Overview and new Developments Radioanalytics

TKI Workshop

Steffen Happel

11/11/2026

TRISKEM
Expertise in Separation Chemistry

Overview

- News
- Reminders/updates:
  - TK200 Resin
  - TK221 Resin
  - Sr-90 in seawater (TK227)
  - Discs (Impregnated membranes)
  - Decommissioning: TK400 et al.
- Upcoming and ongoing
  - TK103 Resin
  - TK104 Resin
  - TK300 Resin
  - TK430 Resin
  - TK230 Resin
  - TK250 Resin
  - At/Bi separation
- Hydrometallurgy
- Other ongoing research….

Cartridge packing

1mL and 2mL cartridges packed fully automatically

Print/label on cartridge body replaced by laser print on cap

Request to facilitate test ‘bio burden’

Before:



After:



TK Resin naming

There is some reason…

Main domain of application

- TK1NN: Environmental monitoring, bioassay,..
- TK2NN: Radiopharmacy
- TK3NN: Analysis of decommissioning samples and nuclear waste
- TK4NN: Geochemistry
- TK5NN: Hydrometallurgy
- TK6NN: ‘custom resins’

Functional groups:

- TK1**0**0/1/2(/3/4) => Crown-ether
- TK2**2**1/2/5/7 => DGA…
- TK2**1**1/2/3 => « organophosphor » acid mixtures

Extension

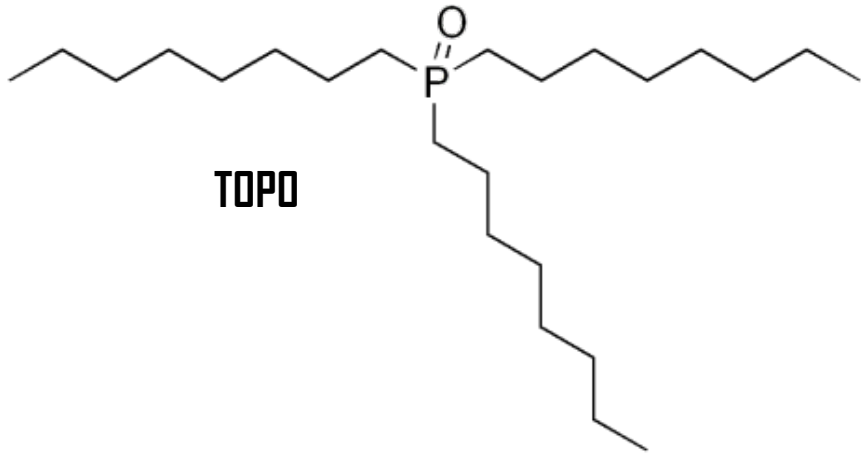






Additional lab space for R&D, QC and production

Reminder: TK200 Resin



TOPO

Based on TOPO extractant

High retention of actinides

Applications:

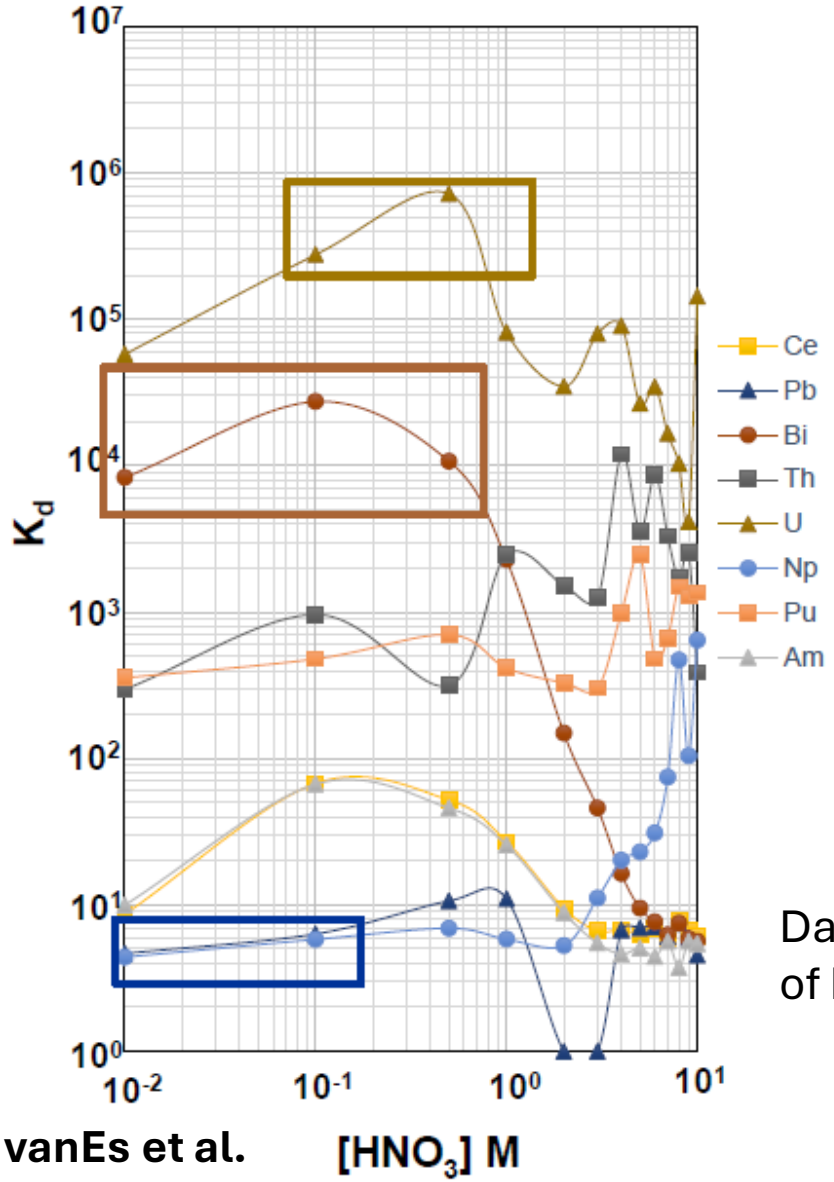
- Use for very efficient U removal from Pu
- Determination of Tc-99 in water samples
- Ga-68 production (in combination with ZR Resin or TK400 Resin)
- Actinide separation from water samples

