Overview and new Developments Radioanalytics

RadWorkshop 2024

Steffen Happel

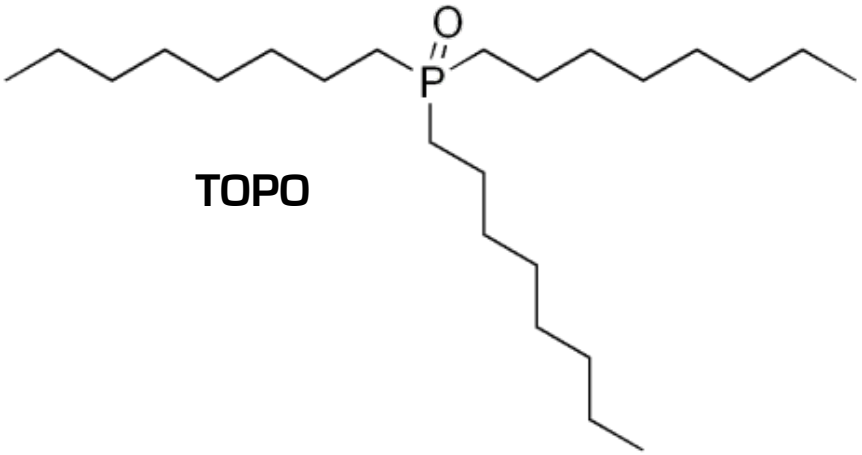
09/09/2024

TRISKEM
Expertise in Separation Chemistry

Overview

- TK200
- TK221
- Sr-90 in sea water
- TK100/1 (Radium)
- TK102
- Tc separation
  - TK201
  - TK202
  - TK200
  - TK-TcScint
- Upcoming: TK-SrScint
- TK400
- Calixarene based resins
- New impregnated membrane filters
- On-going projects

TK200 Resin



TOPO

Based on TOPO extractant

High retention of actinides

- Higher than UTEVA, TEVA

Applications:

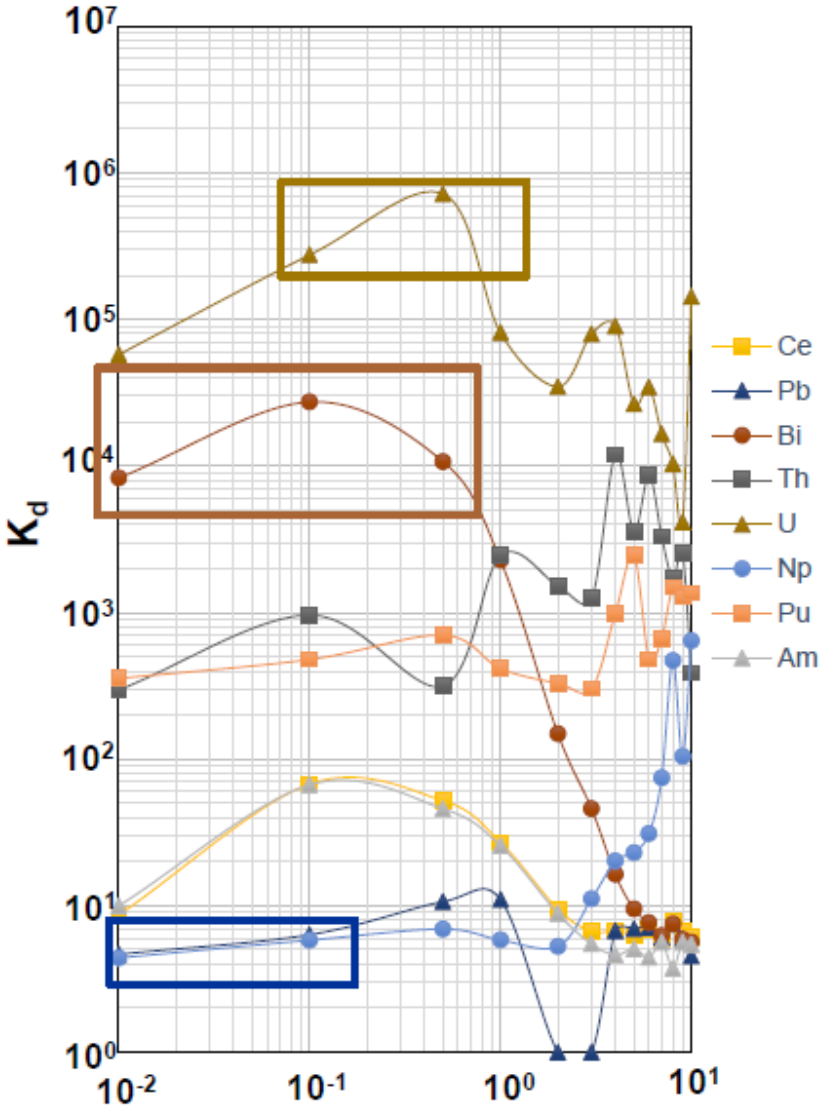
- Use for very efficient U removal from Pu (Wang et al.)
- Determination of Tc-99 in water samples (Ni Yuan et al.)
- Ga-68 production (in combination with ZR Resin)
- Actinide separation from water samples

Extracts actinides even at pH 1 - 2 (nitric acid)

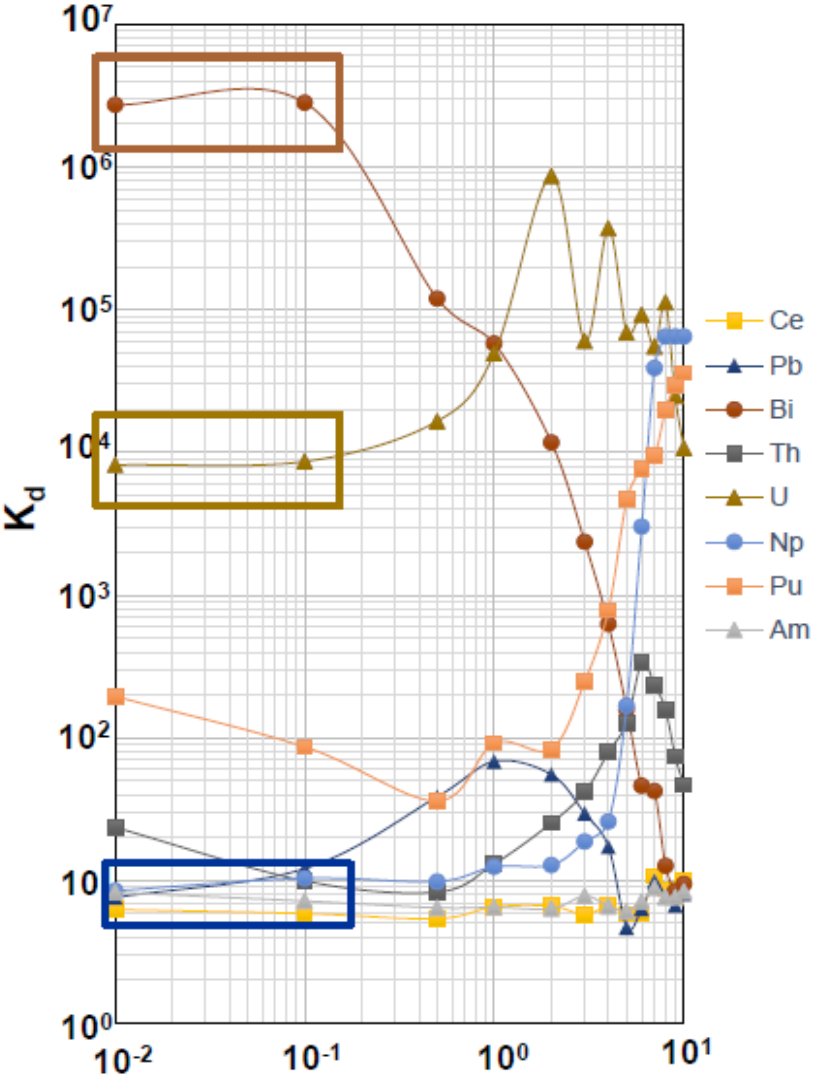
- Preconcentration and purification of selected actinides on same column
- ‘In the field’?

Actinides on TK200

(all data Van Es et al.)

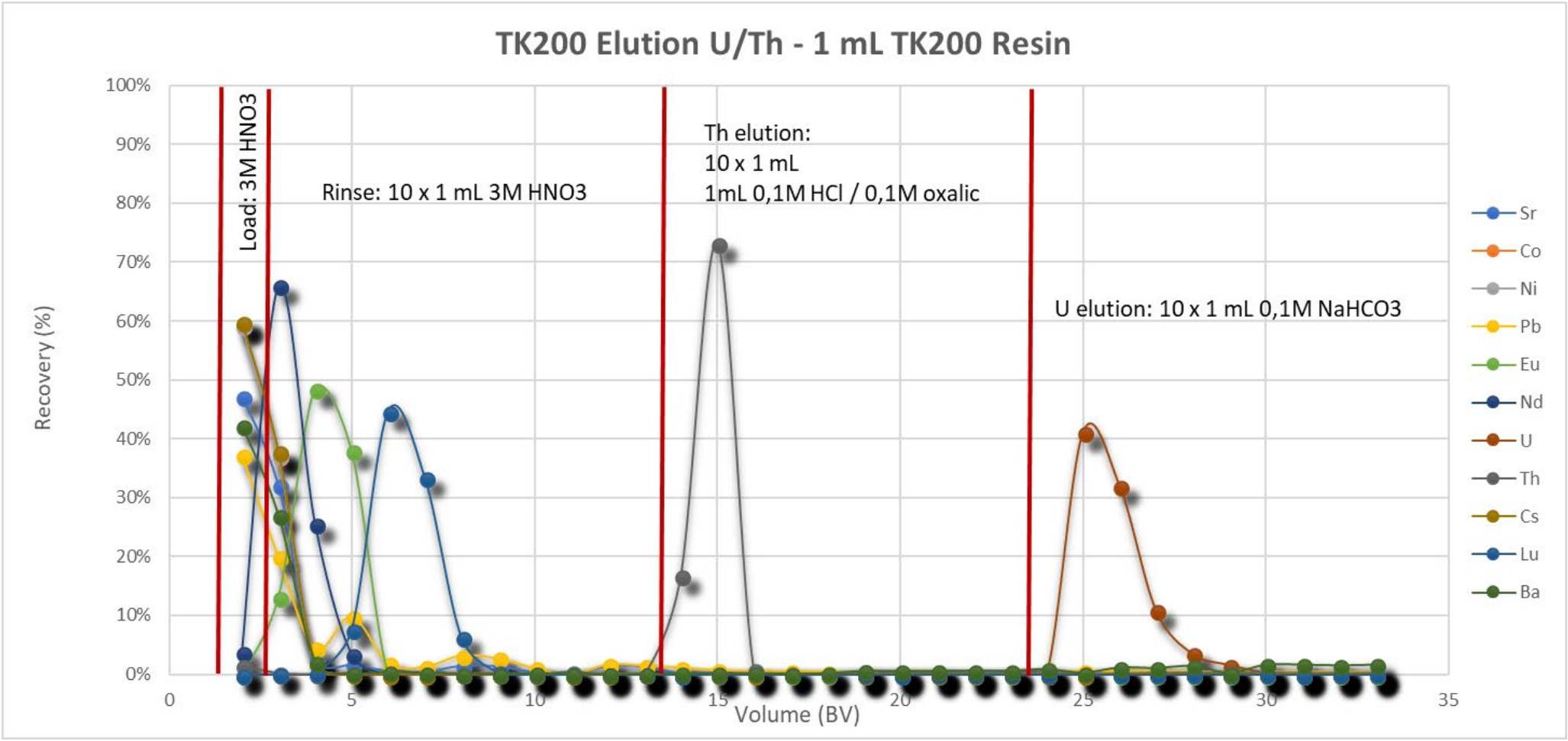


vanEs et al. $[HNO_3]$ M



VanEs et al. [HCl] M

U/Th separation on TK200



Load: 3M HNO_3 or ≥ 1L pH2 (HNO_3)

Very clean U/Th separation

Oxalate instead of carbonate

TK200 Resin - U/Pu separation

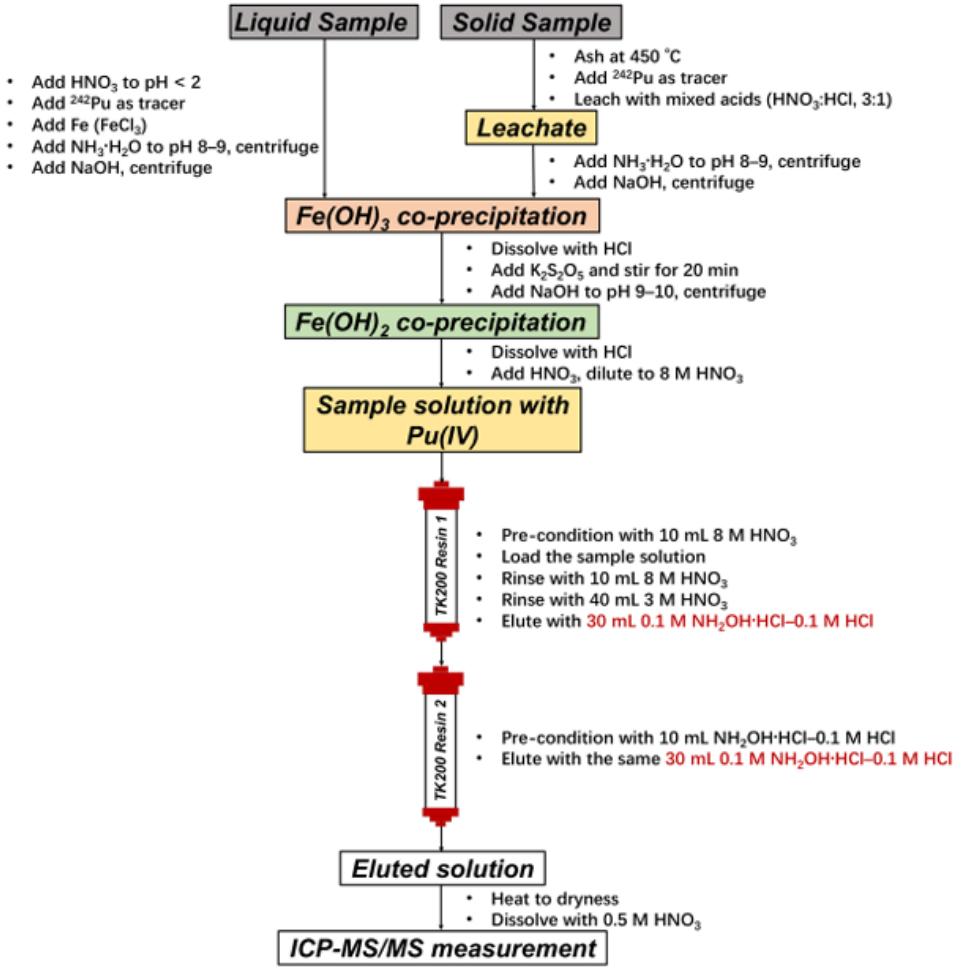


Figure S1. Analytical procedure for determination of plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu)

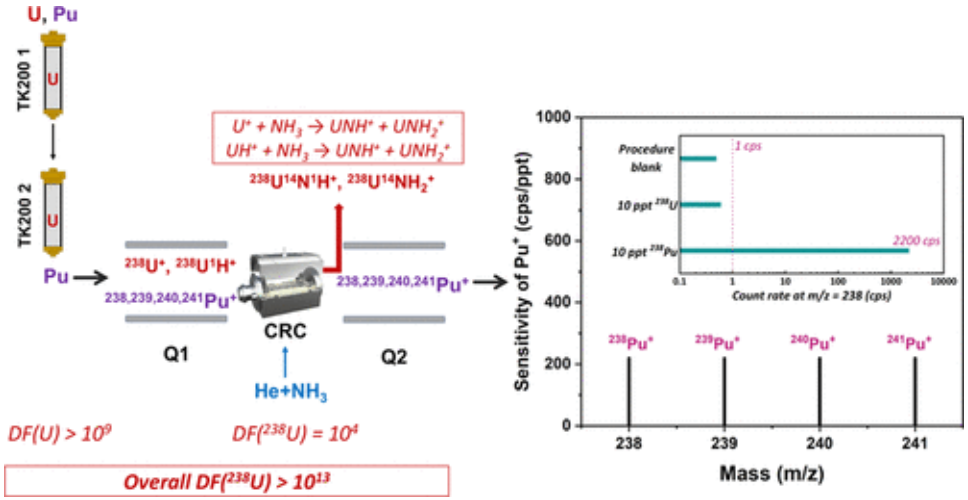
Recent publication by Huang et al.

Better U removal: **$D_f(U) > 10^9$**

Additional U removal via $He+NH_3$

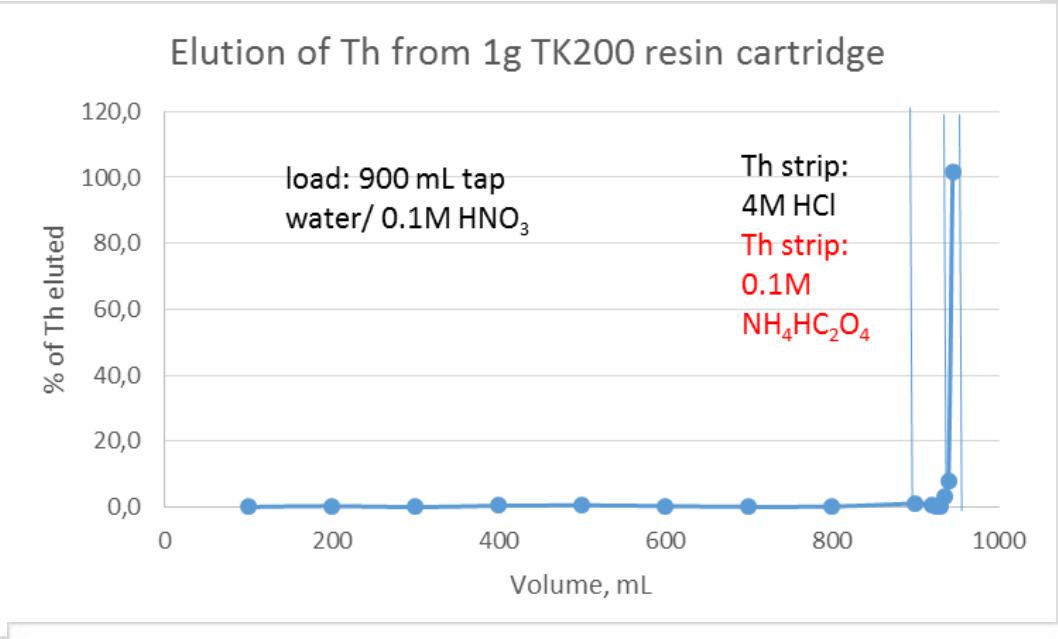
Overall $D_f(U) > 10^{13}$

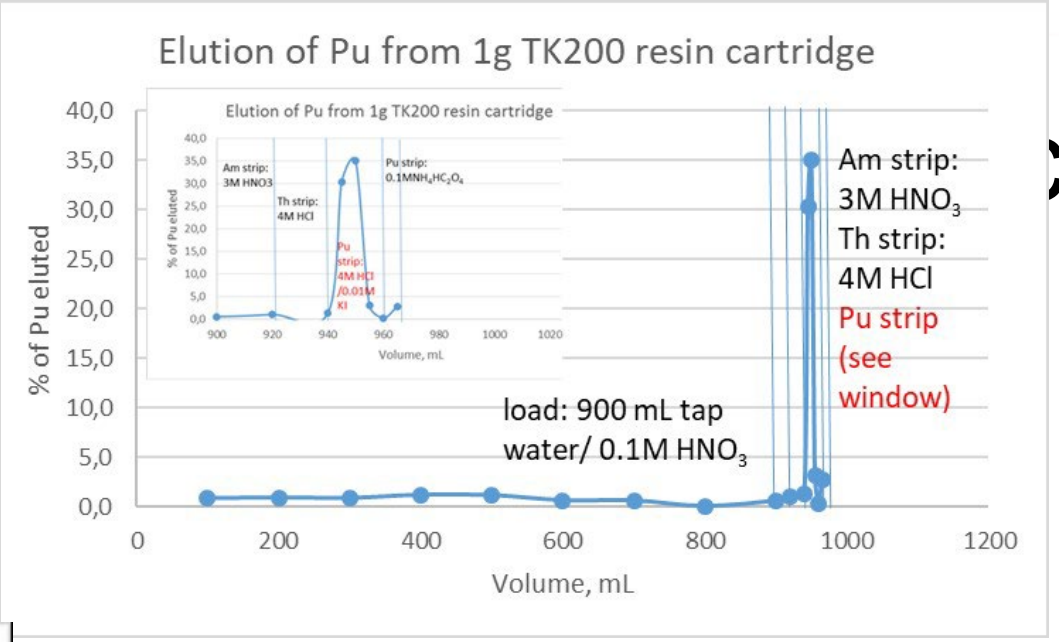
Pu isotopes incl. Pu-238 via ICP-MS/MS

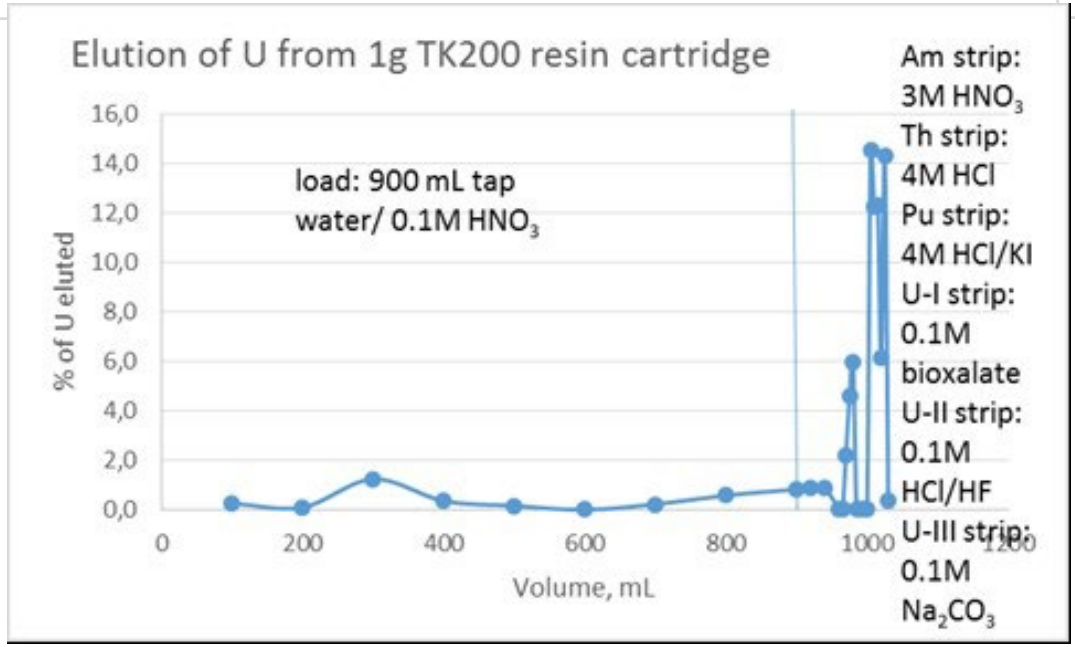


Zhao Huang, Xiaolin Hou, Xue Zhao, Rapid and Simultaneous Determination of 238Pu, 239Pu, 240Pu, and 241Pu in Samples with High-Level Uranium Using ICP-MS/MS and Extraction Chromatography, Anal. Chem. 2023, 95, 34, 12931–12939, https://doi.org/10.1021/acs.analchem.3c02526

