



# TrisKem International

Development of extraction chromatographic resins to meet decommissioning challenges

CARM 2020, NPL Teddington (UK)

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15/01/2020



# TrisKem International

- Based in Rennes (France)
- Independent company since 02/07
  - Formerly part of Eichrom Europe
  - ISO 9001 since 2007
- Sales into >70 countries
- Staff : 21
- R&D, QC and TechSupport group:
  - 3 RadChem PhD, 2 OrgChem PhD, 1 Engineer and 3 Technicians
- R&D: Development of new resins, techniques and applications
- Several domains:



Radiopharmacy  
and  
Nuclear Medicine

Environment and  
Bioassay

Geochemistry  
and  
Metals Separation

Decommissioning

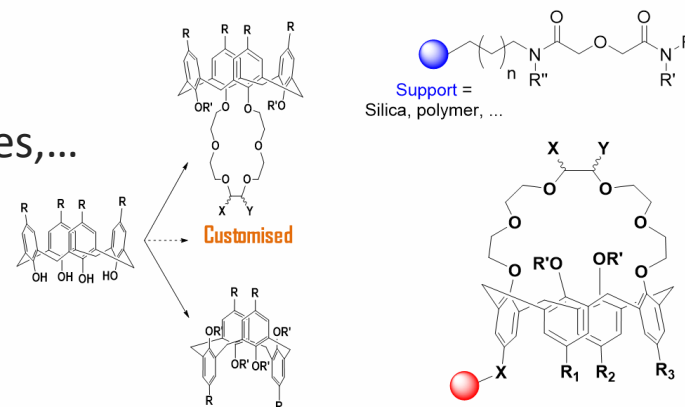
- Production and trade of selective resins and accessories
  - **Mainly extraction chromatographic resins**
  - **PAN embedded inorganic compounds**
  - Functionalized polymers and silicates
  - Analytical and chelating ion exchange resins
- Distribution & commercial agent (mainly Europe):
  - LSC cocktails et al. (Meridian)
  - **New: Radioactive standards (NPL)**
  - Raddec Pyrolyser (H-3 & C-14)
  - PEEK columns
  - ICP & AAS standards (Labkings)
  - Accessories (Zr crucibles, empty columns & cartridges, funnels, vacuum boxes,...)



RADIOACTIVE STANDARD SOLUTIONS



- 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, automatic desiccator, benchtop NMR (43 MHz), surface area and pore size volume analyser, size and shape analyser, pycnometer
  - Production and packing lab with four 20L reactors
- No handling of radioactivity/access to real samples  
=> R&D cooperation
  - Resin and method development “cold” => R&D partner
  - **NPL**, GAU, AWE, RadAnal, NLS,...



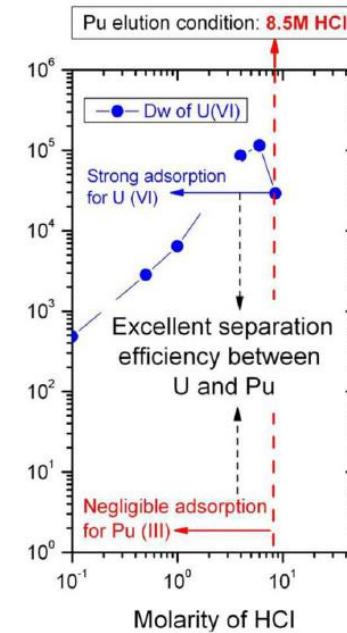


- Analytical applications
  - Wide range of matrices
    - Decommissioning samples (concrete, steel,...), waste monitoring, bioassay, environmental monitoring,...
  - ...and analytes
    - Actinides, fission and activation products,...
  - Focus on **DTMs & rapid methods**
    - **CL Resin** (Cl-36/I-129), **TK100** (Sr in aqueous samples and Sr-90 by ICP-MS), **TK400** (PA, Mo/Nb removal for Zr-93), **TBP Resin** (Sn-121m/6), **CS Resins**, **TEVA**, **UTEVA**, **TRU**, **DGA** (actinides), **NI Resin** (Ni-63), **SR Resin** (Sr-89/90), ...
- Decontamination
  - Treatment of effluents / liquid wastes / environmental waters
    - Removal of radioactive contaminants & heavy metals
    - Inorganic compounds embedded into PAN matrix
    - **Currently CS Resins, more under development**

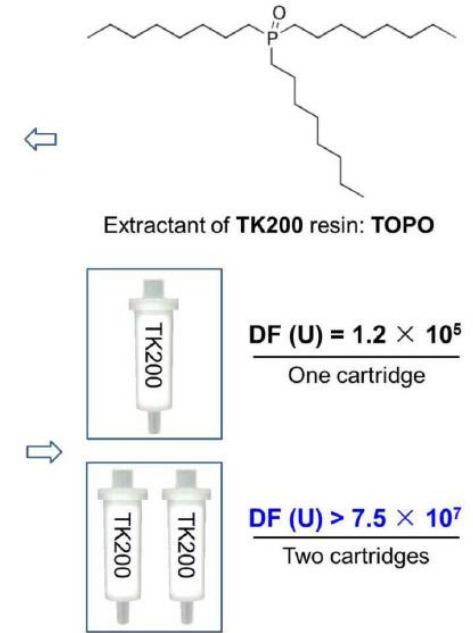
- News/updates
  - TK200 (TOPO based, actinides in water samples...)
  - TK201 (Tc-99)
- Upcoming/beta testing
  - TK TcScint (impregnated plastic scintillation beads for Tc-99)
  - TK202 (Tc-99 from alkaline samples)
  - TK300 (Cs-135/7)
  - TK211/2/3 (lanthanide separation)
- In the pipeline
  - Production upscale/range of new PAN Resins
  - SE Resin (Se-79)
  - Extractive membrane filters
  - ...

# TK200 Resin

- Based on TOPO
- Extracts U, Th, Pu at pH 2
  - Preconcentration and purification of selected actinides on same column
  - Rapid screening of water samples
  - Automated separations/ICP-MS
  - (Sequential) U/Th/Pu separation from water samples



Graphic abstract



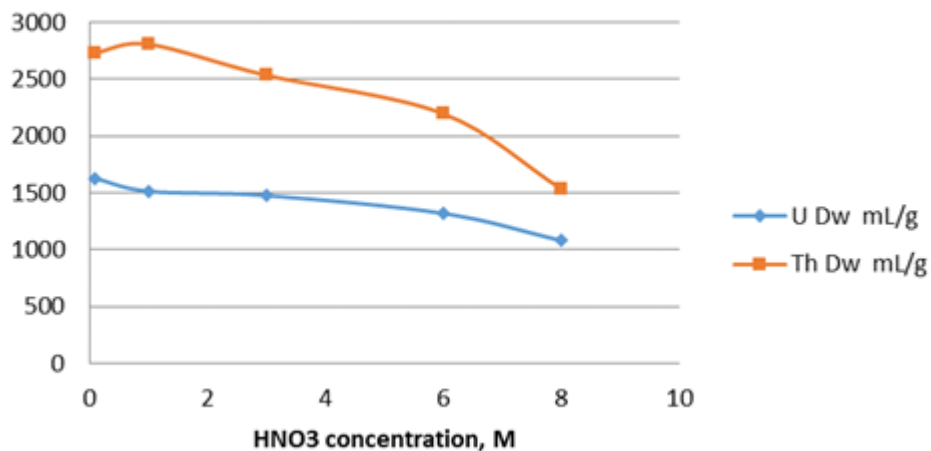
Wang et al. 2019

- High U retention
  - Pu isotope ratios by ICP-MS (U removal e.g. Wang et al, 2 x TK200 => Df >10<sup>7</sup>)
- Other applications:
  - On-going: Pt/Ir, Zn/Cu (Zn production, Zn removal), Sc separation,...
  - Ga-68 production (in combination with ZR Resin)