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

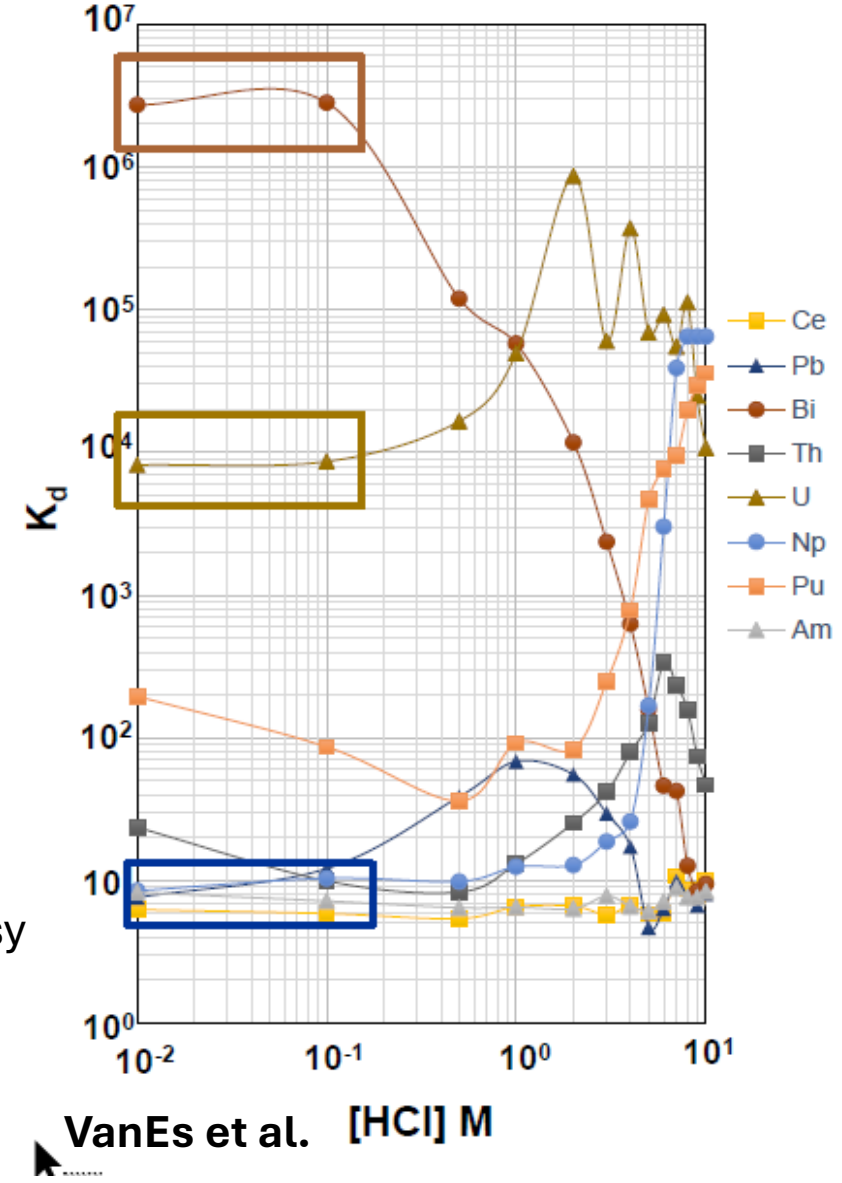
- Preconcentration and purification of selected actinides on same column
- ‘In the field’?

Actinides on TK200

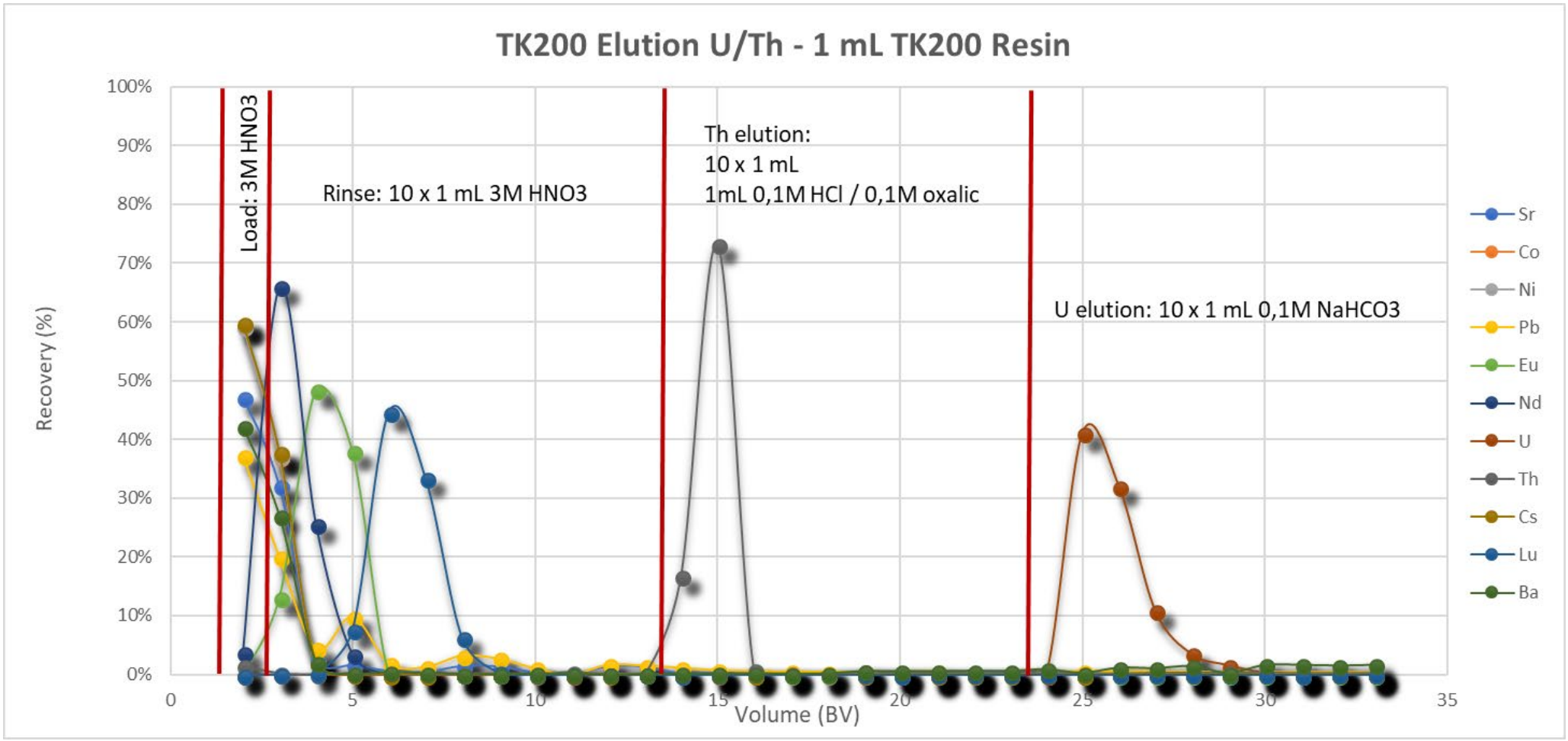
(all data Van Es et al.)