Actinides on TK200 – Application

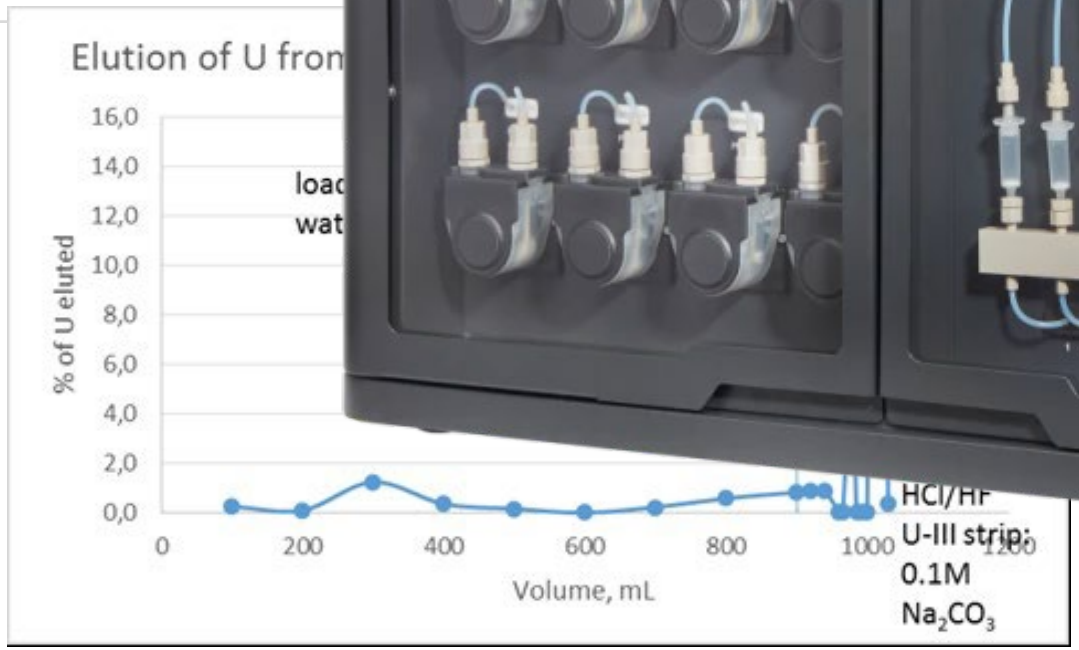






- Data by N. Vajda (RadAnal)
- Method development on-going
- Direct load of U, Th and Pu from acidified water samples (here 900 mL on 2 mL TK200)
- Sequential separation on TK200
- Automatisation & 'in the field' preconcentration'?

Actinides on TK200 – Application



- ping
- from
- ere 900 mL
- n on TK200
- Automatisation & 'in the field' preconcentration'?

TK200 – direct Pu load/separation

One TK200 cartridge

- Preconcentration and purification

Automized separation

Acidified water samples (1 L)

Flow rate 15 mL/min

U DF: 10^4 - 10^5

LoD:

- 0.32 µBq/L Pu-239
- 2.00 µBq/L Pu-240

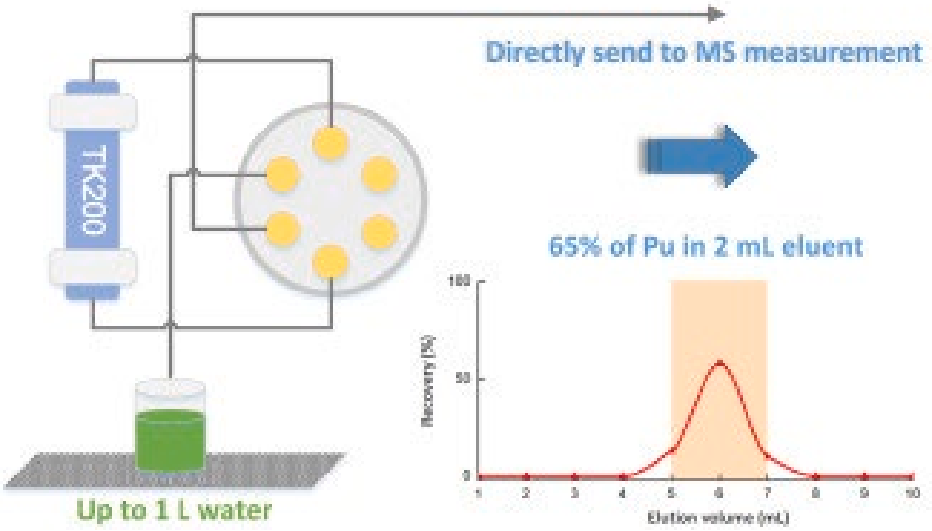
ELSEVIER

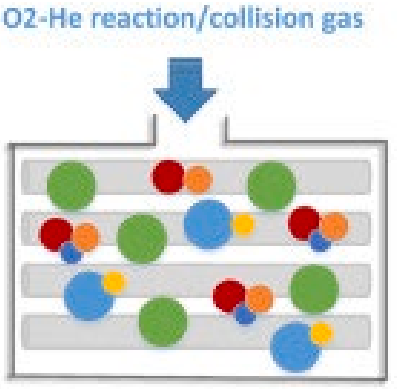
Talanta

Volume 262, 1 September 2023, 124710

A novel strategy for Pu determination in water samples by automated separation in combination with direct ICP-MS/MS measurement

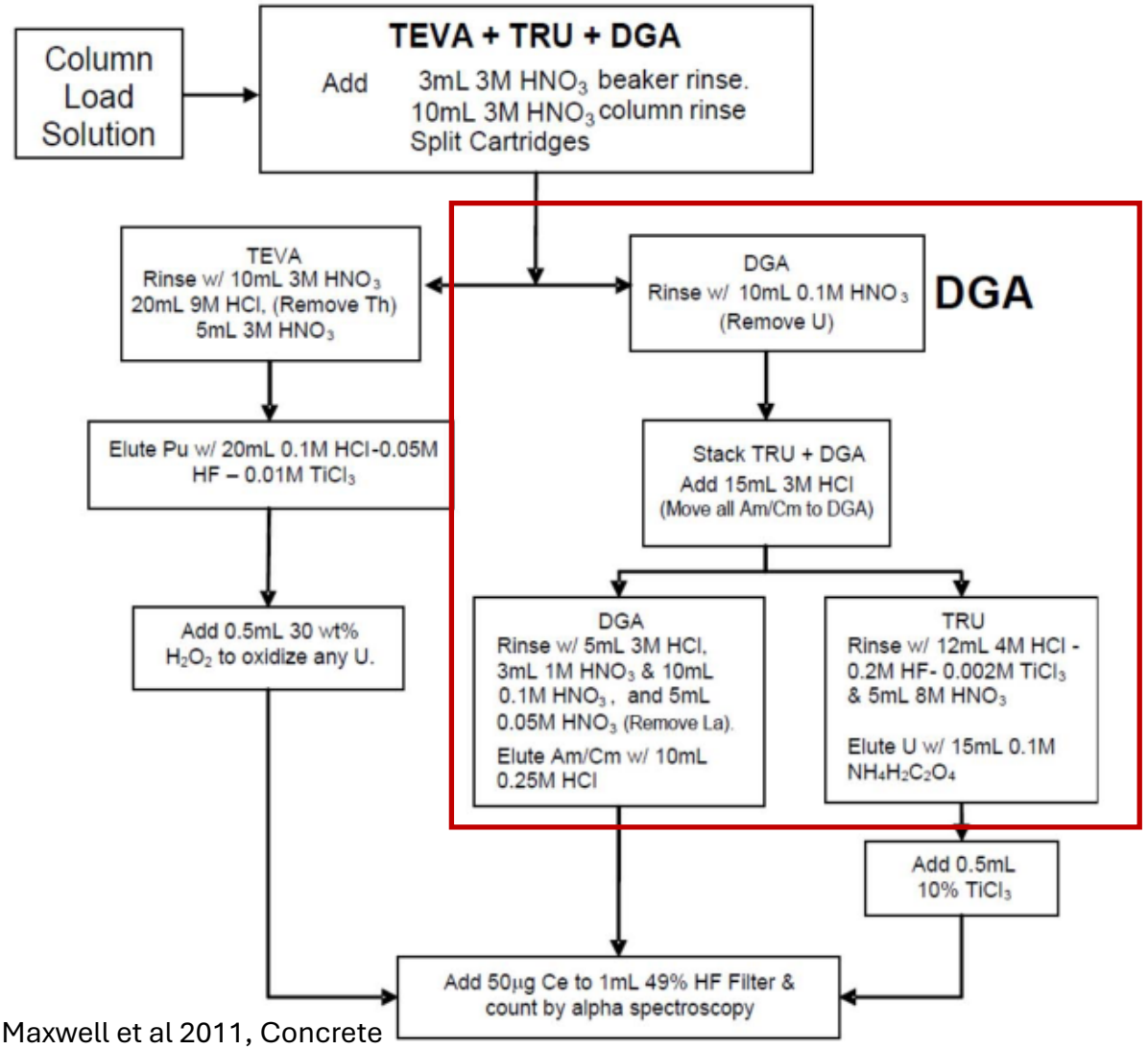
Youyi Ni [a], Wenting Bu [a], Ke Xiong [a], Sheng Hu [a], Chuting Yang [a], Liguo Cao [b]





- Reduced reagent usage
- Minimized labor intensity
- LODs for Pu down to µBq/L

TK221 Resin



Maxwell et al 2011, Concrete and brick samples

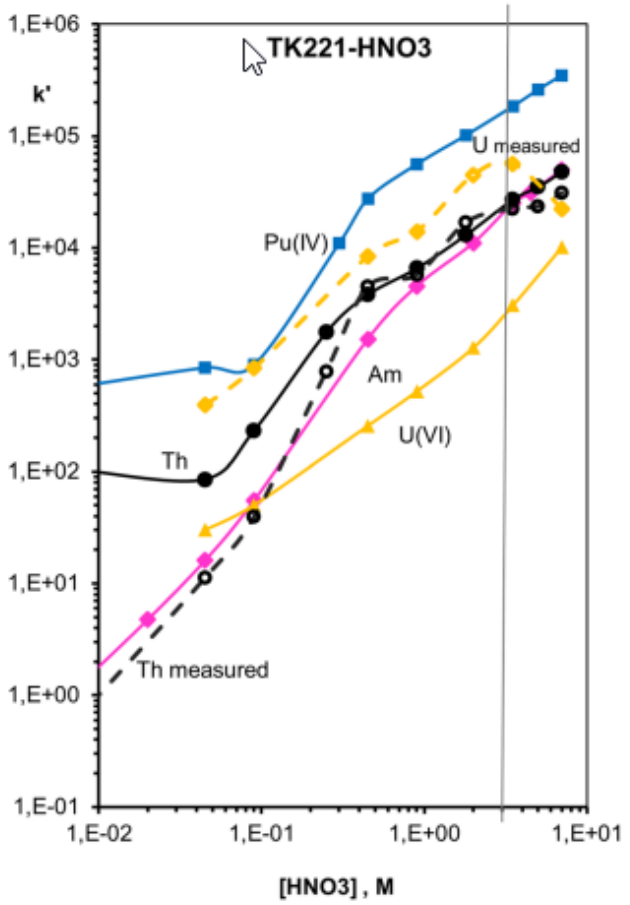
Maxwell et al.

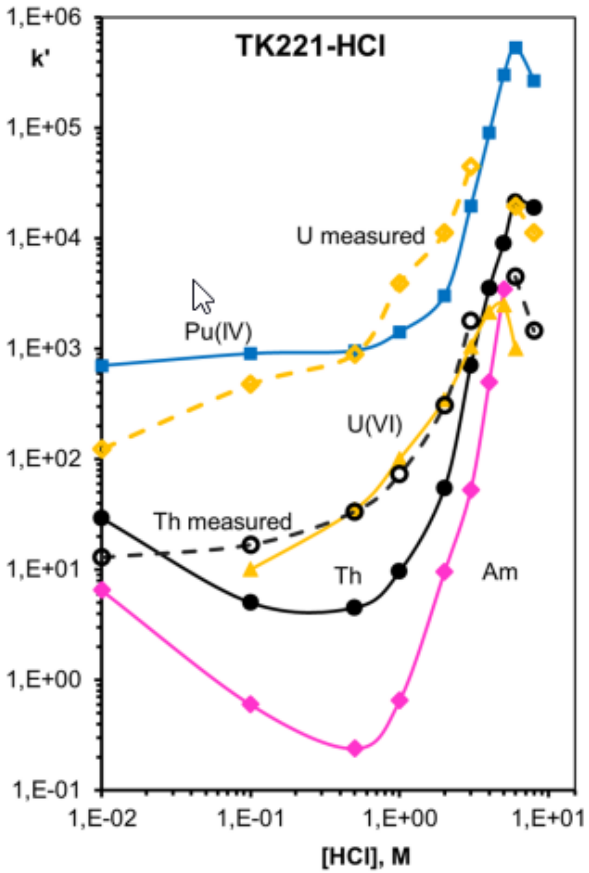
- DGA Resin:
  - High Am retention, rather low U retention
- TRU Resin:
  - Low Am retention, very high U retention
- For high matrix samples often both needed

TK221 Resin

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

- Main applications in RadPharm:
  - Lu, Tb concentration from high acid and elution in small volume of dilute HCl
  - Ac-225 purification
- Applications for the separation of actinides





(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)

TK221 Resin – actinide separation

Modification of DGA Resin

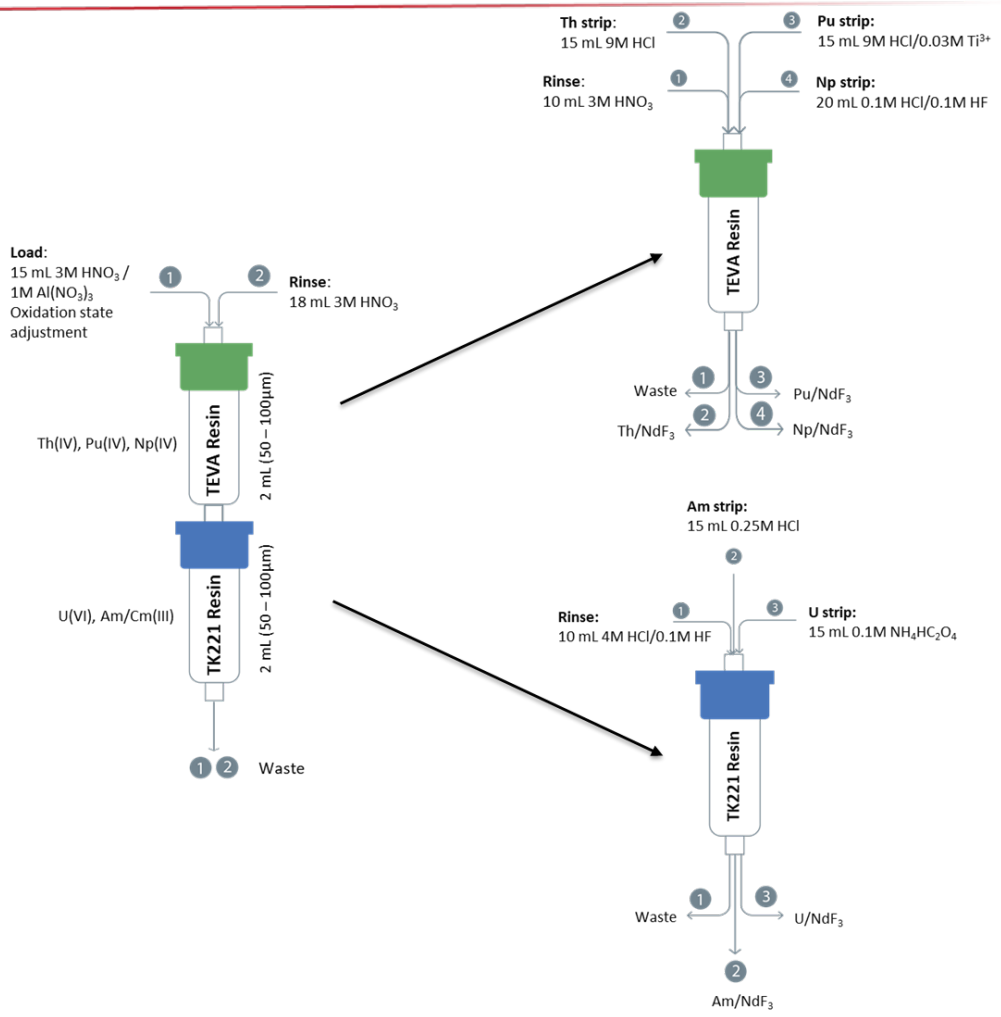
- Contains TO-DGA / phosphine-oxide
- higher load and more radiolysis stable inert support

- Higher U retention than DGA
- Higher Am retention than TRU
  - Potential interest for Actinide separation, particularly Am

Cooperation with Nora Vajda

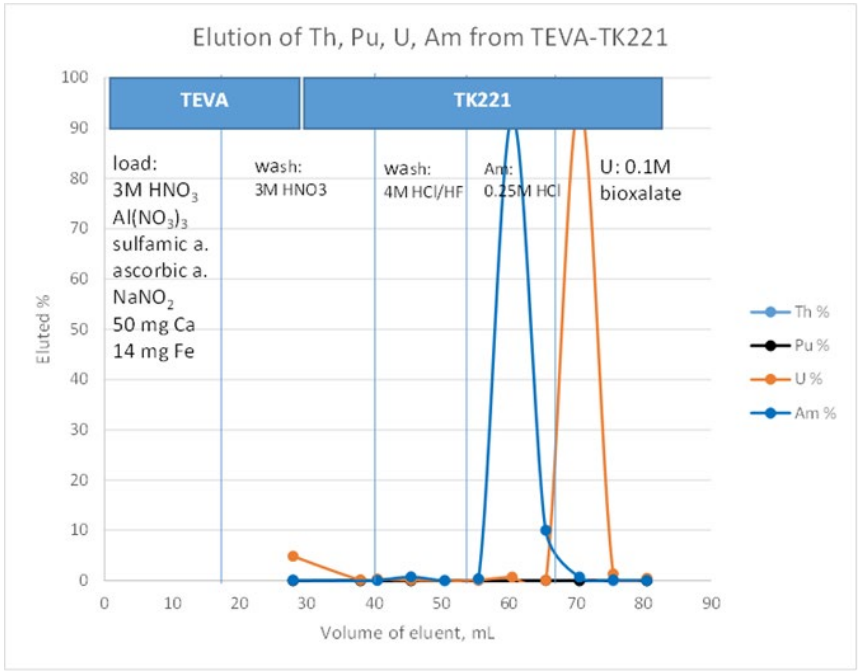
Method development for water samples

- TEVA/TK221 method
- Ideally later also soil and decommissioning samples
- Influence of Fe and Ca



Papp, I., Vajda, N. & Happel, S. *J Radioanal Nucl Chem* (2022). https://doi.org/10.1007/s10967-022-08389-9