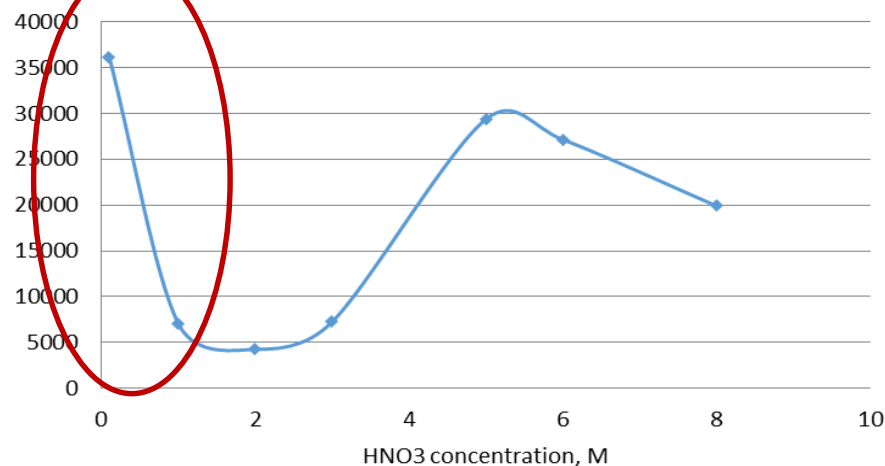
# Actinides on TK200 – HNO<sub>3</sub>

(all data N. Vajda et al)

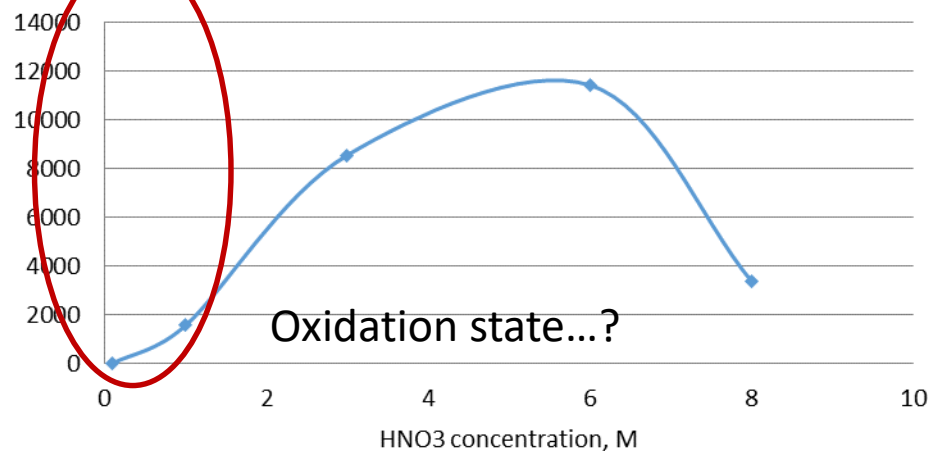
### Dw of U(VI) and Th on TK200, mL/g



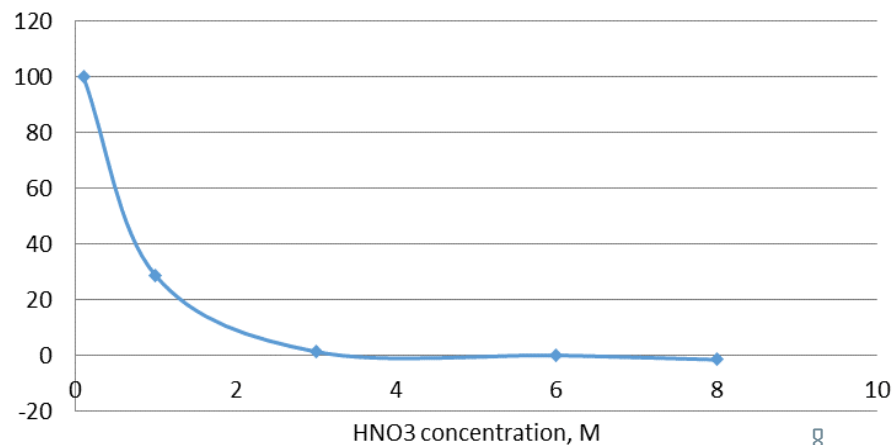
### Dw of Pu on TK200, mL/g



### Dw of Np(IV) on TK200, mL/g



### Dw of Am on TK200, mL/g

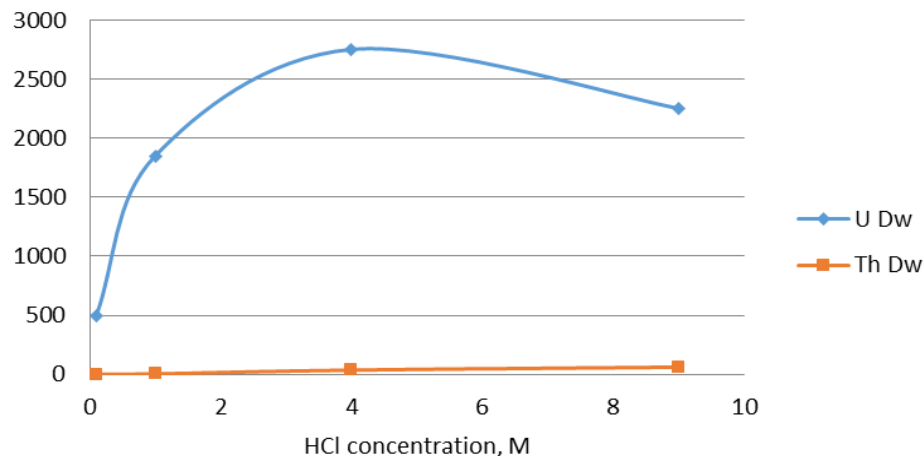




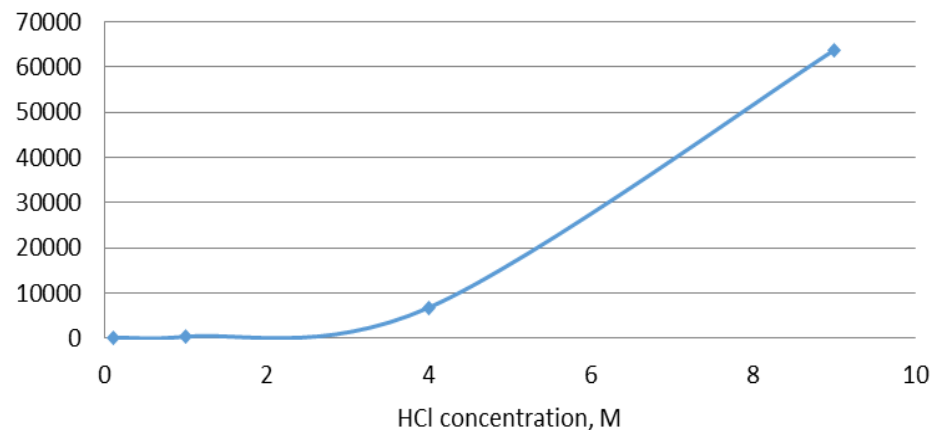
# Actinides on TK200 – HCl

(all data N. Vajda et al)

