - Higher flow rates
  - Ideally for use with water samples (1 – 5L)
  - Use in Passive Sampling (DGT)
  - Under development (incl. respective methods):
    - **TK100 (Sr, Pb, Zn), TK101 (Pb, Ra)**
    - **CL Resin (radio-iodine)**
    - **TK201 (Tc)**
    - Calixarenes (Ra, Cs)
    - …



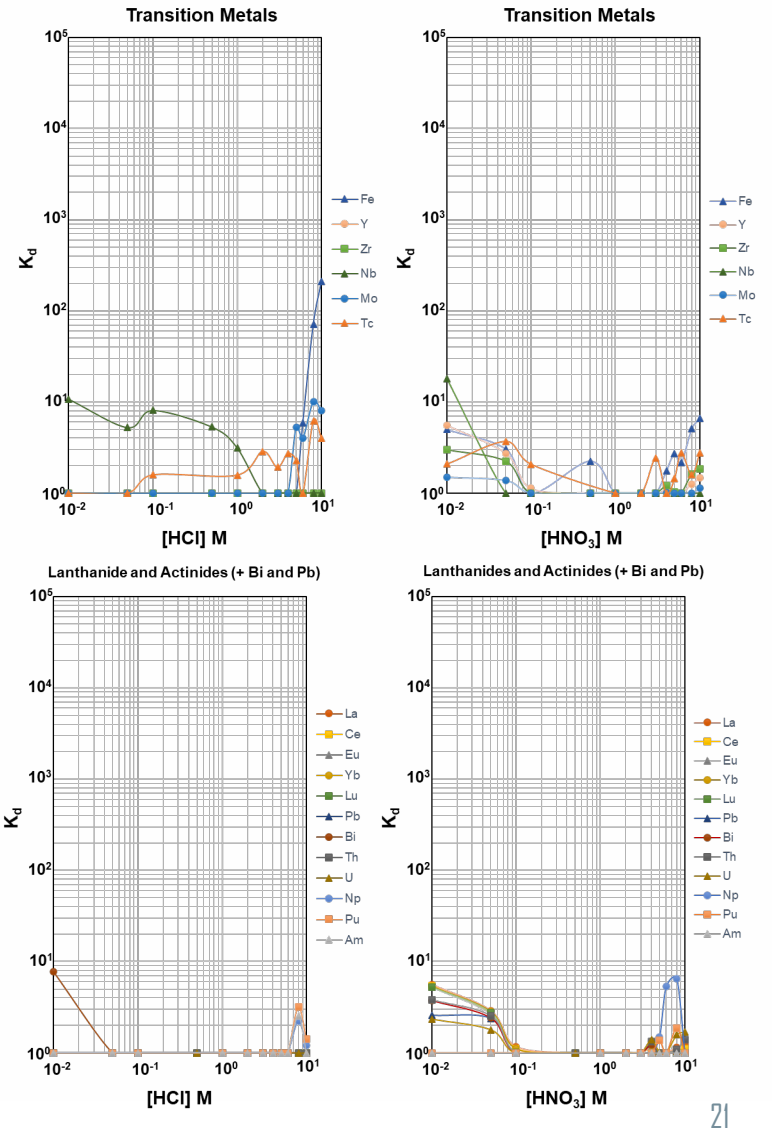
- 'Test sticks'
  - Supported piece of impregnated membrane
  - e.g. DGA for Ca, SR or TK100 for Sr,… i.e. with Uni Southampton
- Various Sheets et al.
  - CU, SR,…
  - Different supports

Upcoming - TK300 Resin

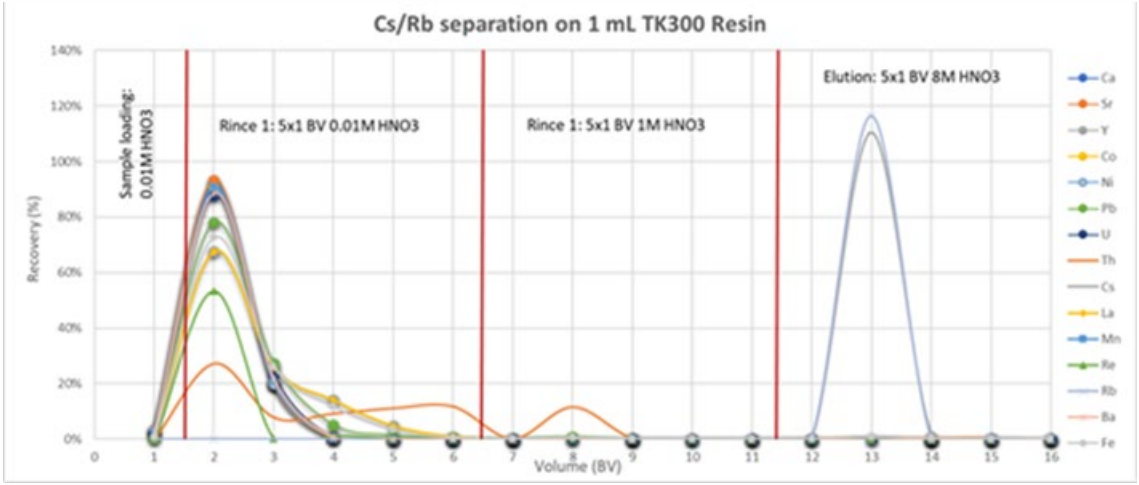
- Macrocycle based Resin
- Cs and/or Rb separation
- Selectivity for Cs and Rb over other elements tested in HNO_3 and HCl
  - Incl. Ba