TK221 Resin



Th and Pu removed with TEVA.
Am and U separation on TK221 Am elution before U

Table 3 Recovery of actinide tracers from spiked water samples

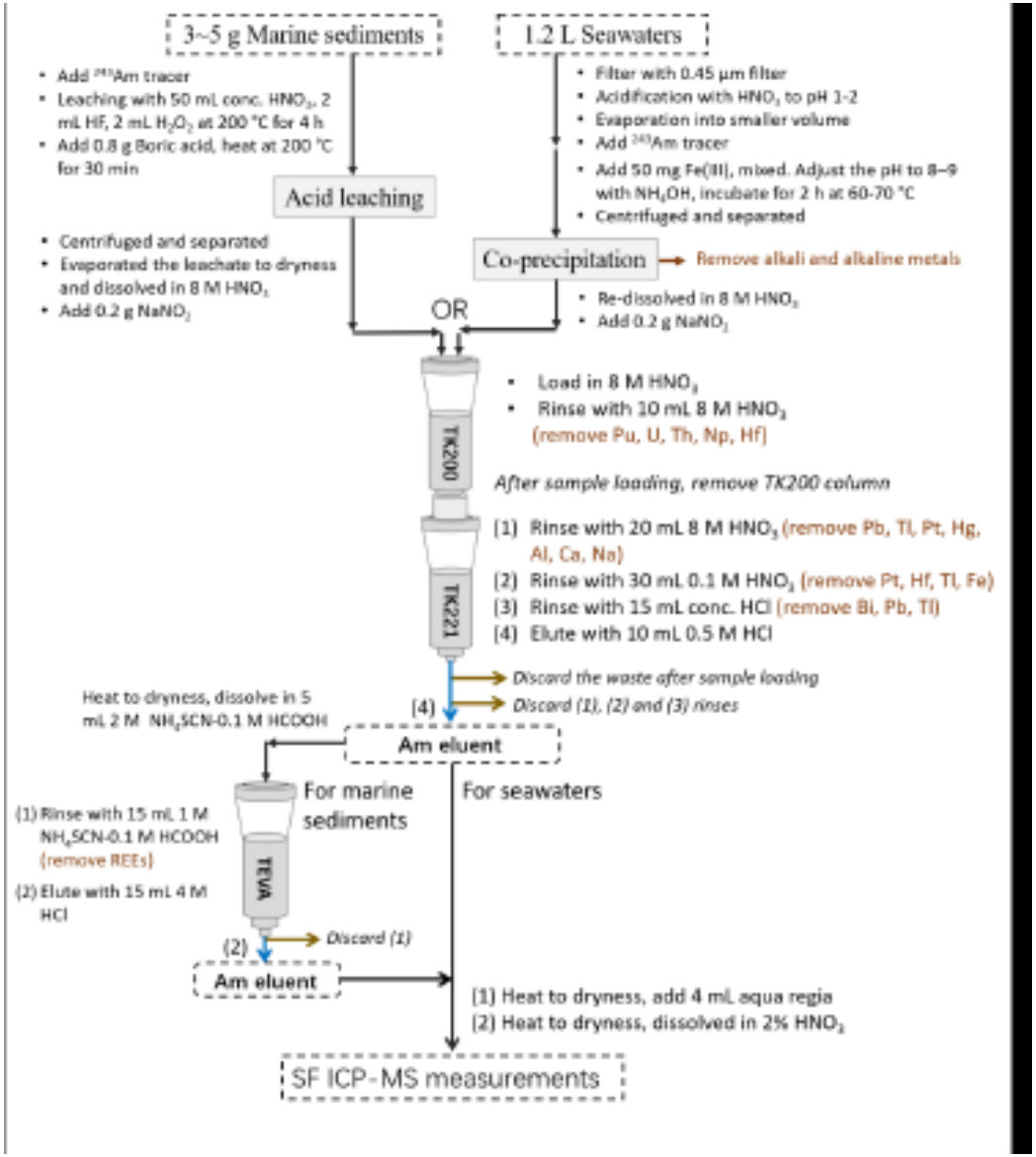
	Actinides determiantion	
	Without Np separation	With Np separation
	Yield	Yield
	%	%
TAP water		
^{230}Th	90 ± 8	86 ± 7
^{239}Pu	108 ± 7	95 ± 7
^{237}Np	–	91 ± 9
^{241}Am	103 ± 7	97 ± 6
^{233}U	103 ± 7	70 ± 7
SEA water		
^{230}Th	71 ± 7	61 ± 6
^{239}Pu	91 ± 7	87 ± 6
^{237}Np	–	93 ± 8
^{241}Am	89 ± 7	92 ± 6
^{233}U	88 ± 7	59 ± 6

Analyte	Target values		Measured values			Relative bias	MARB[a]	Z-score[b]	Test evaluation
	Mean activity concentration	Standard deviation (sd)	Activity concentration	Standard uncertainty	Relative standard uncertainty				
	Bq/kg	Bq/kg	Bq/kg	Bq/kg	%	%	%		
^{239}Pu	5.93	2.27	5.09	0.24	4.7	14	25	0.37	Accepted
^{241}Am	4.85	0.57	4.73	0.15	3.2	2.5	30	0.21	Accepted
^{244}Cm	7.02	2	7.19	0.34	4.7	2.4	25	0.09	Accepted

[a]Maximum Acceptable Relative Bias
[b]Z = |Xreported—Xtarget|/sdtarget

- Method tested on spiked tap and sea water samples
- High yields (88+ for U and Am)
- Analysis of IAEA-TEL-2021–03 WWOPT successful
- On-going: use for solid samples

Tandem TK200/TK221



- Ling Zhang, Emilia Vassileva, Determination of ultra-trace level ^{241}Am in marine sediment and seawater by combining TK200-TK221 tandem-column extraction chromatography and SF ICP-MS, Talanta, 271, 2024, 125724, https://doi.org/10.1016/j.talanta.2024.125724

Conclusion:

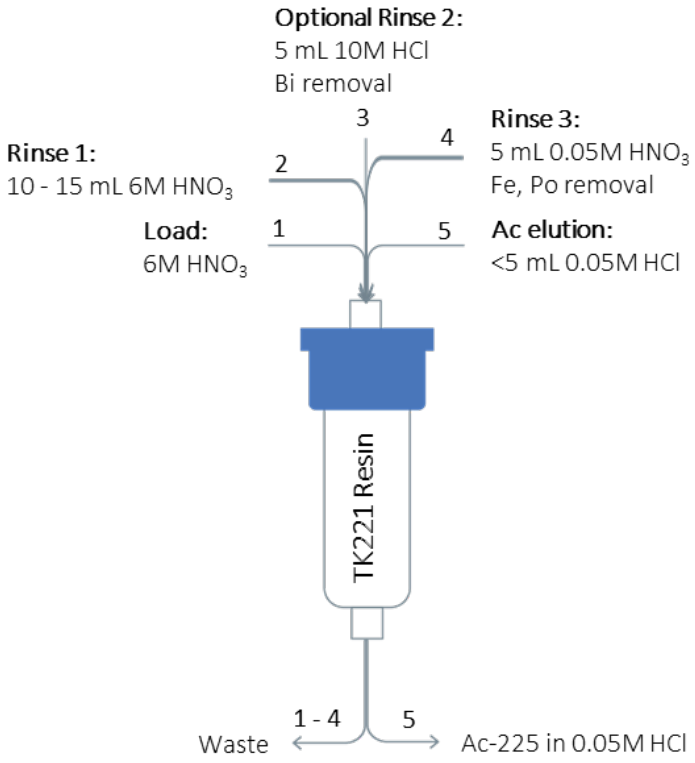
For DGA separation, the decontamination factors (DFs) for Pu, U, and Th were calculated to be $(1.8 \pm 0.4) \times 10^3$, $(3.0 \pm 1.0) \times 10^4$, and 24±6, respectively.

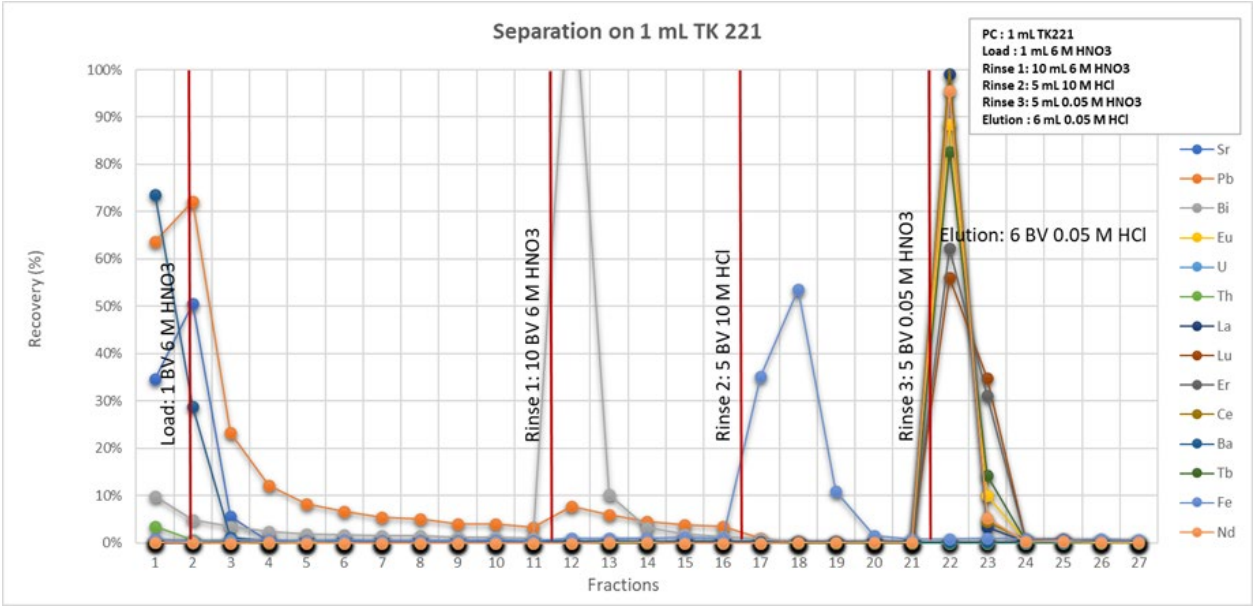
For TK221 separation, the DFs for Pu, U, and Th were $(1.5 \pm 0.2) \times 10^4$, $(2.1 \pm 0.3) \times 10^4$, and $(1.2 \pm 0.1) \times 10^3$, respectively.

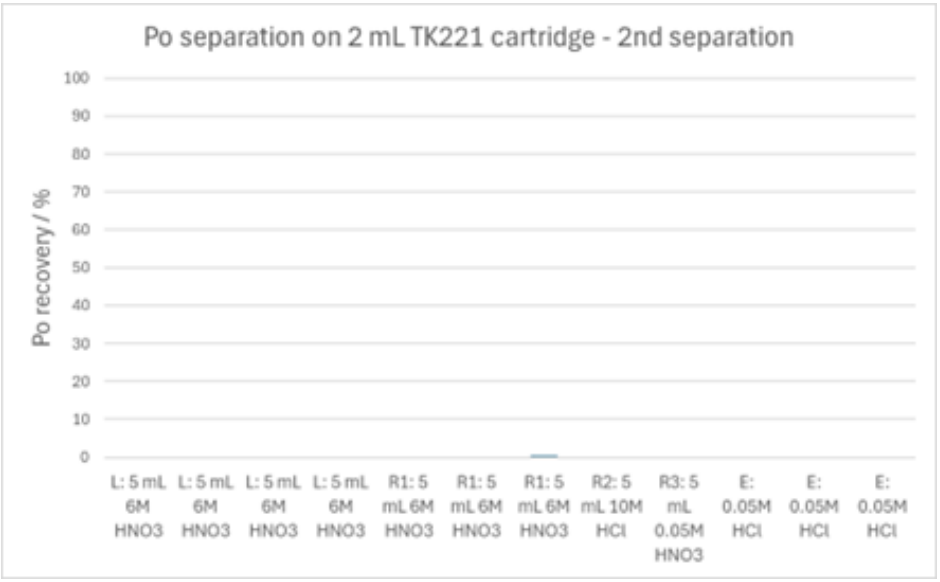
It can be seen that the TK221 resin displayed remarkably better performance for the removal of Pu and Th than DGA resin, while with an excellent decontamination ability of U, close to DGA.

=> Use for Ra-226/8 instead of DGA?

Ac separation => RP presentation







Load from 2 – 6M HNO3
Rinse with 6M HNO_3
10M HCl => Bi removal and
0.05M HNO_3 (Fe removal)
Ac elution in 0.05M HCl
Po remains on TK221

Sr-90 in seawater via DGA – KAERI method

A simple and straightforward technique for analyzing radionuclides in seawater

18 Apr, 2024

Hyuncheol Kim (hckim3@kaeri.re.kr), **Gahyun Kim** (ghkim97@kaeri.re.kr)

Sr-90 in seawater via DGA – KAERI method

Materials and Apparatus

TRISKEM INTERNATIONAL

AMP-PAN (or KNiFC-PAN)

DGA resin

2 mL column

SALT-100 (*WITHTECH Ltd. ; South Korea*)

Eight peristaltic pump
Flow rate: 10 – 100 mL min^{-1}
Applicable with 2 mL/ 5 mL column
https://www.withtech.co.kr/en/busi/new_busiList_5.php

Hidex Q-ARE

Automated Radionuclide Extraction System

Q uick
A utomated
R adionuclide
E xtraction

The most advanced automated radionuclide extraction chromatography system dedicated to radionuclide separation from environmental, food and decommissioning samples.

Quick and easy-to-use unattended radionuclide extraction

User friendly, intuitive and hassle free.

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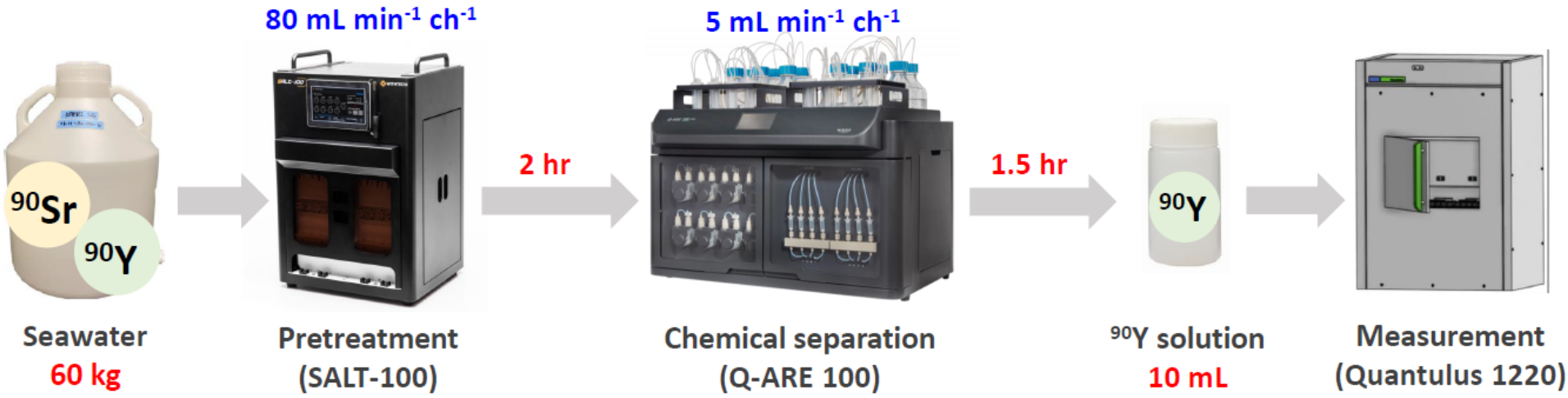
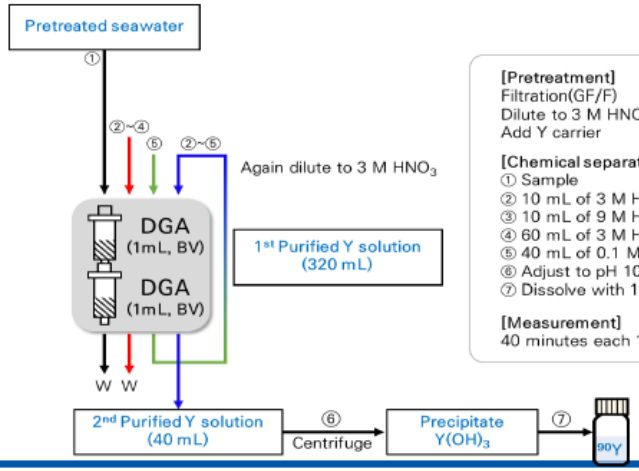
Sr-90 in seawater via DGA – KAERI method

^{90}Sr in seawater; procedure





[Pretreatment]
Filtration(GF/F)
Dilute to 3 M HNO_3 using Conc. HNO_3
Add Y carrier

[Chemical separation]
① Sample
② 10 mL of 3 M HNO_3
③ 10 mL of 9 M HCl
④ 60 mL of 3 M HNO_3/0.3 M HF
⑤ 40 mL of 0.1 M HCl
⑥ Adjust to pH 10 using NaOH
⑦ Dissolve with 10 mL of 0.1 M HNO_3

[Measurement]
40 minutes each 10 times by LSC

Presentation by Hyuncheol Kim at the TrisKem / Raddec Workshop, 18.04.2024
Available on our website
Video also available upon request.

Sr-90 in seawater via DGA – KAERI method

- Rapid automized separation of Y-90 from sea water (60 kg)
- Aim: determination of Sr-90
- Faster than standard methods
- Potential drawback: Sample needs to be adjusted to 2M HNO_3 => large amounts of conc. HNO_3
- Ongoing: modification of DGA to allow loading from 0.2 – 0.5M HNO_3 => significanlty less HNO_3 conc needed for adjustment

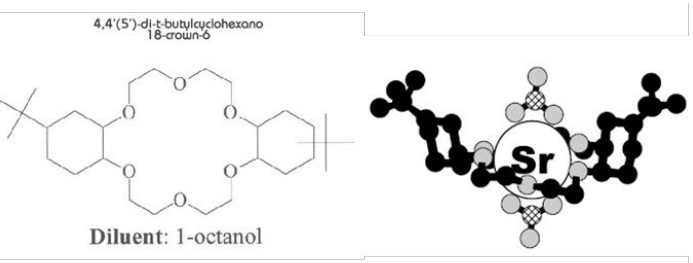
=> TK227 Resin

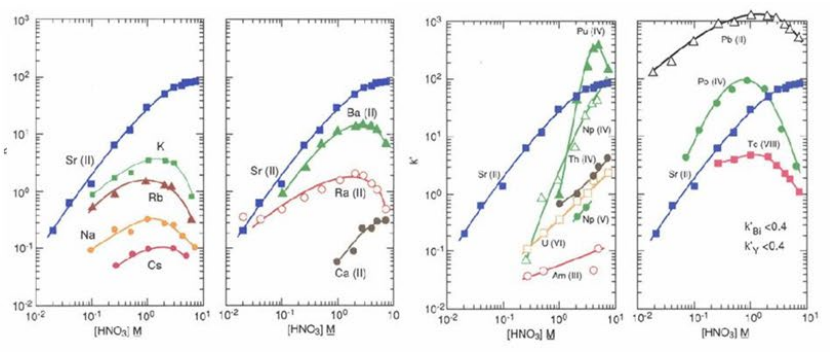
- Similar approach for Am possible?
- SALT / Q-ARE approach also for used Cs-134/7 via AMP-PAN

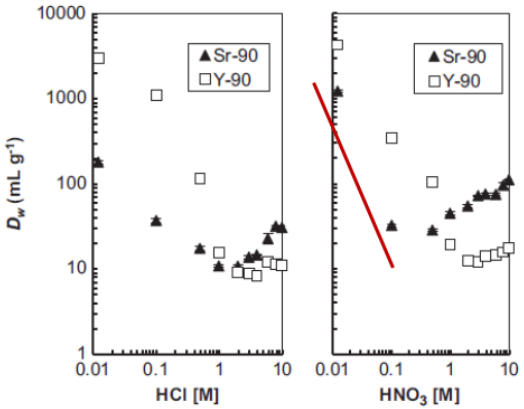
TK100/1 Resins

Based on same crownether as SR Resin

- Different solvents, Sr and Pb uptake also between pH 2 and 7
- Concentration and purification on same column







Typical applications:

- Pb-210 in water samples (up to > 5L per 2 mL column/cartridge)
- Sr-90 by ICP-MS (very high Zr-90 decontamination) => NPL
- Ra-226 by ICP-MS => NPL (Load and purification in one step)
  - Agilent application note

TK100 Resin

Development for measurement of ^{90}Sr and ^{226}Ra by Russel and Van Es from NPL

Rapid Analysis of Radium-226 in Water Samples by ICP-QQQ

Application Note

Nuclear, environmental

https://www.agilent.com/cs/library/applications/8800_ICP-MS_5991-8324EN_radium_analysis.pdf

Authors

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2. Chemistry Department, University of Surrey, Guildford, Surrey, UK

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journal homepage: www.elsevier.com/locate/apradiso

Development of an optimised method for analysis of ^{90}Sr in decommissioning wastes by triple quadrupole inductively coupled plasma mass spectrometry