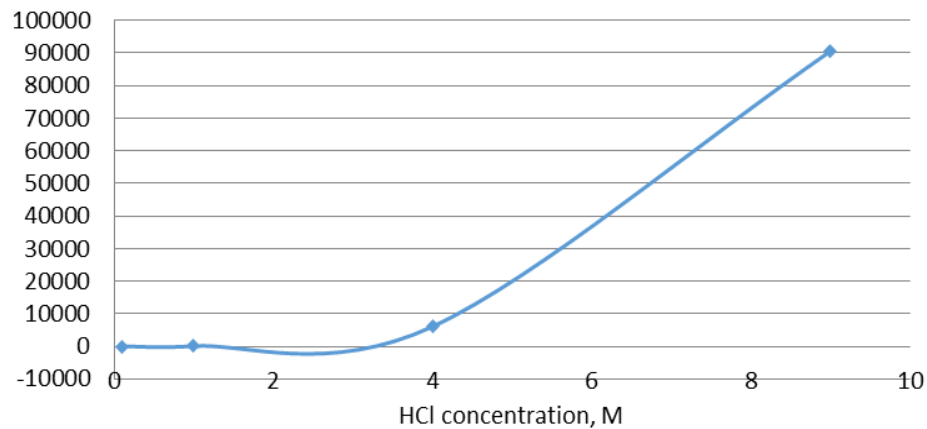
### Dw of U(VI) and Th on TK200, mL/g



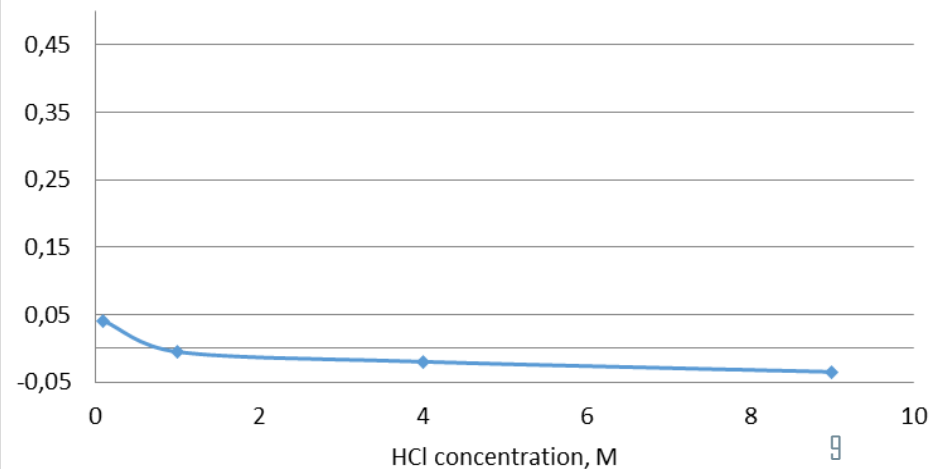
### Dw of Pu(IV) on TK200, mL/g



### Dw of Np(IV) on TK200, mL/g

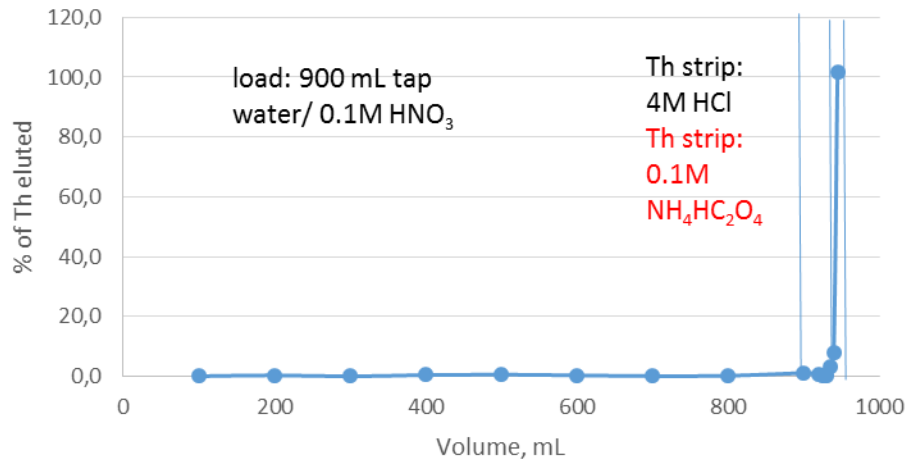


### Dw of Am on TK200, mL/g

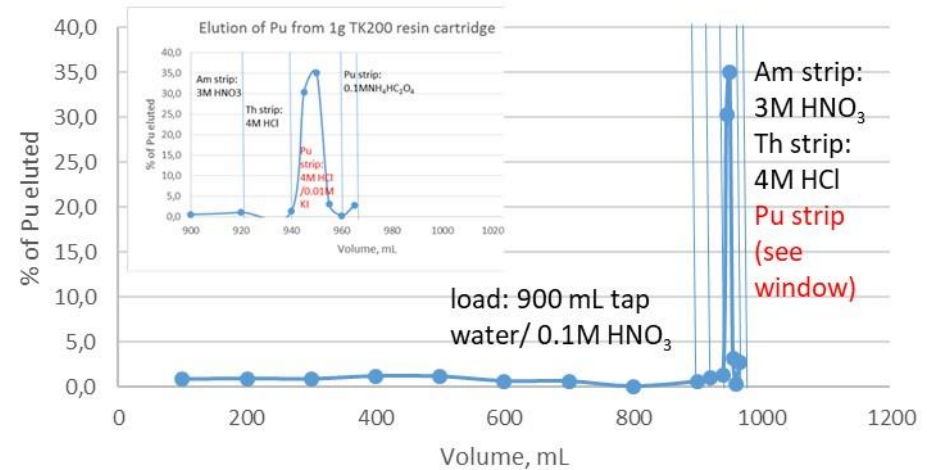


# Actinides on TK200 – Application

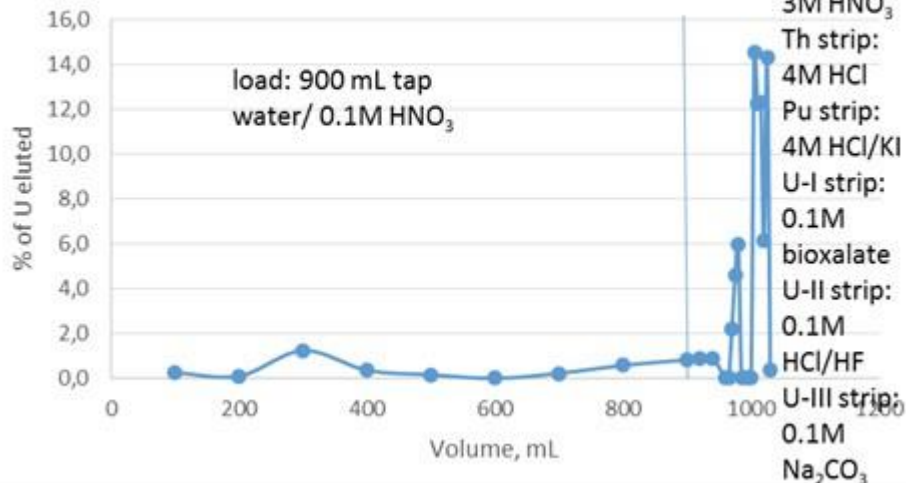
Elution of Th from 1g TK200 resin cartridge