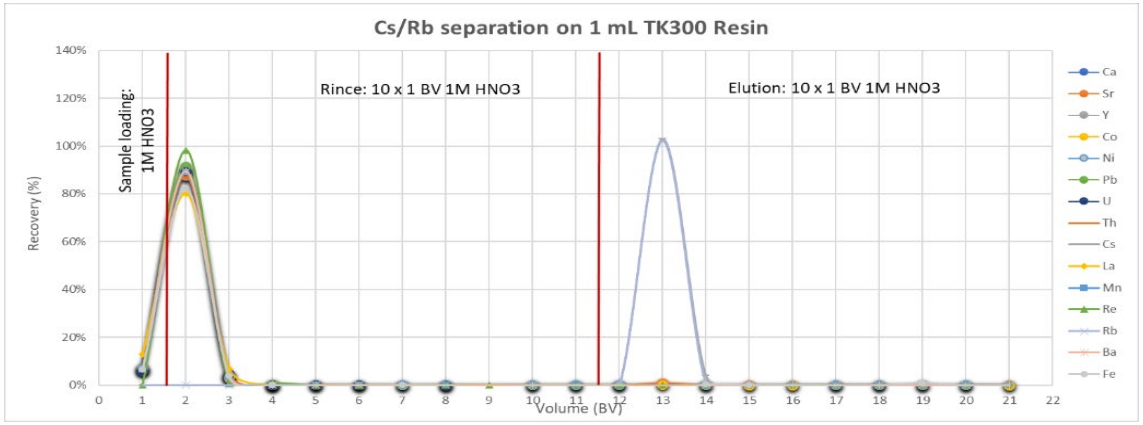
Data provided y B. Russel (NPL)



Upcoming - TK300 Resin



Elution study, Cs and Rb separation from selected elements on TK300 resin, loading from dilute acid.



Elution study, Cs and Rb separation from selected elements on TK300 resin, loading from 1M HNO3

- Separation of Cs and Rb
- Retention over wide pH range (up to 1M HNO_3)
- Cs/Rb separation possible
- Elution in >3M HNO_3
  - Alternative => push resin into LSC vial (=>TEVA)
  - Membrane filters
- Limitations:
  - Limited Cs capacity
  - Interference by K
  - Limits use for environmental samples

➢ Rather suitable for decommissioning samples

Under development

- TK102
  - Modified version of SR Resin
    - Same crown-ether
    - Different solvent, inert support, ratios
  - About ~50% higher k' (Pb, Sr, Ba) and capacity (Pb, Sr to be tested)
  - Method development/testing on-going
    - Incl. Sr-82 production combined with TK100
- TK222
  - TEH-DGA version of TK221 Resin
  - Use in Ac and Sc separation?

‘Industrial’ EXC Resin production

- Requests from hydrometallurgy field
  - Possible applications also in decontamination and valorisation of effluents or decontaminants (e.g. acid)
- Several different resins
- Larger resin beads, larger amounts
  - ~400 – 600µm
  - Challenge: supply of extractants and inert support
    - Extractants: sufficient quality, low pricing, high quantity
- Increase of production capacity for these resins

LabCom « TESMARAC »

- Common ‘virtual’ laboratory
  - Financed by the French ANR
- Subatech (CNRS, Uni Nantes & IMT Atlantique) and TRISKEM
  - Additional support by ModES/CEISAM group (Uni Nantes, molecular modelling)
  - Macrocycles for Ra separation
- Main focus:
  - new selective resins and support materials and
  - new separation and pre-concentration methods with existing support materials for:
    - trace-level DTM Radioactive waste classification and management (e.g. DTM separation)
    - Waste material recycling
    - Assessment of the impact of radioactivity on human beings (e.g. Ra, DGT,…)
    - Radionuclide production for medical purposes (diagnosis and therapeutic uses) incl. e.g. At-211

Some other on-going projects

- Ac separation (incl. Ra recycling)
- Radium
  - New resins and macrocycles
- SE Resin
- Auger emitters
- Improvement of radiolysis stability
- Sr-82
  - TK102/TK100
- Rapid tests
  - Test sticks => Uni Southampton
  - SBSE
  - …
- In field preconcentration
- At separation
  - TK400, Rn-211/At-211 generator,…
- DGT (Diffusive Gradients in Thin Films) => 'bio-availability'
  - E.g. fate of radionuclides in the environment after use in NM
- Separation of DTM
- Microfluidics
- Further projects on decontamination/valorisation

Thank you for your attention!

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Many thanks to all presenters, participants and the NPL!

Hopefully see you again in-person next year

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