B. Russell*, M. García-Miranda, P. Ivanov

National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, UK

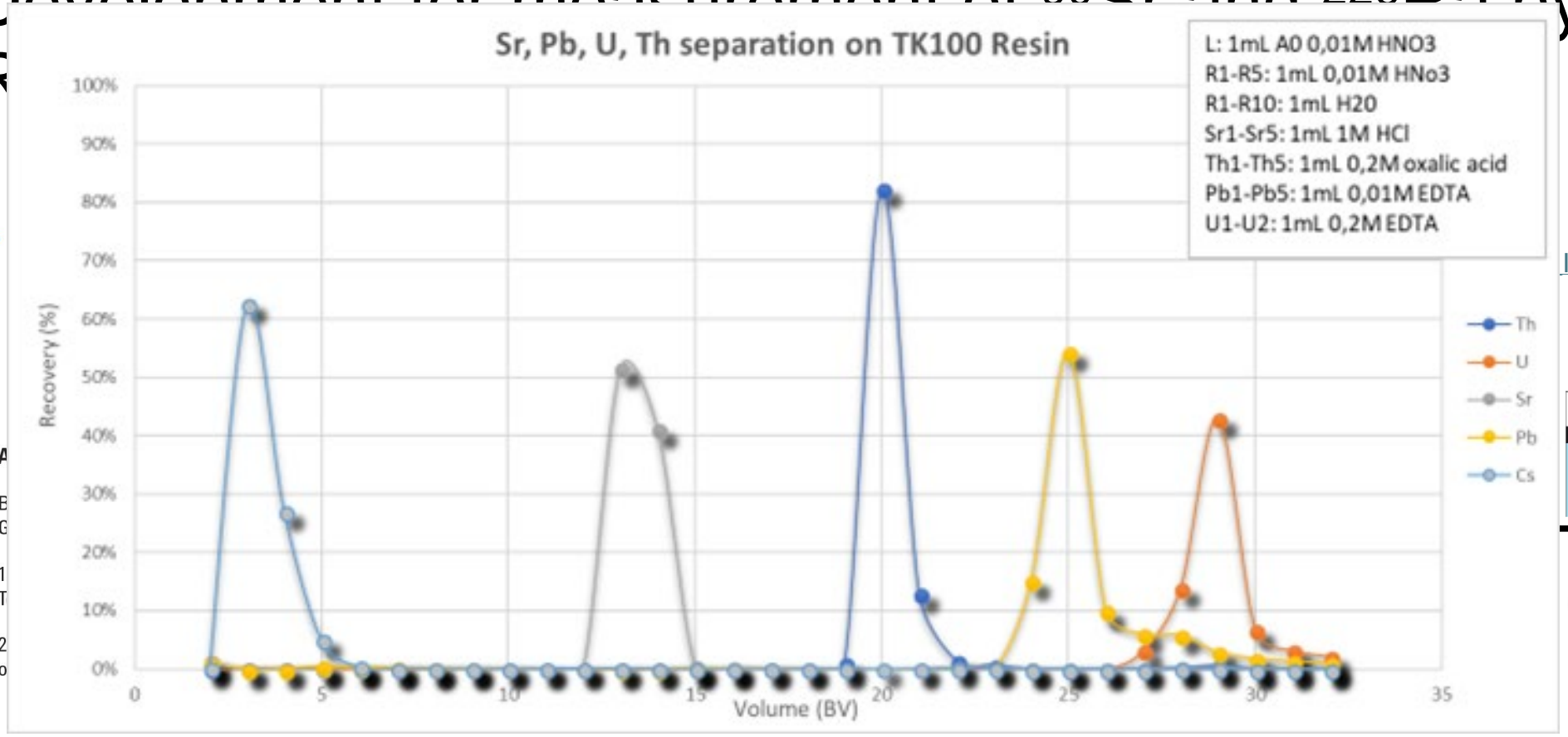
TK100 contains HDEHP

⇒very high Zr retention => high Zr decontamination

⇒ Sr elution in ≥0.5M HCl

TK100 Resin

Development for measurement of ^{90}Sr and ^{226}Ra by R



ICP-

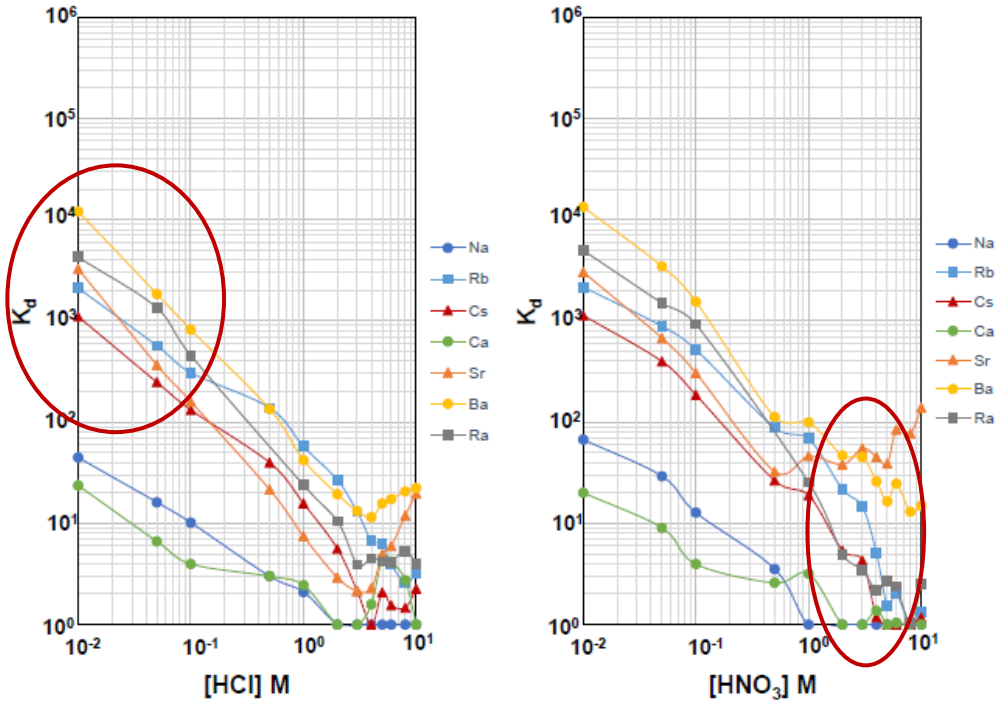
TK100 contains HDEHP

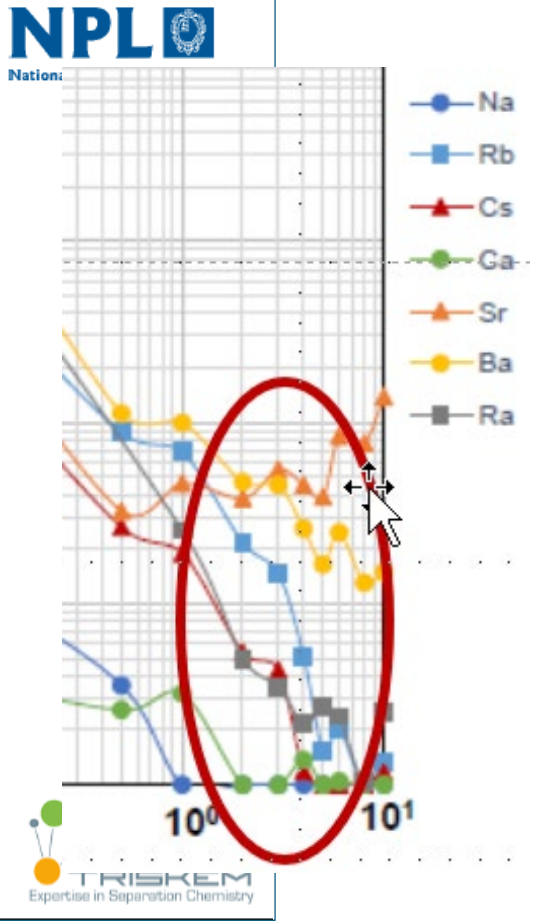
⇒very high Zr retention => high Zr decontamination

⇒ Sr elution in ≥0.5M HCl

TK101 - Radium

TK101 Group 1 and 2

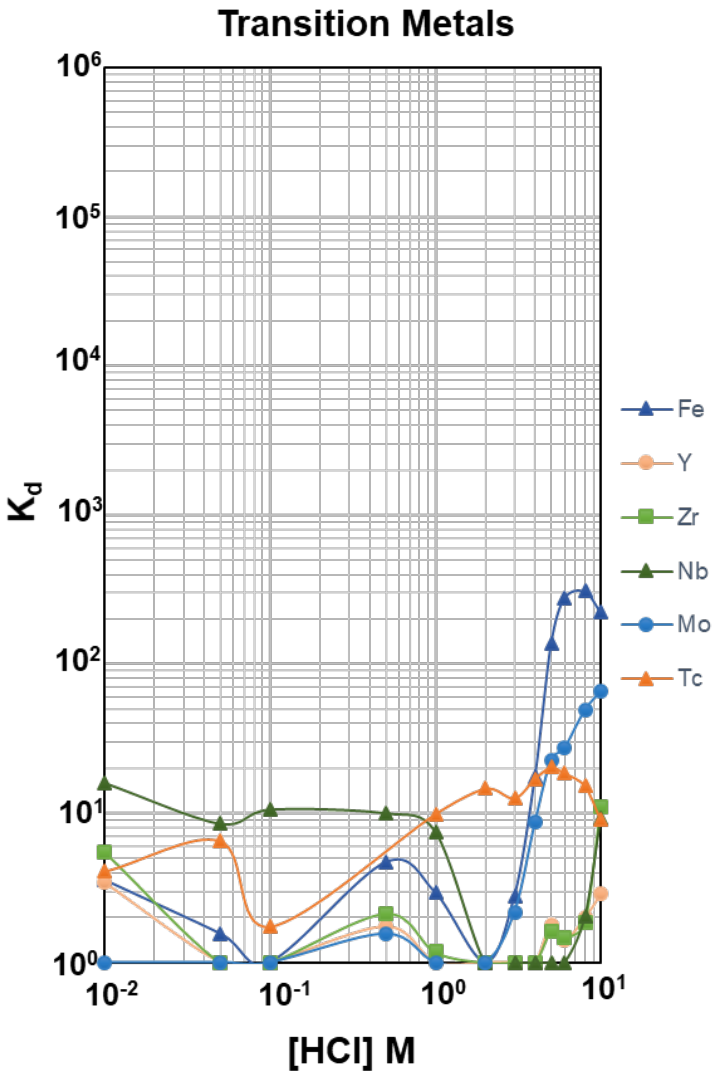


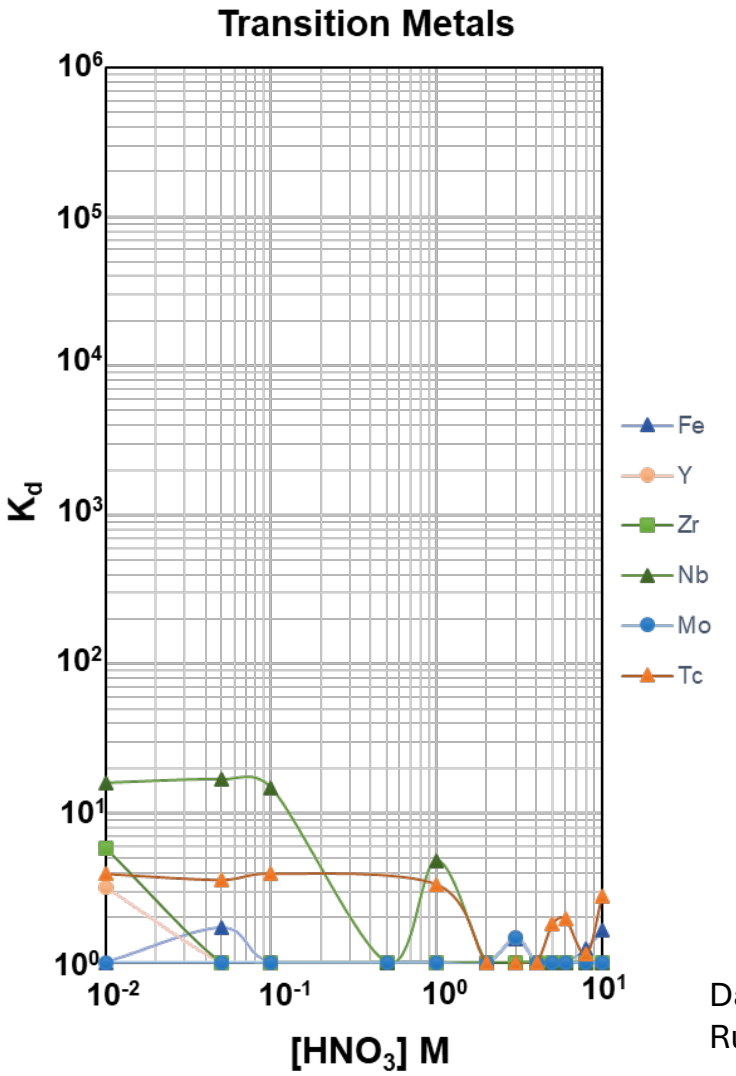


Data provided by Russel et al. (NPL)

- Ra retention from water/dilute acid up to ~0.5M HNO_3/HCl
- At higher conc. selectivity closer to SR Resin/TK102 Resin

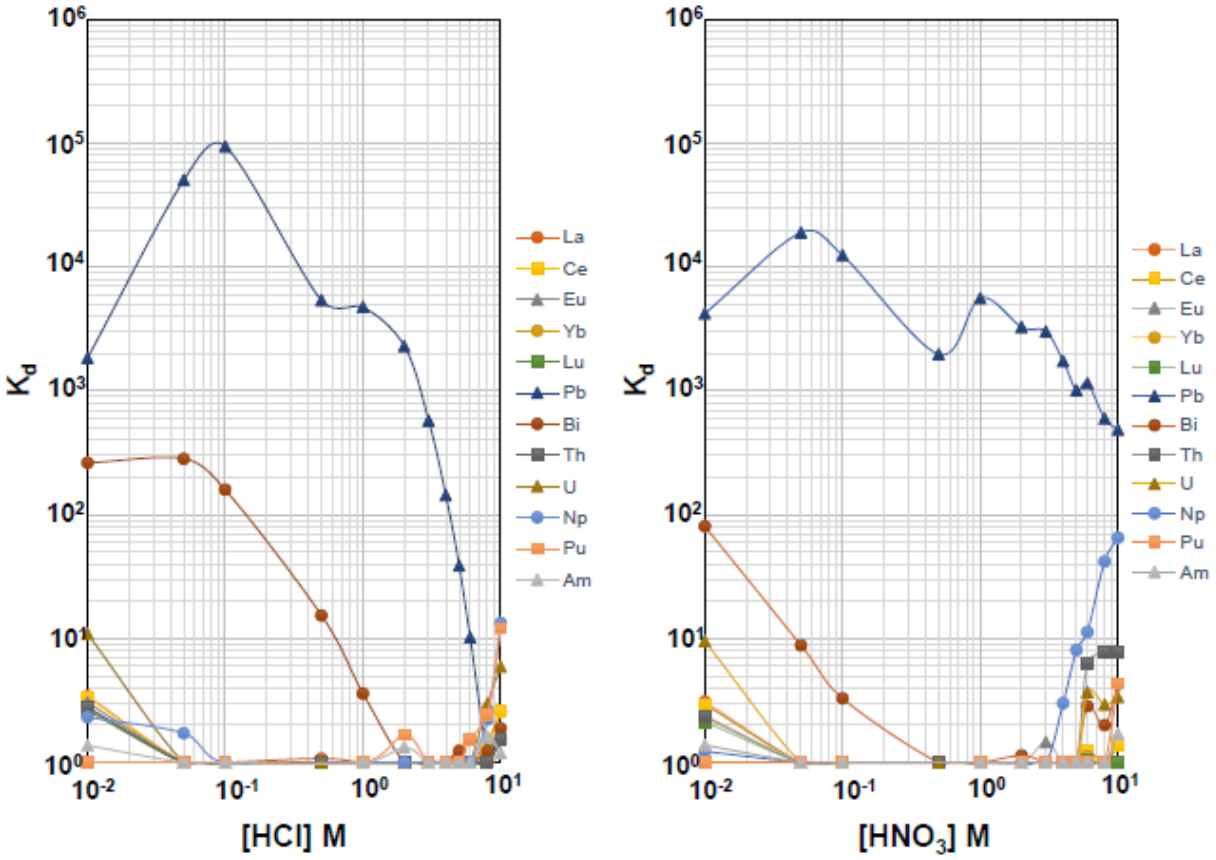
TK101 Transition Metals





Data provided by Russel et al. (NPL)

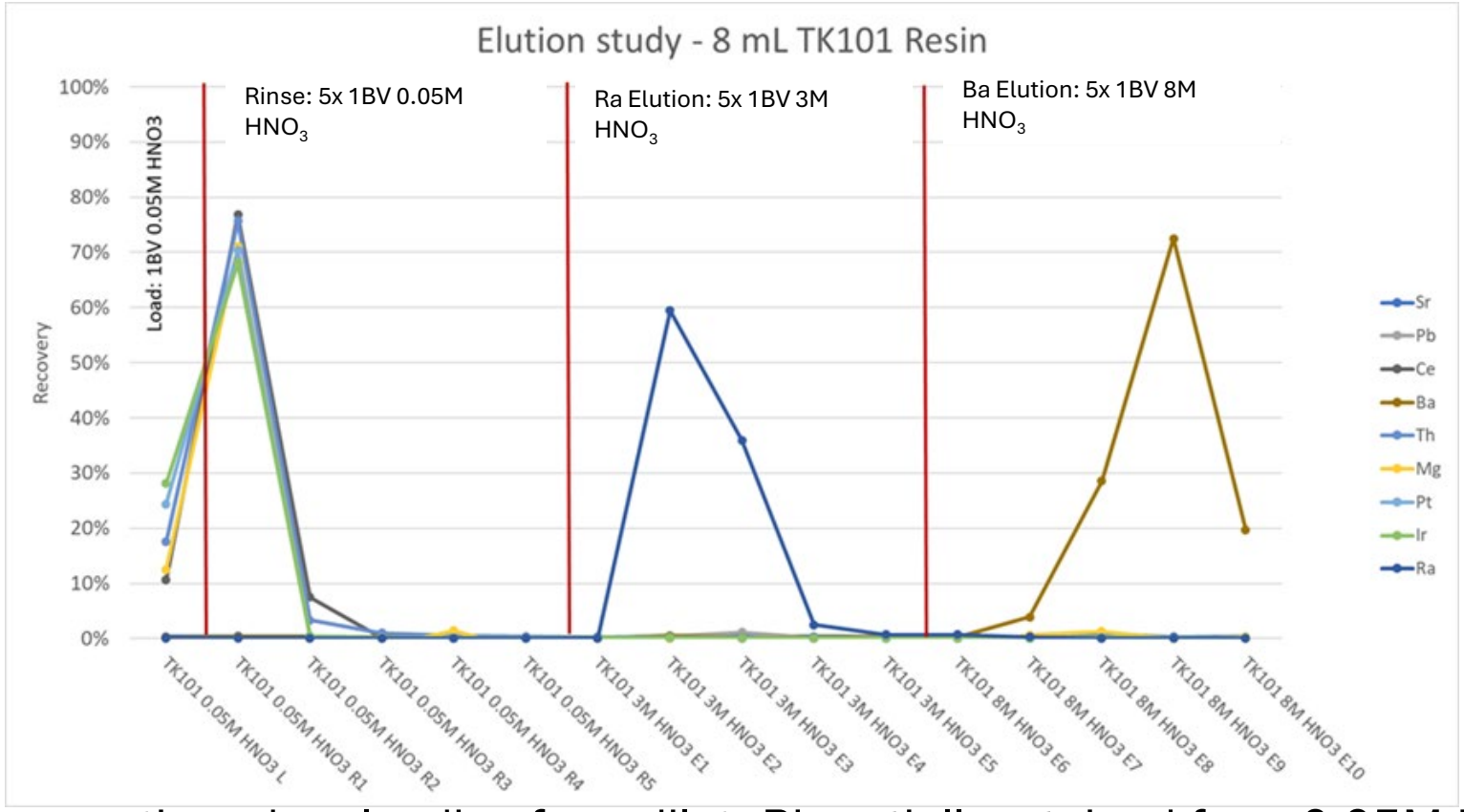
TK101 - Ra



Data provided by Russel et al. (NPL)

- No / extremely low selectivity for Th/U
- Very strong Pb retention => elution in high HCl or citrate

Ra separation on TK101



Good Ra separation when loading from dilute HNO_3/HCl

When eluting Ra in 3M HNO_3, Ba, Pb, Sr remain retained

No retention of U, Th, Pt, Ir,...

Bi partially retained from 0.05M HNO_3/HCl

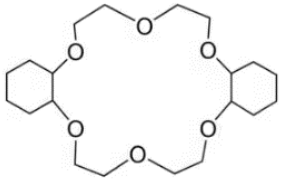
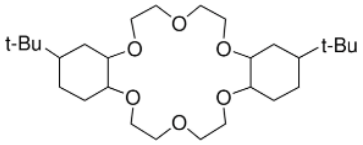
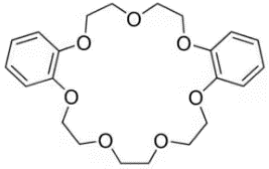
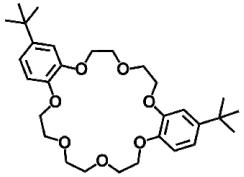
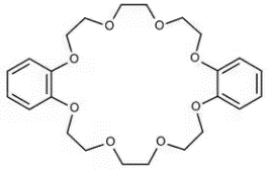
Ra eluted in 3M HNO_3

Further Ba removal via TK102 possible

Tl and Ba eluted in 8M HNO_3

On-going work: test of other crown ethers and diluents

Aim: two resins: a. improved version of TK101 and b. Ra Resin working at elevated acid concentration and elution in dilute acid

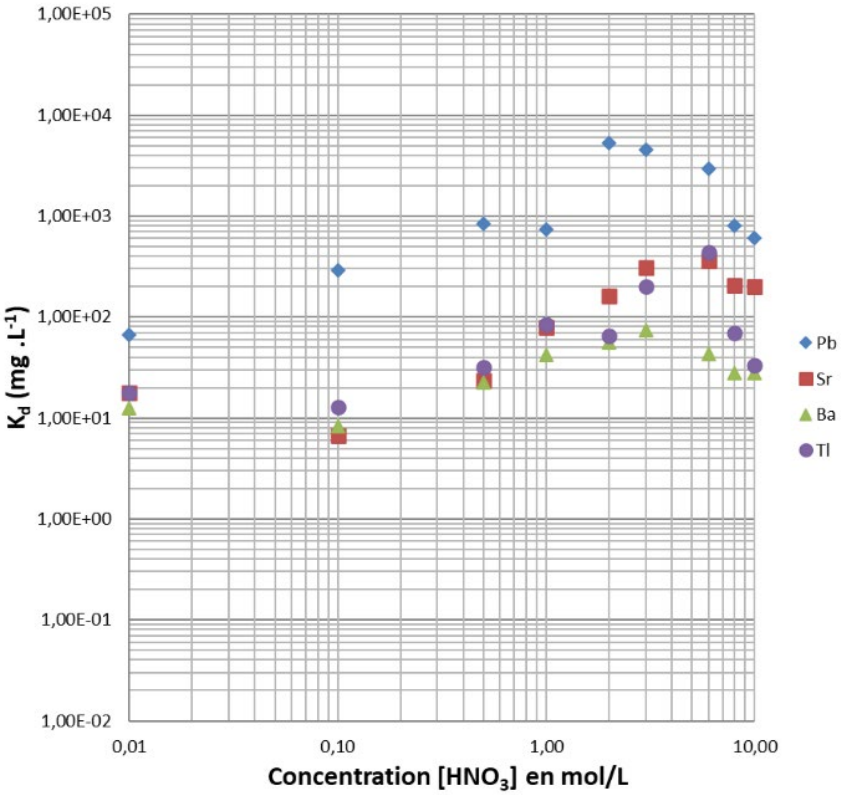
Compound	Name	Abbreviation
	Dicyclohexano-18-crown-6	DCH18C6
	4,4'(4,5')(5,5')-di-tert-butyl-cyclohexano-18-crown-6	DBDCH18C6
	Dibenzo-21-crown-7	DB21C7
	4,4'(4,5')(5,5')-di-tert-butyl-dibenzo-21-crown-7	BDB21C7
	Dibenzo-24-crown-8	DB24C8

