TrisKem International

New Developments in TrisKem
CARM 2023– Hybrid UGM
22/02/23

Aude Bombard

TRISKEM
Expertise in Separation Chemistry

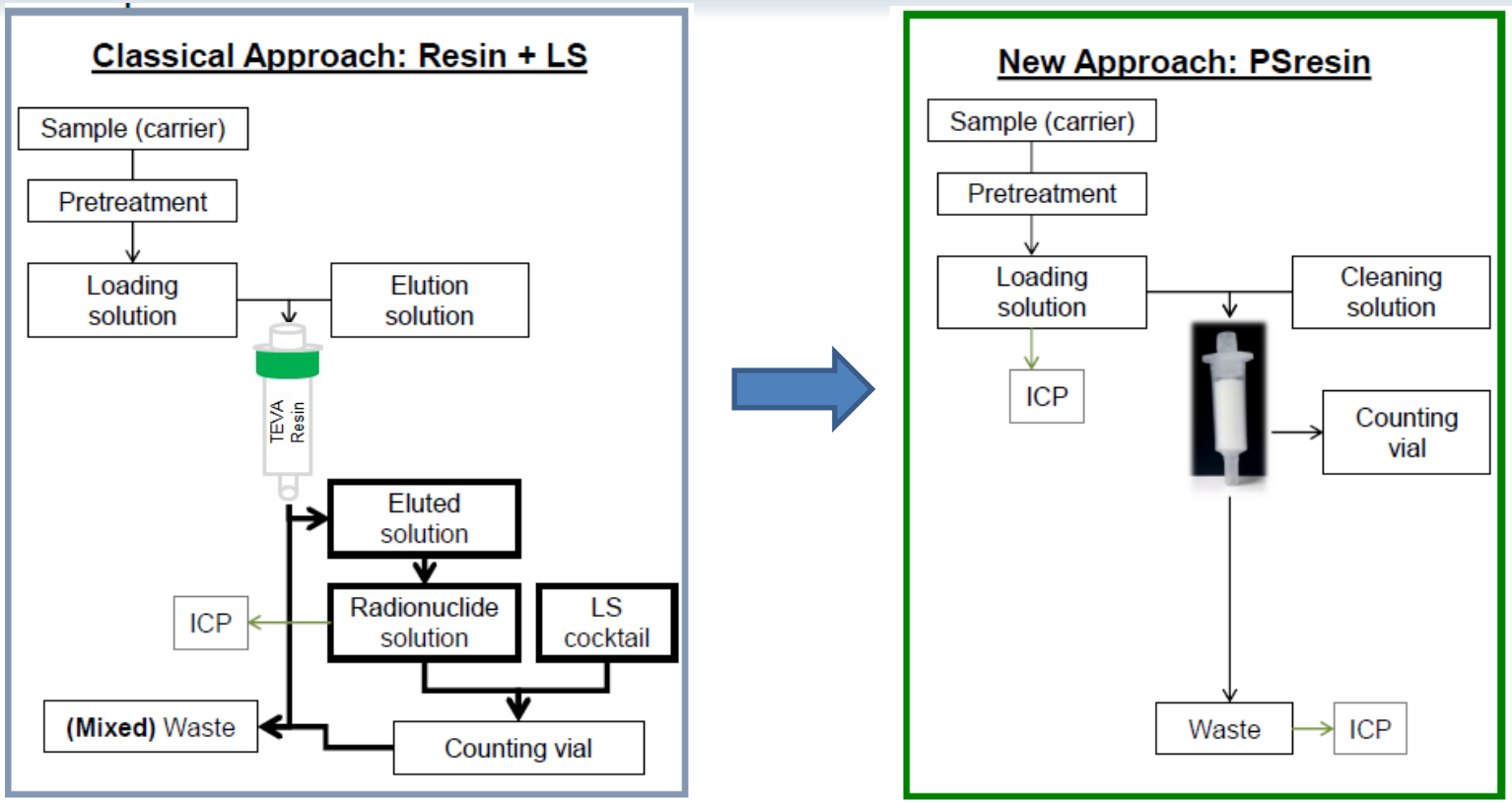
Overview

- New Resins
  - TK-TcScint – Cl-36 measurement (presentation by Ines Llopart)
  - TK202 (presentation by H. Mohamud)
  - TK200
  - TK221 / TK222 (main apps in NucMed – presentation by S. Happel)
  - TK102
  - TK225
- Under development
  - Extractive membranes
  - « Industrial » resins
  - Cs/Rb Resins (presentation by I. Dohvyi)
- Other projects

TK-TcScint

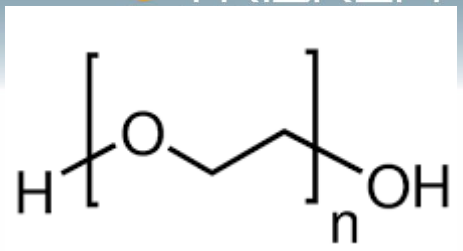
- Plastic scintillating beads impregnated with selective extractant
- Developped by university of Barcelona
  - García, Tarancón, Bagán
- « TK-ElScint » product line
- 1st product: « TK-TcScint »
  - Quaternary ammonium + phase modifier (similar selectivity to TEVA)
  - Environment/decommissioning => Tc-99 by LSC
- Next resins in development with cooperation with the University of Barcelona: Sr-90/Pb-210, Gross-Alpha
  - Other radionulides of interest: **Cl-36**, other β-emiters

TK-TcScint



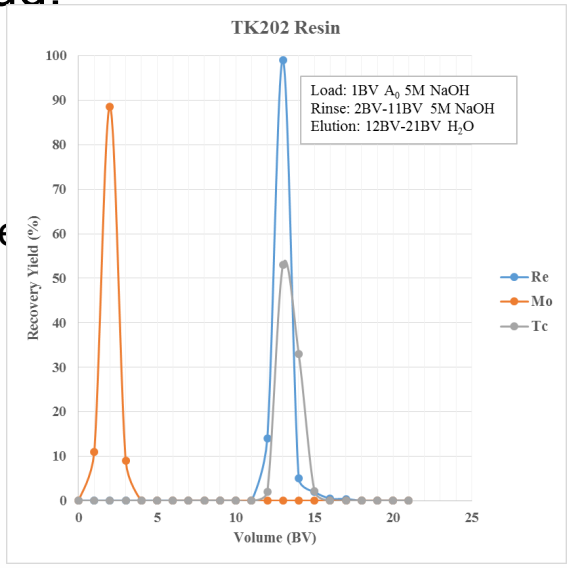
- Direct mesurement of the cartrige by LSC after loading and rinsing
  - NO elution/evaporation/aliquoting => easy automatisation
- Chemical yield via Re/ICP-MS in eluates.

TK202 Resin



- Polyethylene Glycol (PEG) grafted on inert support
- Aqueous biphasic system (ABS)
- Retention of chaotropic anions e.g; TcO_4^- in the presence of Kosmotropic anions (SO_4^{2-}, CO_3^{2-}, OH^-, MoO_4^{2-},…)
- For samples rich in Mo: Tc yield > 90% for 6 – 8g Mo per g TK202
- Results were presented earlier by Hibaaq Mohamud:
- Suited for samples that are fused
  - Load in NaOH or KOH 5-7M
  - Rinse with NaOH or KOH 5-7M
  - Elution with a small volume of water (eluate remains alkaline
    - Load on CEX to neutralise medium and get rid of Na+

    THEN
    - Load on aluminum oxide (AloxA) to get rid of Mo traces
    - Elution in 0.9% NaCl medium



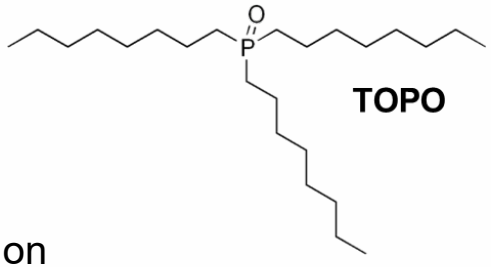
Re/Tc separation from Mo on TK202 Resin

TK200 Resin

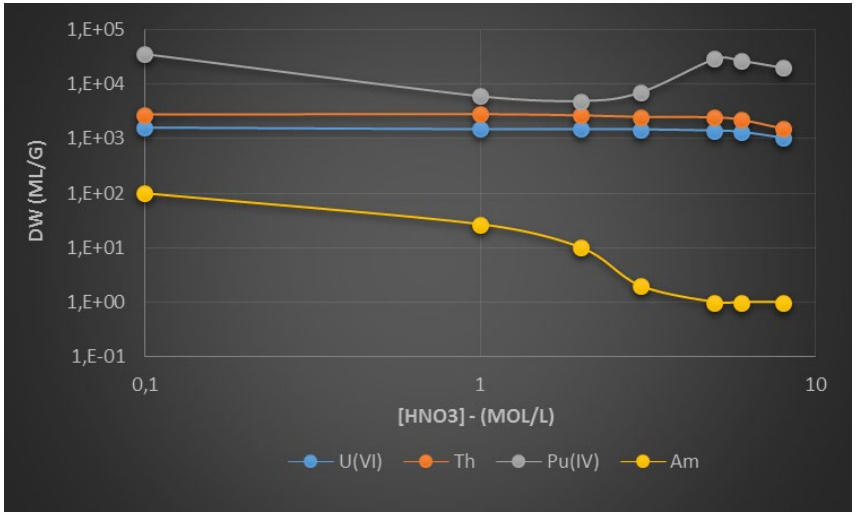
- Resin based on TOPO extractant
- Extracts U, Th, Pu at pH 2 => preconcentration and purification of selected actinides on same column (mainly U)

  => automized separations/ICP-MS
- U/Th separation from water samples
- Efficient U/Pu separation from soil/sediment samples (up to 2g)