Data courtesy of NPL



U/Th separation on TK200



Load: 3M HNO_3 or ≥ 1L pH2 (HNO_3)

Very clean U/Th separation => at high Th amounts (hundreds of µg) Th elution with oxalate incomplete

Oxalate (pH 9 – 10) instead of carbonate for U elution possible

TK200 Resin - U/Pu separation

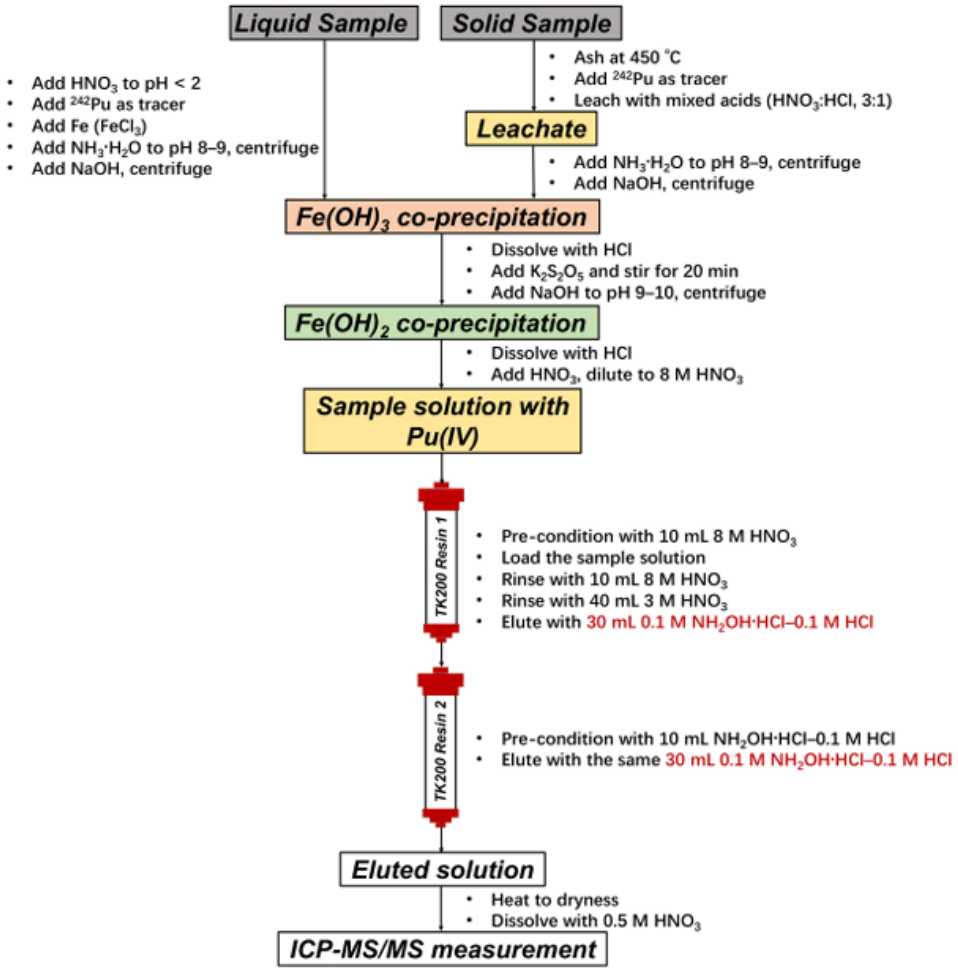


Figure S1. Analytical procedure for determination of plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu)

Recent publication by Huang et al.

U and Pu retained, Pu eluted as Pu(III)