Elution of Pu from 1g TK200 resin cartridge

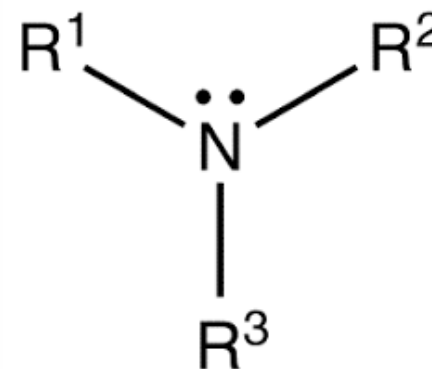


Elution of U from 1g TK200 resin cartridge

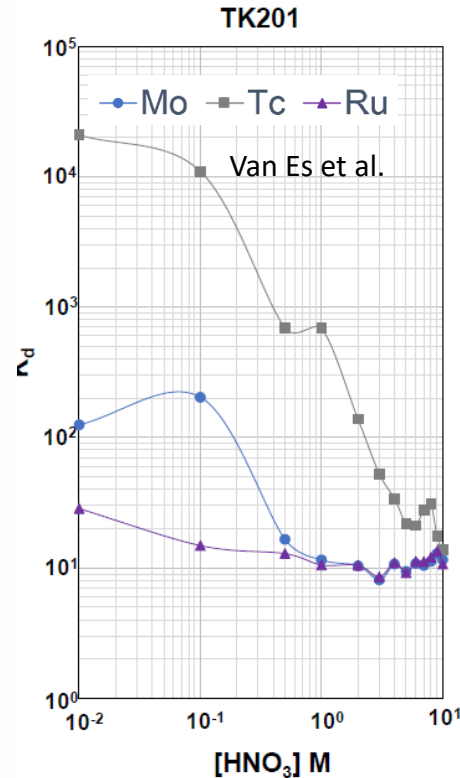
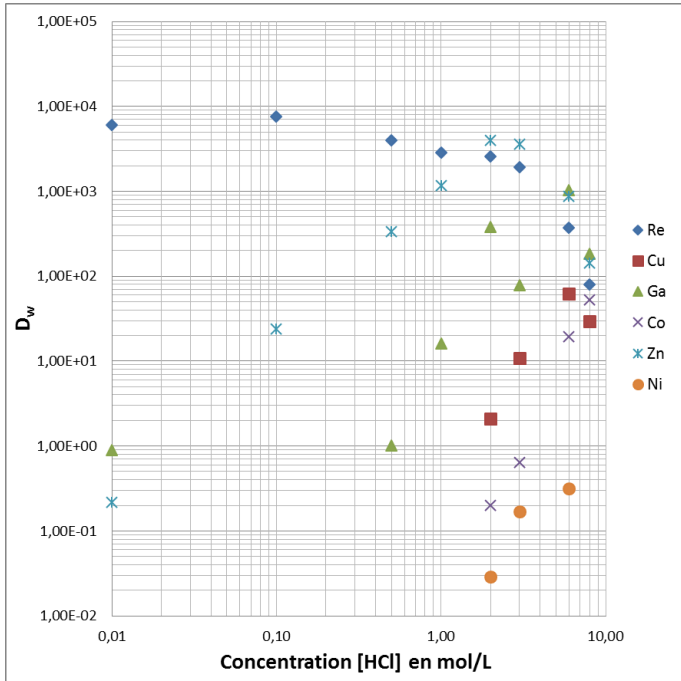


- Currently under improvement with RadAnal (Nora Vajda et al.)
- Aim, direct load of actinides from acidified water
- Sequential separation

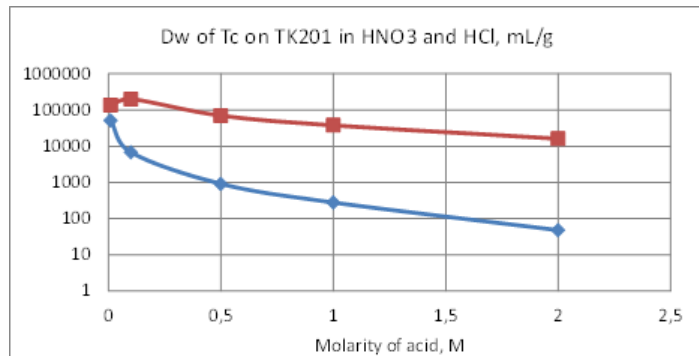
- Tertiary amine based resin
  - Weaker anion exchanger compared to TEVA
  - Elution under softer conditions
    - $> 2M \text{ HNO}_3$  or  $\geq 0.5M \text{ NH}_4\text{OH}$
  - Main application Tc-99
  - New  $D_w$  and elution data by NPL
  - Other applications:
    - Cu separation (Cu-64 from solid Ni-64 targets)
    - U/Pu separation?



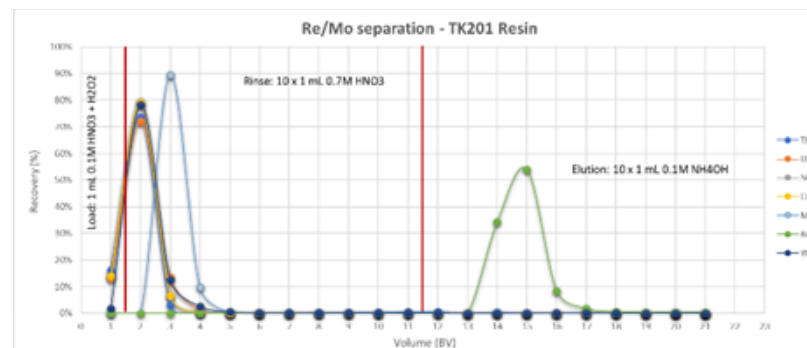
# TK201 – Dw data Tc/Re



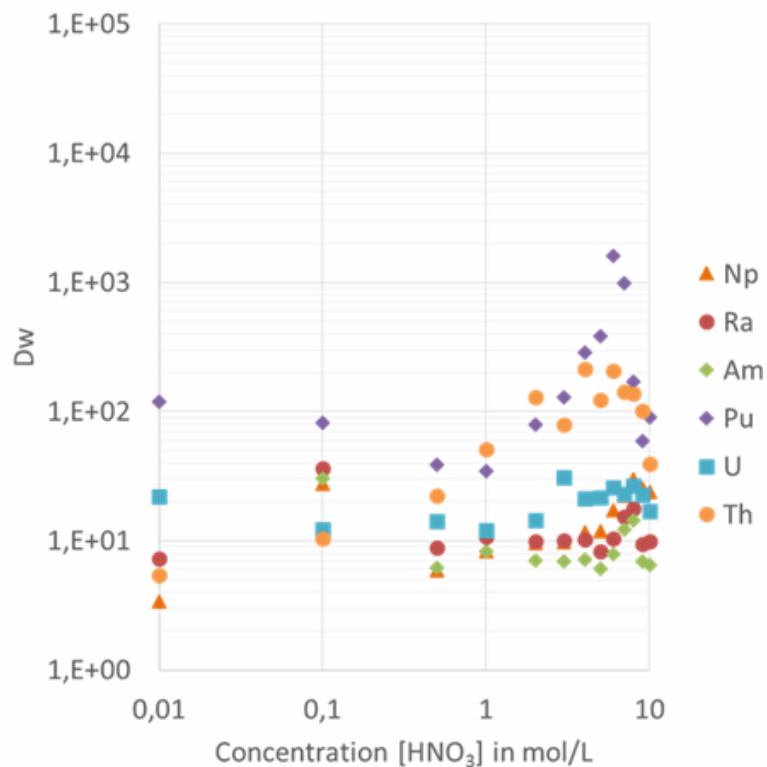
- Re/Tc uptake between  $pH \leq 2$  and  $\sim 2M$  HCl
- Tc retention higher than Re
  - Chemical yield via Re...
- Tc shows higher retention in HCl than in  $HNO_3$
- Low selectivity for Ru in  $HNO_3$
- Low retention of Mo in  $HNO_3$  at  $> 0.5M$
- High Tc selectivity over Mo at  $\geq 0.7M$   $HNO_3$
- Clean Mo separation



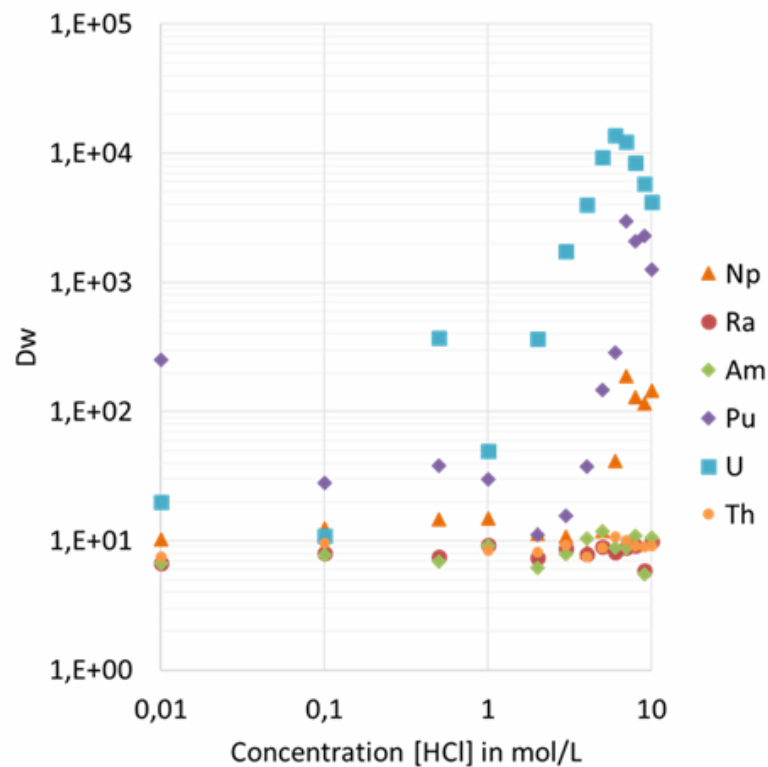
Vajda et al. — Tc Dw in  $HNO_3$  mL/g — Tc Dw in HCl mL/g