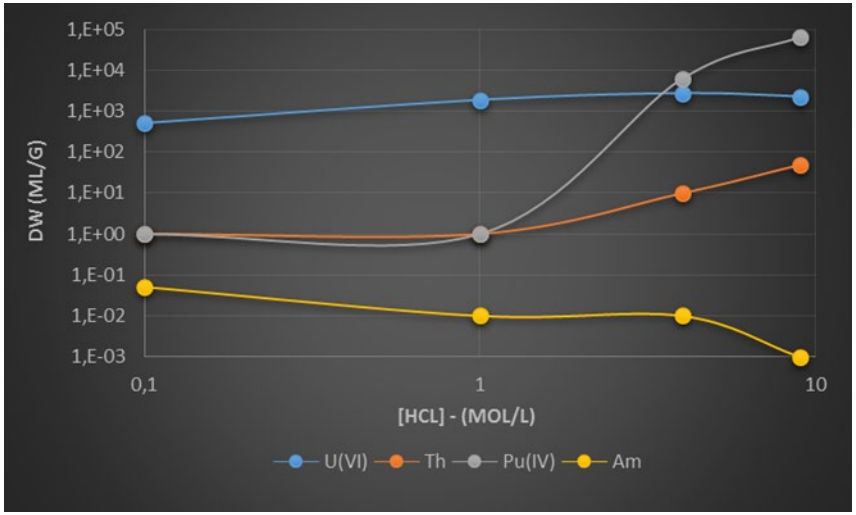
- Other applications:
  - Nuclear medecine
    - Ga-68 production (in combination with ZR Resin)
    - on-going: Pt/Ir, Zn/Cu (Zn production, Zn removal), Sc production



TK200 Resin – Dw Studies



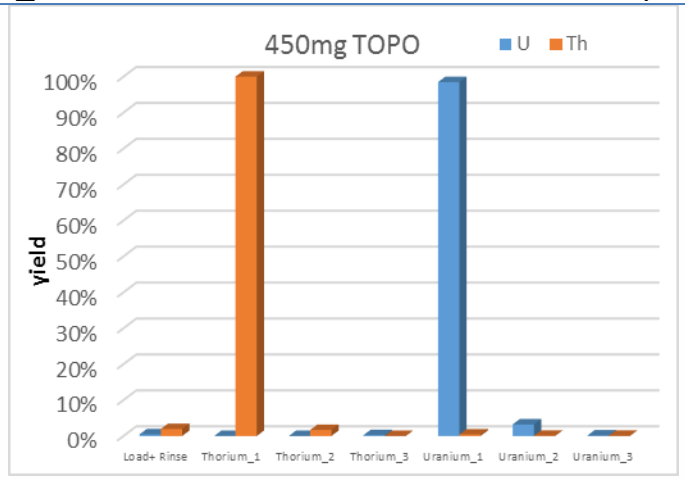
- Retention of Am < 0,1M HNO_3;
- U/Th/Pu uptake over the whole acidity range studied;
- High uptake of Bi from 0,01 – 2M HNO_3 => possibility to separate from Pb in case of MS measurement;
- Uptake of Sn from 0,1 – 10M HNO_3 (alternative to TBP Resin).



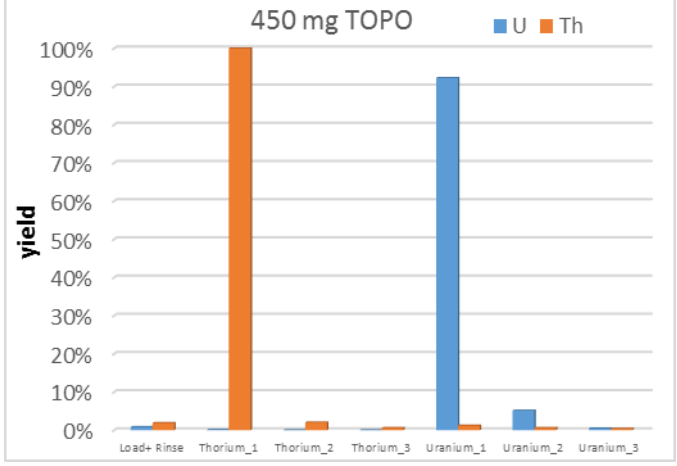
- No retention of Am ;
- U/Th uptake over the whole acidity range studied;
- Pu uptake from 3-10M HCl – no retention below 3M HCl;
- High uptake of Bi from 0,01 – 3M HCl => possibility to separate from Pb in case of MS measurement;
- High uptake of Sn over the whole acidity range studied (alternative to TBP Resin)

TK200 Resin – Elution studies for U/Th separation from acidic solutions

Load+ Rinse	5mL Load 3 M HNO_3 + 5mL 3 M HNO_3
Th_1	10 mL 0.1 M HCl-0.1 M oxalic acid
Th_2	5 mL 0.1 M HCl-0.1 M oxalic acid
Th_3	5 mL 0.1 M HCl-0.1 M oxalic acid
U_1	10 mL 0.1 M Ammoniumoxalate pH 9
U_2	5 mL 0.1 M Ammoniumoxalate pH 9
U_3	5 mL 0.1 M Ammoniumoxalate pH 9



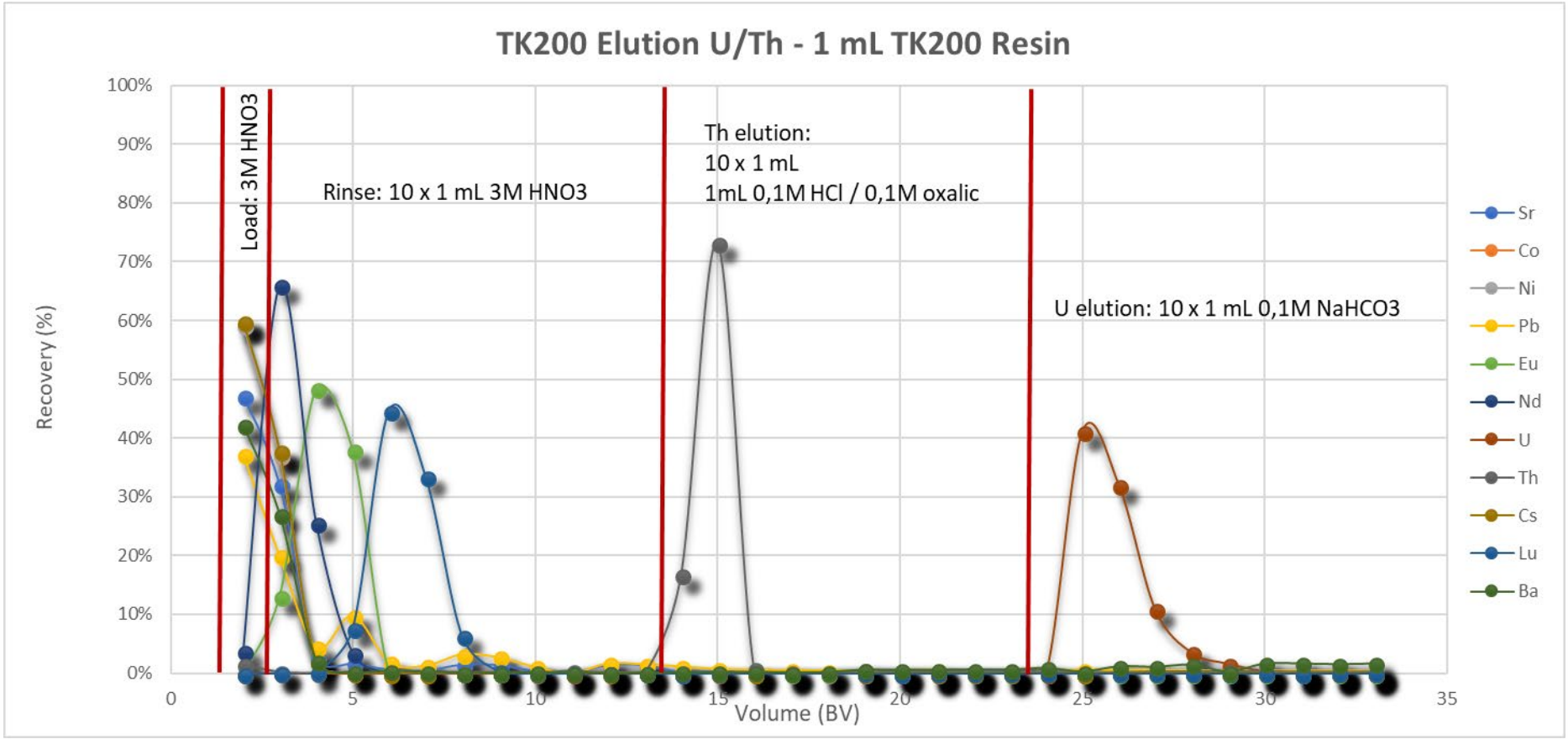
Load+ Rinse	5mL Load 3 m HNO_3 + 5mL 3 m HNO_3
Th_1	10mL 0.1 m HCl-0.1 m oxalic acid
Th_2	5 mL 0.1 m HCl-0.1 m oxalic acid
Th_3	5 mL 0.1 m HCl-0.1 m oxalic acid
U_1	10 mL 0.1 m $NaHCO_3$
U_2	5 mL 0.1 m $NaHCO_3$
U_3	5 mL 0.1 m $NaHCO_3$



Th selectively separated from U and recovered quantitatively

U quantitatively recovered with 15mL of various solutions depending on needs

U/Th separation on TK200



- Load: 3M HNO_3 or ≥ 1L pH2 (HNO_3)
- Very clean U/Th separation
- Alcaline oxalate instead of carbonate

TK200 Resin - U/Pu separation (Wang et al – 2019)

