TrisKem International

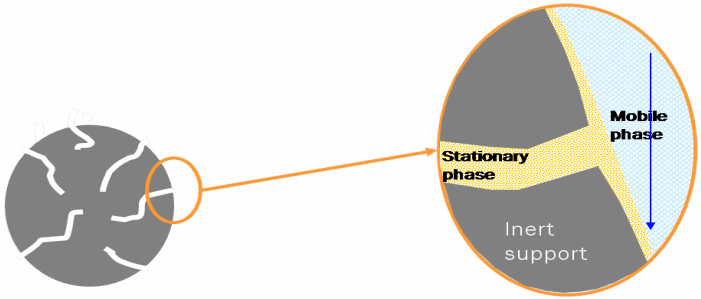
On the development of new extraction chromatographic materials for the separation of difficult to measure radionuclides

Steffen Happel
18/10/2021

TRISKEM
Expertise in Separation Chemistry

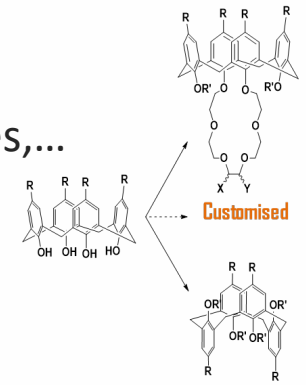
TrisKem International

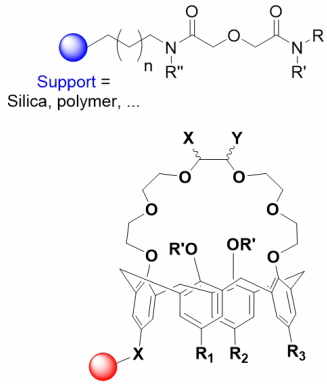
- Based in Rennes (France)
- Independent company since 02/07
  - Formerly part of Eichrom Europe
- SME / Staff : 19
- R&D, QC and TechSupport group:
  - 3 RadChem PhD, 2 OrgChem PhD, 5 Technicians
- R&D: Development of new resins, techniques and applications
  - Mainly extraction chromatographic resins
- Applications in several domains



R&D TrisKem International

- Two R&D labs:
  - Synthesis Lab (new resins and extractants)
    - Incl. grafted resins (silica or polymers), macrocycles,…
  - Application Lab
    - Preparation of extraction chromatographic resins
    - Resin characterisation and method development





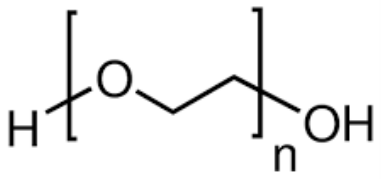
- Equipment:
  - ICP-MS, IC, TOC, TGA, IR, BET, microtrac,…
  - Access production and packing lab with four 20L reactors

- No handling of radioactivity => R&D cooperation
  - Resin and method development “cold” => R&D partner (NPL, RadAnal, Subatech, UBarca,…)

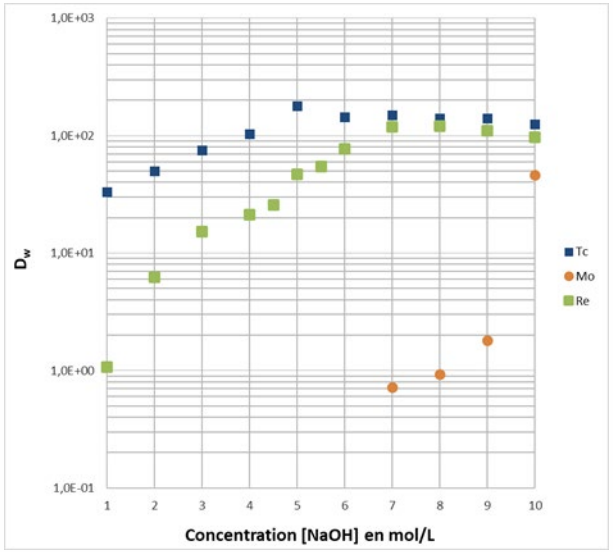
Tc-99 - new TK202 Resin

- Based on Polyethylene Glycol (PEG)

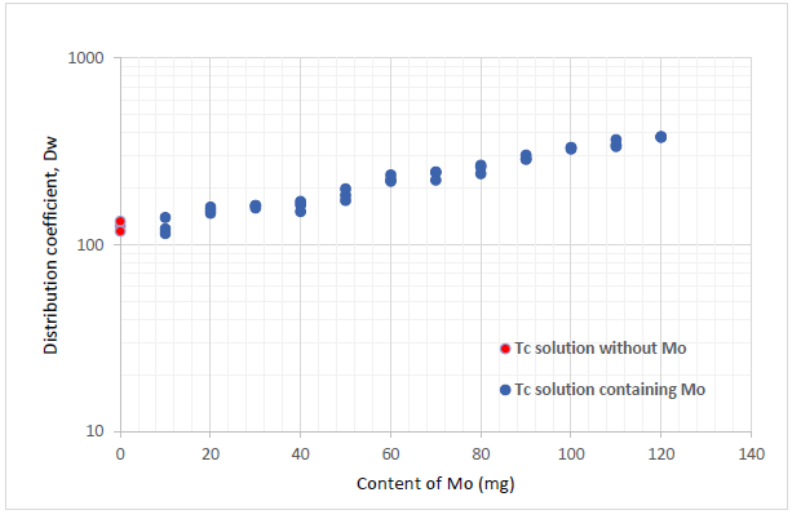
grafted on inert support



- 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-} ,…)
  - Originally: Separation of Tc-99m from high masses of Mo



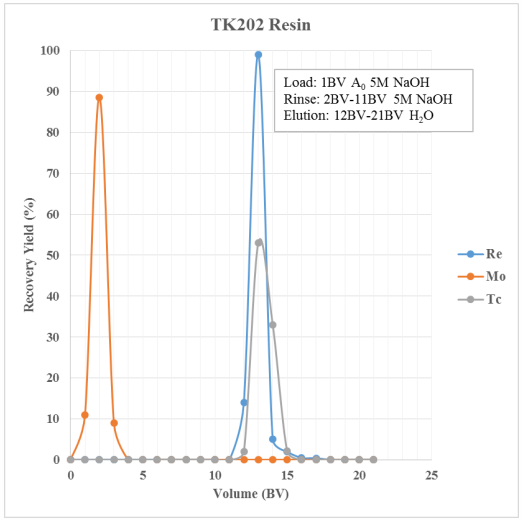
Dw values for Tc, Re and Mo on TK202 Resin, at varying NaOH concentrations. Tc data taken from Cieszykowska et al.(2).



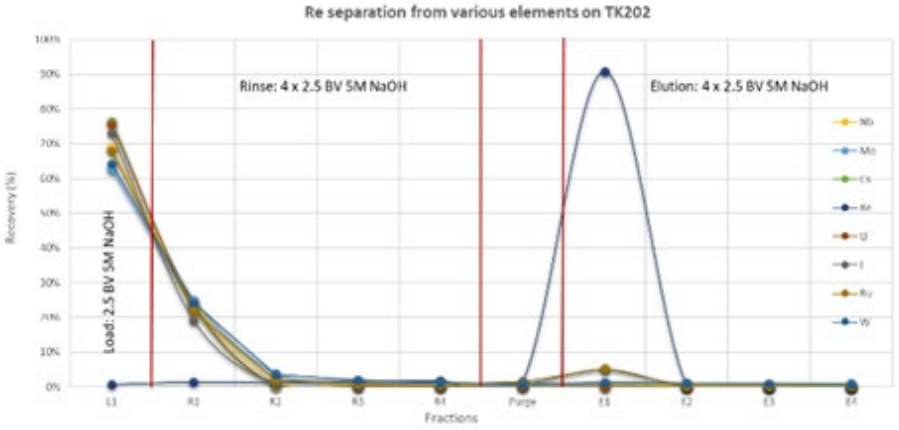
Dw values for Tc in 5M NaOH using 40 mg TK202 Resin, increasing amounts of Mo. Data taken from Cieszykowska et al.