# TK201 – Dw data actinides

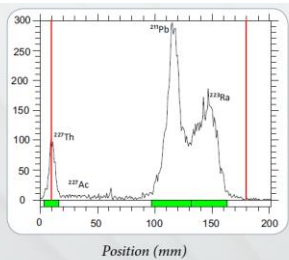


- Pu well retained at elevated HNO<sub>3</sub>
- Th fairly well retained

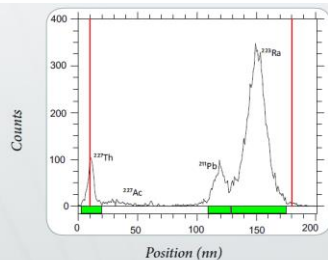


- High U and Pu uptake at high HCl
- Np retention good-ish at high HCl
- Elution at low HCl

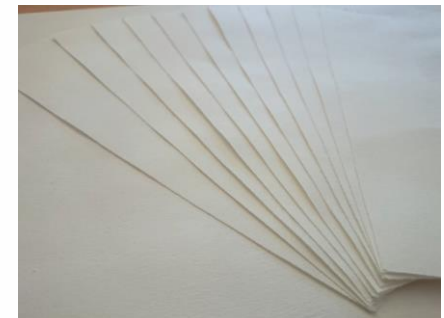
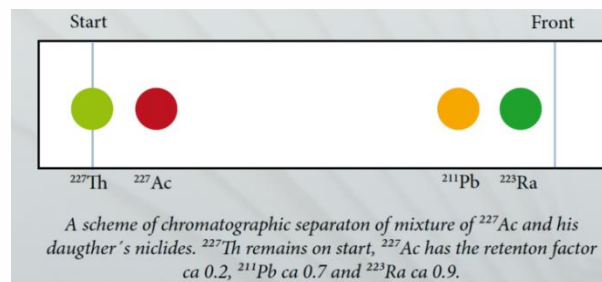
- Originally: QC of radionuclides and generator eluents (p.ex. Ra-223, Ac-225/Bi-213, Pb-212, Ge-68/Ga-68 ...)
  - TLC scanner or radiometer/LSC after cutting
- More types of sheets upcoming (selectivities/extractants)
- 2D TLC under development => use in screening/ decommissioning
  - Quadratic sheet, two runs (90° turn in-between) with different acids => 2D pattern
  - Measurement e.g. with Ai4r Beaver system (high res  $\alpha/\beta$  discrimination counting) or autoradiography



Radiochromatogram measured immediately after separation. Low abundant radiations of  $^{227}\text{Ac}$  were not detected.



Radiochromatogram measured one hour after separation. Decay and ingrowth of  $^{211}\text{Pb}$  is clearly visible.



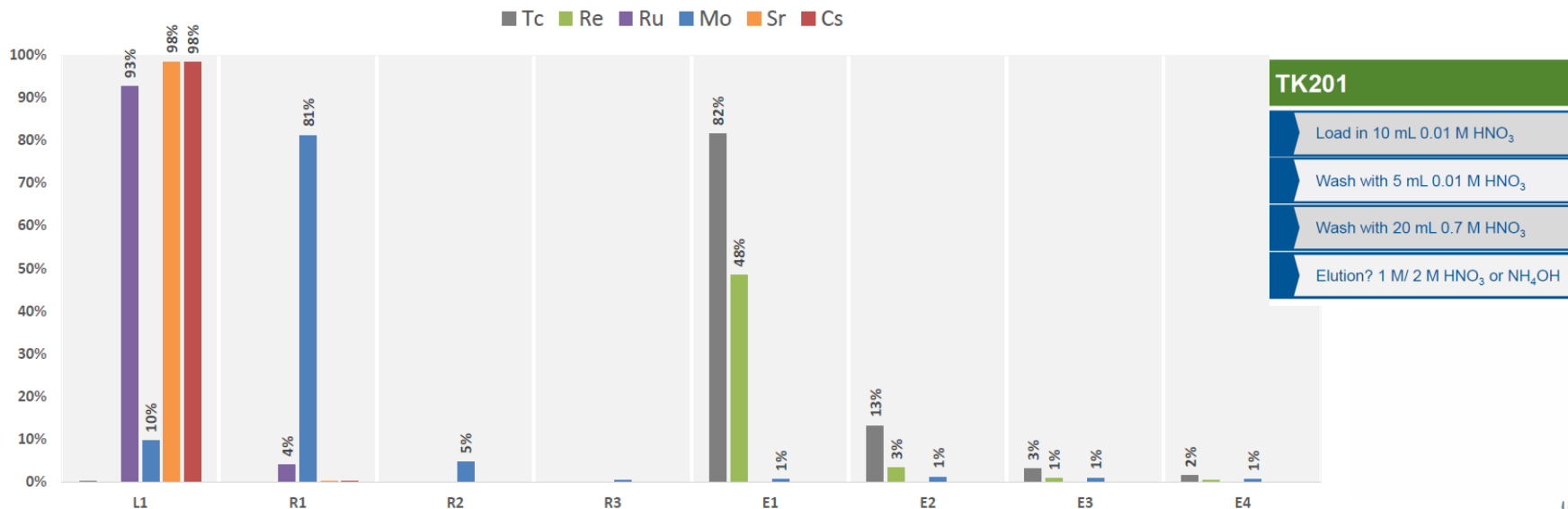
# TK201 Resin – Elution

- Load of sample at pH 1-2 to fix Re & Tc
- Mo elution at 0.7M HNO<sub>3</sub>
- Interferences removed during load/rinse
- Preferable elution options: ≥ 0.5M NH<sub>4</sub>OH
- Other options under evaluation: TK200, TK202, TK201/TBP

## Elution Study (TK201) 0.5 M NH<sub>4</sub>OH

**Load:** 10 mL 0.01 M HNO<sub>3</sub>  
**Wash:** 10 mL 0.7 M HNO<sub>3</sub>  
**Wash:** 5 mL 0.01 M HNO<sub>3</sub>  
**Elution:** 20 mL 0.5 M NH<sub>4</sub>OH

### Proposed Method



- Impregnated Scintillating Resin (PSm)
  - Plastic scintillator beads impregnated with selective extractants
    - Developed by Uni Barcelona
    - Direct measurement of cartridges
    - No elution/addition of LSC Cocktails
- « TK **El**Scint » range of products
- First: « TK TcScint » => Aliquat336 (+ long-chained alcohol) impregnated
  - Environmental monitoring => Tc-99
  - Tc-99 Detection efficiency >85%
  - Load/Rinse like TEVA Resins
  - Chemical yield via Re/ICP-MS
- Final beta testing after upscale
  - Please indicate if interested
- Additional resins upcoming

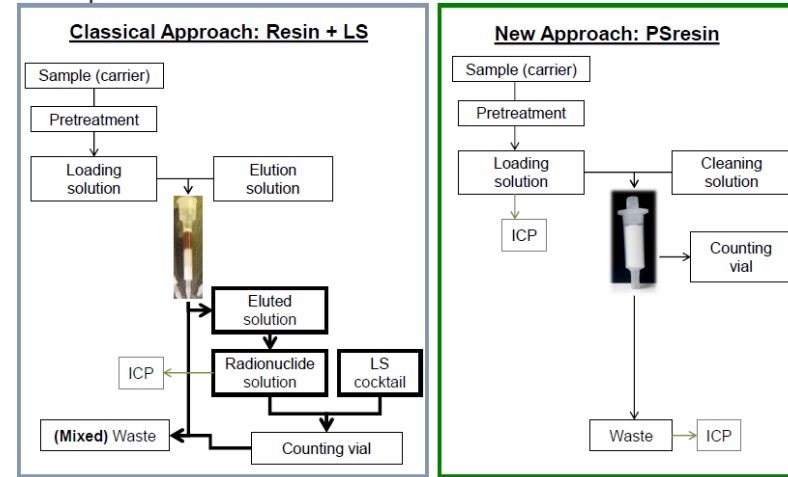
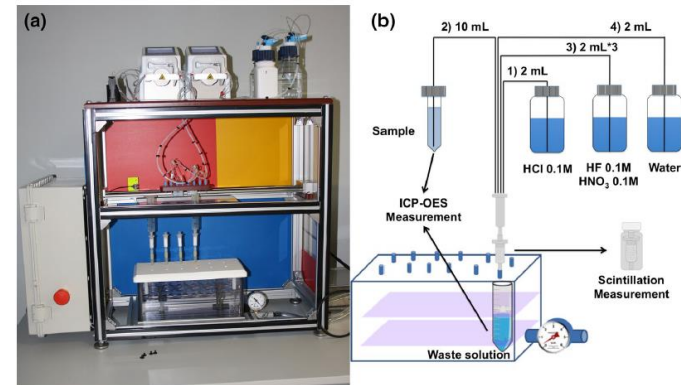


Fig. 1 Openview automated modular separation system (OPENVIEW-AMSS) (a) and scheme of separation (b)



Coma et al.