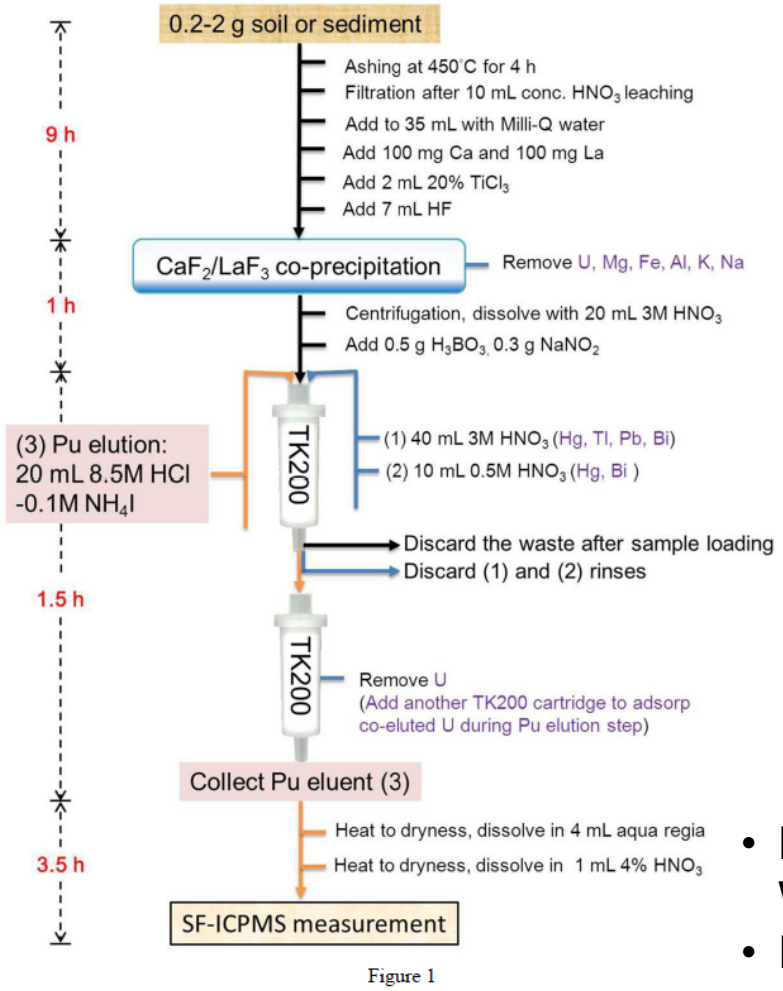
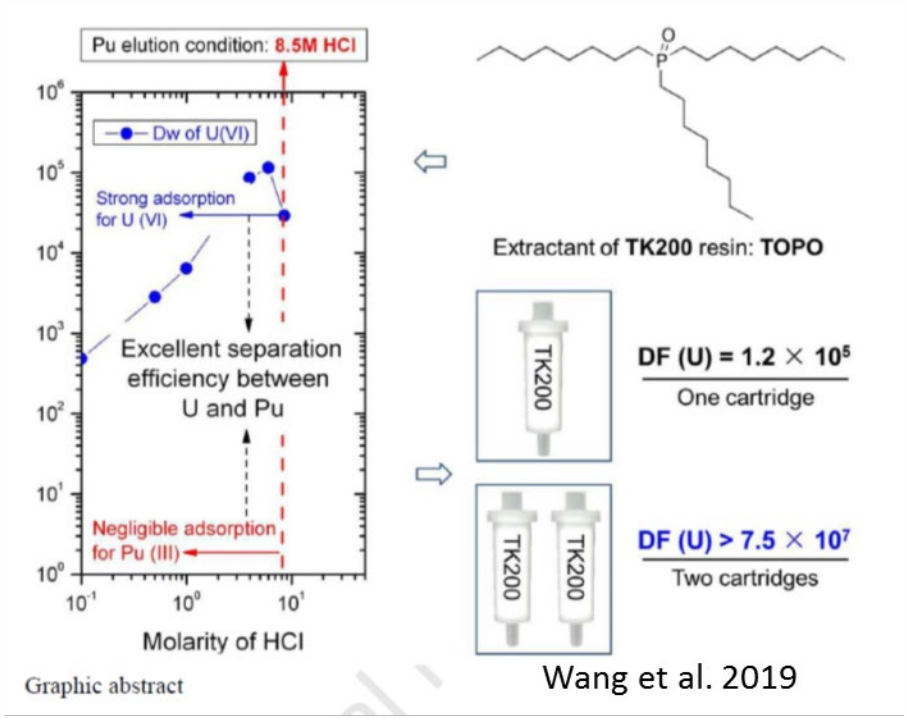


Figure 1



- Pu isotope ratios by ICP-MS (U removal e.g. Wang et al, 2 x TK200 => Df >10^7)
- Pu elution as Pu(III) in 8,5M HCl/0,1M NH_4I
  => U remains fixed on resin in these conditions

TK200 Resin – Conclusions

- Preconcentration of actinides from pH1-2 solutions => medium usually used to preserve samples for storage and prior to analysis
- Th/U and U/Pu Separations are efficient
- Possibility to extract/concentrate Sn and Cd in HCl and elute in low HNO_3 concentration.
- Zr/Hf are well extracted in HCl (1-10M) and HNO_3 (whole studied range)

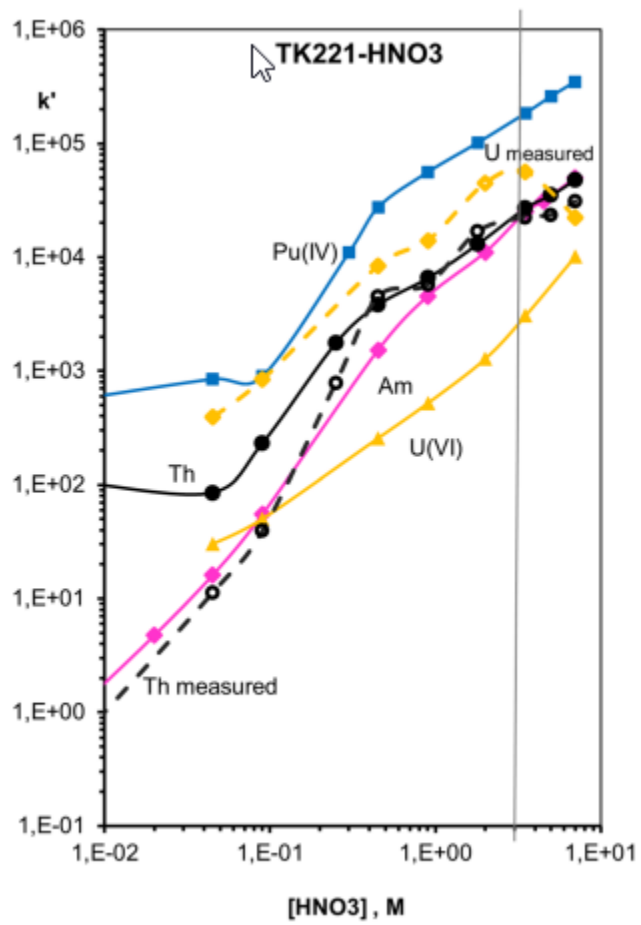
TK221 Resin

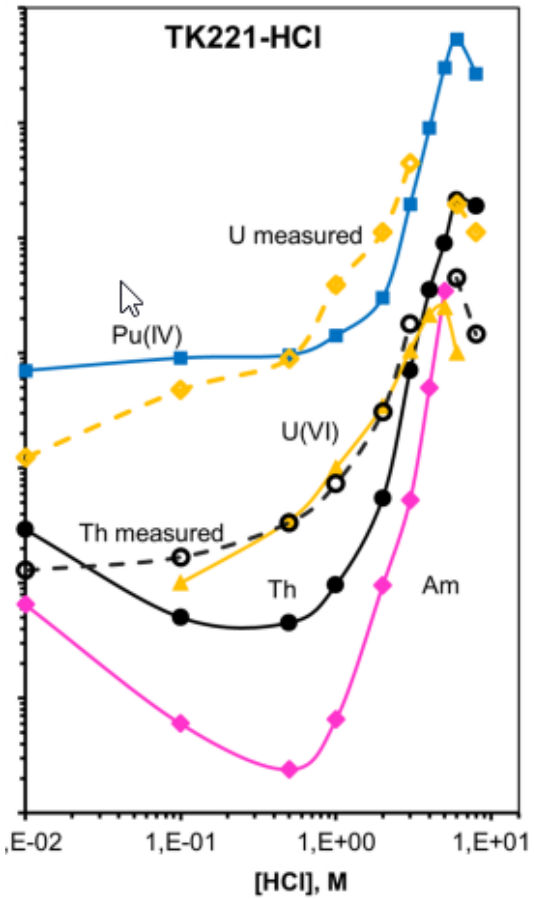
(Papp, I., Vajda, N. & Happel, S. An improved rapid method for the determination of actinides in water. *J Radioanal Nucl Chem* **331**, 3835–3846 (2022). https://doi.org/10.1007/s10967-022-08389-9)