Tc-99 - new TK202 Resin

- Tc retention from high NaOH (preferably 5 - 7M NaOH)
  - e.g. after alkaline fusion of decommissioning samples
- Re may serve as internal standard
- For high Mo samples:
  - Tc rec. > 90% for 6 – 8g Mo per g TK202
- Elution with water
  - Elution in small volume
    - Will still be alkaline
  - Pass through CEX for neutralisation and
  - through aluminium oxide for trace Mo removal and recovery as 0.9% NaCl solution



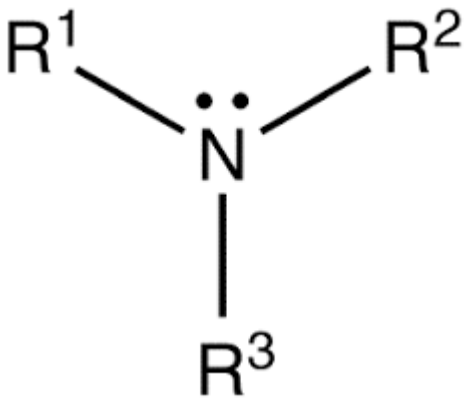
Re/Tc separation from Mo on TK202 Resin



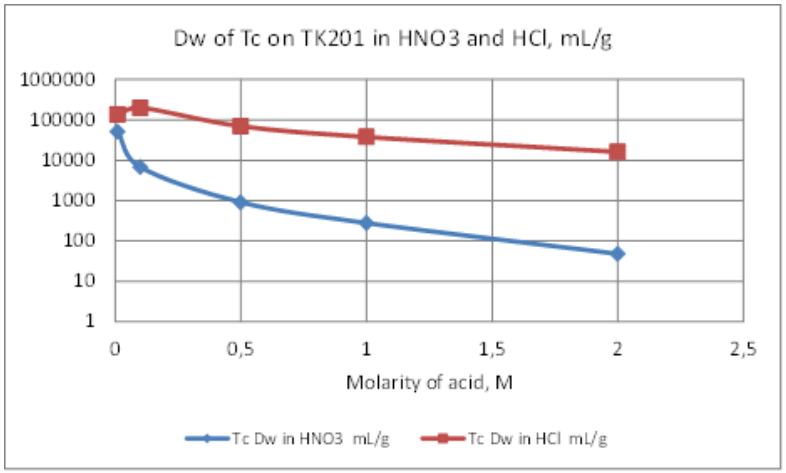
Re separation from selected elements on 2 mL TK202 Resin cartridge, load and rinse at 1 BV/min, elution at 0.25 BV/min.

Tc-99 - TK201 Resin

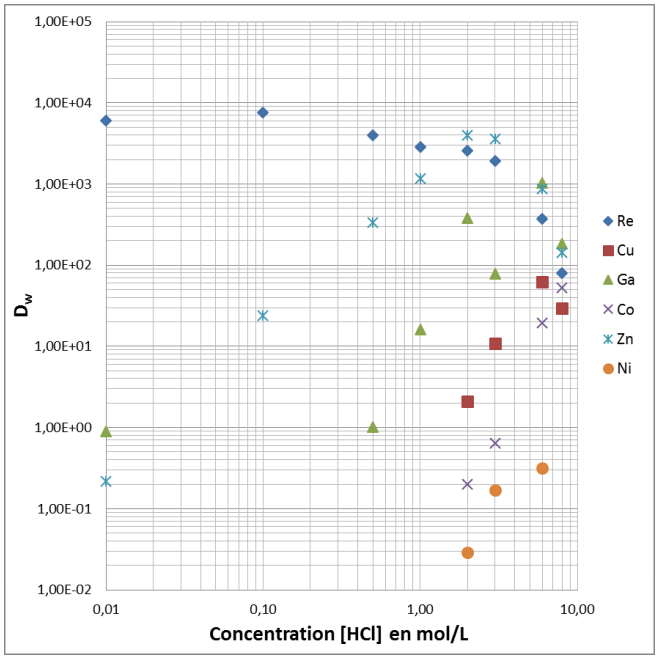
- Based on tertiary amine (weak Anion Exchanger) impregnated on inert support
- Main applications:
  - Cu separation
    - In combination with TBP resin for Cu-64 and
    - With CU Resin for Cu-67 production
  - Tc separation
    - Similar selectivity to TEVA but easier to elute
    - Environmental monitoring
    - Decommissioning

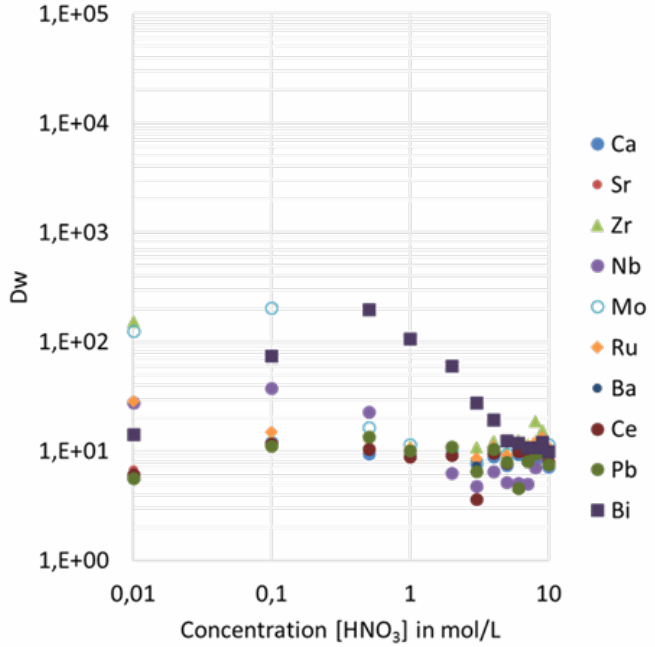


Tc-99 - TK201 Resin



Data provided y N. Vajda (RadAnal)





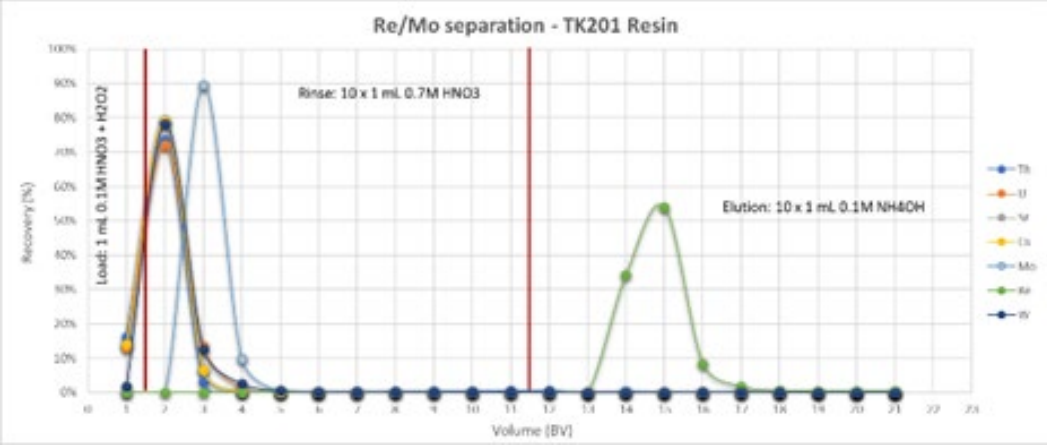
Data provided y B. Russel (NPL)

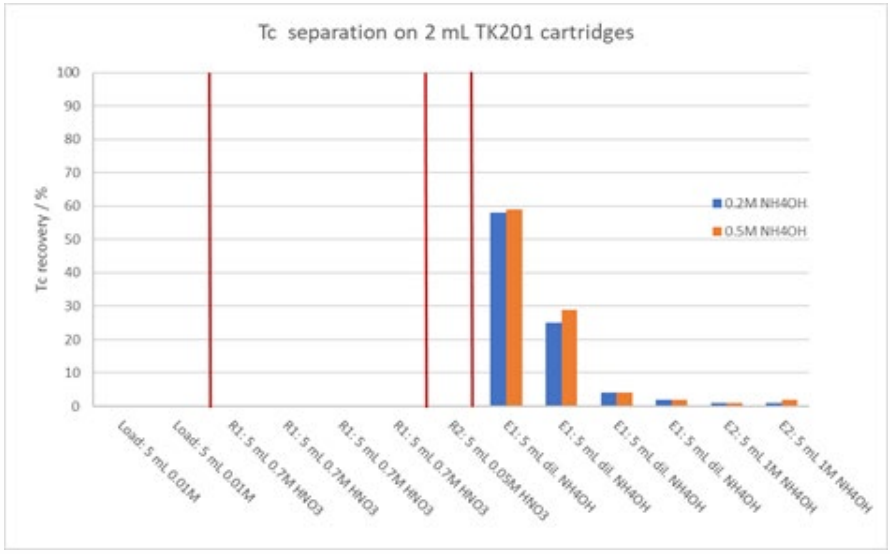
- High Tc and Re uptake in HCl (incl. ≥2M)
- HNO_3: only high uptake at low concentration
- Very low Mo retention at ≥0.5M HNO_3
  - Tc/Mo separation
- Tc/Re elution in elevated HNO_3