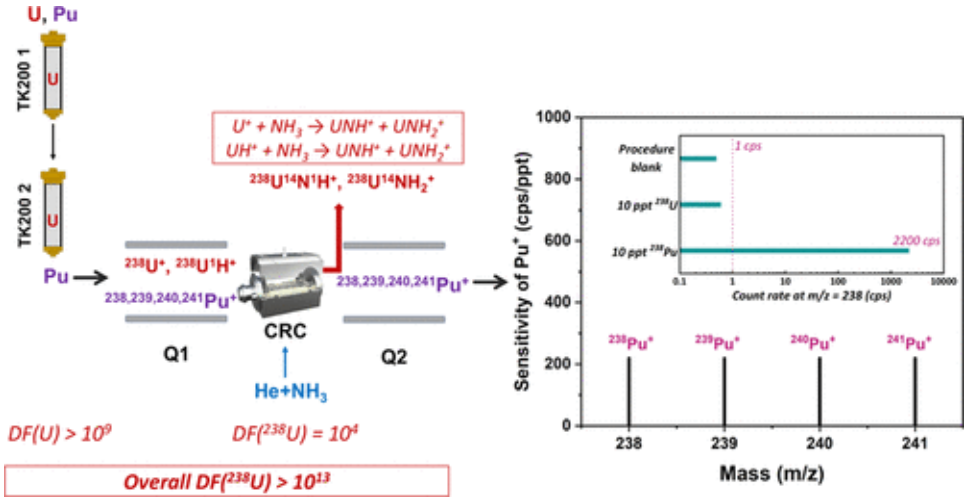
2nd TK200 U removal only

U removal via 2x TK200: **$D_f(U) > 10^9$**

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

TK200 Resin: new applications

ELSEVIER

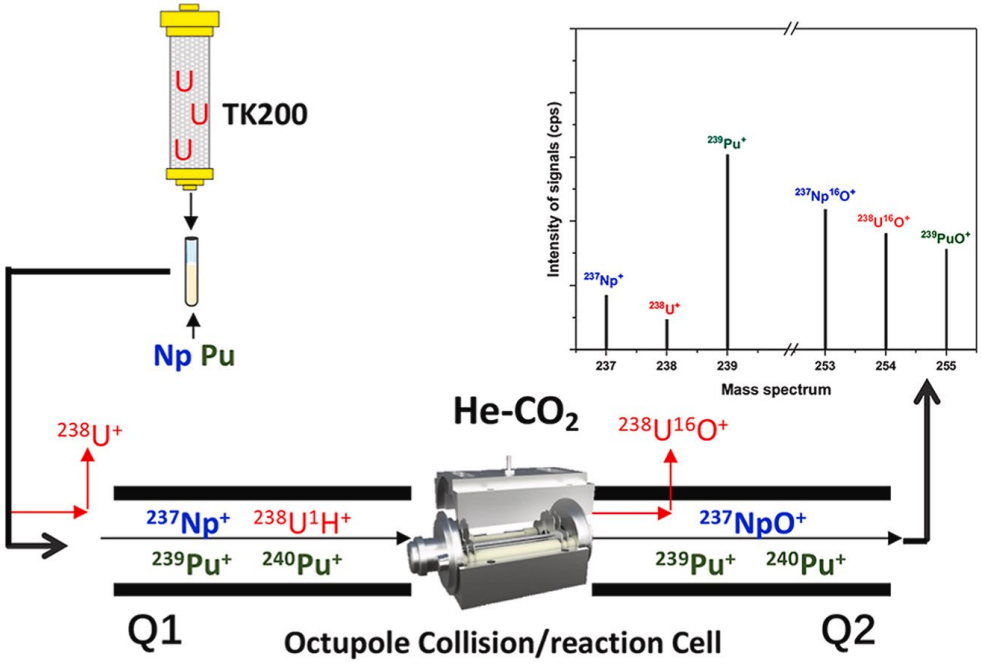
Talanta

Volume 265, 1 December 2023, 124798



Simultaneous determination of femtogram levels of ^{237}Np, ^{239}Pu, and ^{240}Pu in environmental solid samples using extraction chromatography and ICP-MS/MS

Zhao Huang [a b d], Xiaolin Hou [a b c] ✉, Jixin Qiao [a], Xue Zhao [b c e]



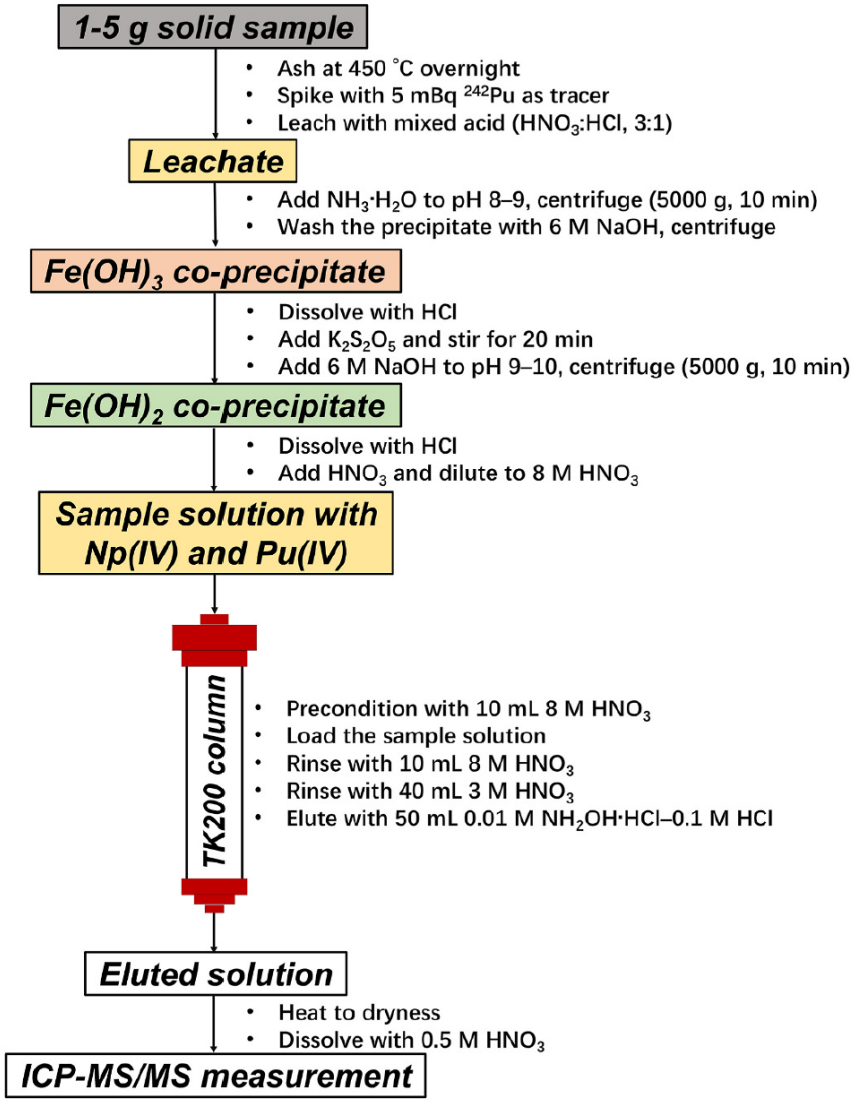


Fig. 1. Sample pretreatment procedure and optimized conditions for the simultaneous separation of Np and Pu.