TRISKEM
Expertise in Separation Chemistry

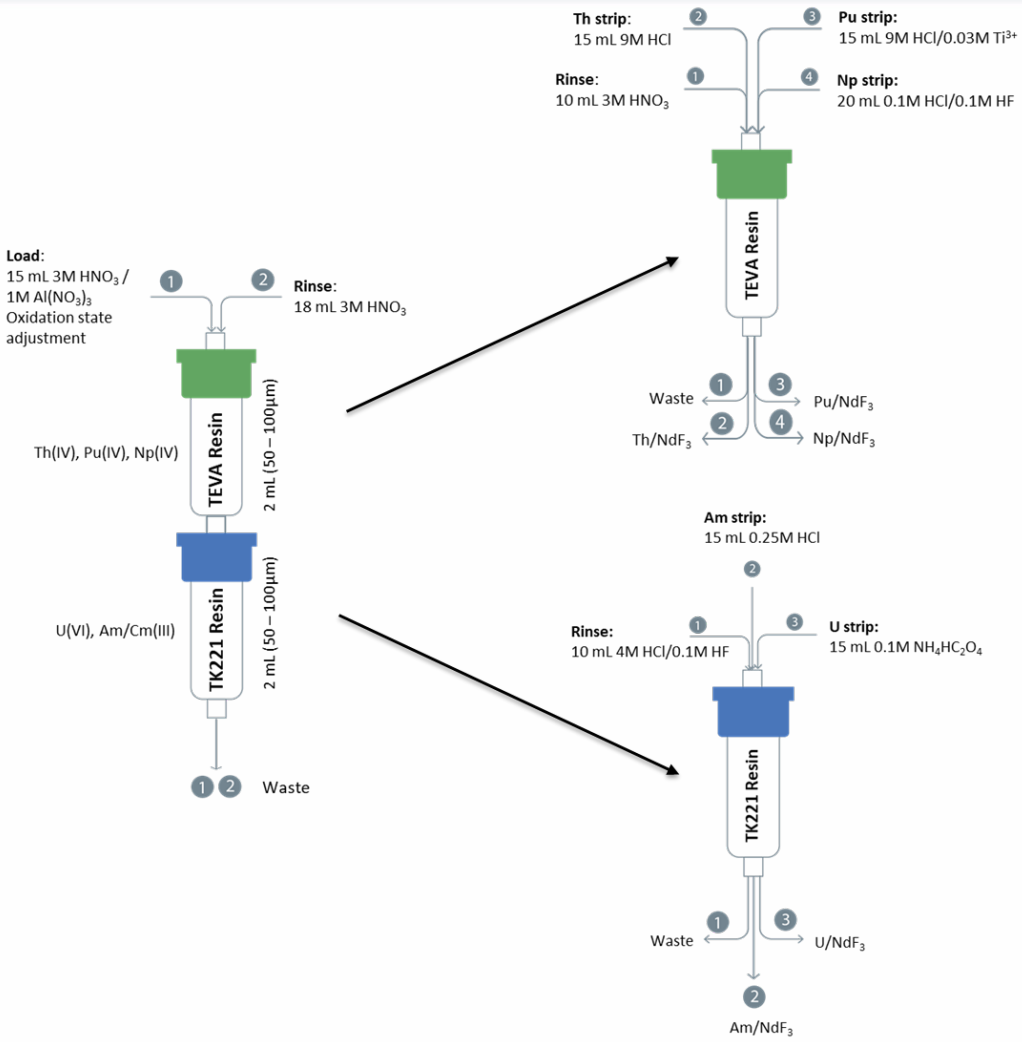
Resin based on a mixture of diglycolamide and phosphine oxide + traces long chained alcohol on inert support.

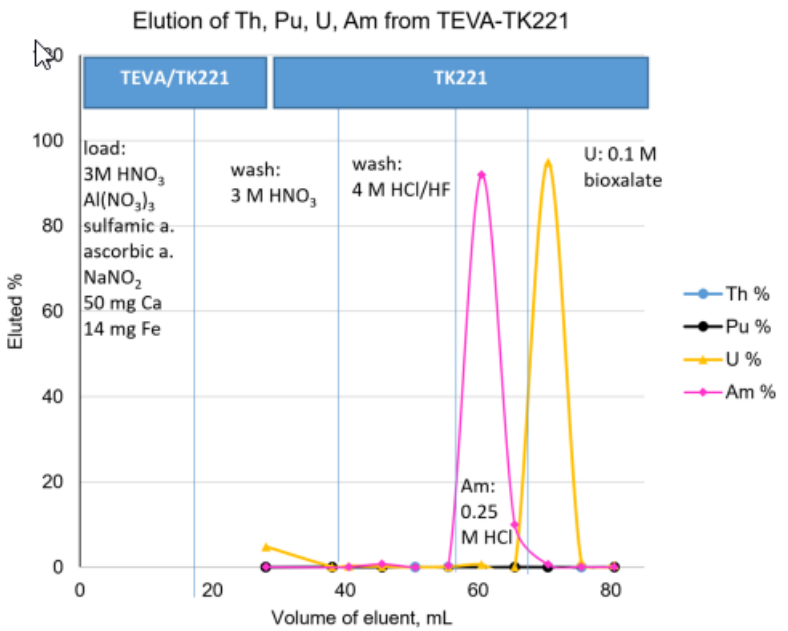
- Main applications in radpharm
- Applications for the separation of actinides





TK221 Resin (Papp, I. et al. *J Radioanal Nucl Chem* **331**, 3835–3846 (2022). https://doi.org/10.1007/s10967-022-08389-9)





TK221 Resin	Yield (%)	Am (%)
RN	Without Np separation	With Np separation
TAP WATER		
Am-241	103 +/- 7	97 +/- 6
U-233	103 +/- 7	70 +/- 7
SEA WATER		
Am-241	89 +/- 7	92 +/- 6
U-233	88 +/- 7	59 +/- 6

TK222 Resin

- Same as TK221 Resin but based on TEHDGA
- About same properties as TK221 Resin

- More information in Steffen Happel's presentation

TK102 Resin

- Modified version of SR Resin
  - Same crown-ether
  - Solvent, inert support and ratios => different
- Work by Illarion Dohvyi (Poster during ERA14), Marine Bas, Soumaya Khalfallah, Nora Vajda, Steffen Happel
- Separating Methods under development

TK102 Resin - Determination of Kd values

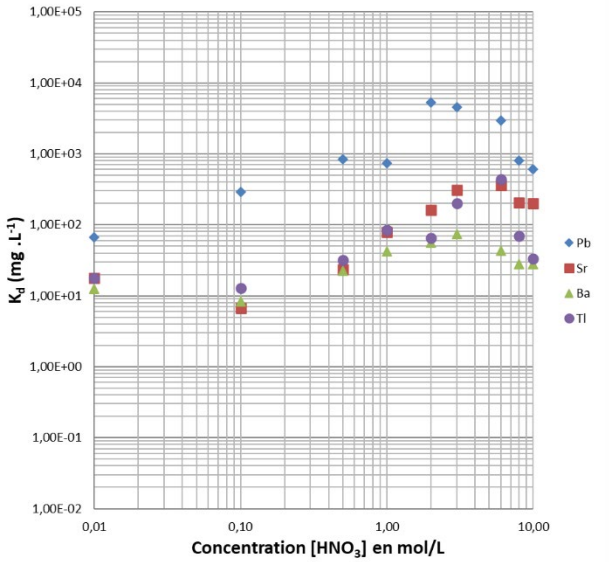


Fig. 1: Distribution coefficients of selected elements on TK102 Resin in HNO_3

► Sr, Ba, Pb and Tl show high D_W in HNO_3

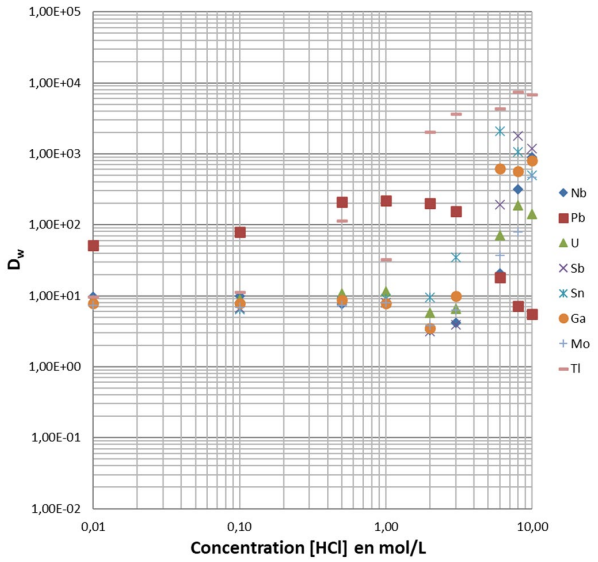


Fig. 2: Distribution coefficients of selected elements on TK102 Resin in HCl

► Pb, Tl, Sn, Sb, Ga show hight D_W in HCl

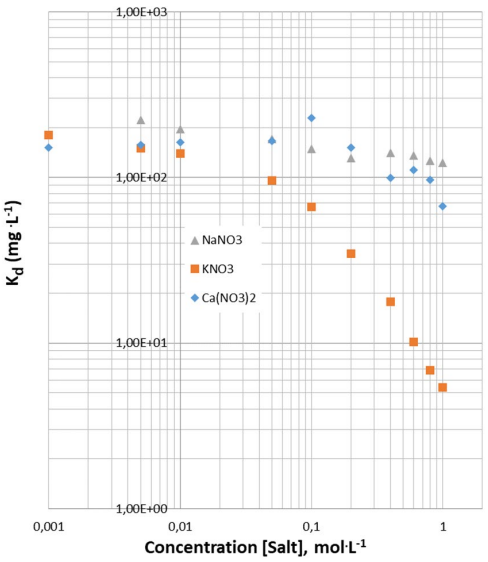


Fig. 3: Distribution coefficients of Sr on TK102 Resin in
3 M HNO_3 in the presence of different salts

►D_w Sr decreases by 30% with $NaNO_3$ up to 1 M,

► no effect of KNO_3 and $Ca(NO_3)_2$ up to 0,05 M.

TK102 Resin - Determination of capacity (column experiment)

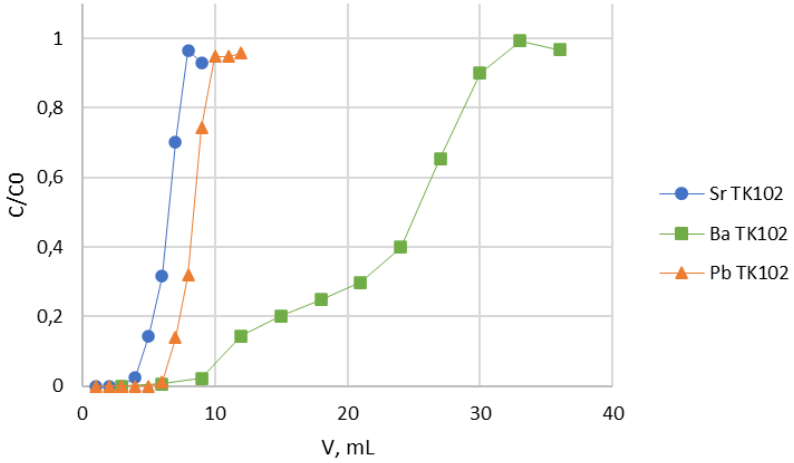


Fig. 4. Sorption curves of Sr, Ba and Pb on TK102.