TK201 Resin – Elution curve

- Load of sample at pH 1-2 t
- Interferences removed during load/rinse
- Most other elements removed during load and first rinse
- Clean Mo elution at 0.7M HNO_3
- Elution of Re ≥1M HNO_3 possible, for Tc (& Re) >2M HNO_3
  - Higher HNO_3 => smaller elution volumes
- Preferable elution option:

  ≥ 0.2M NH_4OH (~10 – 15 mL)
- Still requires elution…





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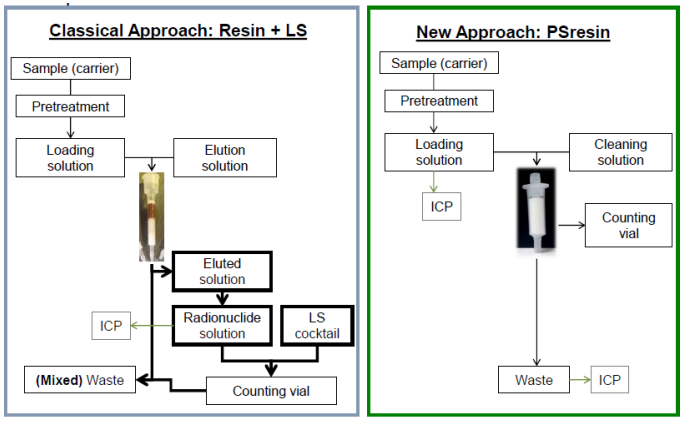
Tc-99 – New: TK TcScint

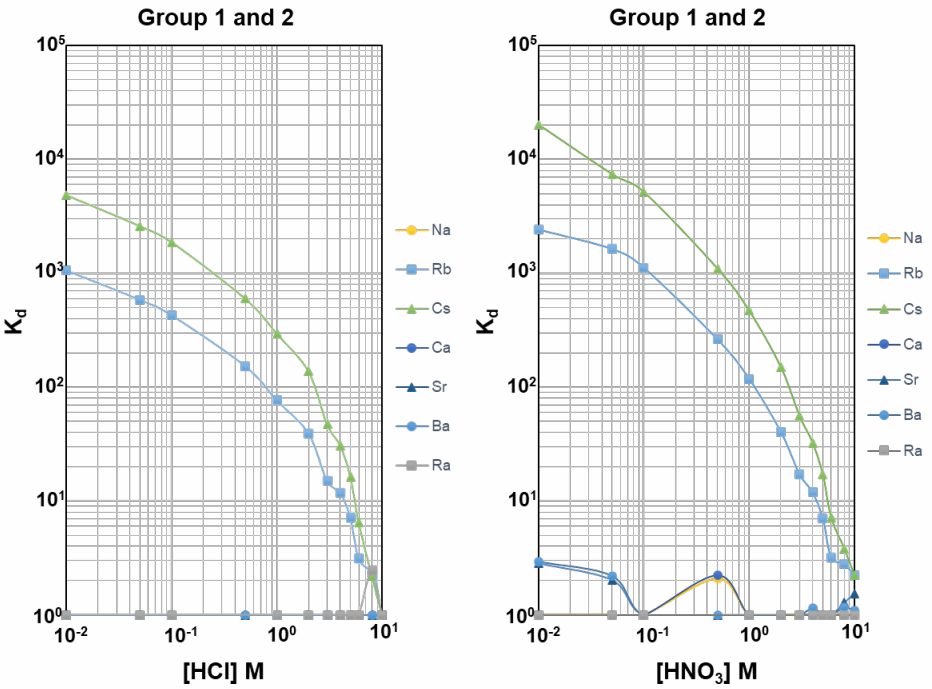
- Based on Plastic Scintillating microspheres (PSm)
- Scintillating beads impregnated with selective extractants
- Developped by García, Tarancón & Bagán
- Now available at TKI
- « TK ElScint » range of products
- First: « TK TcScint »
  - Aliquat based > selectivity similar to TEVA



- Environmental/decommissioning monitoring => Tc-99 by LSC
- Direct measurement of cartridges after loading in LSC counter
  - Radioprotection, safety, hands-on-time, waste…
- Chemical yield via Re/ICP-MS in effluents

Upcoming - TK300 Resin

- Macrocycle based Resin
- Cs and/or Rb separation
- Selectivity for Cs and Rb over other éléments tested in HNO_3 and HCl



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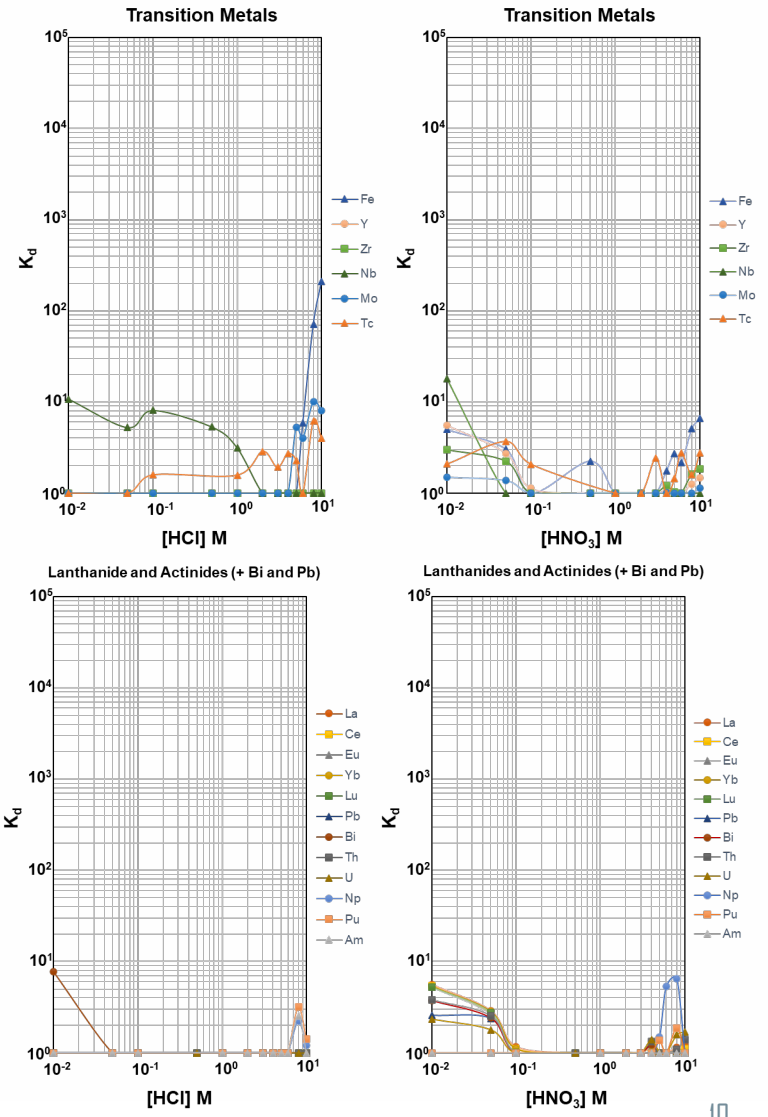
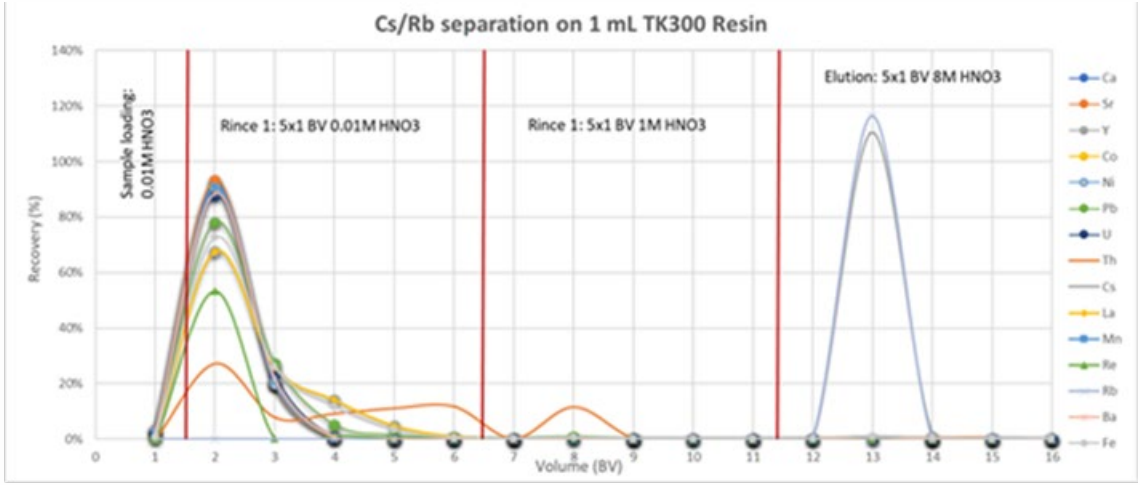
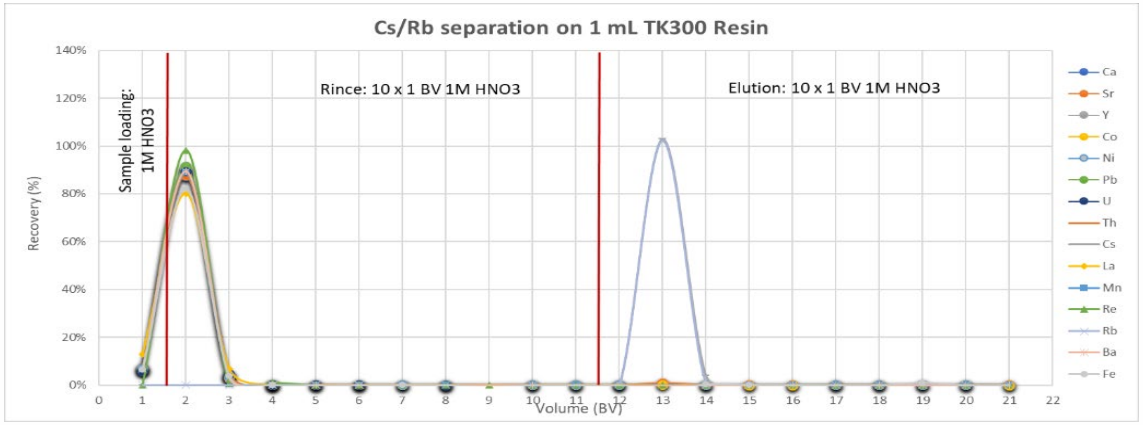