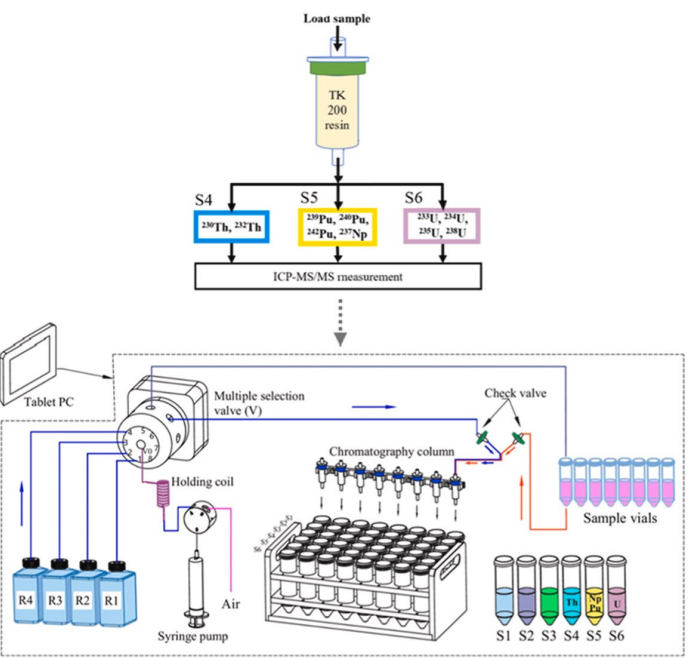
TK200 Resin: new applications

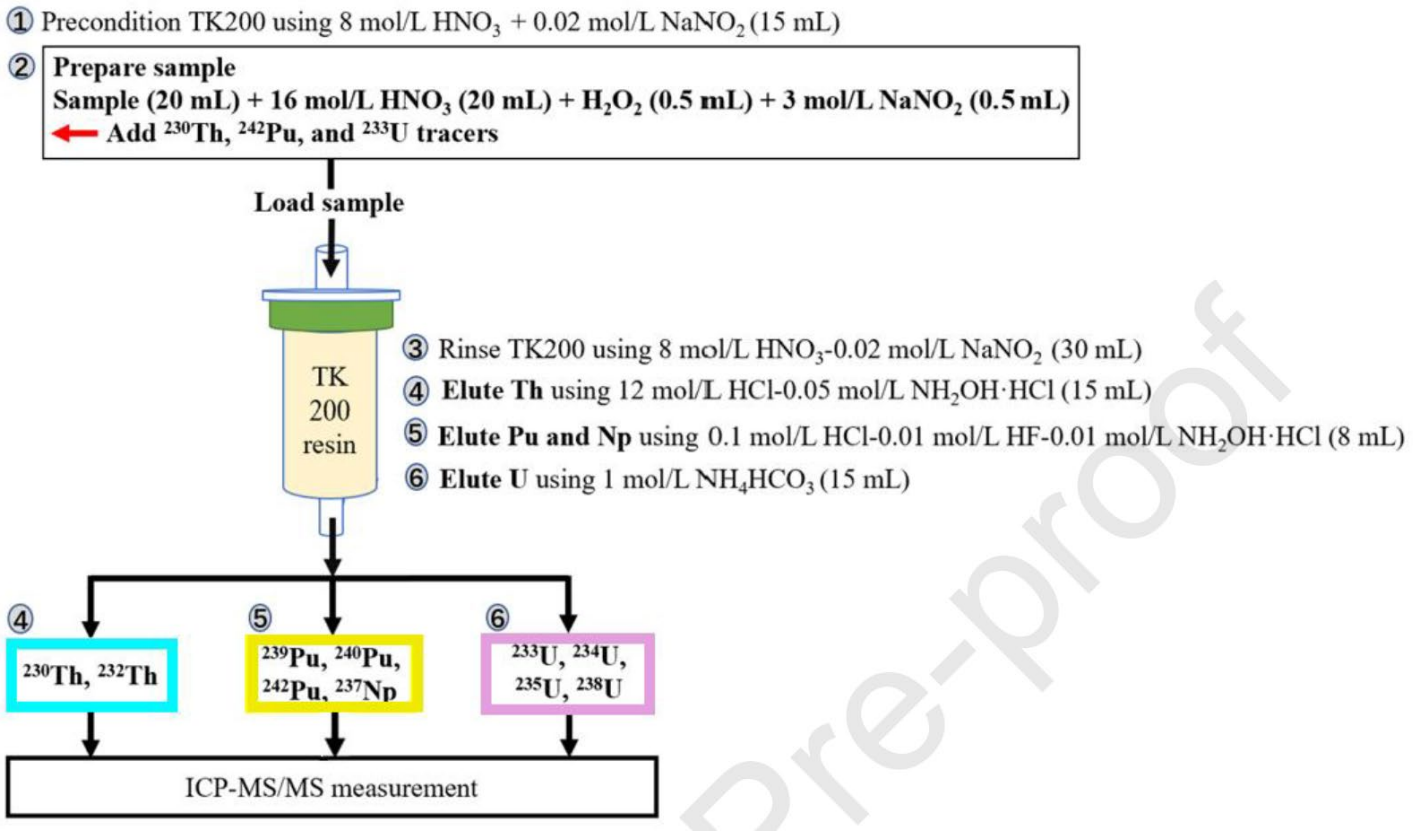
Talanta
Volume 306, 15 August 2026, 129700

Development of emergency radio-bioassay method for Th, Pu, Np and U in urine samples using single-column chromatography, automated operation system and ICP-MS/MS

Maoyi Luo [a b c], Rong Guo [a], Yang Wu [a b], Yunshi Xiao [a], Ni Yuan [a b], Jing Zhang, Quan An [a b], Liye Liu [a b], Taeko Shinonaga [a b d]