Table 1 TK102 capacities for Sr, Ba, Pb in 3 M HNO_3 from results of different experiments.

Element	Capacity in column experiment, mg/g	DEC, mg/g	TDEC, mg/g	Langmuir maximum capacity, mg/g	Maximum theoretical capacity, mg/g
Sr	41.6	27.2	40.9	39.7	45.5
Ba	12.8	6.7	19.9	*	70.8
Pb	94.1	74.3	97.2	98.0	106.9

* – cannot be determined under the conditions studied due to limitations in the solubility of $Ba(NO_3)_2$ in HNO_3.

TK102 Resin - Determination of capacity (Langmier isotherm)

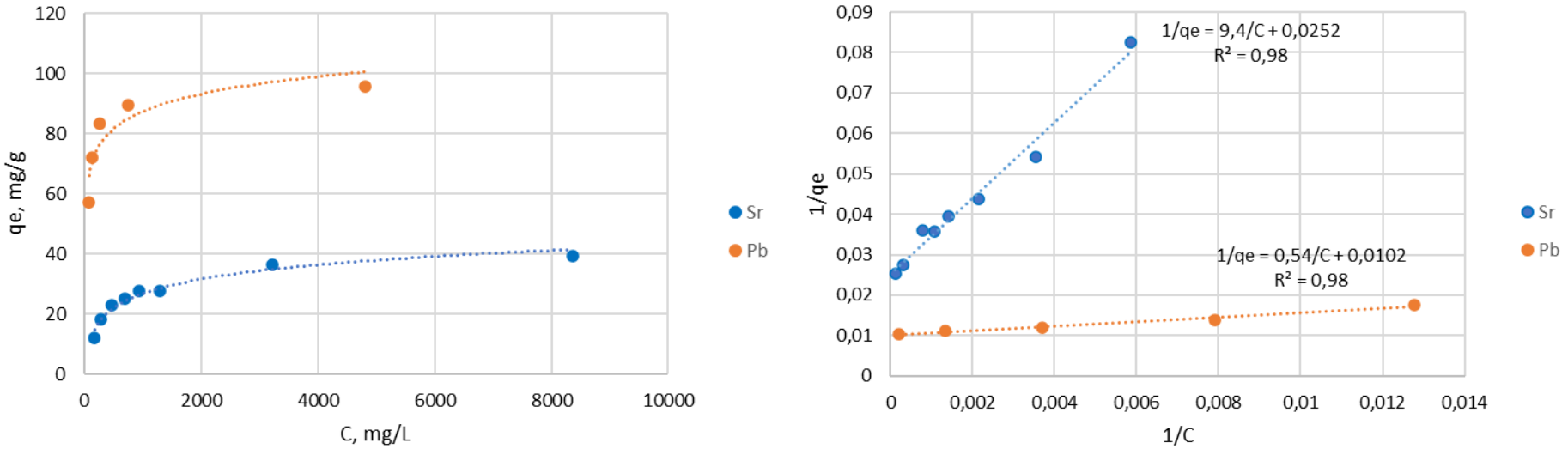
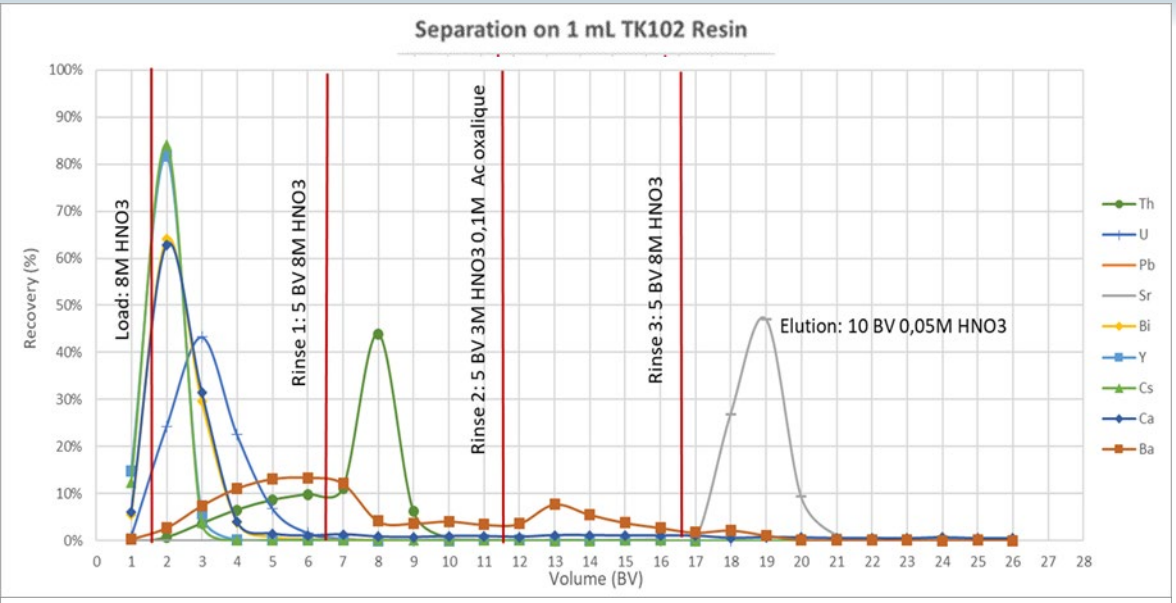
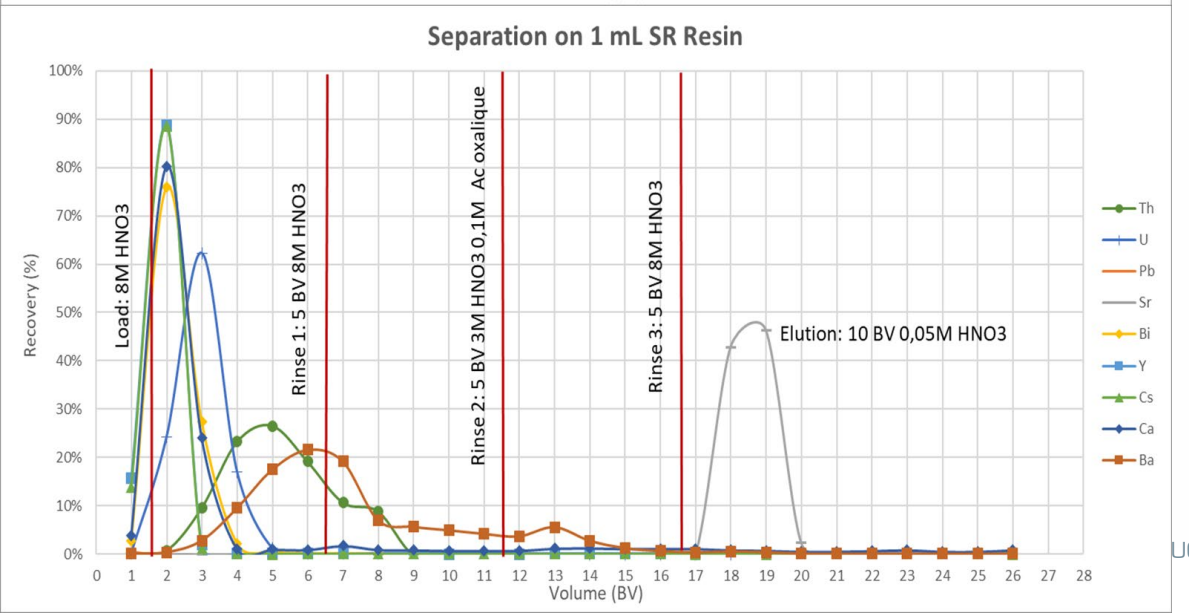


Fig. 5. Sr sorption isotherms with TK102: q_e – C plot (a), linearized in coordinates: $1/q_e$ – $1/C$ plot (b),