Upcoming - TK300 Resin



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



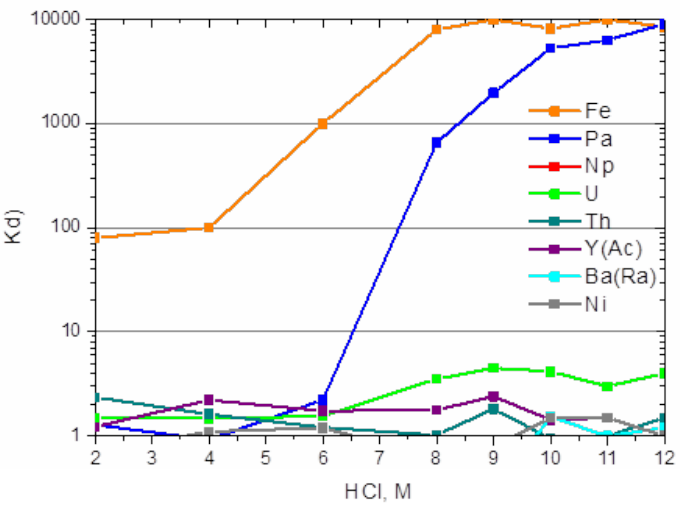
Elution study, Cs and Rb separation from selected elements on TK300 resin, loading from 1M HNO3

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

➢ Rather suitable for decommissioning samples

TK400 Resin

- Long chained alcohol
  - First work by Knight et al. on Np/Pa separation
- Retention only at high HCl concentration (>6M HCl), elution in low HCl, water,…
- Main application: Pa separation
- Also retains Mo, Fe, Po, Ga, Nb, Nb,…
- Higher Fe capacity than e.g. TRU Resin
- Currently being tested with in an ongoing DTM separation project with Subatech



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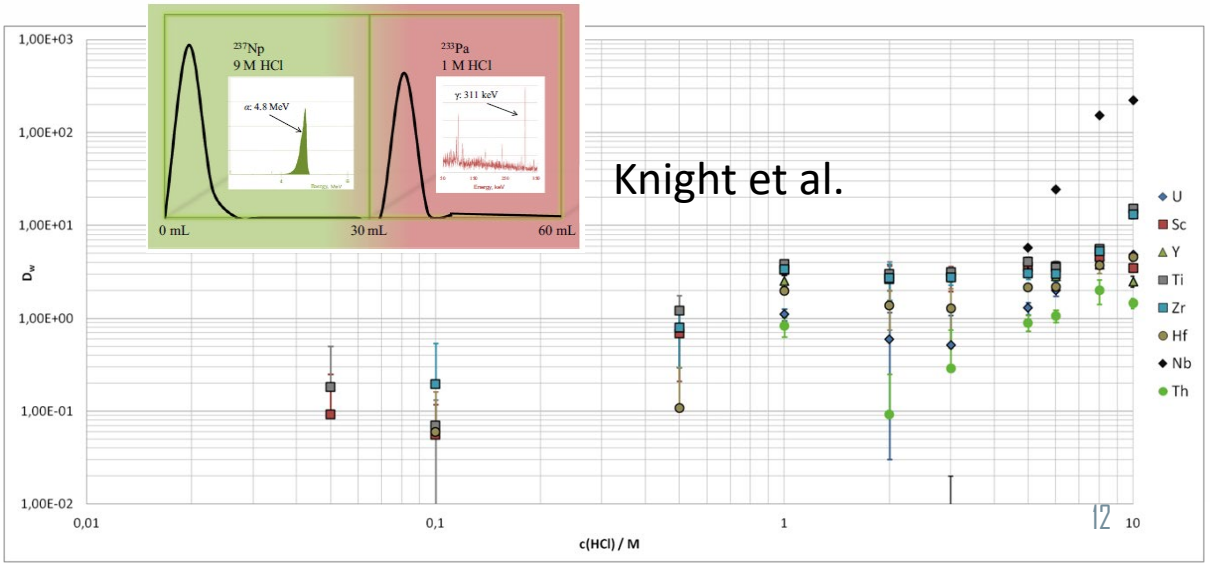
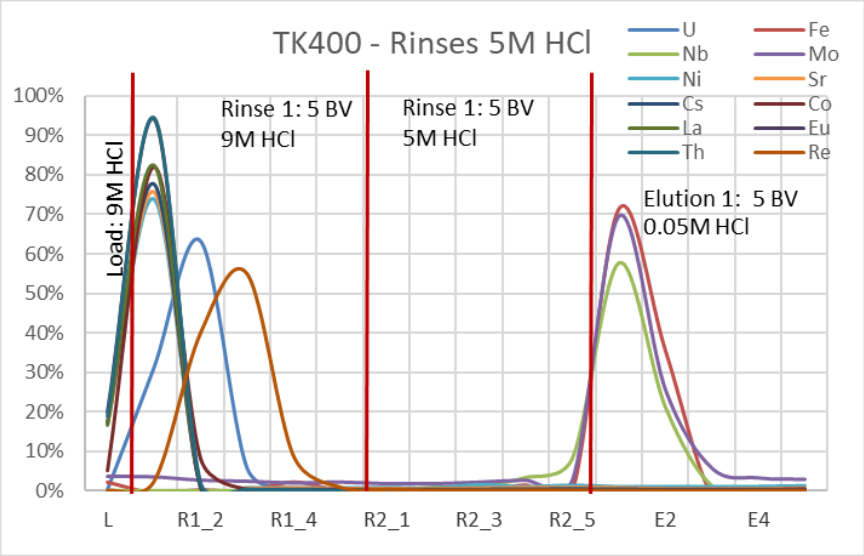
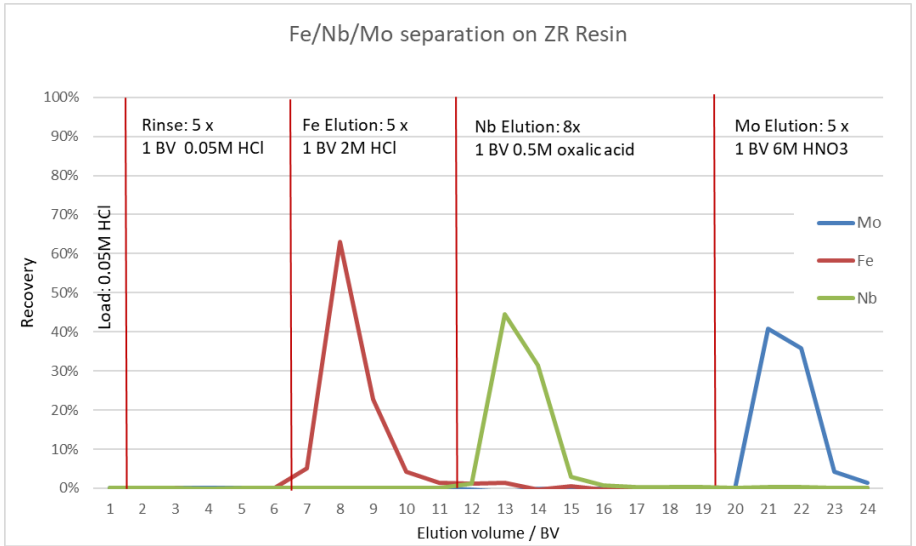