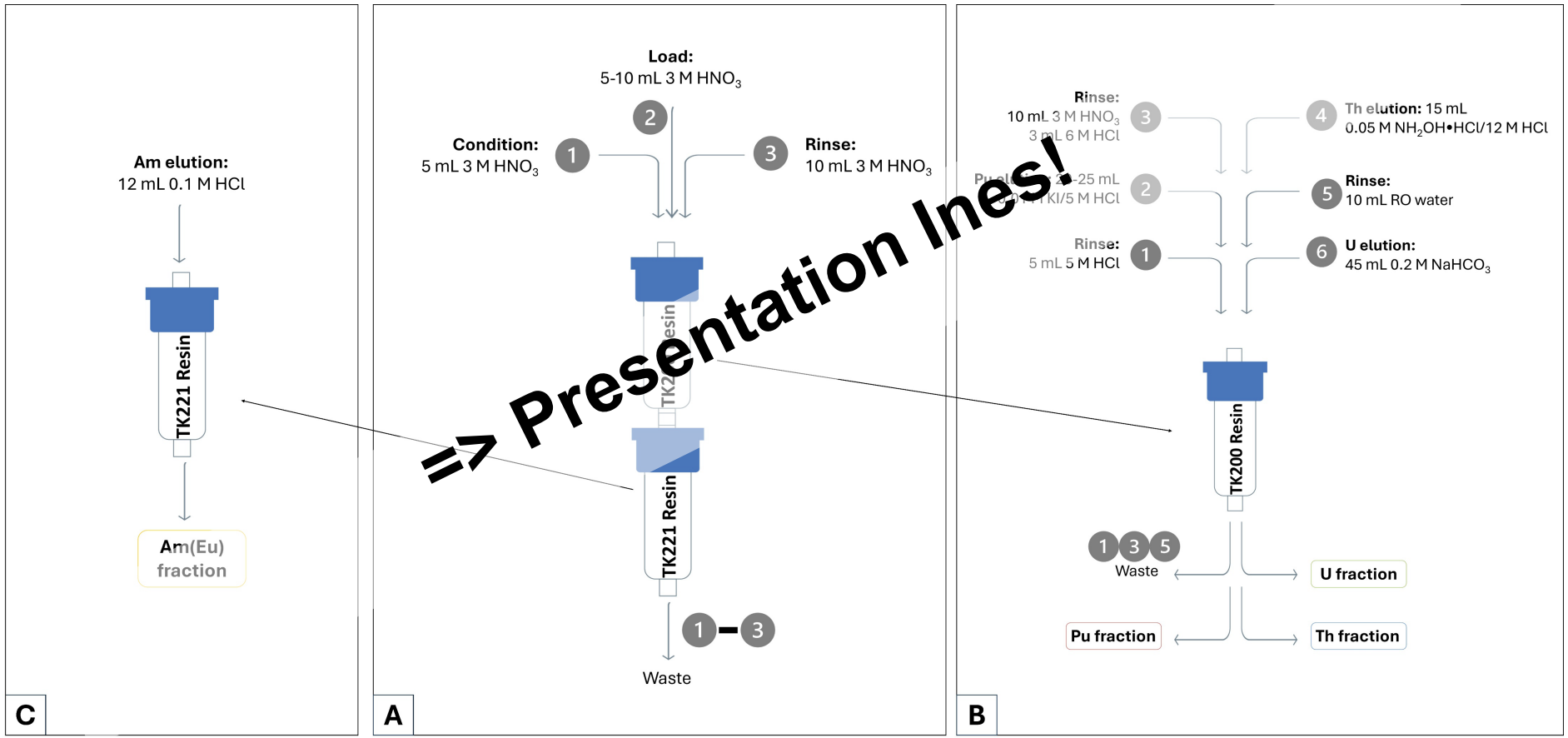
Sequential AC separation
Th elution quite harsh…
Pu and Np co-eluted
>96% yield
$D_F > 10^3$
Am not included…





Pre-proof

On-going: integration of TK221



=> Presentation Ines!

Load from 3M HNO_3 after redox adjustment

Separation of U, Pu and Th on TK200

Am passes through onto TK221 => IAEA - MEL paper

TK200 – direct Pu load/separation

One TK200 cartridge

- Preconcentration and purification

Automized separation

Acidified water samples (1 L)

Flow rate 15 mL/min

$D_F(U)$: 10^4 - 10^5

LoD:

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

ELSEVIER

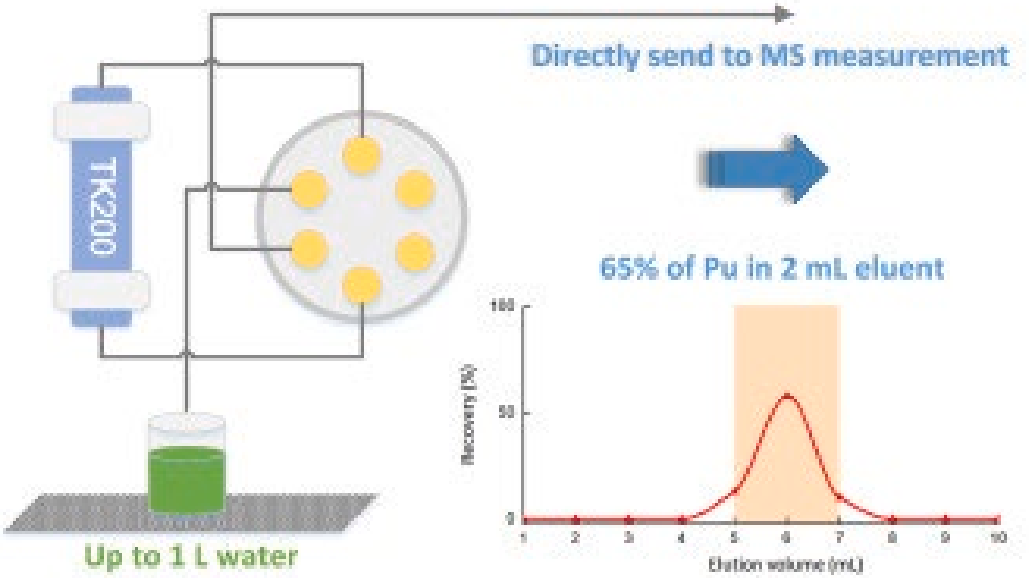
Talanta

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]