$$\frac{1}{q_e} = \frac{1}{K_L \cdot q_m \cdot C_e} + \frac{1}{q_m}$$

TK102 Resin – Elution curves comparison Vs SR Resin regarding Sr

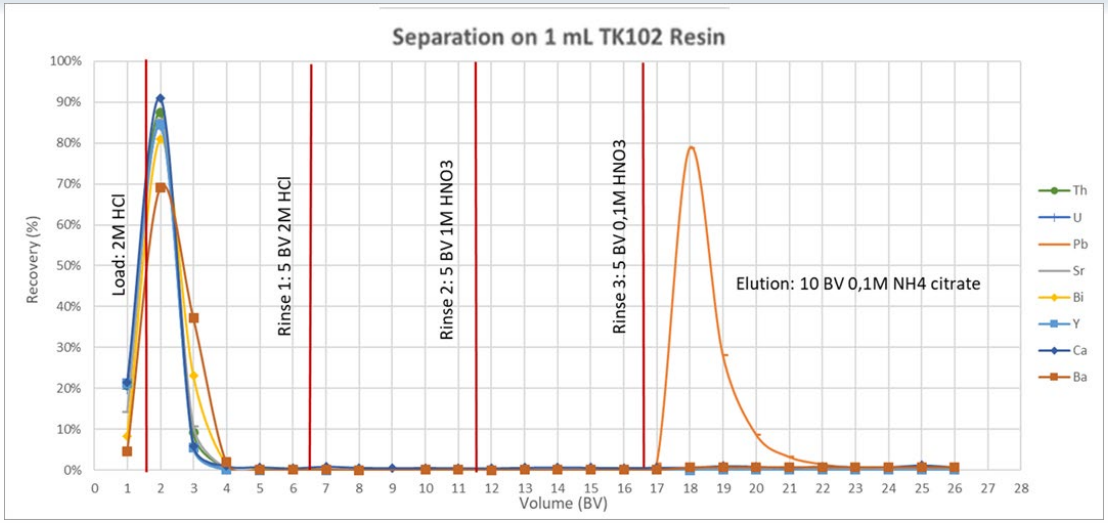


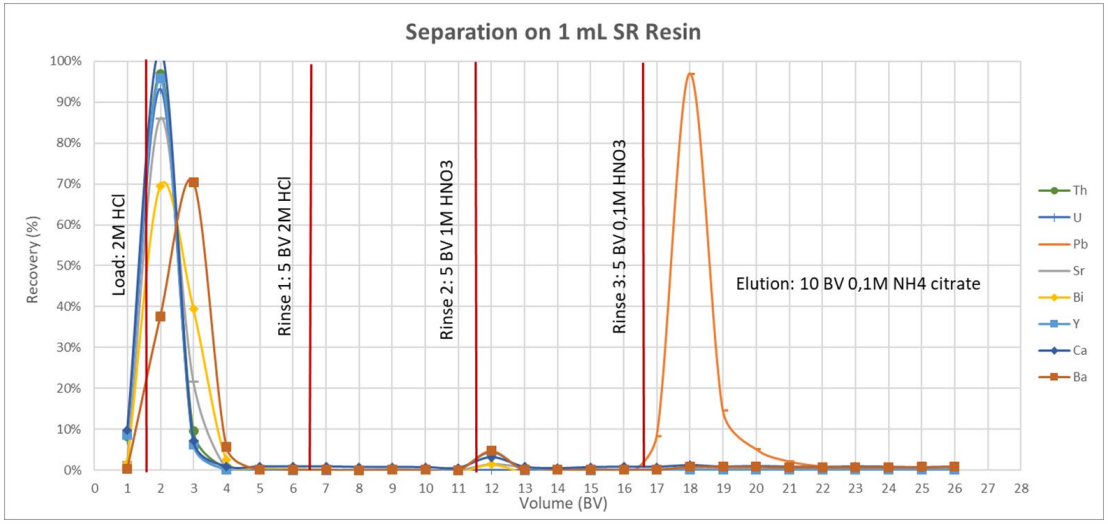


TK102 Resin vs SR resin:
Sr elution study in 8M HNO_3 load medium

Resins TK102 and SR similar for the separation of elements Th/U/Pb/SR/Ca/Bi/Y/Ca and Ba

TK102 Resin – Elution curves comparison vs SR Resin regarding Pb

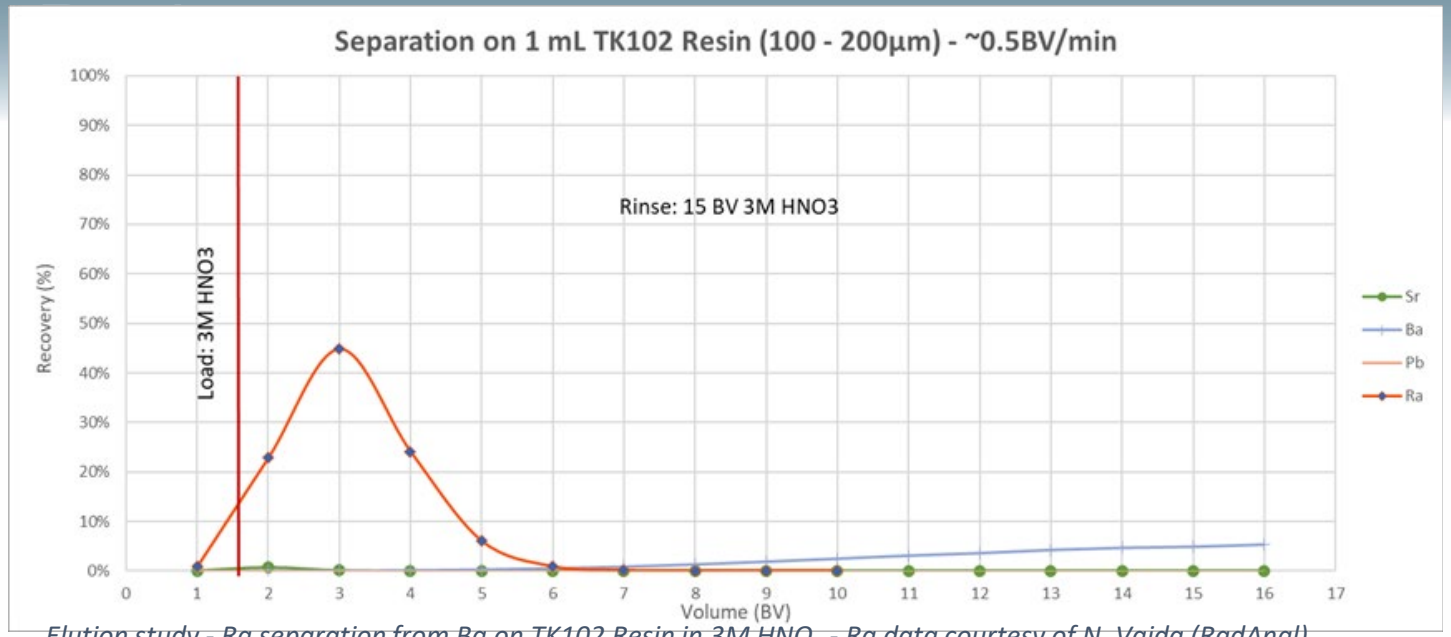




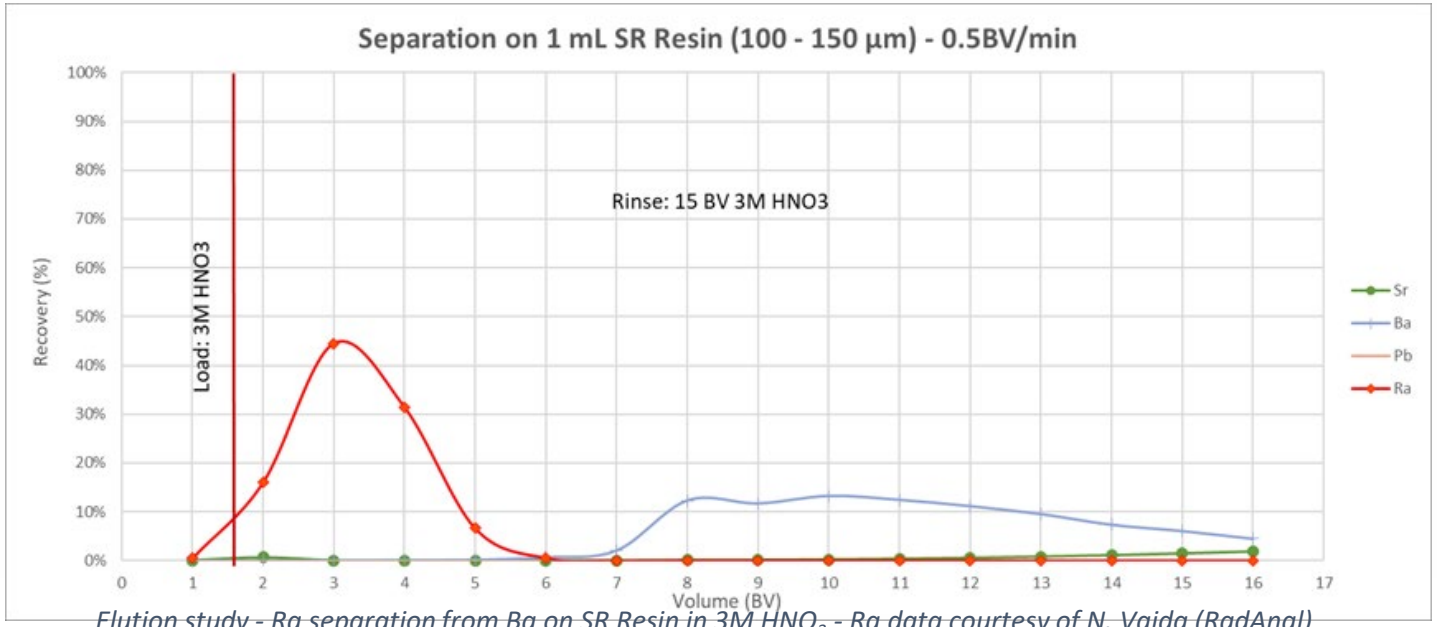
TK102 Resin vs SR resin:
Pb elution study with 2M HCl loading medium

Resins TK102 and SR similar for the separation of elements Th/U/Pb/SR/Ca/Bi/Y/Ca and Ba

TK102 Resin – Ba/Ra behaviour vs SR



Elution study - Ra separation from Ba on TK102 Resin in 3M HNO_3 - Ra data courtesy of N. Vajda (RadAnal)



Elution study - Ra separation from Ba on SR Resin in 3M HNO_3 - Ra data courtesy of N. Vajda (RadAnal)

- Ra eluted in the 6 BV @ 3M HNO_3
- Sr/Pb and Ba remained fixed on resins
- Ba on TK102 => possibility to separate Ra and Ba (conditions and tests to be continued)

TK225 Resin (1/3)