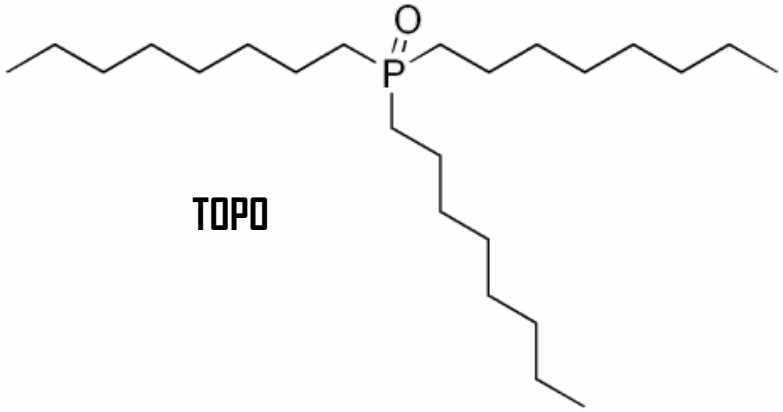
Fe/Mo/Nb separation





- 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 and Mo eluted in dilute HCl => separation on ZR Resin
- Can also be used to remove Nb from Zr (e.g. stacked TK400/UTEVA) or Pu-241

TK200 Resin



TOPO

- Based on TOPO extractant
- High retention of actinides
- Extracts actinides even at pH 2
  - Preconcentration and purification of selected actinides on same column
  - ➢ Automized separations
- Typical applications:
  - Actinide separation from water samples
  - Use for very efficient U removal from Pu (Wang et al.)
  - Ga-68 production (in combination with ZR Resin)
  - On-going: Pt separation, Pd separation, Zn separation

Actinides on TK200 – HNO_3
(all data N. Vajda et al)

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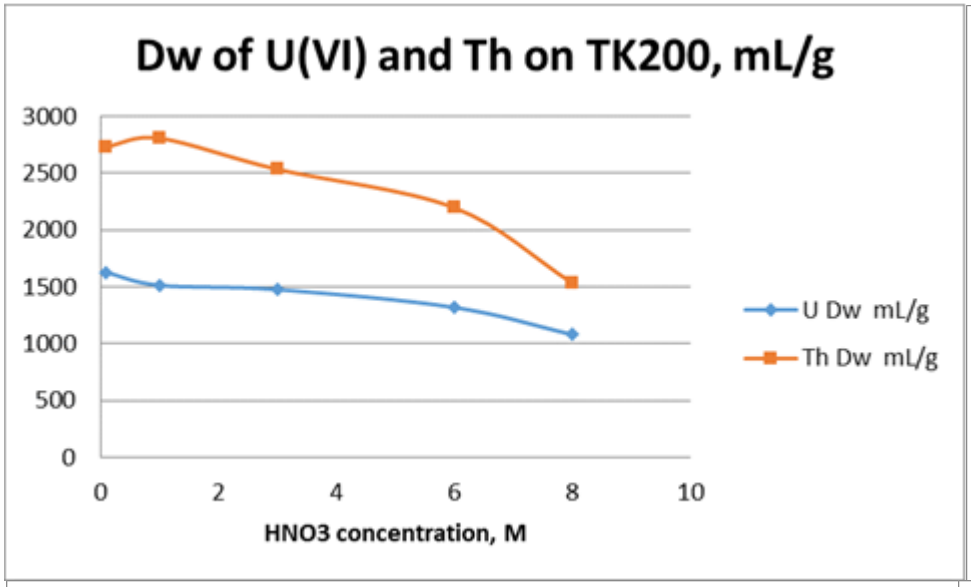