# TK202 Resin

- PEG covalently bound onto polymer
- Tc retention from high NaOH (5M NaOH)
- Tc Elution with water
  - Allows for additional purif on AlO<sub>x</sub> (trace Mo)
- Original application: Separation of Tc from elevated amounts of Mo
  - Tc retention increased by Mo
  - Tests at Polatom with simulated Mo targets
    - Poster presented at ISTR2019 (Vienna, 28/10/19 – 01/11/19)
    - Tc recovery > 90% for 6 – 8g Mo per g of TK202
    - Tc recovery > 80% for 12g Mo per g of TK202
- Looking for beta testers: Tc in decommissioning samples after alkaline fusion

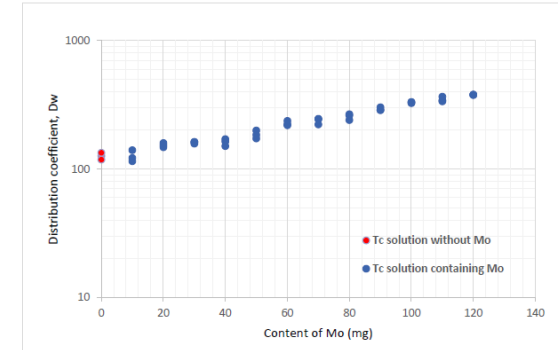
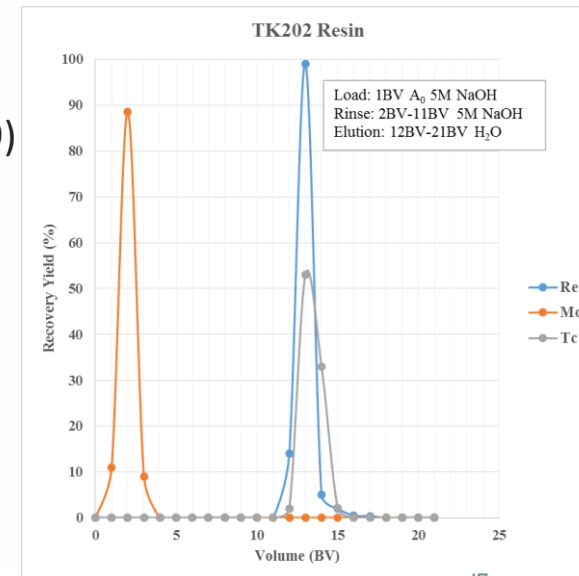


FIG. 6. Distribution coefficients for <sup>99m</sup>Tc in 5M NaOH on TK 202 resin versus molybdenum mass. Cieszykowska et al.



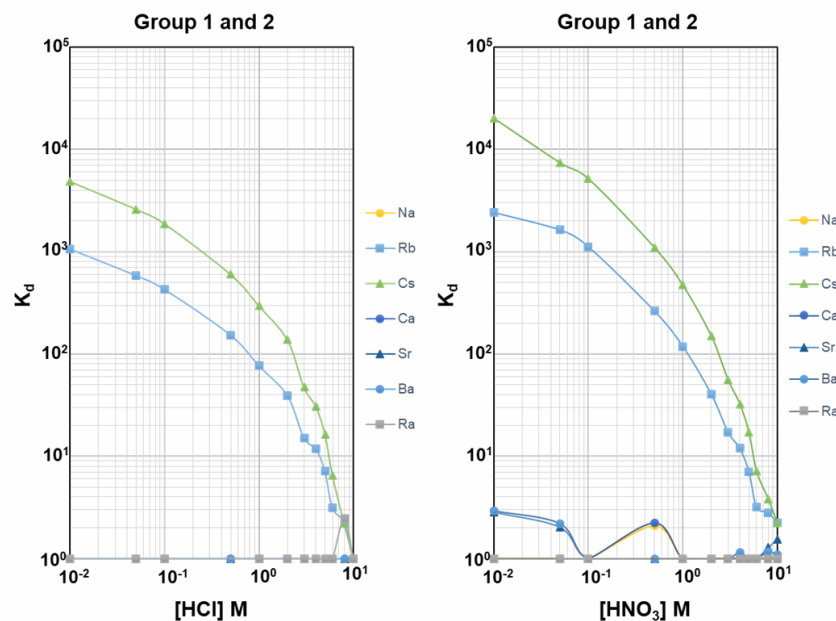
# TK300 – Cs and Rb separation

## Calixarene based resin for Cs and Rb separation

### ➤ Applications:

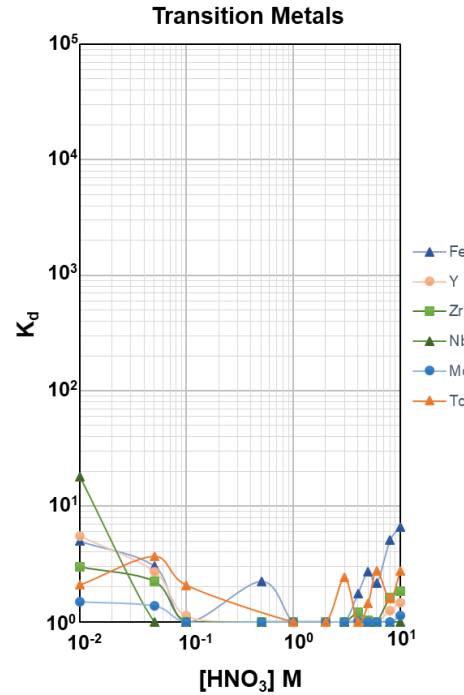
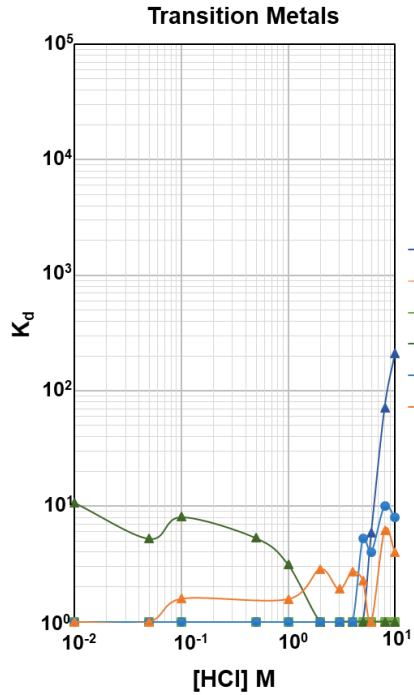
- Cs-135/7 by ICP-MS from water, environmental or decommissioning samples
- Sr/Rb dating in geochemistry