Presentation I. Dovhyi at NRC10

TK102 Resin

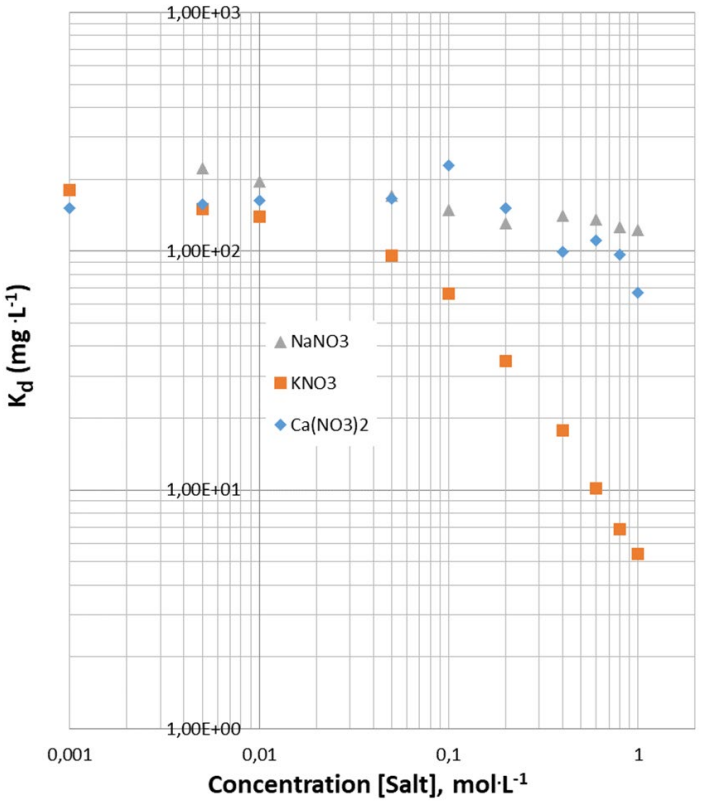
- Modified version of SR Resin
  - Same crown-ether
  - Dliuent, inert support and CE/D ratios => different
  - Higher Sr, Pb and Ba retention than SR Resin
  - **Less bleeding of organic materials**
    - Should lead to better shelf life
- Work by Illarion Dohvyi (Poster during ERA14), Marine Bas, Soumaya Khalfallah, Nora Vajda, Steffen Happel
- Originally optimisation for Ra/Ba separation

TK102 Resin - Determination of Kd values



Distribution coefficients of selected elements on TK102 Resin in HNO_3

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

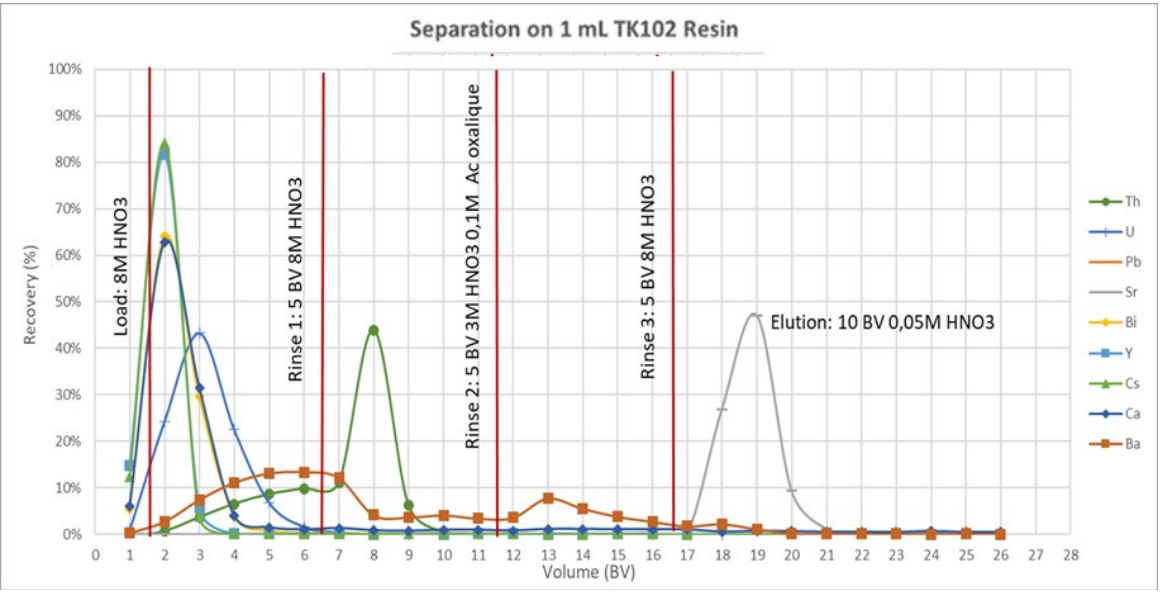


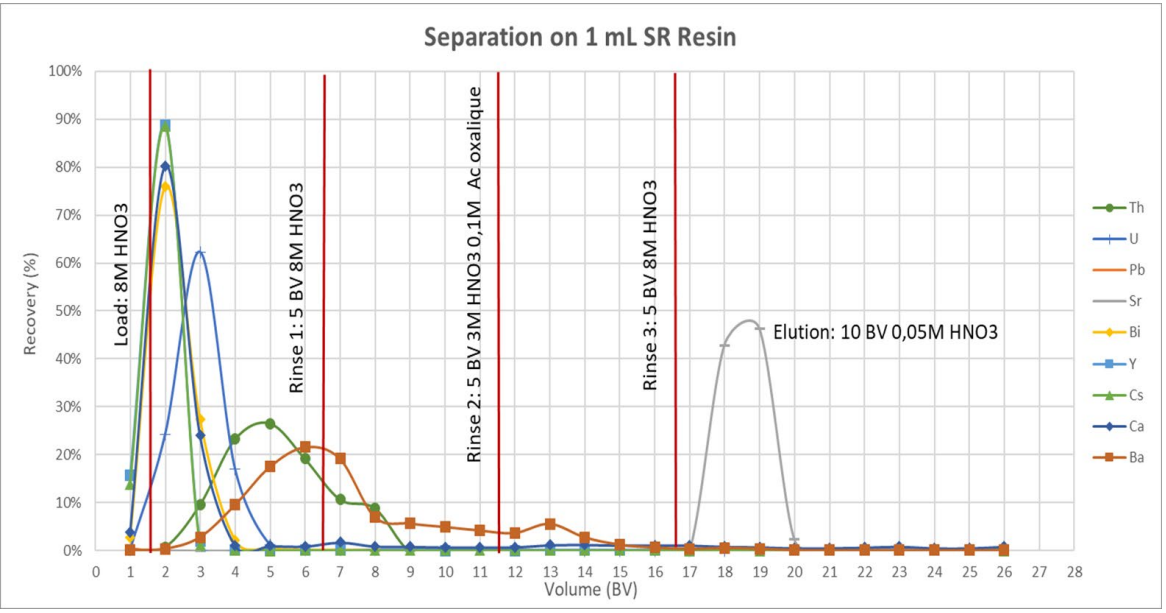
Distribution coefficients of Sr on TK102 Resin in 3 M HNO_3 in the presence of different salts

► 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 – Elution curves comparison vs SR Resin - Sr separation

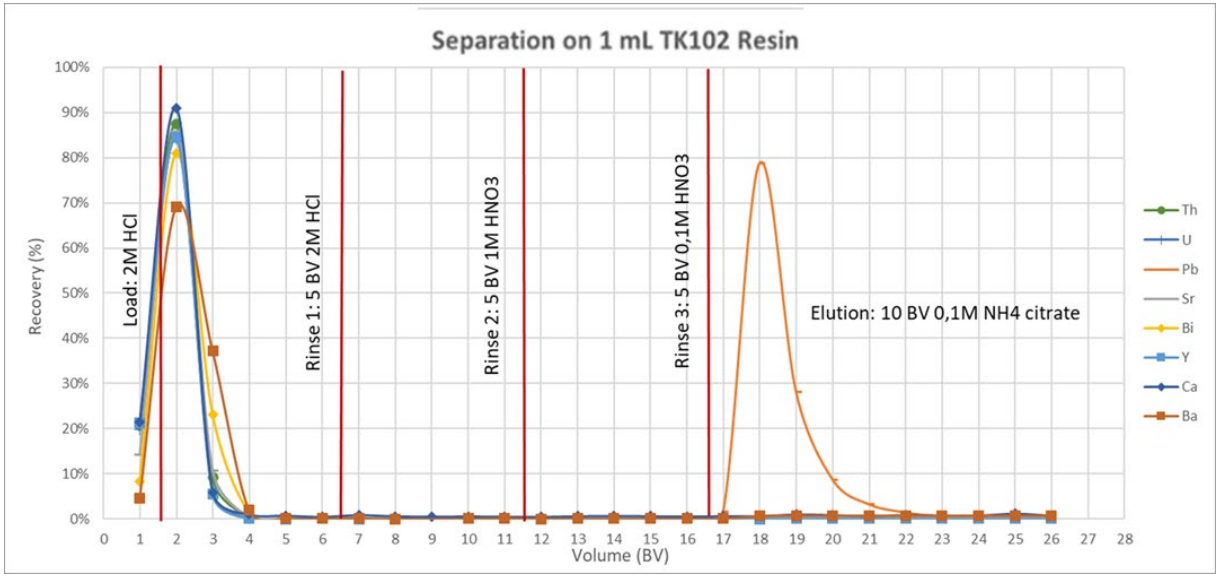


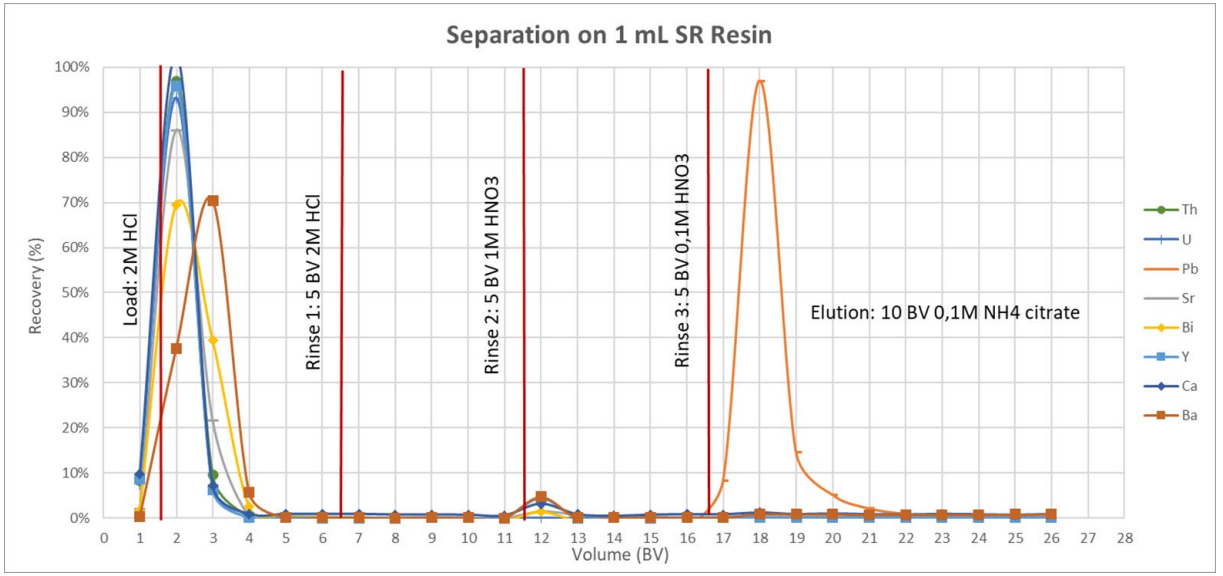


TK102 Resin vs SR resin:
Sr elution study in 8M HNO_3 load medium

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 - Pb separation

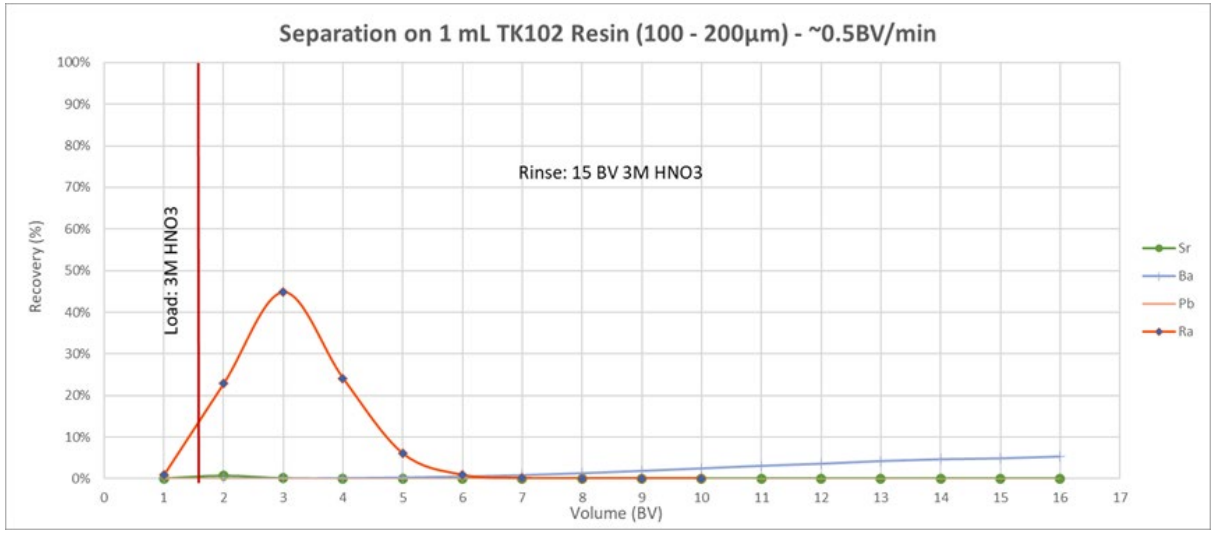


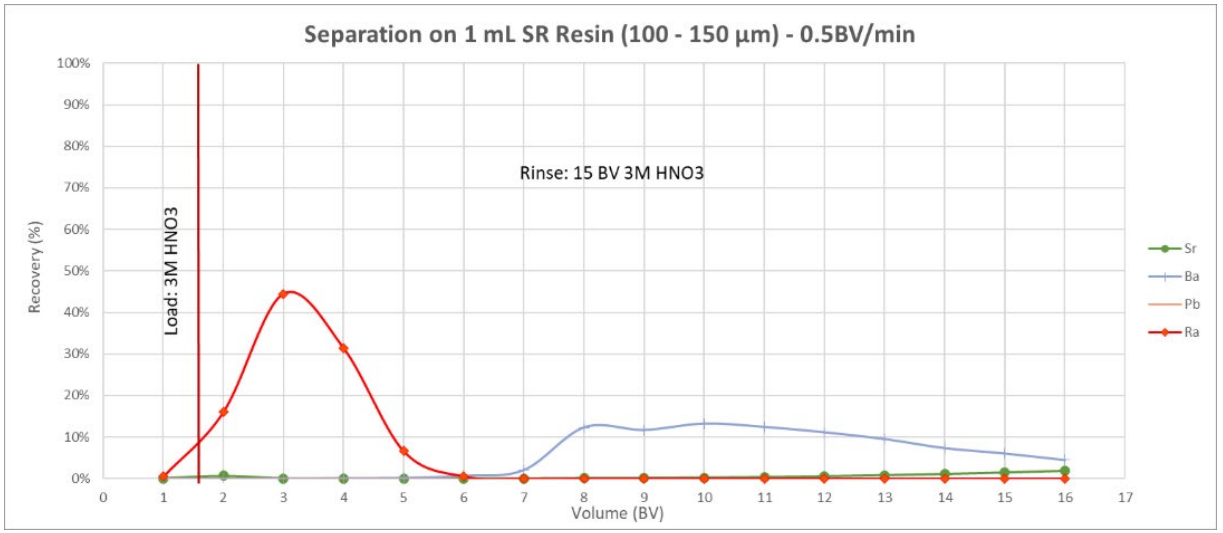


TK102 Resin vs SR resin:
Pb elution study with 2M HCl loading medium

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

Ra/Ba separation





- SR Resin: high Ba breakthrough starts after 7 – 8 bed volumes
- TK102 Resin: significantly lower Ba breakthrough
- Suitable for Ba removal from Ra at 3M HNO_3

Tc-99 separation

Tc-99 (difficult to measure – DTM Radionuclide) – 100% beta emitter

TEVA resin allows for Tc separation but quantitative elution needs highly acidic medium

➢ New resins resins developped for loading from both acidic or alkaline media and elution in slightly alkaline or water

TK201 resin

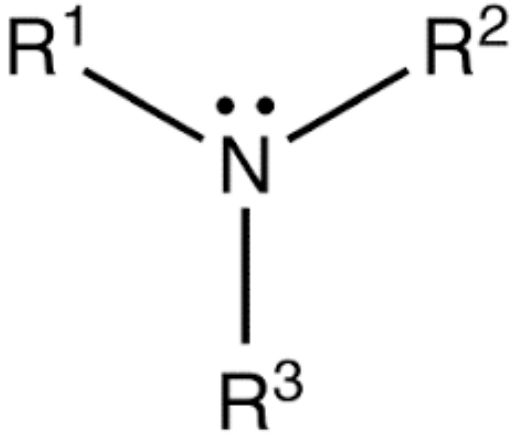
TK202 resin

TK-TcScint

TK201 Resin

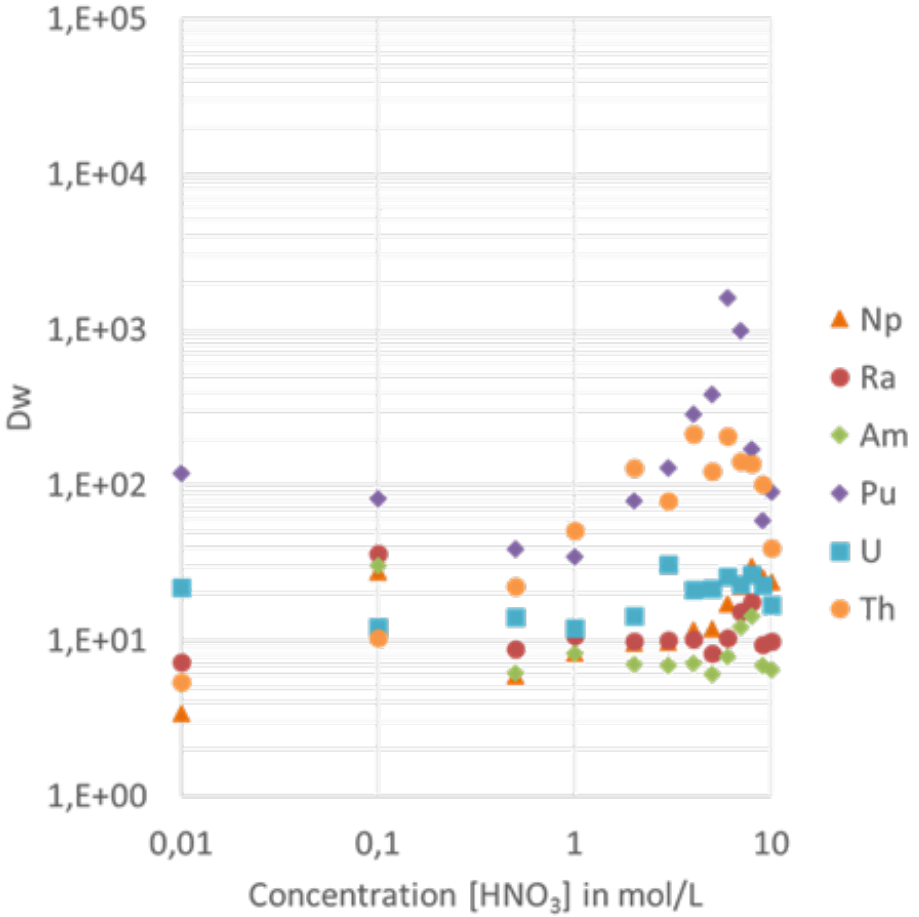
Based on tertiary amine (weak Anion Exchanger) impregnated on inert support

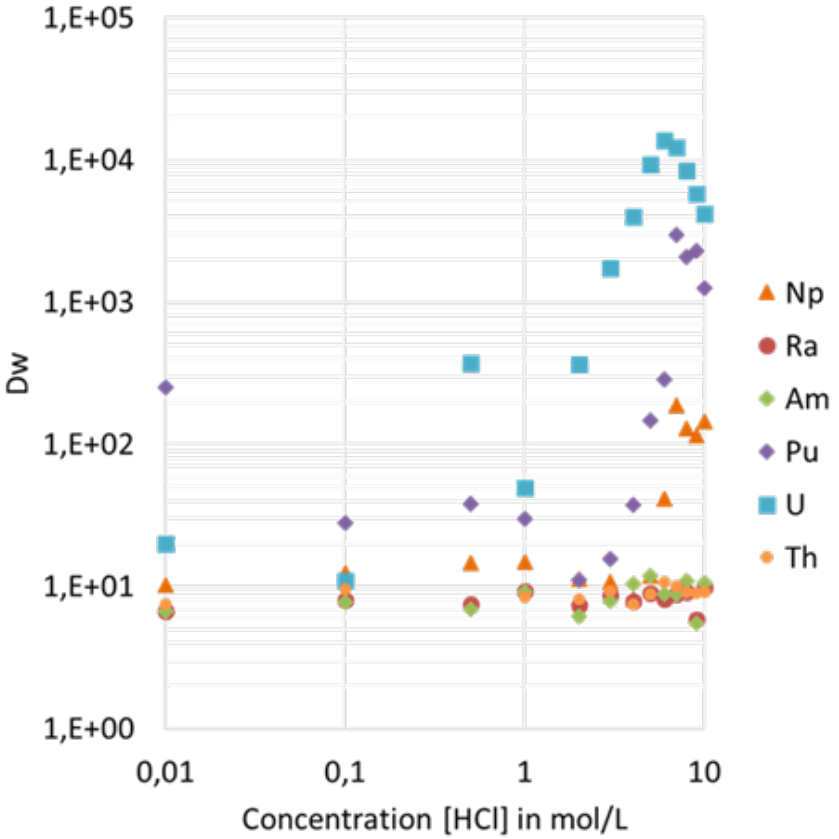
Main applications:



- Tc separation
  - Environmental monitoring
  - Decommissioning
  - Similar selectivity to TEVA but easier to elute
    - Use of NH_4OH or 2M HNO_3
- Cu separation
  - On-going development
  - Radiopharmacy

TK201 – Actinides



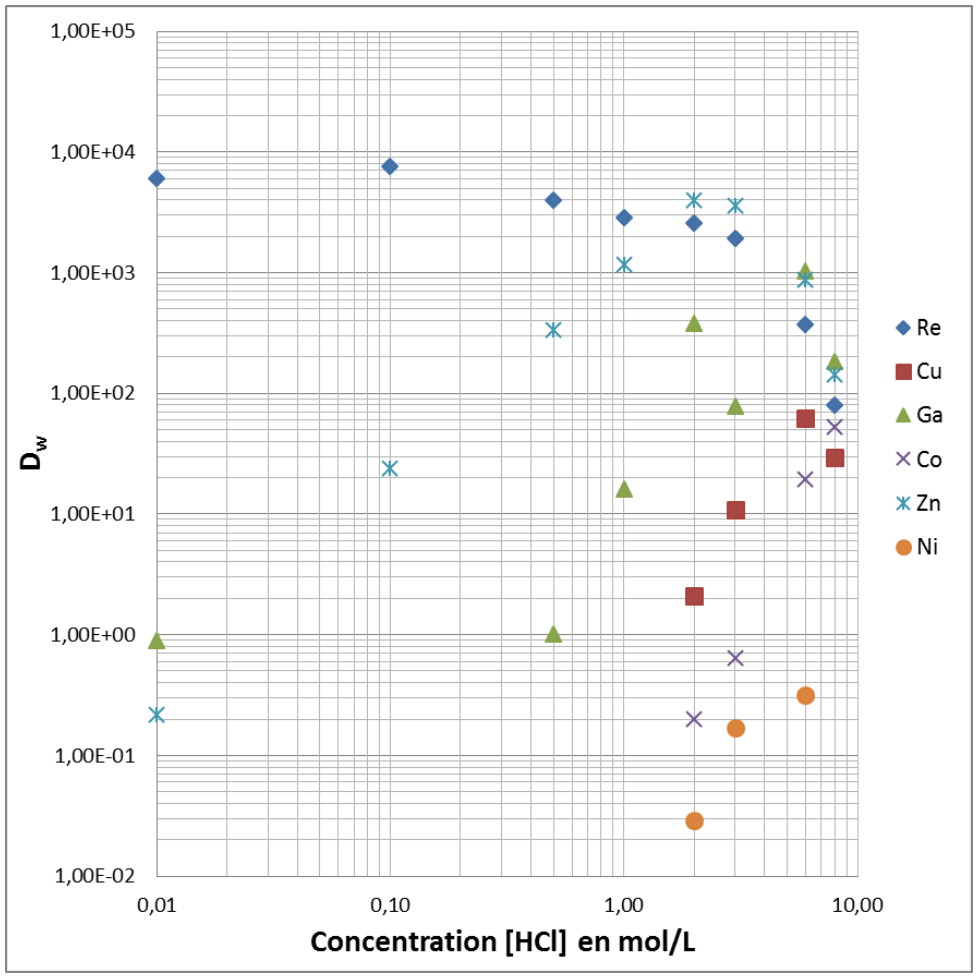


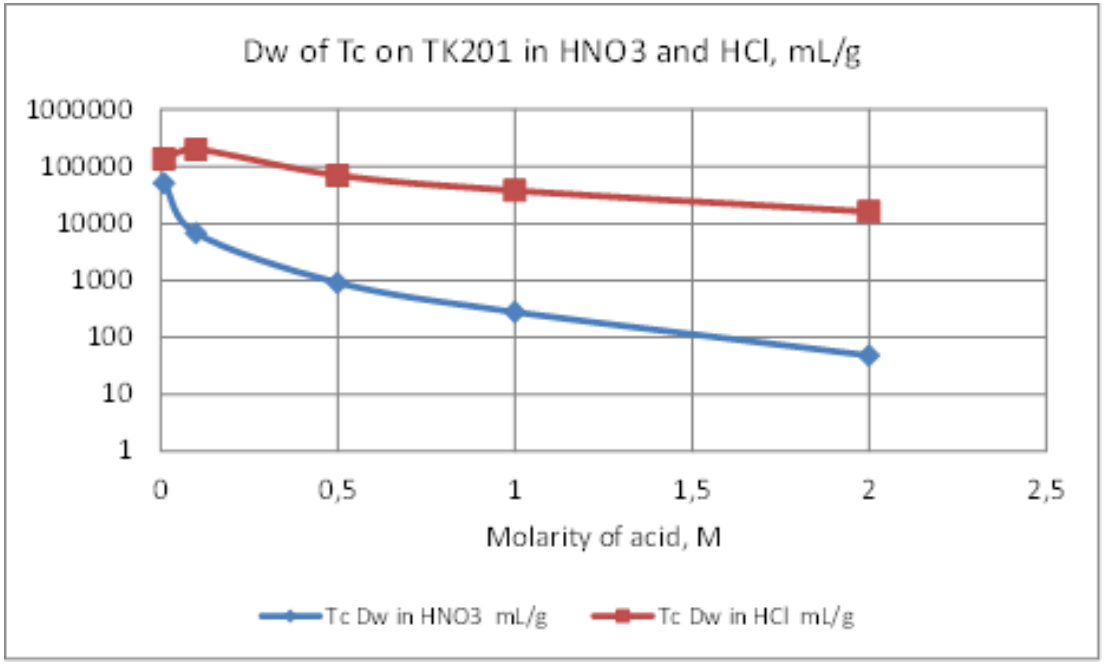
- Re uptake between pH 2 – 5M HCl
- In HNO_3 medium, Re fixed at pH 1-2

- High U and Pu uptake at high HCl
- Elution at low HCl

Data Russel et al. NPL

TK201 – Dw values





Pu well retained at elevated HNO_3

Tc well retained at c(HNO_3) <1M

Tc retention significantly higher in HCl

No Mo retention at > 0.7M HNO_3

TK201 Resin – Elution curve

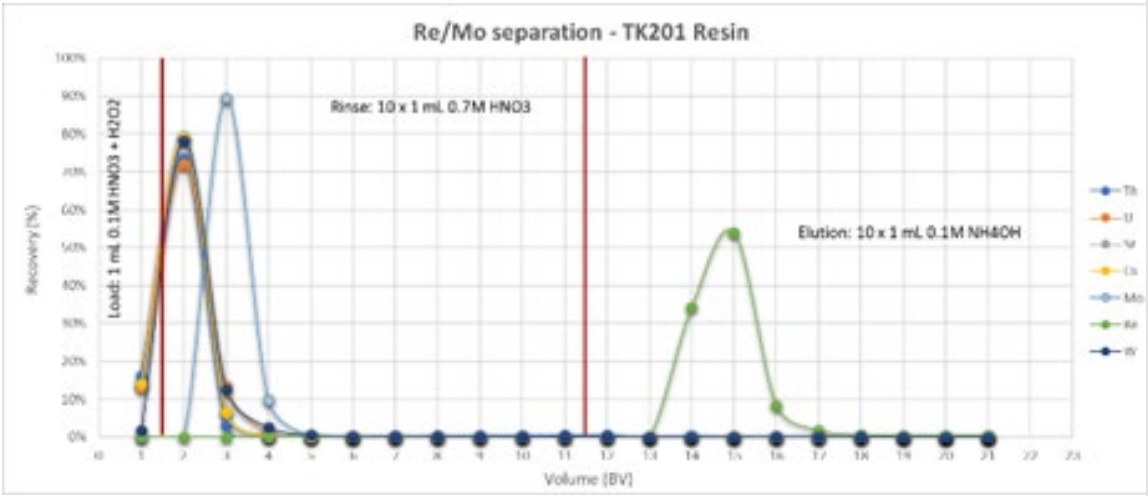
Load of sample at pH 1-2 to retain Re & Tc

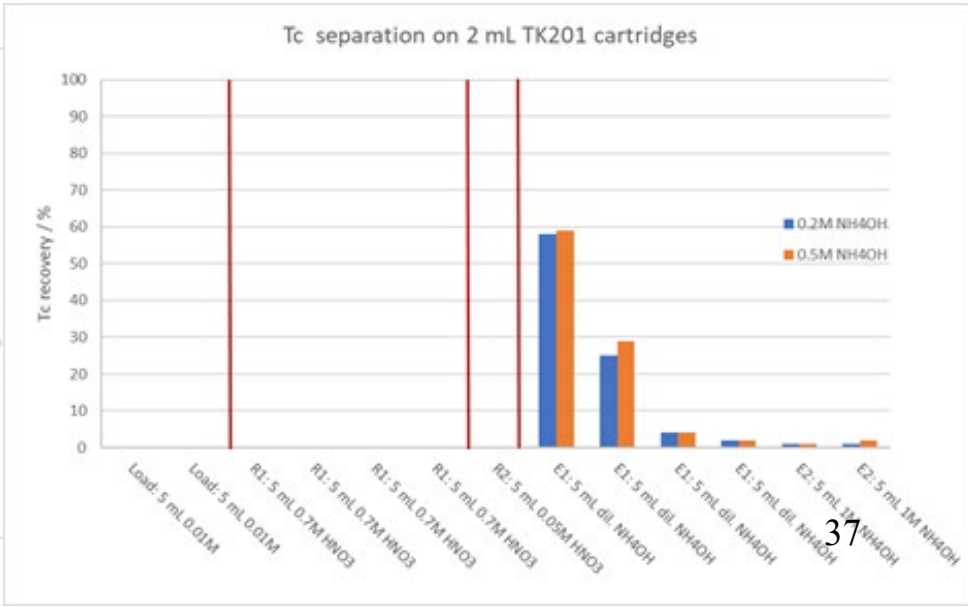
Interferences removed during load/rinse

Mo elution at 0.7M HNO_3

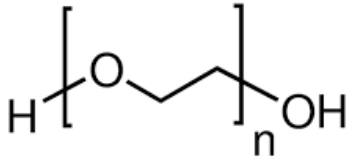
Elution of Re @ ≥1M HNO_3 possible, for Tc >2M HNO_3

Preferable eluton options: ≥ 0.2M NH_4OH





TK202 Resin

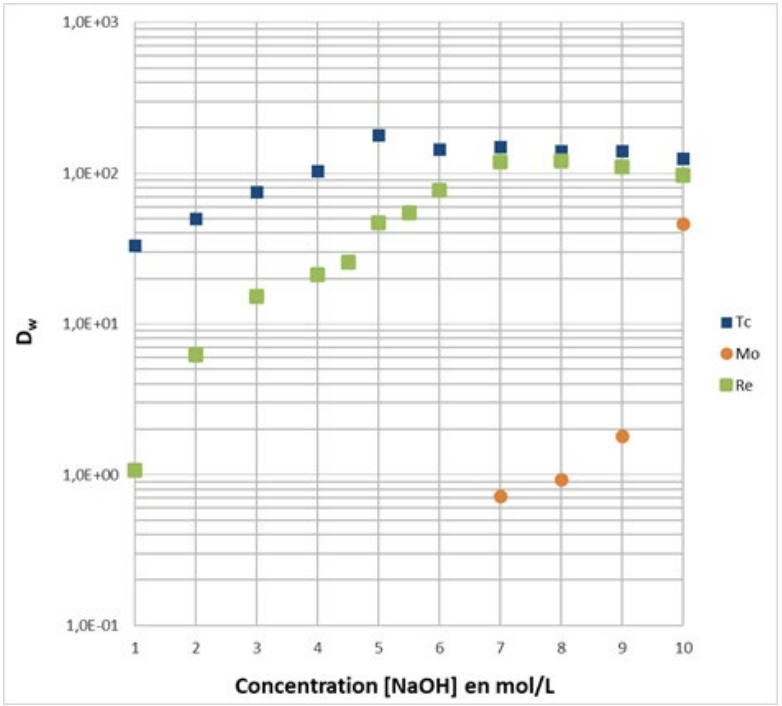


Polyethylene Glycol (PEG) grafted on inert support

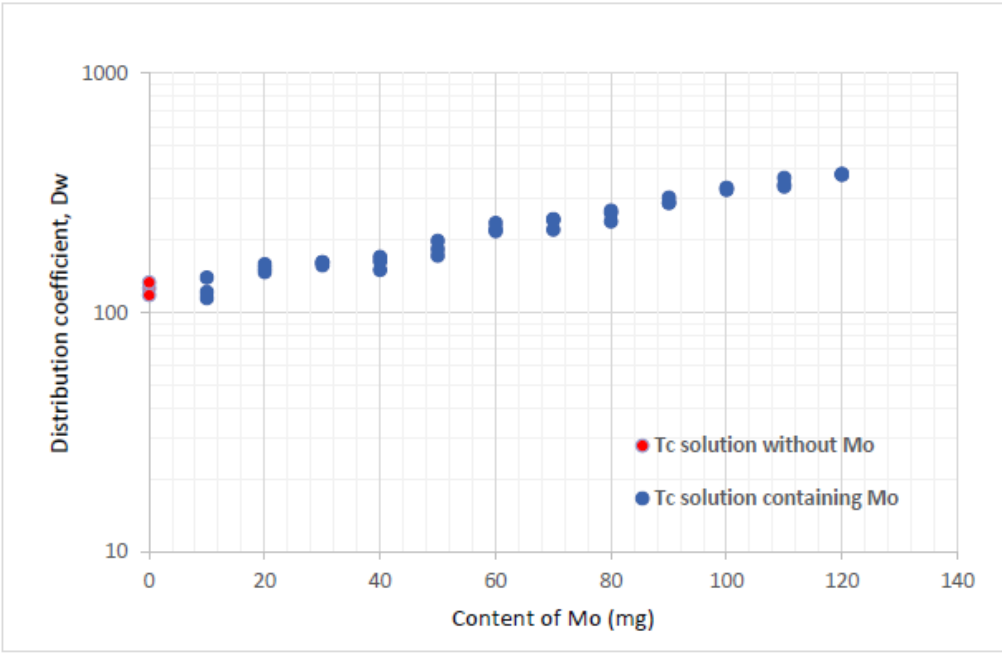
Aqueous biphasic system (ABS)

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



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

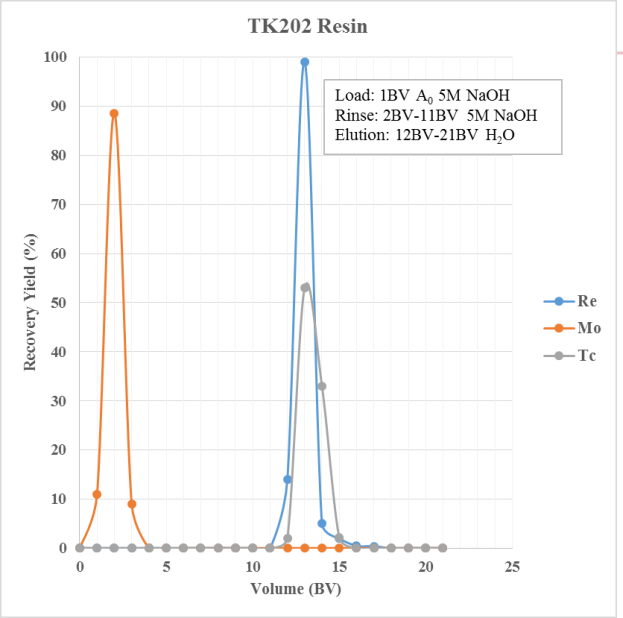
Retention of Tc from concentrated NaOH medium (5 - 7M)

- Alkaline Fusion e.g. decommissioning samples
- Dissolution of Mo target
- Clean separation from other tested elements

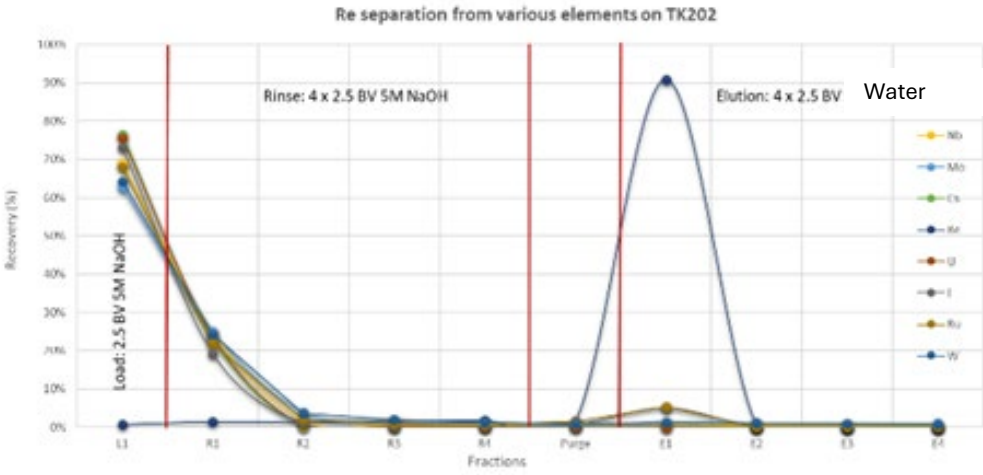
Re can be used as internal standard

Elution in a small volume of water

- Eluat remains alkaline
- Load on CEX to neutralise medium + remove Na^+ THEN
- Load on aluminum oxide to remove last Mo traces + elution in 0.9% NaCl



Re/Tc separation from Mo on TK202 Resin



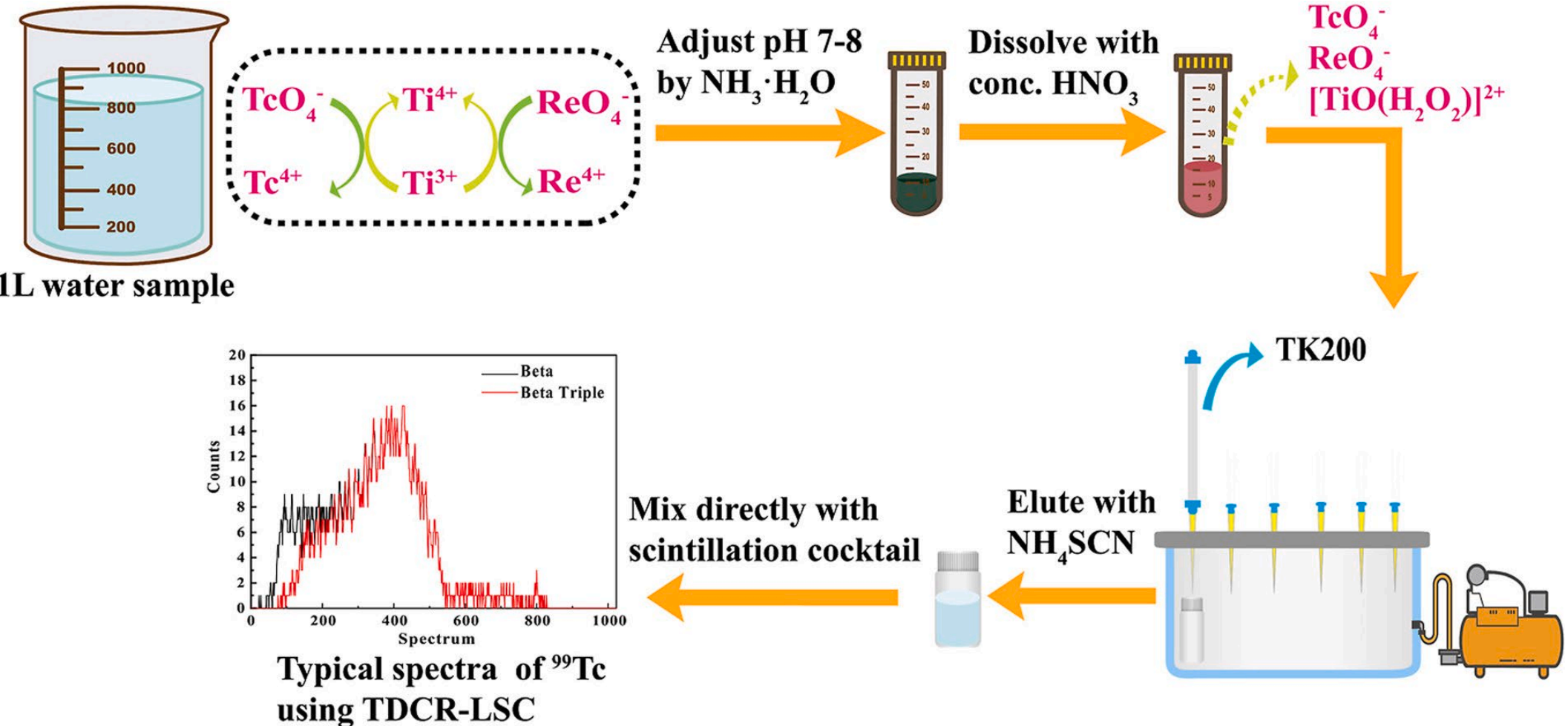
Re separation from selected elements on 2 mL TK202 Resin cartridge, load and rinse at 1 BV/min, elution at 0.25 BV/min.