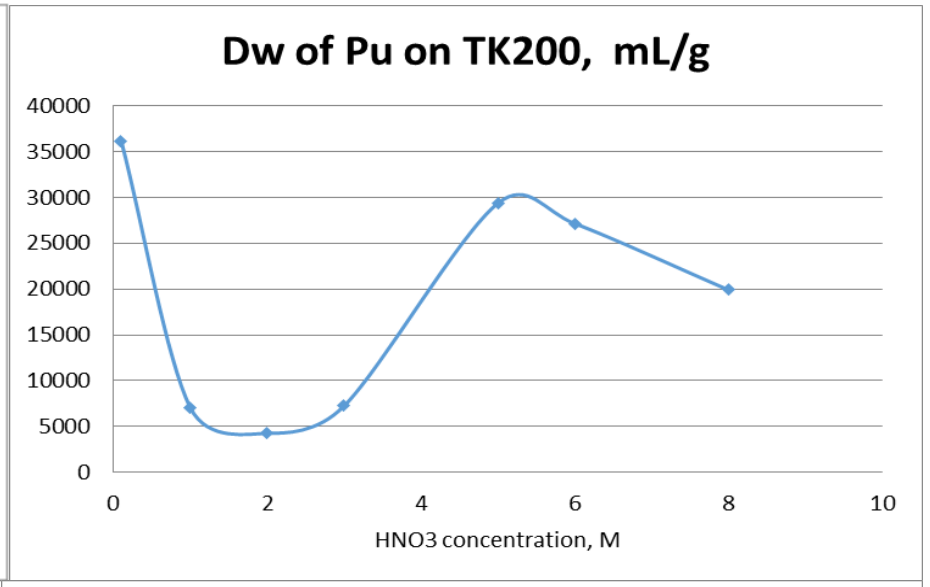

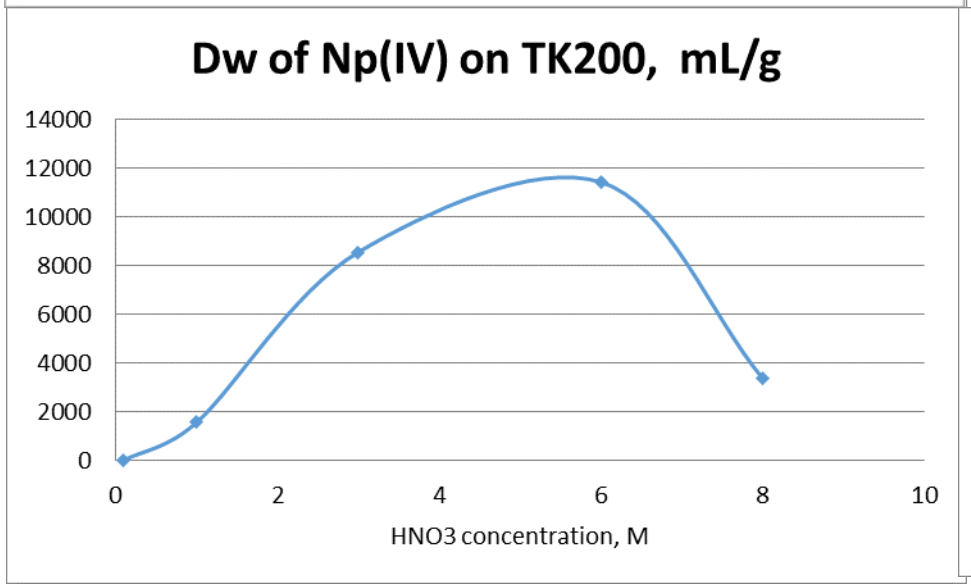

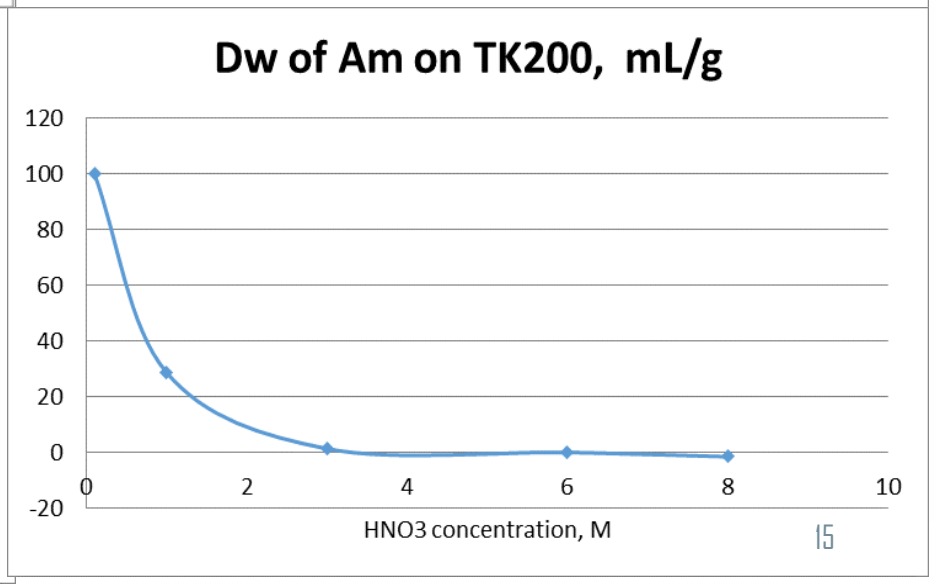

Actinides on TK200 – HCl
(all data N. Vajda et al)

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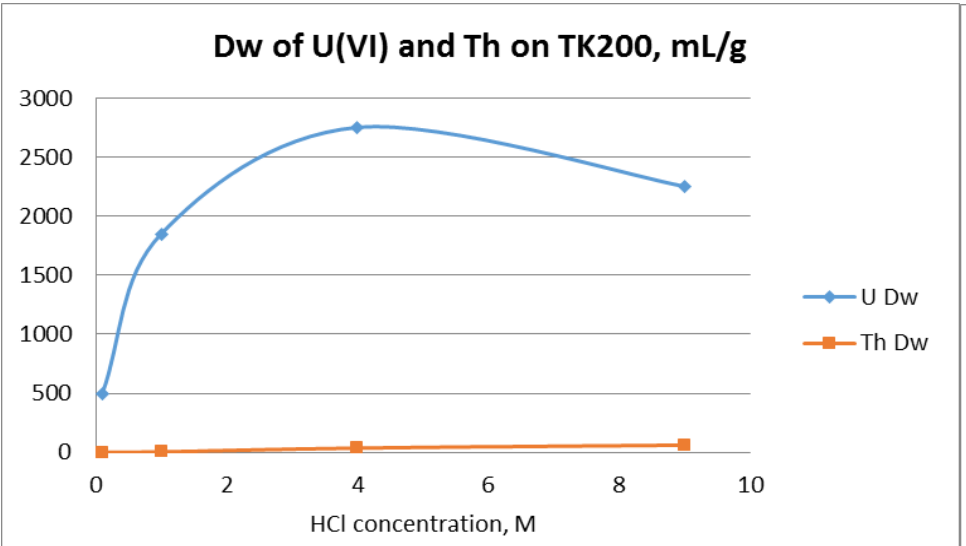
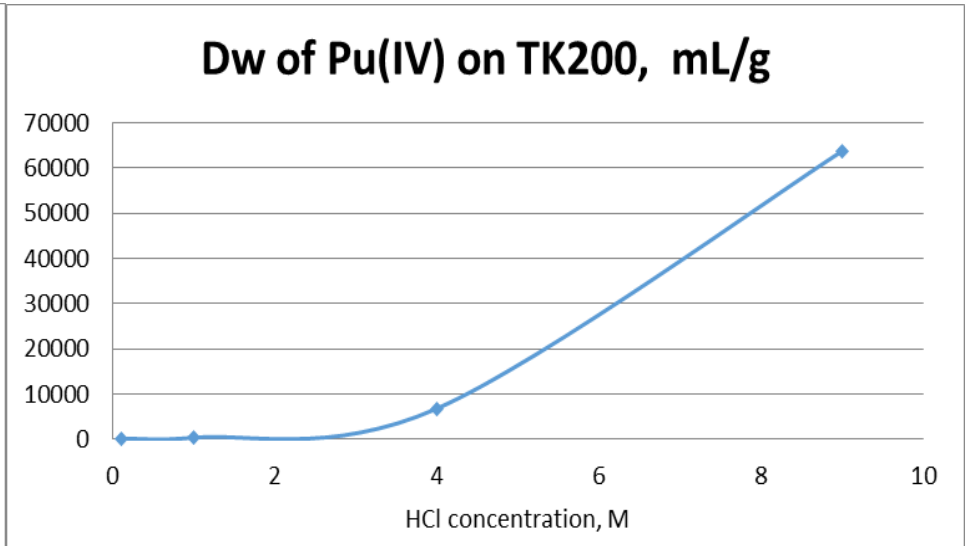
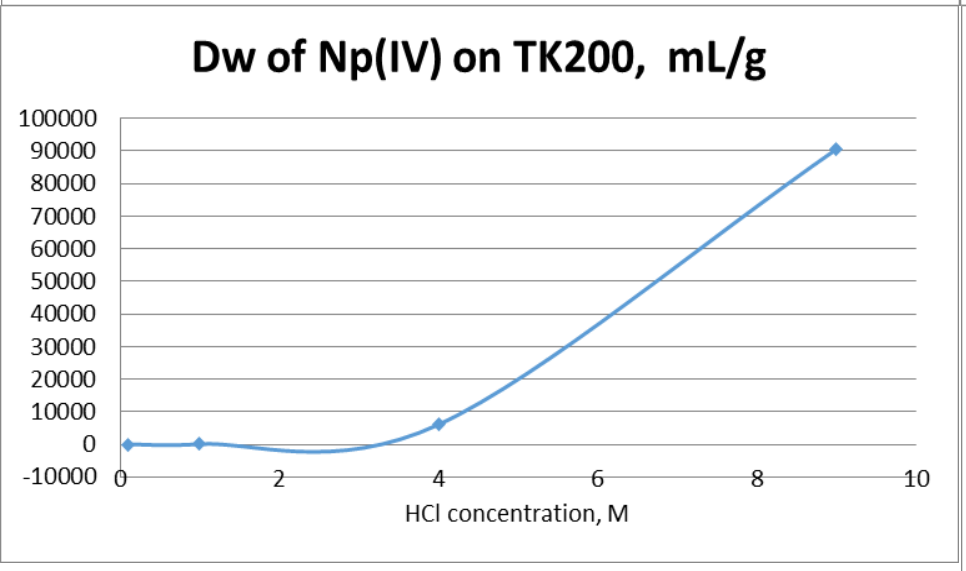
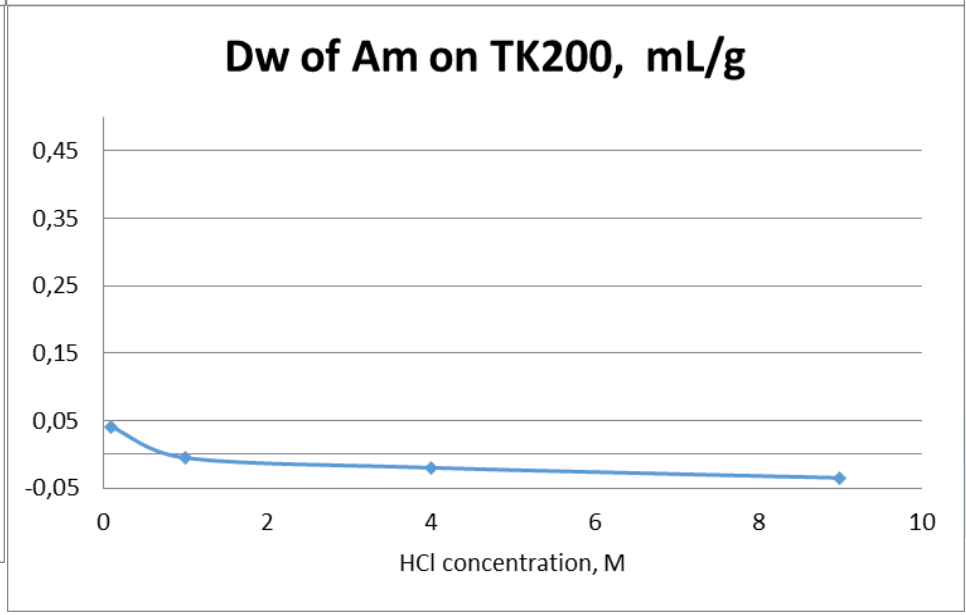
Expertise in Separation Chemistry