### TK300 Group 1 and 2

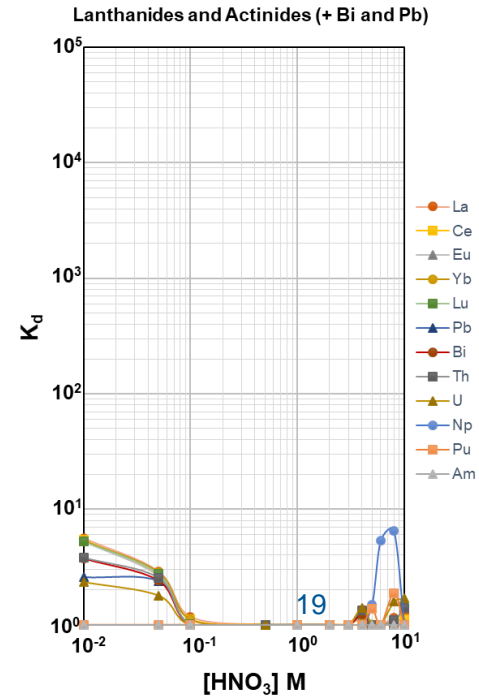
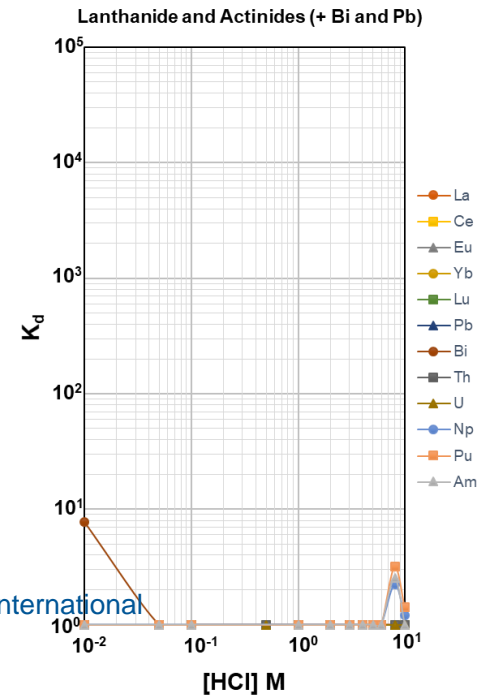


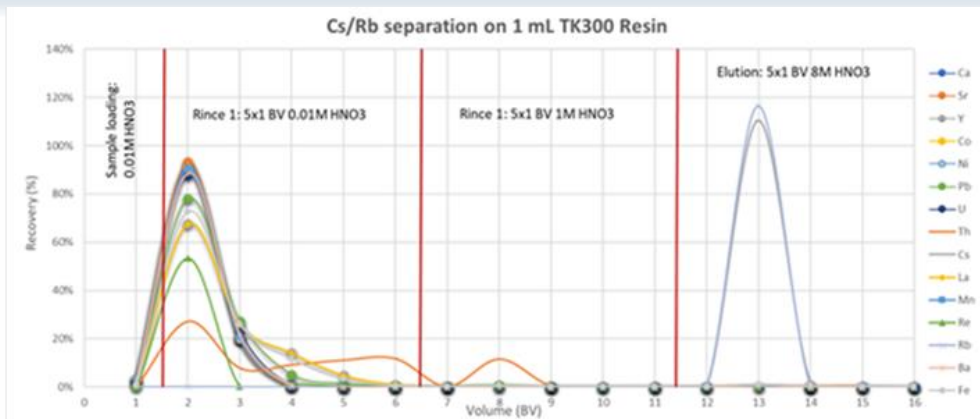
- High Cs retention up to 1 or 2M HNO<sub>3</sub>, elution in higher acid
- Rb well retained but less than Cs => Cs/Rb separation possible

# TK300 other elements



- Very little retention of other elements

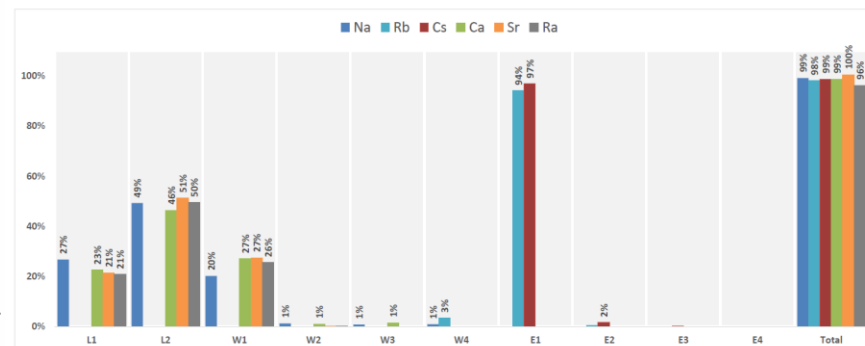




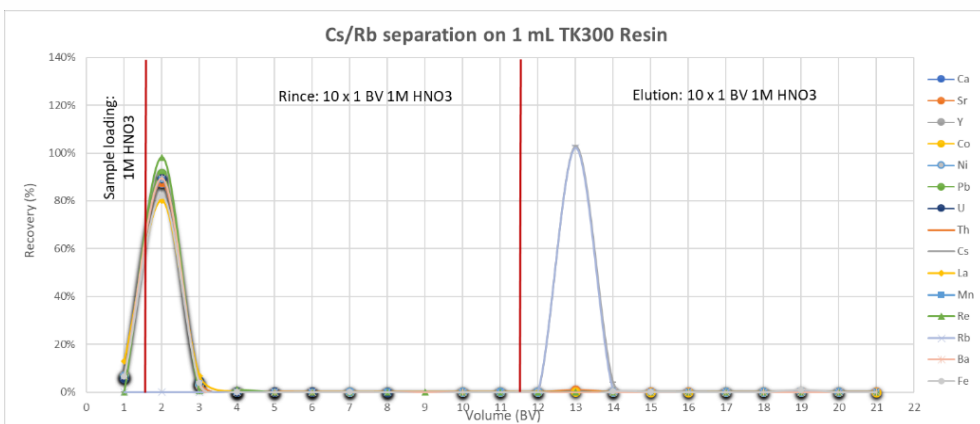
Elution study, Cs and Rb separation from selected elements on TK300 resin, loading from dilute acid.

## Elution Study (TK300)

Load: 10 mL 0.01 M HNO<sub>3</sub>  
 Wash: 15 mL 0.1 M HNO<sub>3</sub>  
 Wash: 5 mL 1 M HNO<sub>3</sub>  
 Elution: 20 mL 8 M HNO<sub>3</sub>



Van Es et al.



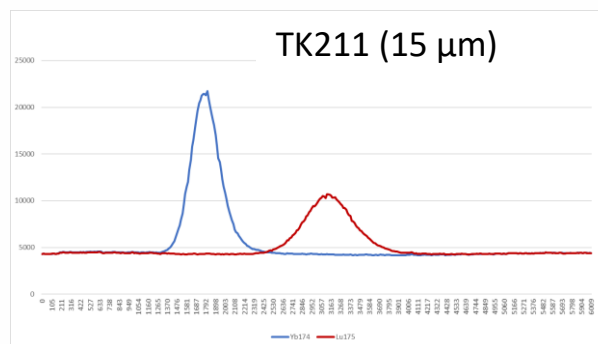
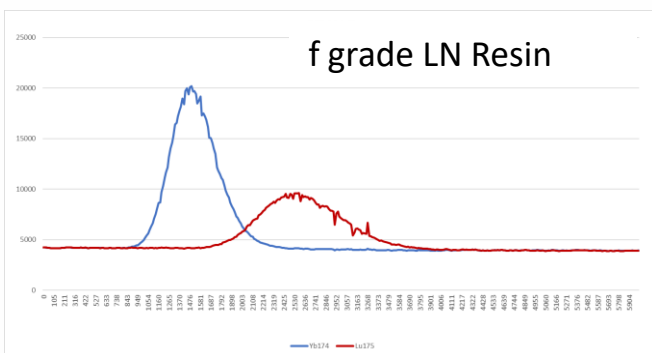
Elution study, Cs and Rb separation from selected elements on TK300 resin, loading from 1M HNO<sub>3</sub>

- First round of beta-testing on-going
- K interference => problematic for some environmental samples
- Suitable for Decommissioning samples?
- Might need to increase capacity
- Currently under evaluation