TK200 Resin

Journal of Environmental Radioactivity
Volumes 251–252, October 2022, 106954

Rapid determination of ^{99}Tc in water samples using $Ti(OH)_3$-TcO_2 co-precipitation and TK200 resin by liquid scintillation counting

Ni Yuan [a], Quan An [a], Shan Xing [a b], Xiongxin Dai [a], Xiaolin Hou [c d], Yonggang Yang [a], Yan Ma [a]



TK200 Resin

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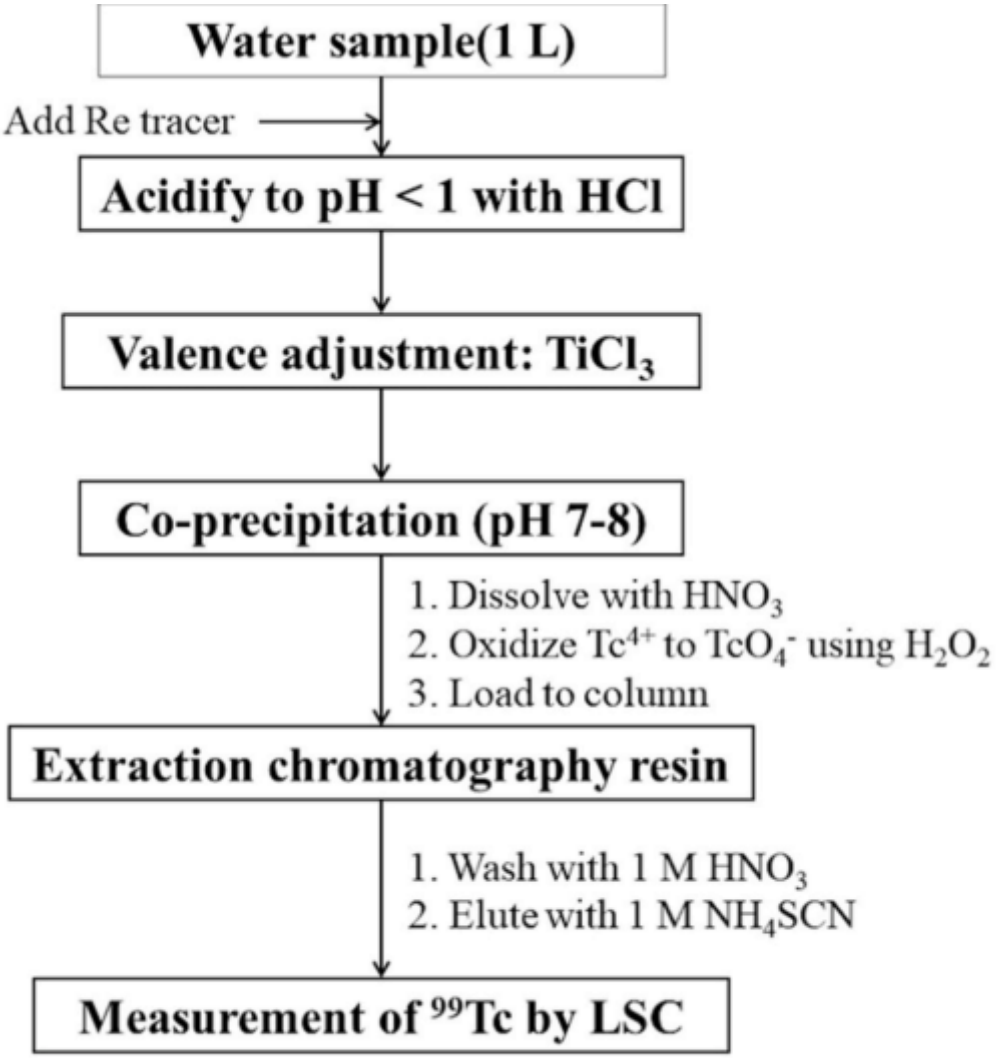
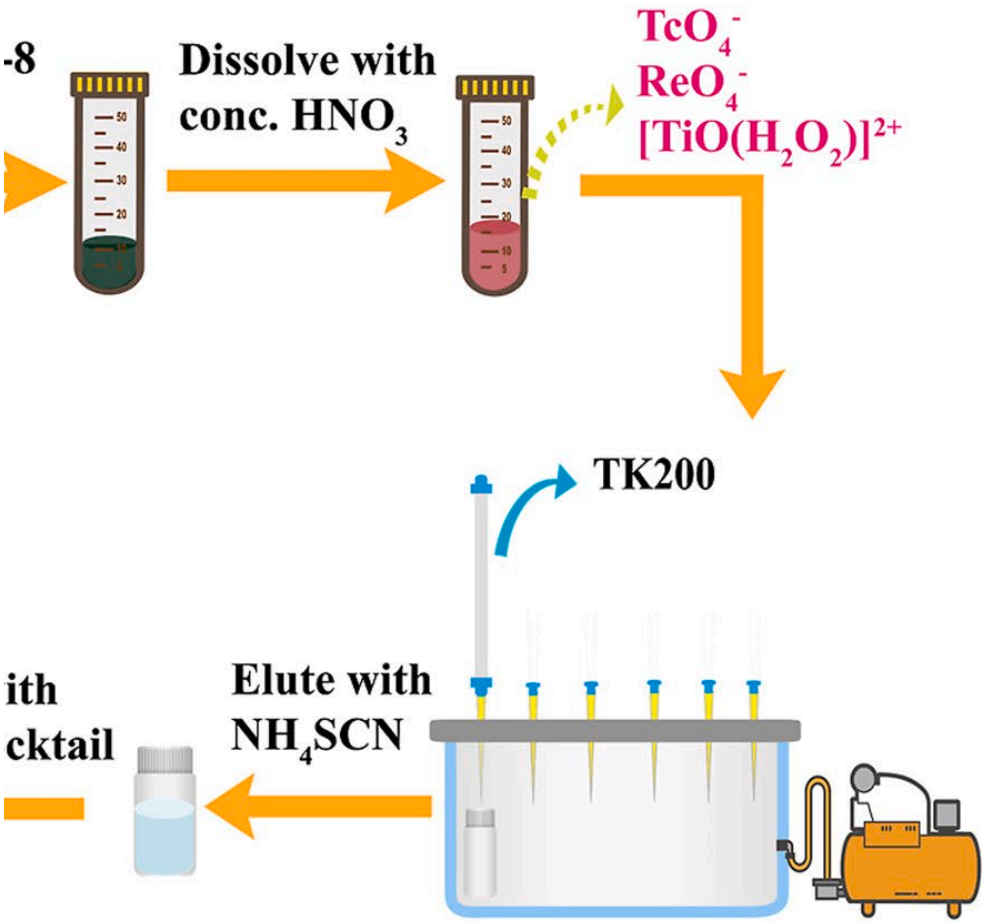


Fig. 1. Schematic diagram of the chemical procedure for separating ^{99}Tc from the water sample.



using TDCR-LSC

TK-TcScint

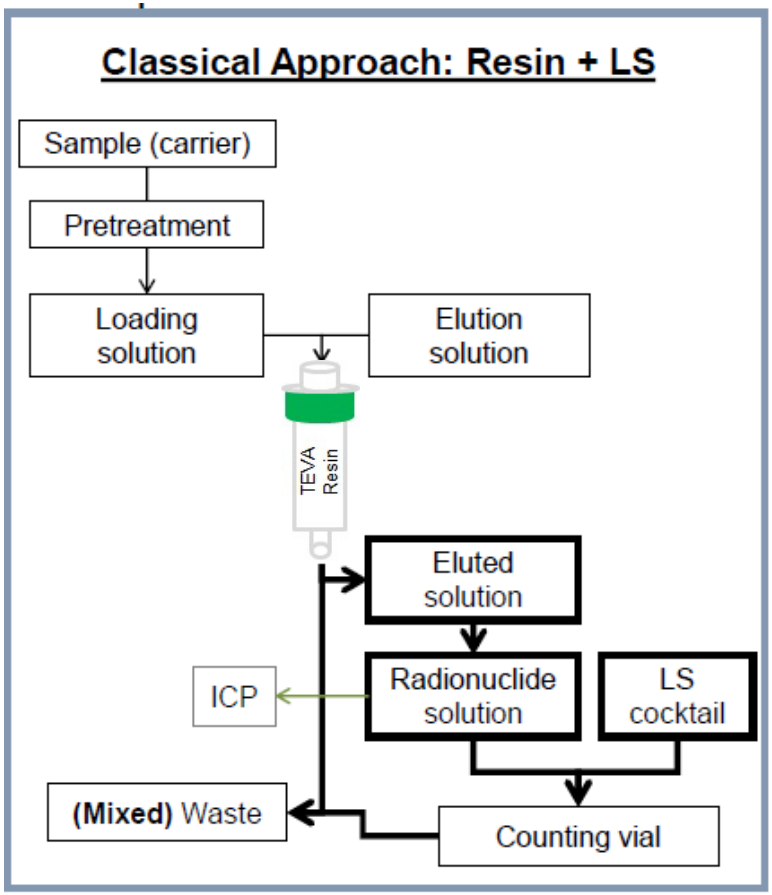
Plastic scintillating beads impregnated with selective extractant

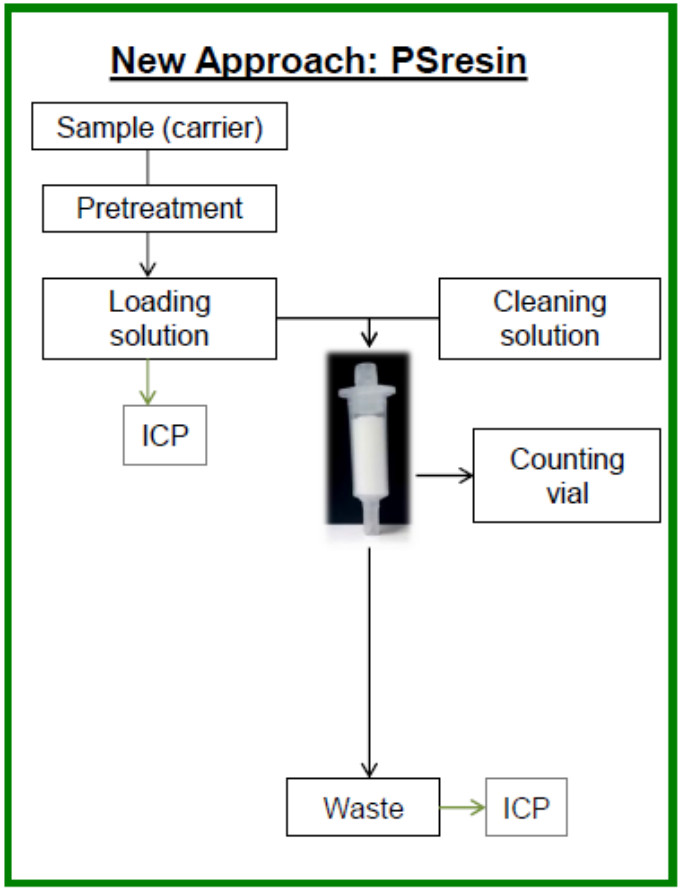
Developped by university of Barcelona

- 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
  - Coming soon: TK-SrScint
    - Sr and Pb
  - More products under development

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.

TK-TcScint

Use of TK-TCScint in aqueous/urine samples for Tc-99 determination (Garcia et al., TKI UGM Cambridge 2018)

MOP:

2ml cartridge using Vacbox

1mg Re carrier

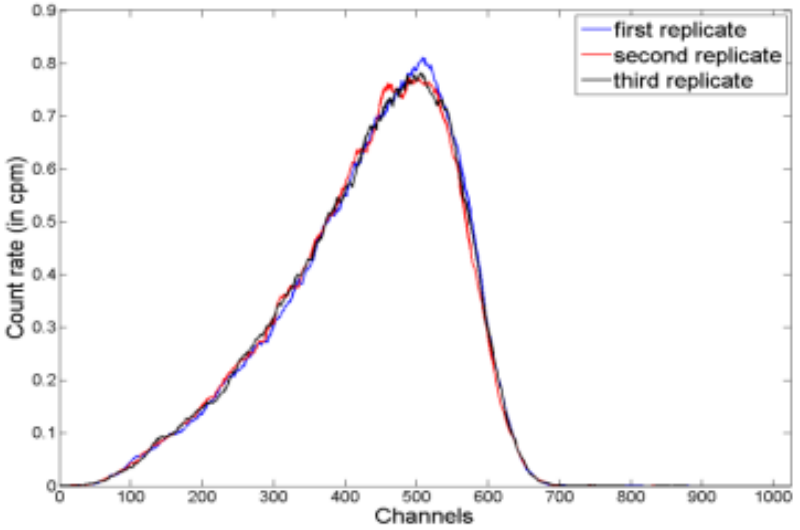
Precondition with 2ml 0.1M HCl

Load 10ml sample in 0.1M HCl

Rinse 4x2ml DI H_2O

Results

Recovery of Rhenium (by ICP-OES)	> 98.8 %
Recovery of ^{99}Tc (by LS):	> 98.8 %
^{99}Tc Detection Efficiency (%):	89.5(0.6)
Background (cpm):	1.09
Quenching Parameter (SQP(E)):	787(7)



Upcoming new product

- After TK-TcScint second product of impregnated Plastic Scintillation microsphere (PSm) line
- Based on SR/TK102 Resin crownether
- Samples available

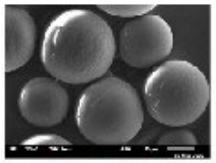
TRISKEM
Expertise in Separation Chemistry

UNIVERSITAT DE BARCELONA

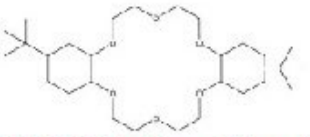
Coming soon: TK-SrScint

Plastic Scintillation microspheres (PSm) impregnated with a selective extractant Developed by Tarancón & Bagán at Universitat de Barcelona

- Based on **SR Resin** crownether and fluorinated alcohol used in TK102 Resin
- Selectivity similar to **SR** and **TK102 Resin**



TK-SrScint Resin



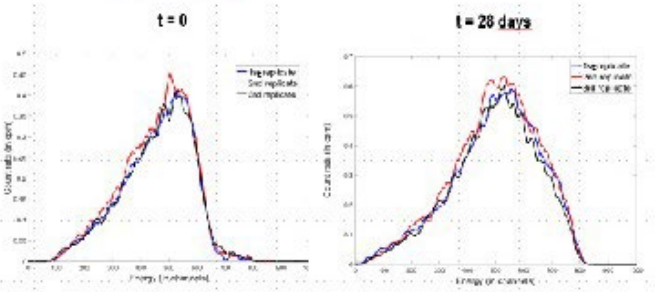
4,4'(5')-di-t-butylcyclohexano-18-crown-6

Available as ready-to-use 2mL cartridges:

- Compatible with vacuum boxes
- Facile automatization

Direct measurement of cartridges :

- No elution/addition of LSC Cocktails
- Detection efficiency:
  - t=0 > 85%*
  - t=28 days > 185%*
- Tested on milk* and river water* samples
- Sr yield ≥ 85%, deviation: < ±10%



Sr-90 spectra on TK-SrScint at t=0 (after Sr-90/Y-90 separation) and after 28 days (Y-90 ingrown), measured on a 300SL (Hidex)

Advantages:

- Less hands-on time
- Faster turn around time
- Less radioactively contaminated waste
- No mixed wastes

Application:

Sr-90 determination in environmental and decommissioning samples

Literature:

- Baudat, E., Gautier, C., Bagán, H. et al. Optimization of a new radiochemical method based on extraction chromatographic resins and plastic scintillation for measurement of 90Sr in nuclear waste. J Radioanal Nucl Chem. https://doi.org/10.1007/s10967-024-09396-8. 2024
- *I. Giménez, J. Rotger, E. Apellániz, H. Bagán, J. Tent, A. Rigol, A. Tarancón. A new method based on selective fluorescent polymers (PSresin) for the analysis of 90Sr in presence of 210Pb in environmental samples. Applied Radiation and Isotopes, Volume 199, 110879. https://doi.org/10.1016/j.apradiso.2023.110879. 2023.
- *Marina Sáez-Muñoz, M.; Bagán, H.; Tarancón, A.; García, J.F.; Ortiz, J.; Carlos, S.; Martorell, S. Rapid methods for radiostrontium determination in aerosol filters and vegetation in emergency situations using PS resin . Journal of Radioanalytical and Nuclear Chemistry, 322:1397-1408. https://doi.org/10.1007/s10967-019-06779-0. 2019.
- Marina Sáez-Muñoz, M.; Bagán, H.; Tarancón, A.; García, J.F.; Ortiz, J.; Martorell, S. Rapid method for radiostrontium determination in milk in emergency situations using PS resin. Journal of Radioanalytical and Nuclear Chemistry. 315, 543–555. 2018
- H. Bagán, A. Tarancón, G. Rauret, J.F. García. Radiostrontium separation and measurement in a single step using plastic scintillators plus selective extractants. Application to aqueous sample analysis. Analytica Chimica Acta, 686, 1-2, 50-56. 2011.

TK400 Resin

Long chained alcohol

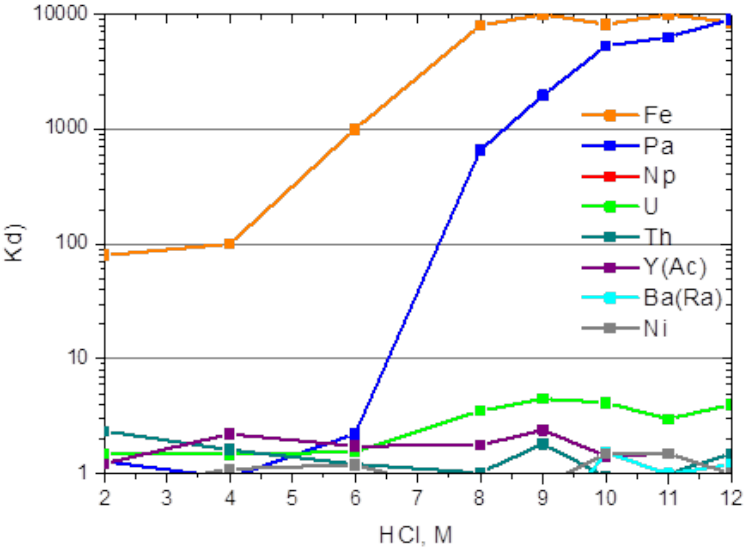
- First work by Knight et al. on Np/Pa separation

Retention only at high HCl concentration (>6M HCl), elution in low HCl, water,…

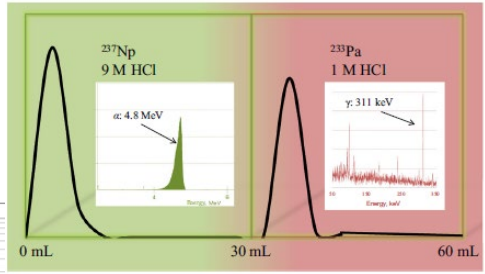
Main application: Pa separation

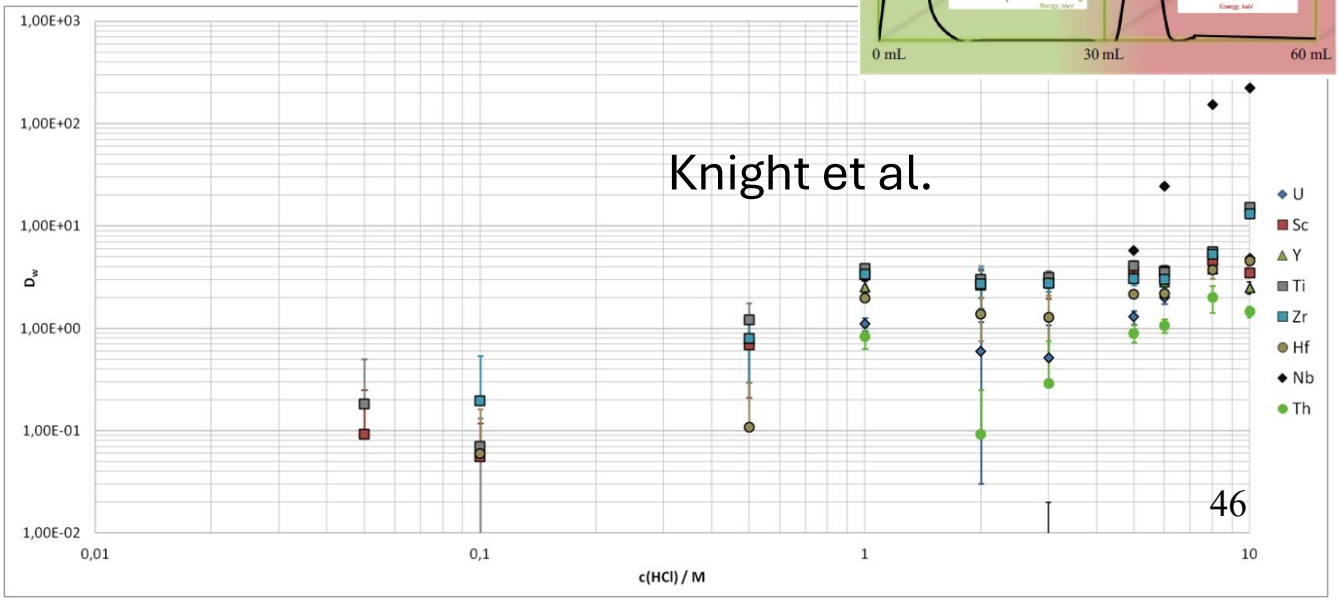
Also retains **Mo, Fe**, Po, Ga, **Nb**,… working on Sb

Higher Fe capacity than e.g. TRU Resin (~15mg Fe/g TK400)



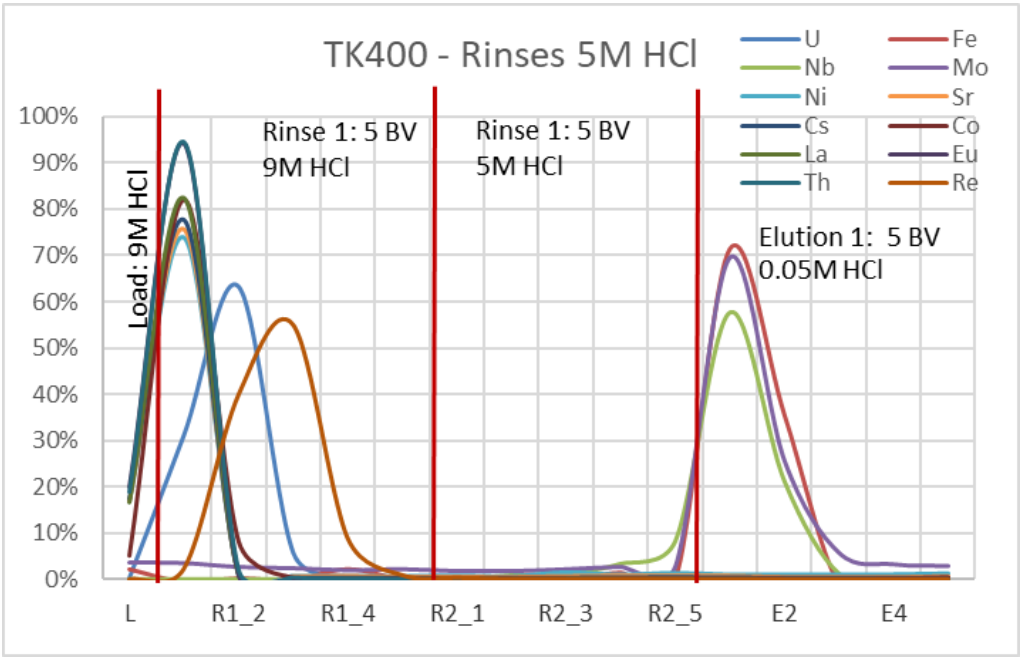
Data provided y B. Russel (NPL)

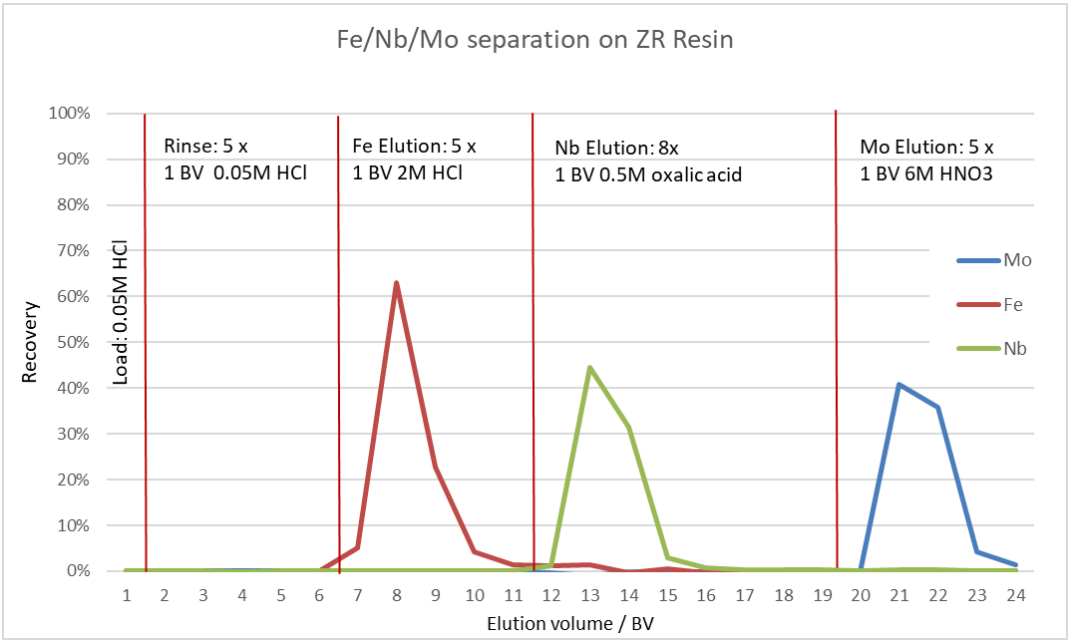




Knight et al.