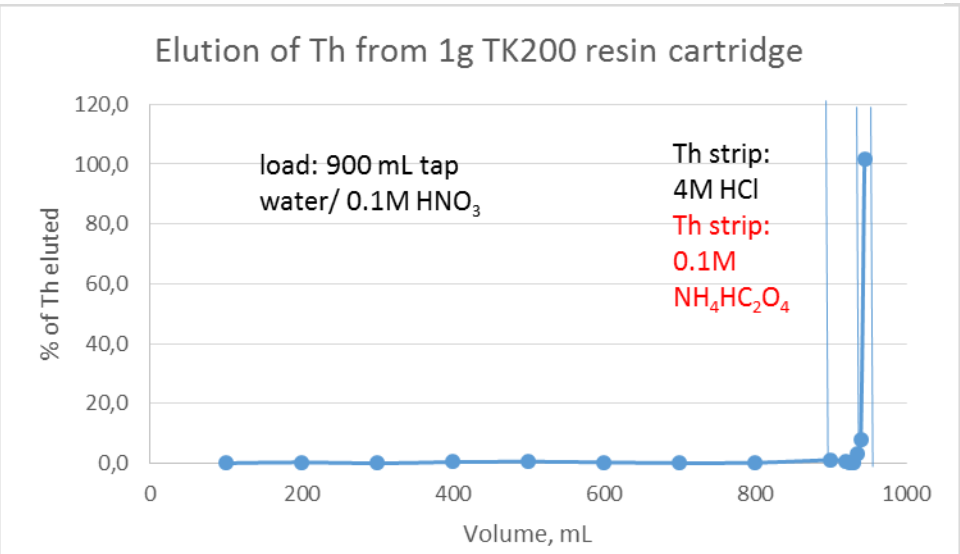


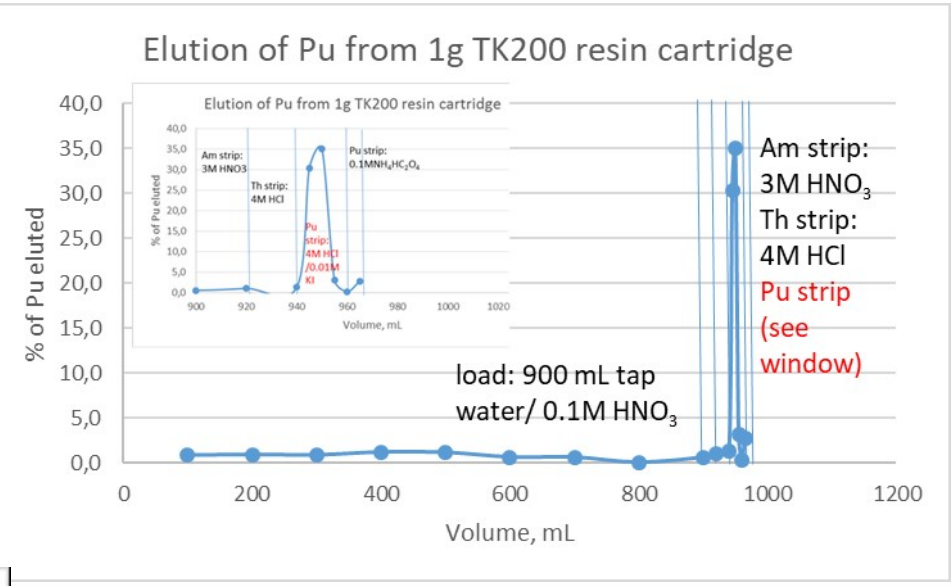


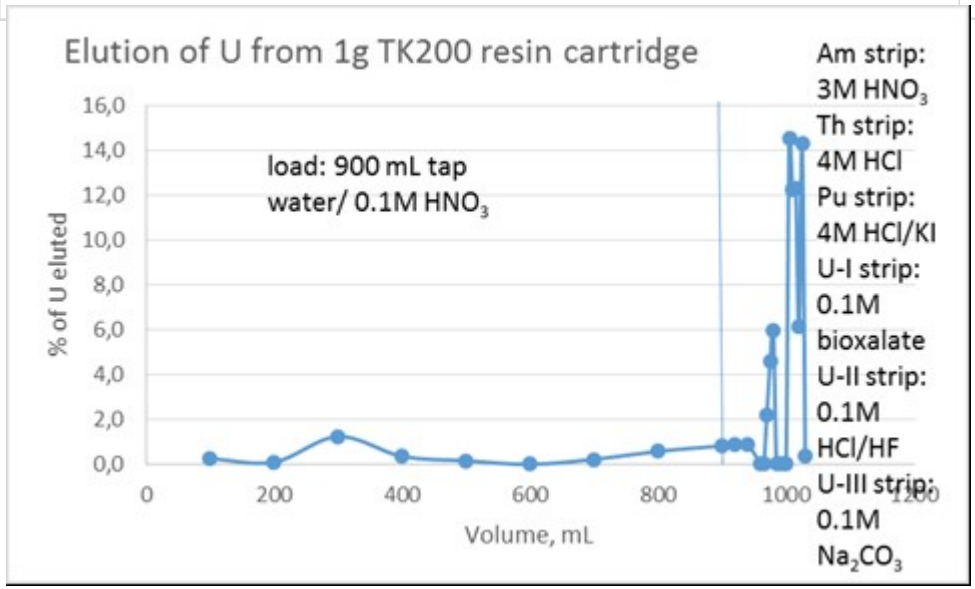




Actinides on TK200 – Application



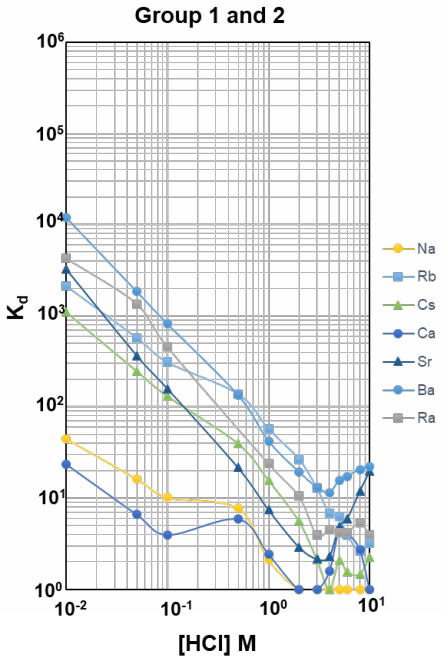


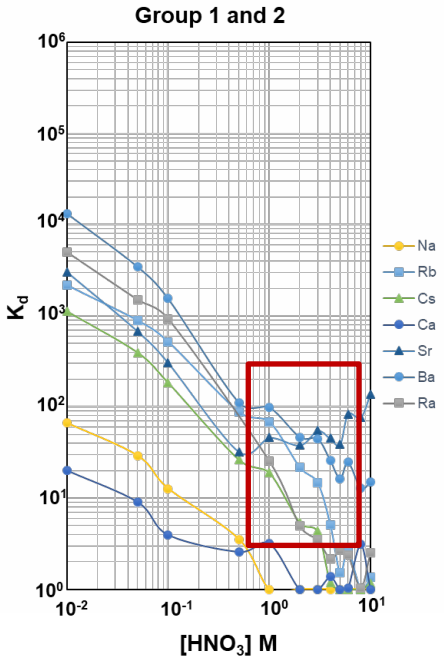


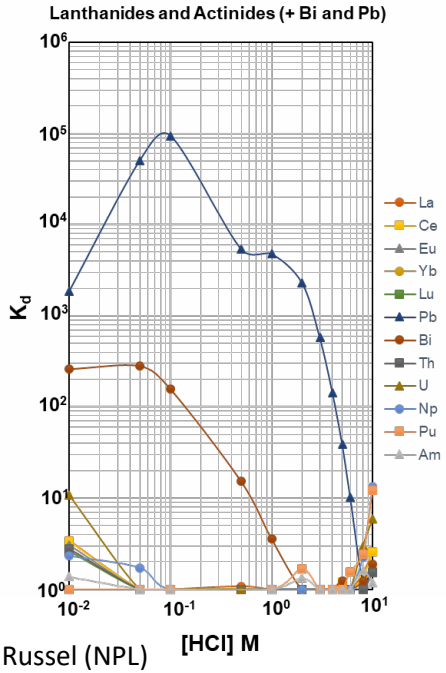
- Data by N. Vajda (RadAnal)
- Method development on-going
- Direct load of actinides (U, Pu, Th) from acidified water samples
- Sequential separation on TK200
- 'In the field preconcentration'?

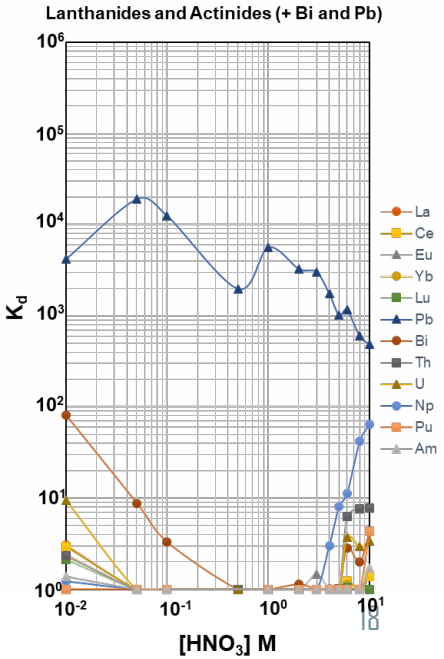
On-going: Radium

- Original work (e.g. van Es et al., Agilent Application note) on TK100 (1L ground water)
  - U, Pb and Th also retained => Work on sequential method still on-going
- TK101 Resin – SR Resin crown-ether in ionic liquid
  - High retention Ra, Ba, Sr, Pb and Cs/Rb from dilute mineral acid or water, no retention of U or Th
  - Ra elution at ≥1M HNO_3, separation from Ba and Sr seems possible, Pb retained
  - Rather suitable for ICP-MS, α-spec or preconcentration for LSC (further purification needed)
- On-going project => calixarene based resins (first publication in prep.)





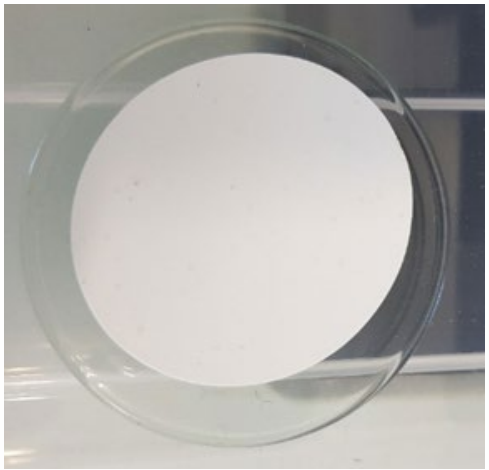




Data provided y B. Russel (NPL)

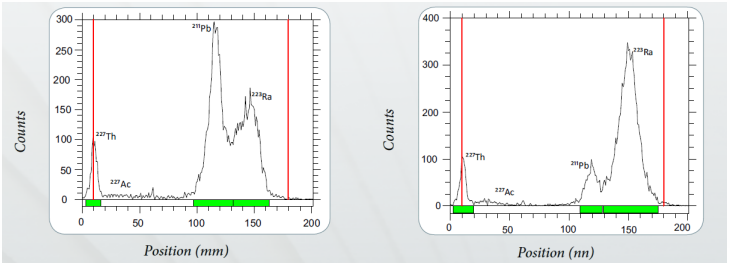
Under development

- Range of **extractive membrane filters (MF)**
  - Rapid separation (up to 50 mL / min)
  - Preferably for use with water samples (0.5 – 5L)
  - Sampling in the field
  - Passive Sampling (DGT)
  - Under development:
    - TK201 (Tc)
    - TK100 (Sr, Pb), TK101 (Pb, Ra)
    - CL Resin (iodine)
    - Calixarenes (Ra)
    - TK300 (Cs)
    - …
- Range of 'Test sticks'
  - Pieces of impregnated membrane on support
  - E.g. DGA for Ca,… (JCU, Usouthampton)



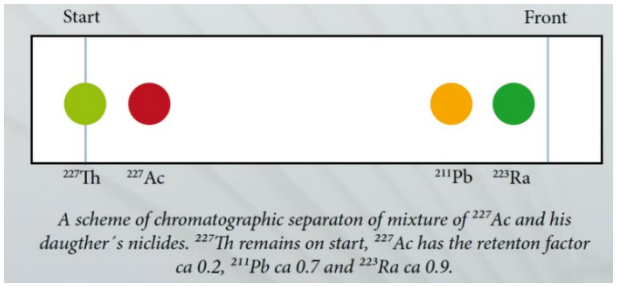