Main application:
Removal of radiolanthanides from acidic effluents

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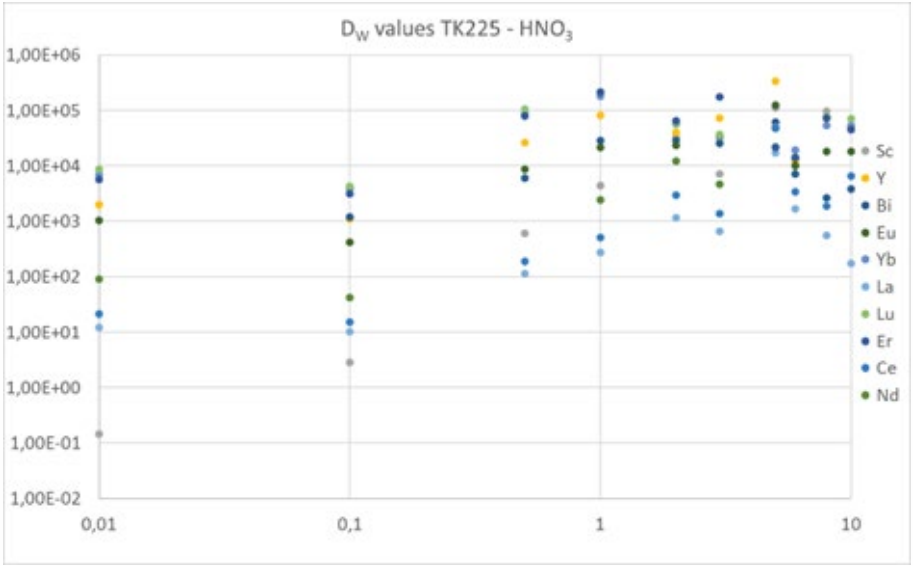
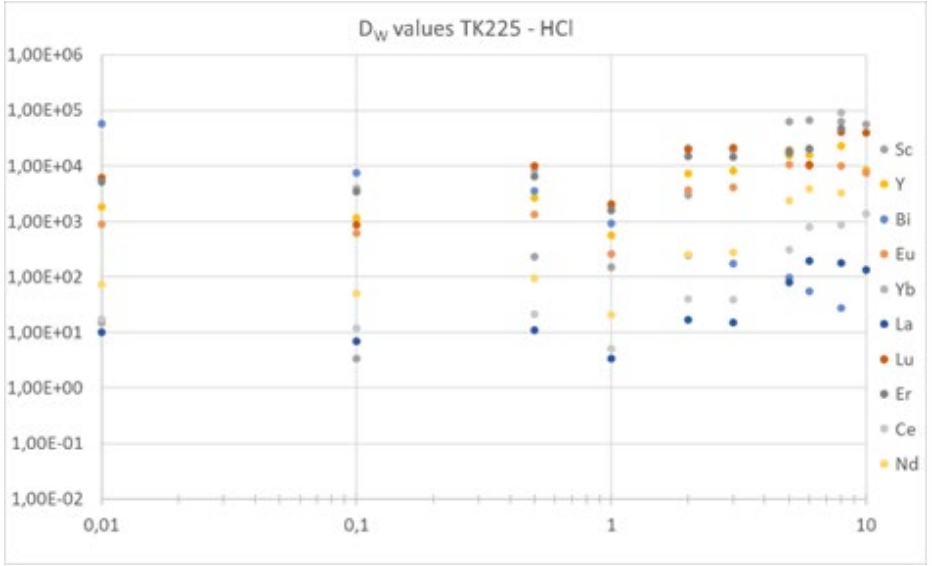
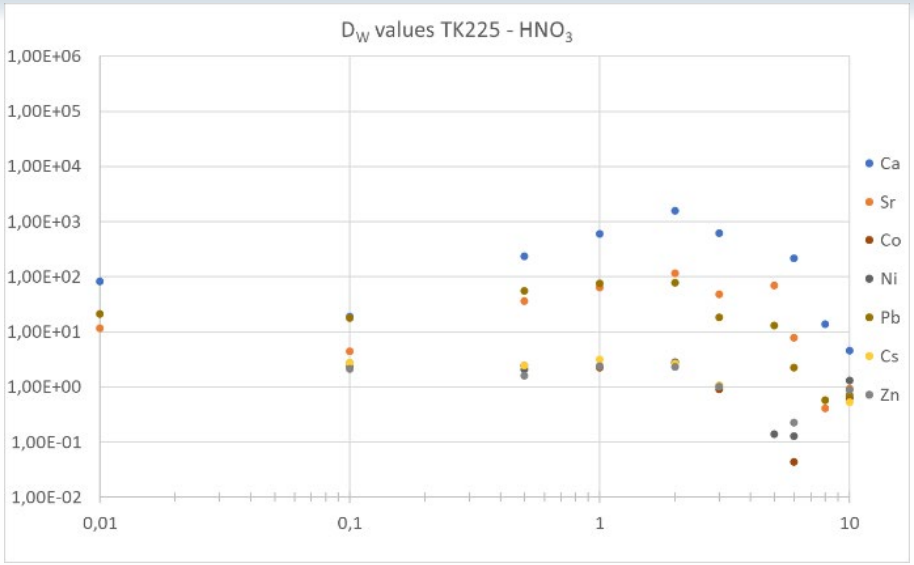
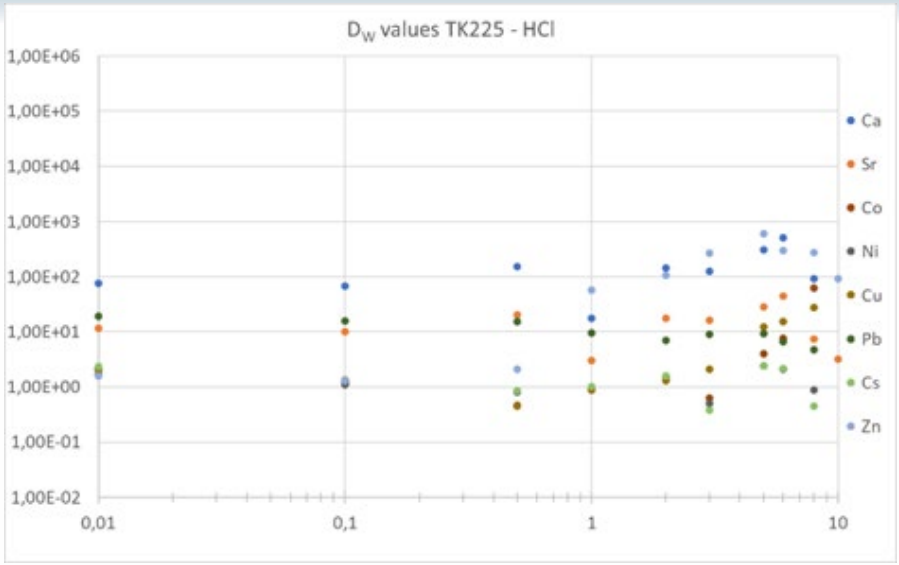
- Resin based on TO-DGA and ionic liquid
- Selectivity similar to DGA,N Resin
- Presence of ionic liquid => increase of the selectivity towards trivalent elements (difficult to remove from the resin)





TK225 Resin (2/3)

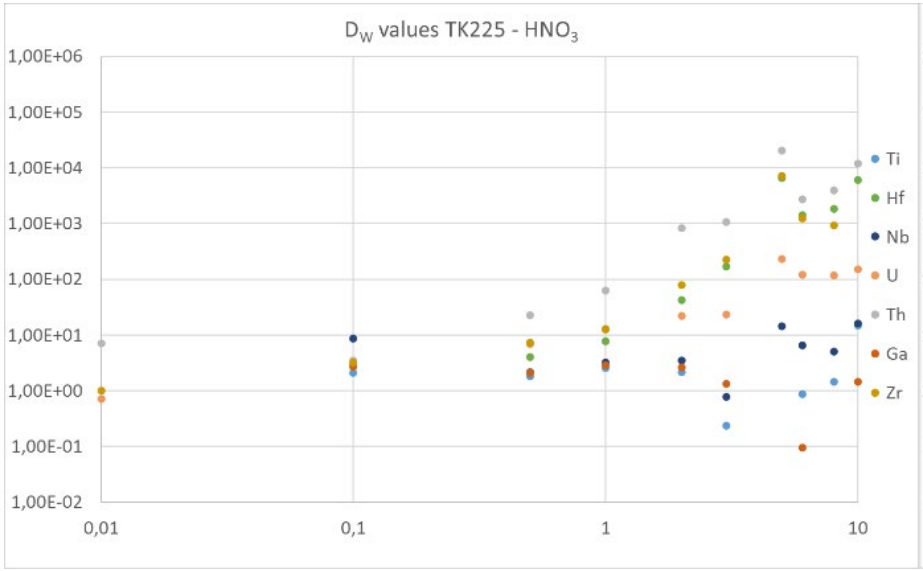


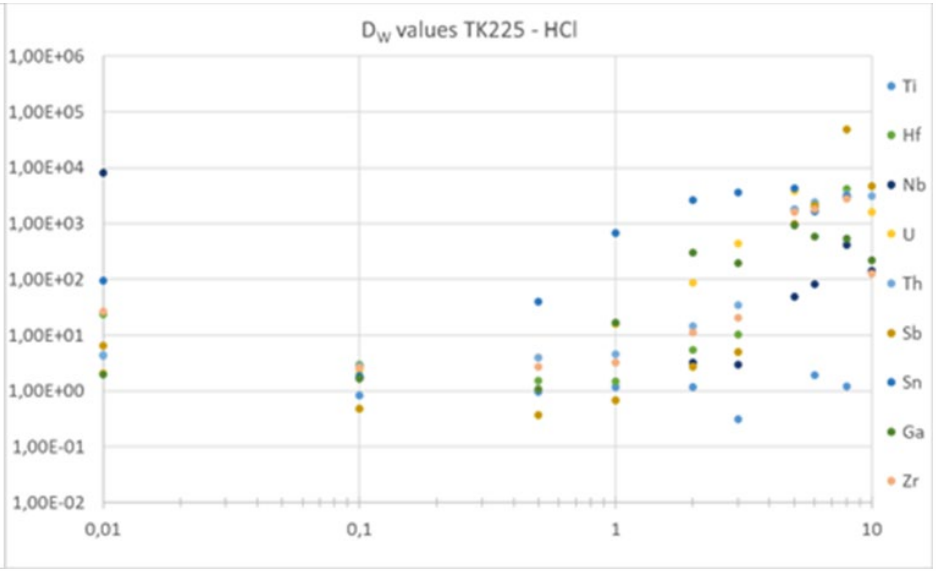


TK225 resin shows retention for Ca

=> Methods under development for Ca specific separation

TK225 Resin (3/3)