TK200 – direct Pu load/separation

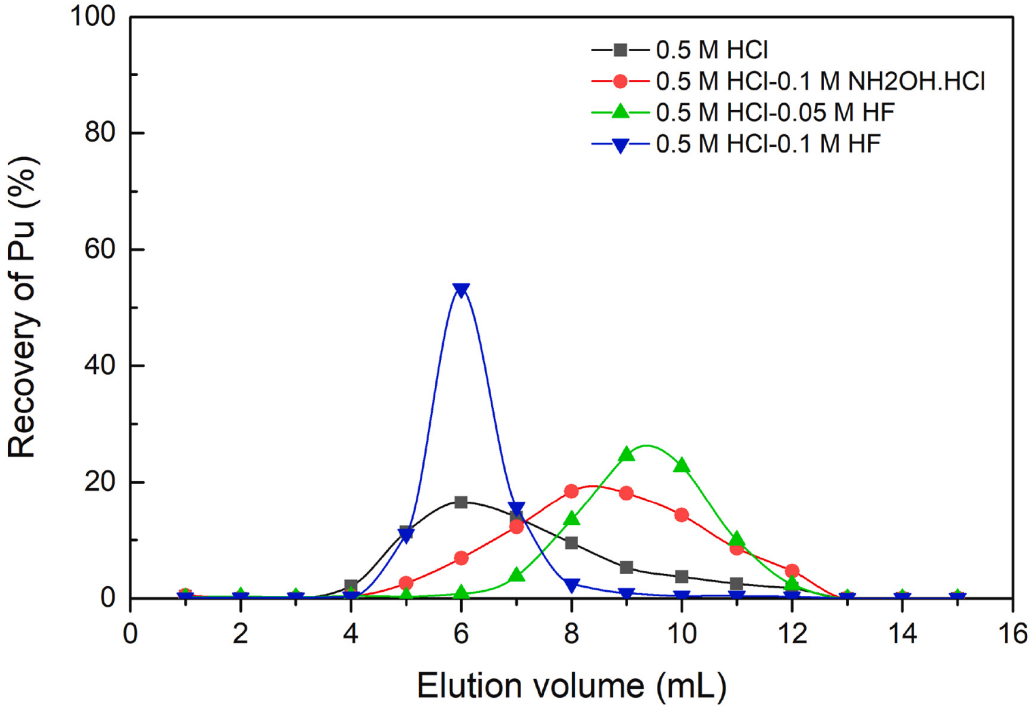
One TK200 cartridge

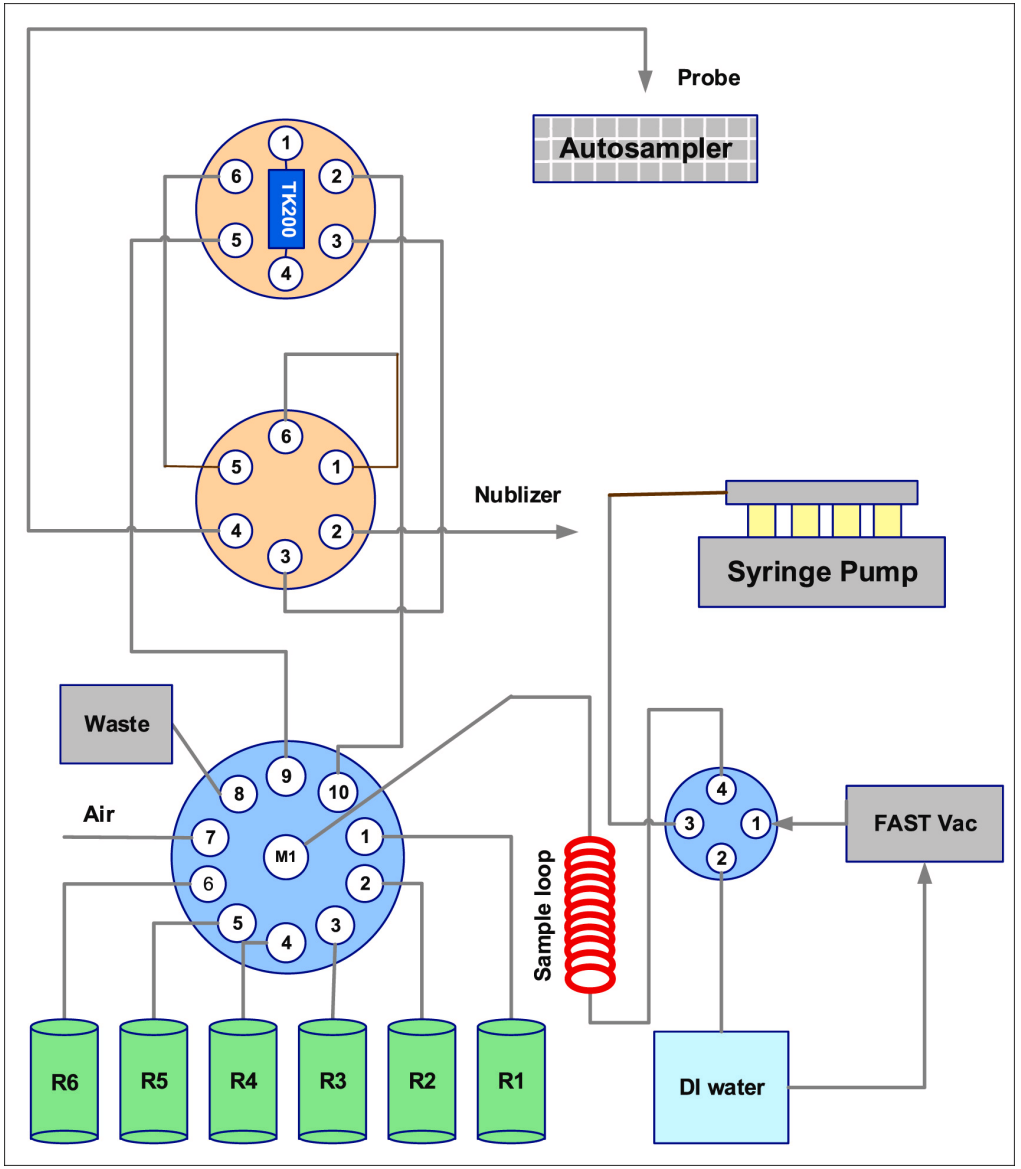
- Preconcentration and purification

Automized separation