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

Calixarene based resins for Cs separation

AMP-PAN and KNiFC-PAN well suitable for Cs concentration from aqueous matrices but:

Cs elution difficult, leading to high matrix Cs containing solutions

- Use of NH_4OH, $Sr(OH)_2$ followed by AIX and CEX

Use of calixarene based resins instead

Original work: TK300 Resin

- High Cs/Ba selectivity
- Load from water up to 1M HNO_3
- Interference by K
- Low Cs capacity
- Home made calixarene => upscale too difficult

Calixarene based resins

Aim: two resins

- Separation of Cs and Rb from neutral to weak acid and elution with strong acid
- Separation of Cs and Rb from elevated acid and elution with water or weak acid
- Use of ionic liquids or short-chained alcohols as diluents

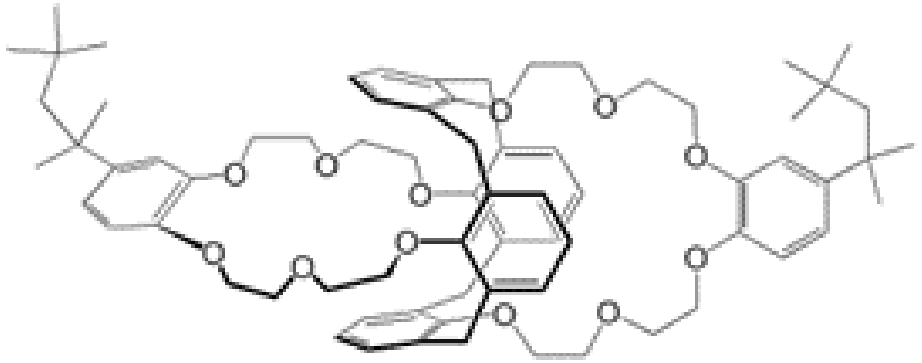
Preparation of 13 test resins (PR) based on commercially available calixarenes

Characterisation of these resins

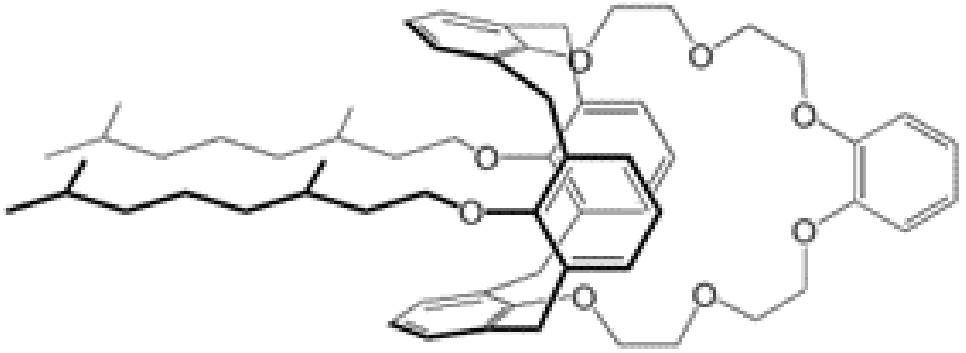
- D_W values of different element on test resins in HNO_3 and HCl
- Influence of interfering ions (like potassium) on Cs separation
- Breakthrough and full capacities
- Elution tests for Rb and Cs separation

Work performed by Illarion Dovhyi, presented at last TKI/Raddec Workshop (18.04.2024) => visit our website for more data

Tested Calixarenes



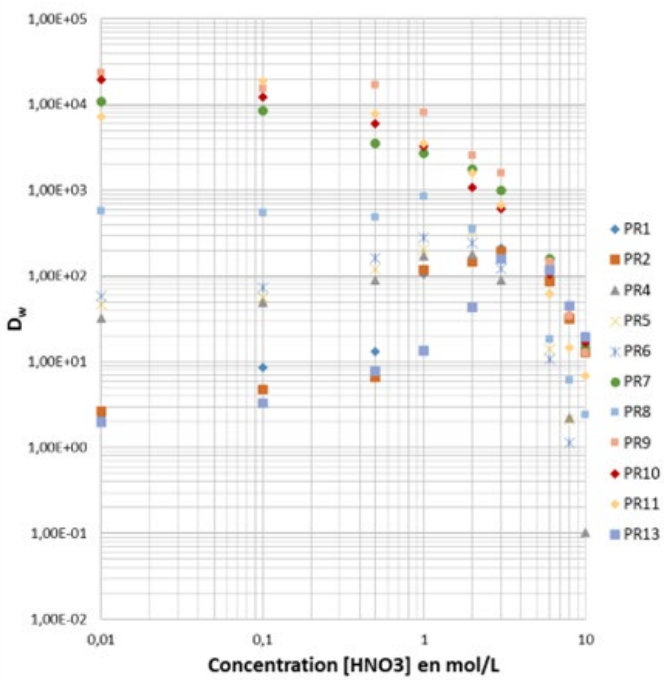
Calix[4]arene-bis(tert-octylbenzocrown-6, $C_{72}H_{92}O_{12}$ (BOBCalix)



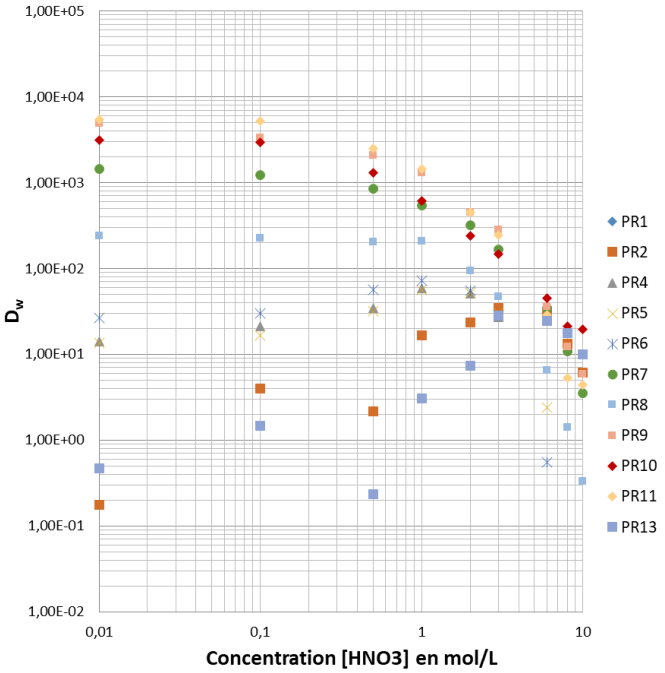
1,3-alt-25,27-Bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6, $C_{62}H_{82}O_8$ (MAXCalix)

Calix[4]arene-bis[4-(2-ethylhexyl)benzo-crown-6], $C_{72}H_{92}O_{12}$ (BEBHCalix)

D_W values of selected cations in HNO_3



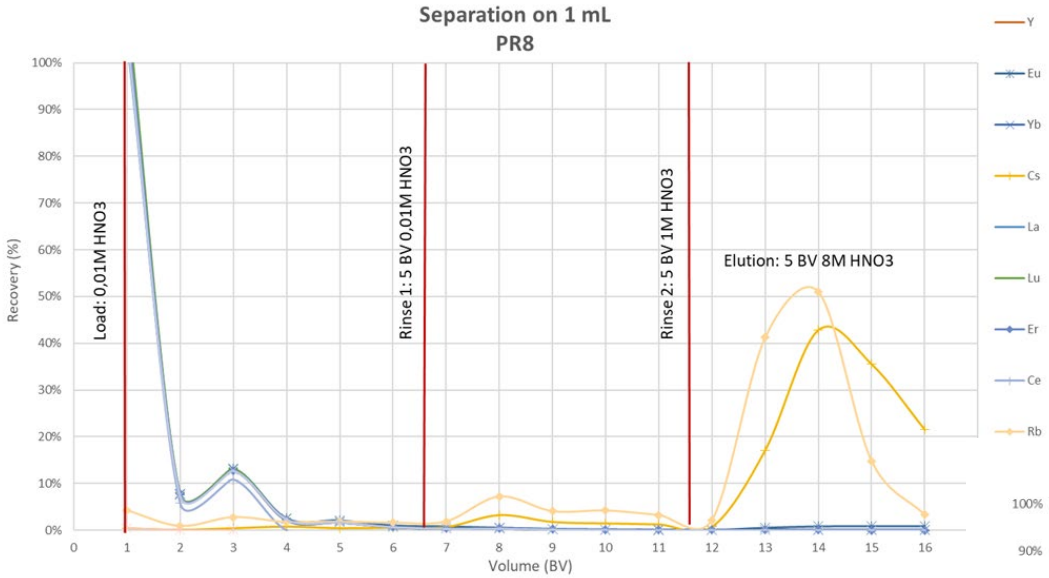
Acid dependency of D_W for Cs^+ on PR1-13 in HNO_3



Acid dependency of D_W for Rb^+ on PR 1-13 in HNO_3

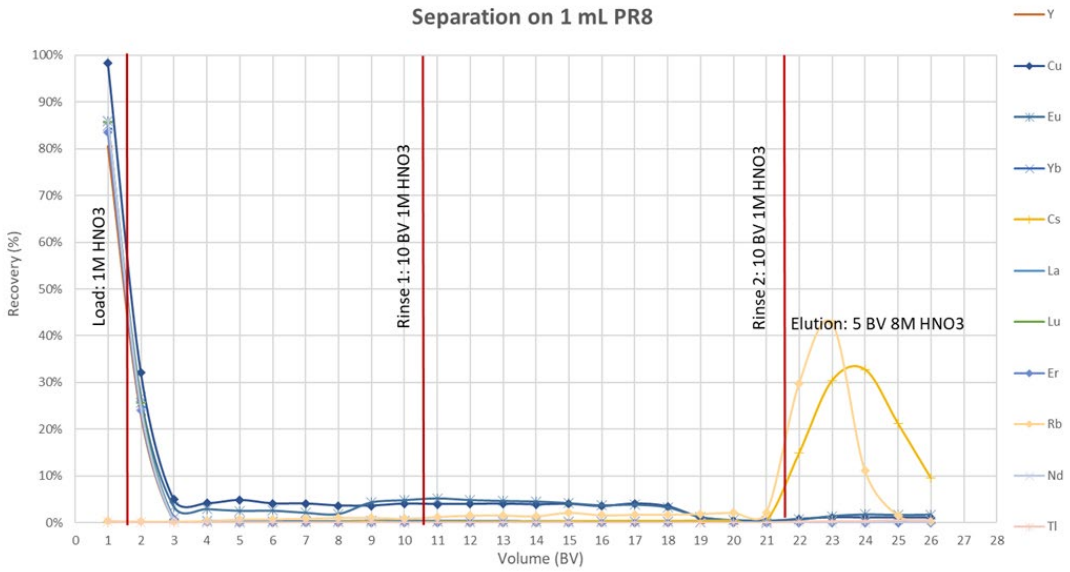
- Generally, D_W Cs > Dw Rb, other elements (Ag, Al, Ba, Bi, Ce, Co, Cu, Er, Eu, Ga, Hf, La, Lu, Mo, Nb, Nd, Ni, Pb, Re, Sb, Sc, Sn, Sr, Th, U, Y, Yb, Zn, Zr) not retained from HNO_3
- Ionic liquid based resins: very high D_W from 0.01M to ≥1M HNO_3
- Other test resins (non IL) low Cs/Rb extraction from low acid, maximum at 2 – 3M HNO_3
- Generally strong decrease of retention at very high HNO_3

Elution tests with selected test resins



Separation of Rb and Cs on PR8 (loading in 0,01 M HNO_3)

- Generally high selectivity for Cs and Rb, interferents well removed
- Cs elution required >5 BV 8M HNO_3



Separation of Rb and Cs on PR8 (loading in 1 M HNO_3 solution)

Under development: range of impregnated membrane filters

Tesmarac
joint research laboratory

On-going work: development of impregnated membrane filters

First filters under beta testing:

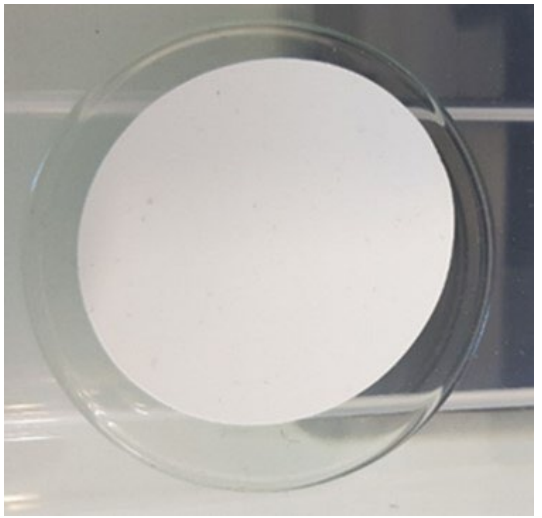
- TK100 (DGT of Sr, Pb, Zn, LN in soil samples)
- TK201 (determination of Tc-99 in aqueous samples)
- CL for iodine,...
- 25mm and 47mm

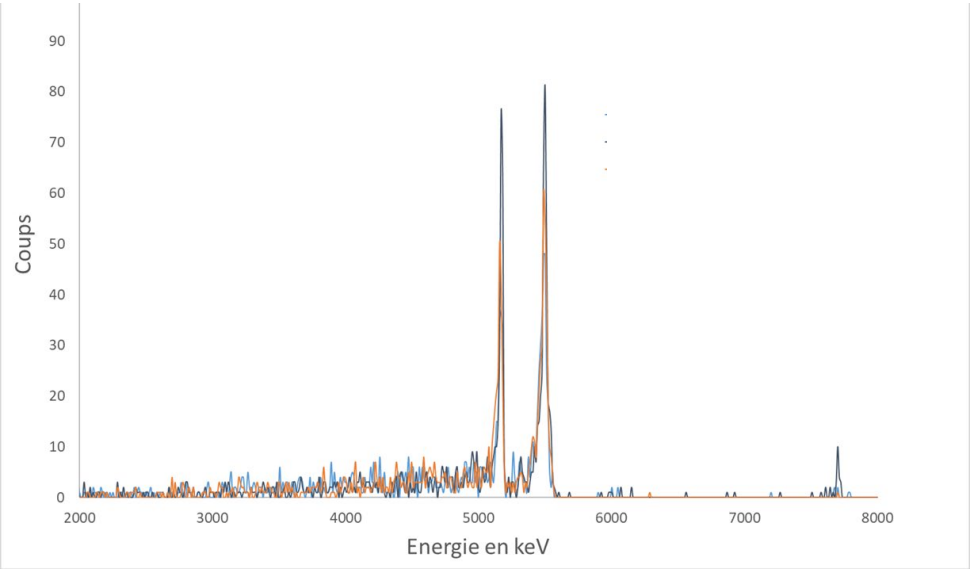
Example: membrane filter for gross alpha measurement

pH 2, 10mL/min, typically 100mL samples

High retention of actinides

Glue on disc => alpha spec





Alpha sprectrum, Am-241 & Pu-239, ~50mBq each

Passive sampling

- TK100 discs
- Wagner et al.
- Passive sampling via DGT (Diffusive Gradiant in Thin films) => ‘bio-availability’
- Published: Sr and Pb isotope ratios in soil samples, Zn also possible
- On-going: Sr-90

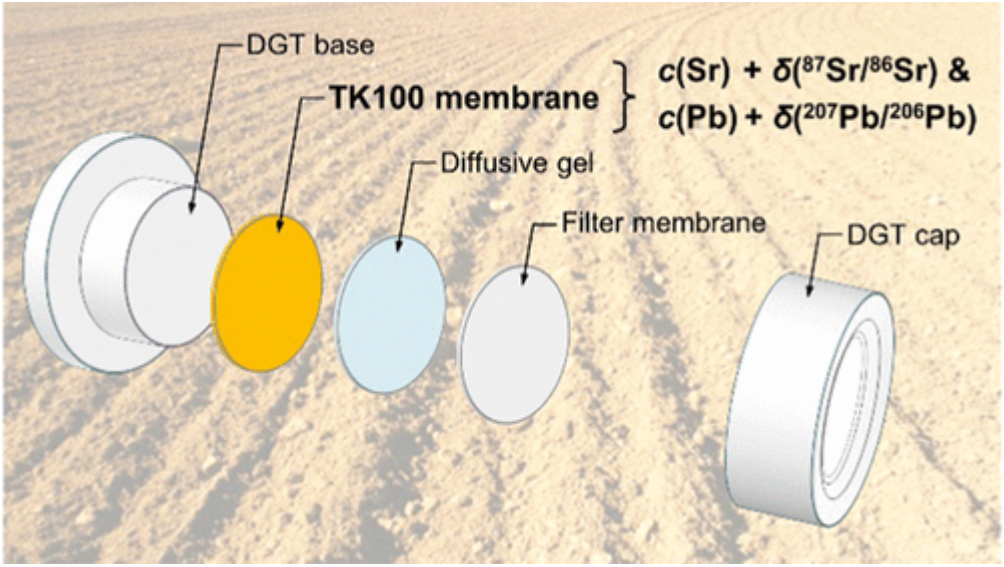
analytical chemistry

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*

Cite This: *Anal. Chem.* 2022, 94, 6338–6346 Read Online

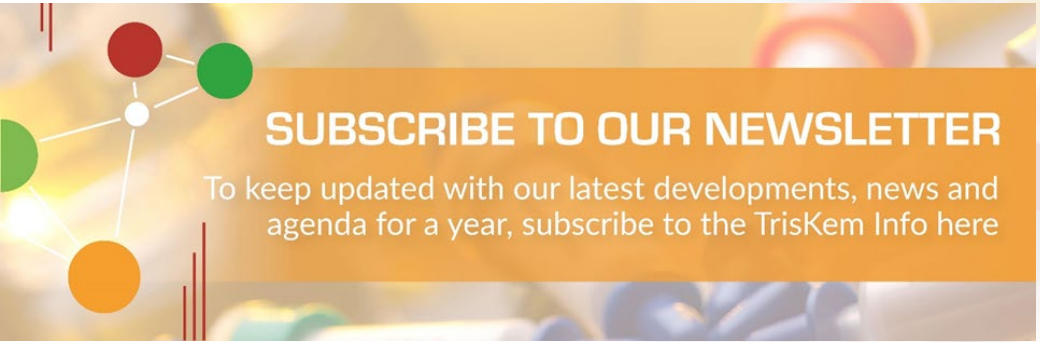


Some other on-going projects

- Rapid tests
  - Impregnated PSm resins
  - Range of 'Test sticks'
    - Suitable impregnated support
    - JCU => rapide isotope ratio analysis by MS (metallomics)
    - NPL
    - Uni Barcelona
- Passive sampling (DGT)
- Separation of DTM
  - SE Resin => Se-79
  - Zr-93, Fe, Mo, Nb,…
- Decontamination
  - PAN based materials (e.g. AMP-PAN)
- Fate' of RN in the environment
  - Separation methods
  - Mainly longer lived RN (=> therapy)
    - Ac-225/7, Lu-177(m), radioiodine,…
  - Quantification
- In-field preconcentration
  - Impregnated membranes
  - Cartridges
- Microfluidics
- Other 'geometries' &

'Non-resin' separation materials

Thank you for your attention!



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