DGA Sheets

- Originally developed by CVUT Prague
- TO-DGA (normal DGA) and TEH-DGA (branched DGA)
- QC of radionuclides and generator eluents
  - Ra-223, Ac-225/Bi-213, Pb-212, Ge-68/Ga-68, Sr-90/Y-90,…
  - TLC scanner or radiometer/**LSC after cutting (Ge-68, Sr-90)**
- More types of sheets under development
  - **SR (Sr-90/Y-90 QC) in beta testing**, TK201, LN, ZR, UTEVA,…
- 2D TLC under development => use in decommissioning
  - Quadratic sheet, two runs (90° turn in-between) with different acids => 2D pattern
  - Initial screening with autoradiography,… potentially followed by LSC after cutting

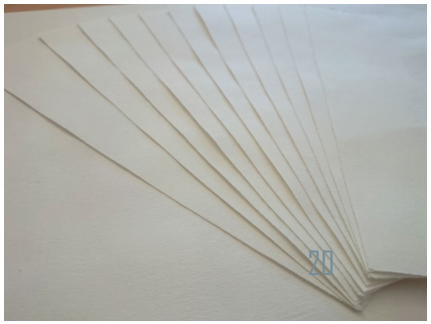


Radiochromatogram measured immediately after separaton. Low abundant radiatons of ^{227}Ac were not detected.

Radiochromatogram measured one hour afer separaton. Decay and ingrowth of ^{211}Pb is clearly visible.



A scheme of chromatographic separaton of mixture of ^{227}Ac and his daugther´s niclides. ^{227}Th remains on start, ^{227}Ac has the retenton factor ca 0.2, ^{211}Pb ca 0.7 and ^{223}Ra ca 0.9.



Some other on-going projects

- SE Resin
- Optimised DTM separation schemes
  - E.g. Subatech (LabCom TESMARAC)
- Rapid tests
  - Test sticks
  - SBSE
- TK221 instead of TRU or DGA
  - Higher Dw for Am than TRU
  - Higher Dw for U than DGA
    - N. Vajda (RadAnal)
- In the field sampling
  - Cartridges or discs
- DGT (Diffusive Gradients in Thin Films) => 'bio-availability'
- Lanthanide separation
  - TK221, TK211/2/3
- Separation of radiometals for use in nuclear medicine
- Li Resin
- Microfluidics
- Upscale => resins for hydrometallurgy/recycling
  - Larger quantities and bead sizes

Thank you for your attention!

TRISKEM
Expertise in Separation Chemistry