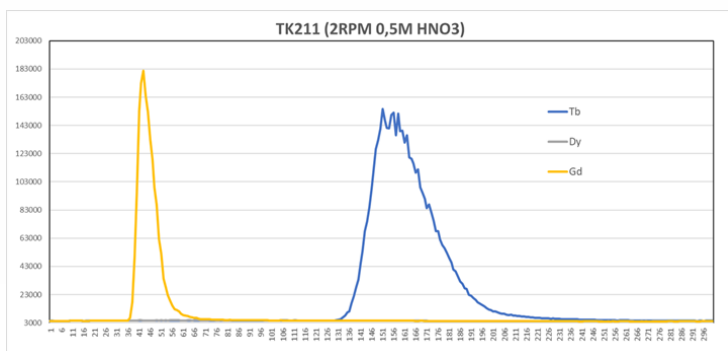
# • Lanthanide separation

## • TK211/2/3

- Based on LN/LN2 and LN3 extractants
- On-bead mix of different extractants for improved selectivity
- 15  $\mu\text{m}$  resin beads for improved lanthanide separation (10  $\mu\text{m}$  also possible)
  - Narrower peaks for better separation
  - PEEK column/pump driven separation



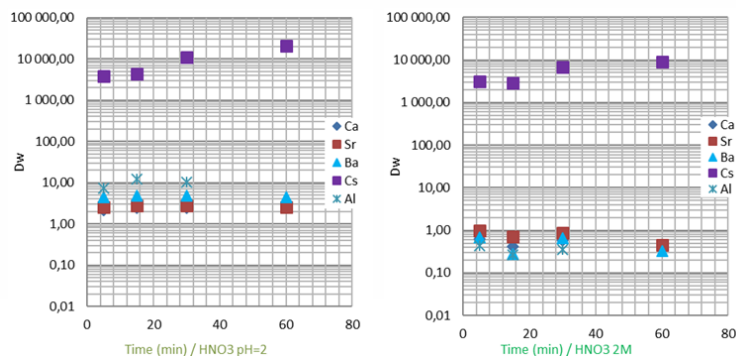
Lu/Yb separation  
Comparison (run  
under identical, non-  
optimum conditions):



Gd, Tb, Dy separation

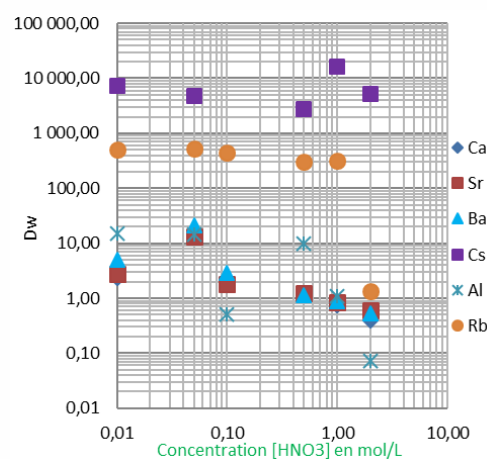
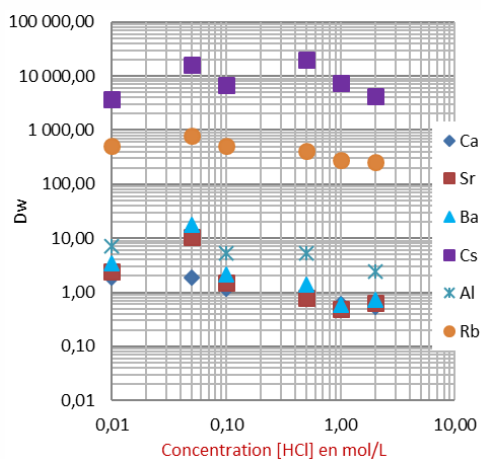
# PAN based resins

- Knowledge transfer from CVUT (Prague)
- Already providing AMP-PAN, KNiFC-PAN (both Cs) and MnO<sub>2</sub>-PAN (Ra) mainly for analytical purpose
  - Typical example: determination of Cs-134/7 in 100L seawater samples
- Increasing demand for larger amounts for decontamination
  - Decontamination of effluents => radionuclides, heavy metals, pollutants...
- PAN based resins
  - High content of inorganic compounds (up to ~85%)
  - Mechanical stability
  - Control of particle diameter
  - High porosity/active surface => fast kinetics



Park et al.

- Platform technology
  - Control/choice of wide range of selectivities
  - Variety of inorganic compounds embedded in organic matrix
  - Choice of polymer depending on matrix pH (e.g. highly alkaline)
  - AMP & KNIc for Cs, SbO for Sr/Y, TiO for actinides, Sr and activation products, FeO for Se, SnO<sub>2</sub> or CeO<sub>2</sub> for Ge, ZrP for Sr et al., NaBiO<sub>3</sub> for Am/Cm separation, MnO<sub>2</sub> for Ra,...



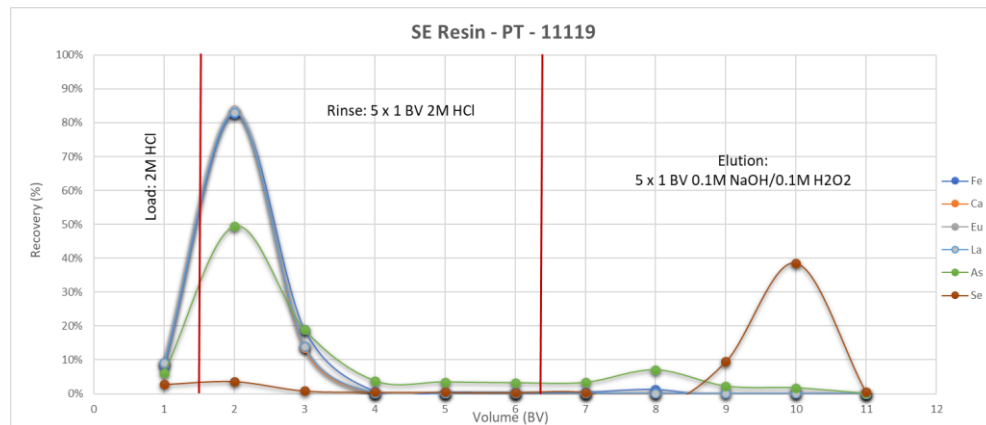
AMP-PAN selectivity in various concentrations of HNO<sub>3</sub>/HCl

- Upscale for large scale production under development
  - 100s of kg to tons per year
  - Various PAN Resins

# Other developments

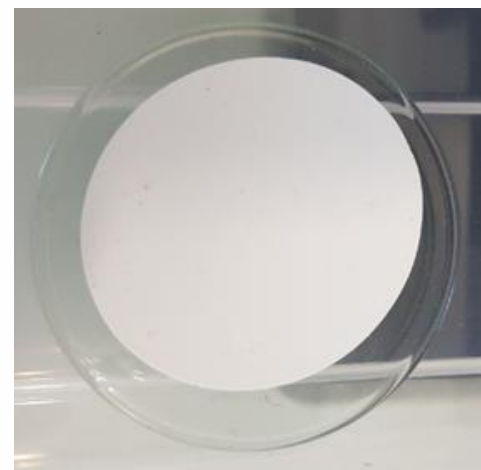
## SE Resin

- Se(IV) retention from HCl
- Piazselenol chemistry
- Se(VI) elution under oxidizing conditions



## Extractive membranes

- High flow (up to 50 - 100 mL/min)
- Preferably for use with water samples (1 – 5L)
- Product range under development:
  - TK201 (Tc)
  - TK100 (Sr), TK101 (Pb, Ra)
  - TK200 (actinides)
  - TK300 (Cs)
  - AC (gross alpha),...





- Improved Ni separation
- Rapid tests => e.g. Uni Southampton
- DGT/passive sampling
  - Cs, I, Pu, Ra, Sr, Pb
- Functionalised polymers & silicates,...
  - e.g. DGA, macrocycles,...
- Use of DGA Sheets for screening
  - 2D TLC + autoradiography/imaging
  - Development of other sheets (TK201, CU, UTEVA,...)
- Li Resin
- Improvement of radiolysis stability
- Spin coating
- Microfluidics
- Non-resin separation systems...
- New accessories e.g. new 4 position box, gauge,..



Thank you for your attention!



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