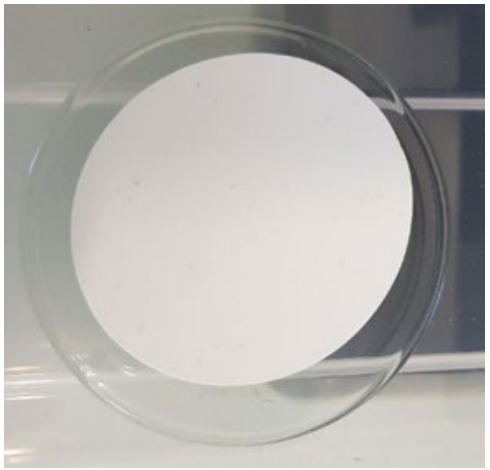


TK225 resin shows retention for Th, Zr and Hf

TK225 resin shows retention for Sb, Sn, Zr and U

Coming products – impregnated filtering membranes

- New product line: **impregnated filtering membrane (MF)**
  - Fast flow rates
  - Use with water samples (1 – 5L),
    But also
  - Use as Passive Sampling (DGT)
  - In development (including procedures):
    - **TK100 (Sr, Pb, Zn), TK101 (Pb, Ra)**
    - **CL Resin (radio-iodine)**
    - **TK201 (Tc, Re)**
    - Calixarenes (Ra, Cs)
    - …

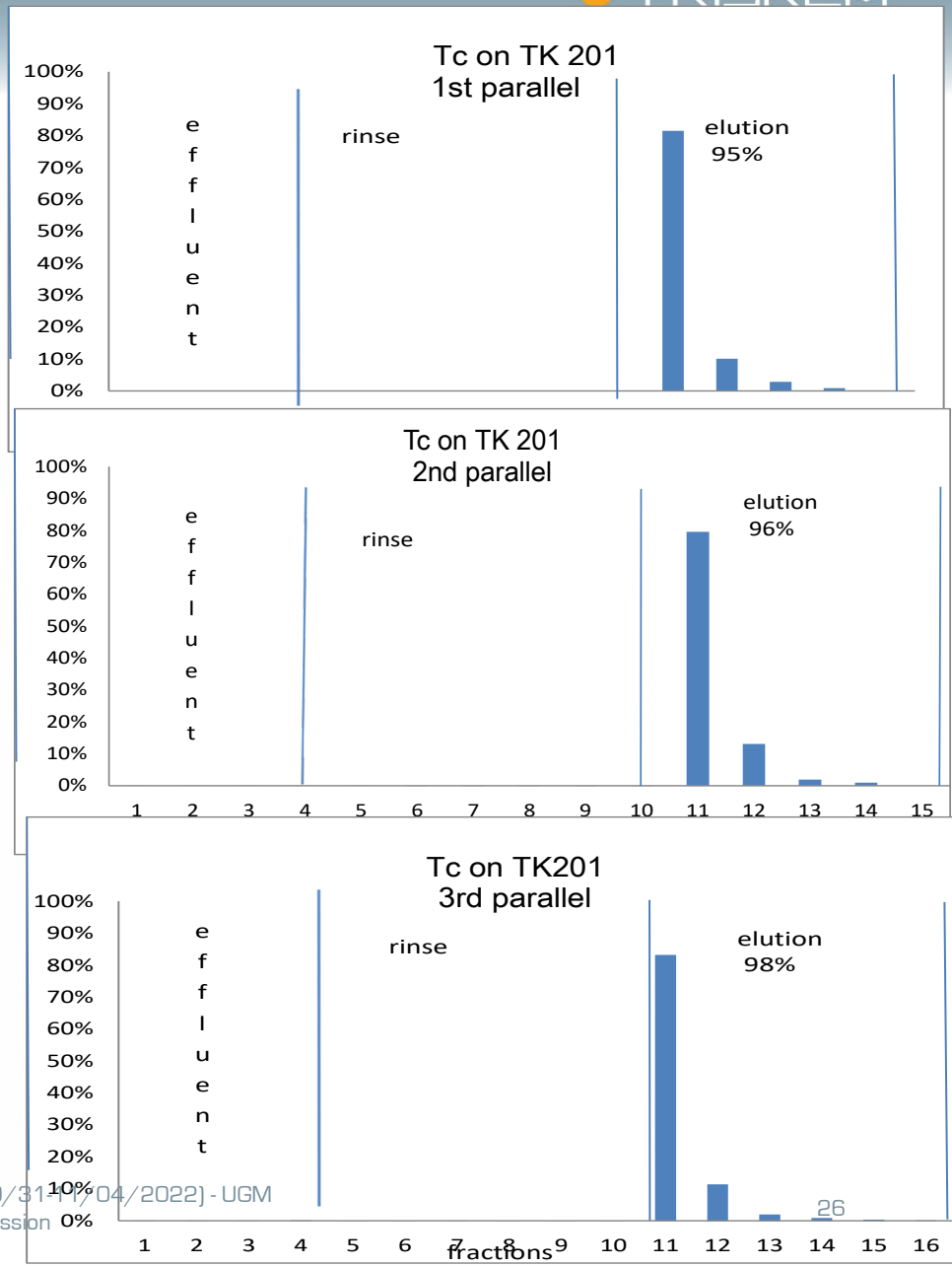


TK201 membranes: Tc separation

fraction		1st parallel		2nd parallel		3rd parallel	
		eluted %	unc %	eluted %	unc %	eluted %	unc %
1	Ef1	LD	-	LD	-	LD	-
2	Ef2	LD	-	LD	-	LD	-
3	Ef3	LD	-	LD	-	LD	-
4	Ef4	LD	-	LD	-	LD	-
5	R1	LD	-	LD	-	LD	-
6	R2	LD	-	LD	-	LD	-
7	R3	LD	-	LD	-	LD	-
8	R4	LD	-	LD	-	LD	-
9	R5	LD	-	LD	-	LD	-
10	R6	LD	-	LD	-	LD	-
11	El1	81.5%	0.5	79.6%	0.5	83.2%	0.5
12	El2	10.1%	1	13.1%	1	11.4%	1
13	El3	3%	2	1.9%	3	1.9%	3
14	El4	1%	5	1.0%	4	0.9%	5
15	El5					0.4%	9
16	El6					0.1%	20

Eluent yield %	95%	96%	98%
Total yield %	95%	96%	98%

- Tc **fully retained** on TK201 disc from 1 L tap water acidified with HNO_3 @ pH 2 spiked with Tc,
- **NO** Tc leakage detected during loading nor rinsing steps,
- **> 95% of Tc eluted/recovered** with 20 mL 2M NH_4OH.



TK100 membranes

- Already in use for passive sampling of Sr and Pb

analytical chemistry

pubs.acs.org/ac Article

Selective Diffusive Gradients in Thin Films (DGT) for the Simultaneous Assessment of Labile Sr and Pb Concentrations and Isotope Ratios in Soils

Stefan Wagner, Jakob Santner, Johanna Irrgeher, Markus Puschenreiter, Steffen Happel, and Thomas Prohaska*

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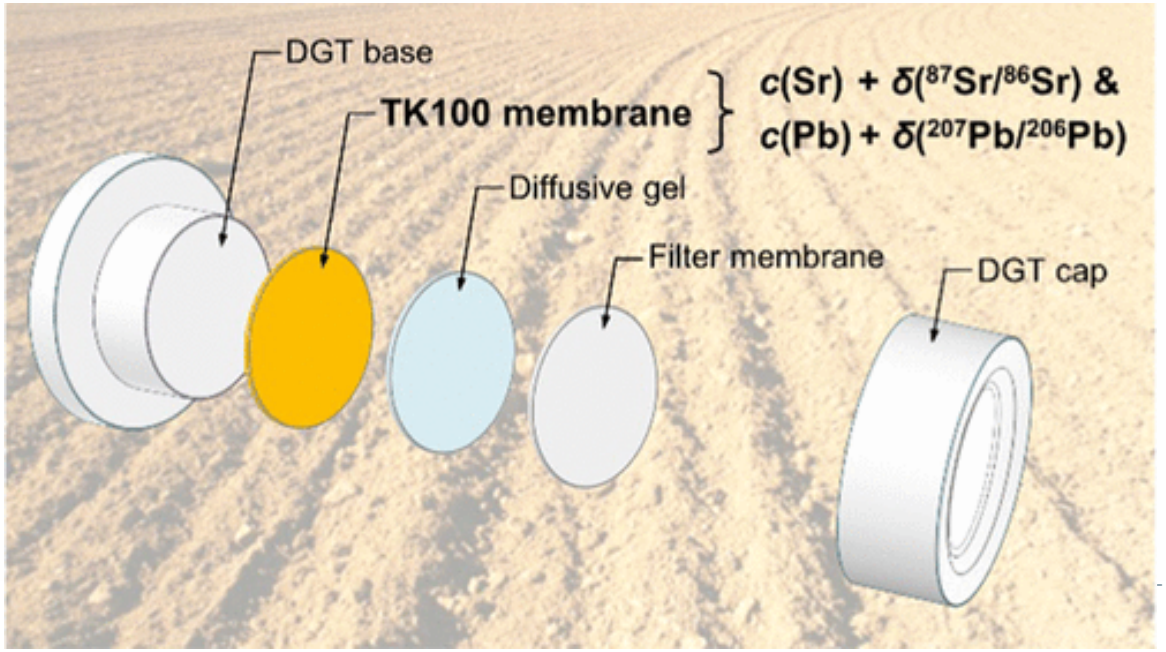

Production of « industrial » extraction chromatographic resins

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- Requests from hydrometallurgy area
  - Possible applications in decontamination and valorisation of effuents or decontaminent (e.g. acid)
- Different resins
- Bigger particle size support ~400 – 600µm
- Higher amount of resins requested
  - Challenge: supply of extractant and inert support
    - Extractants: sufficient quality, low costs, high quantities
- Increase of production capacity for these resins

Under development - Cs/Rb Resins

- See Ilarion Dohvyi's presentation just after this one!
- For the on-going projects, see Steffen Happel's presentation at the end of this session

Thank you for your attention!

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