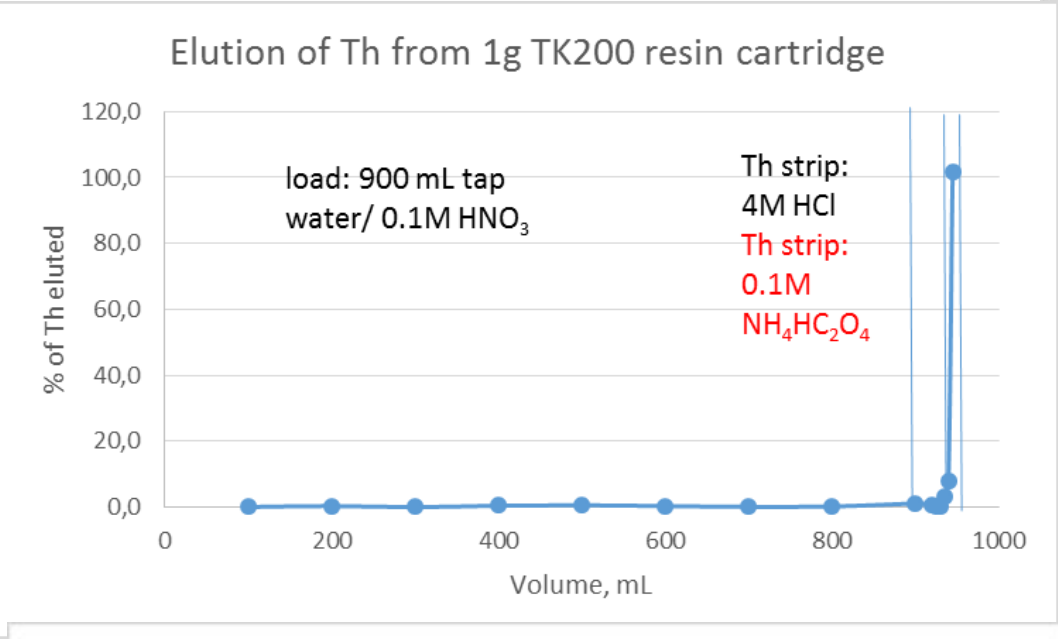
Acidified water samples (1 L)

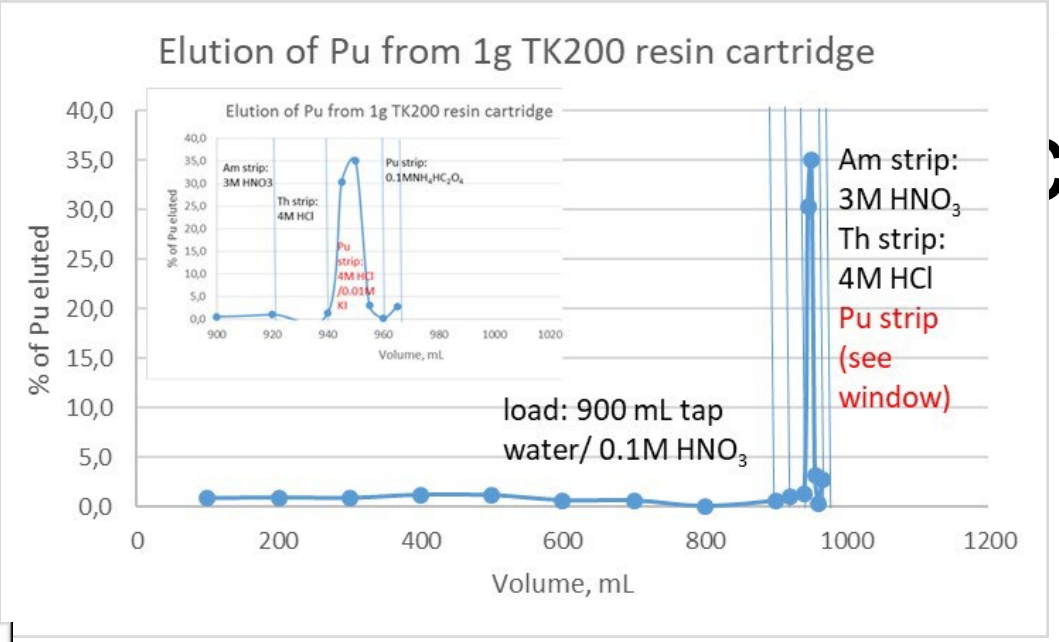
Flow rate 15 mL/min

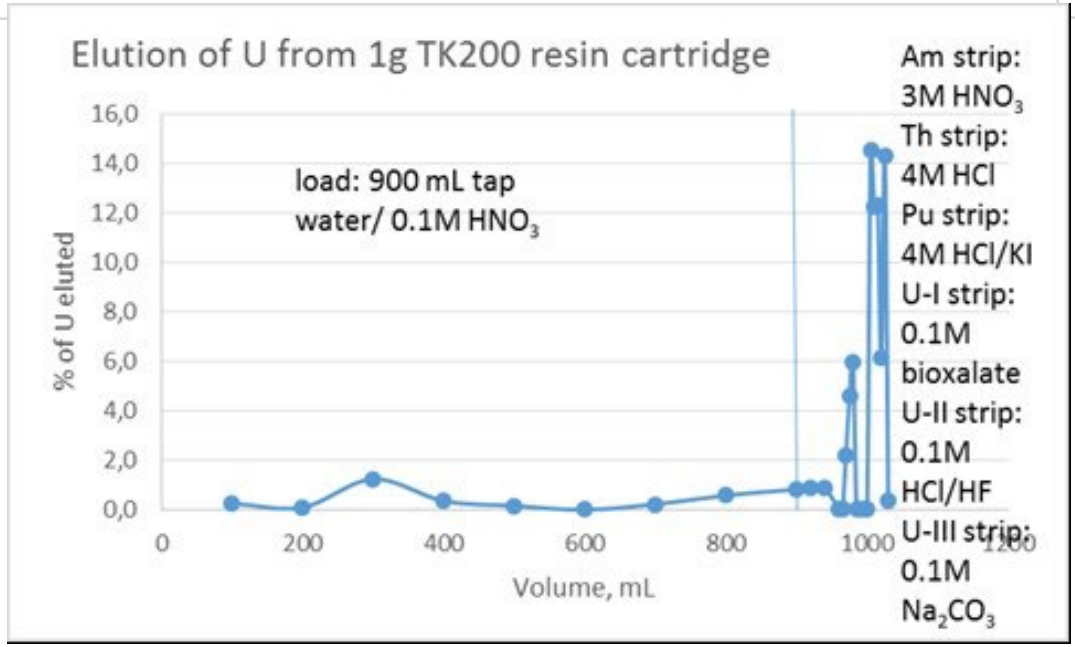




Direct load on TK200 – U, Pu, Th

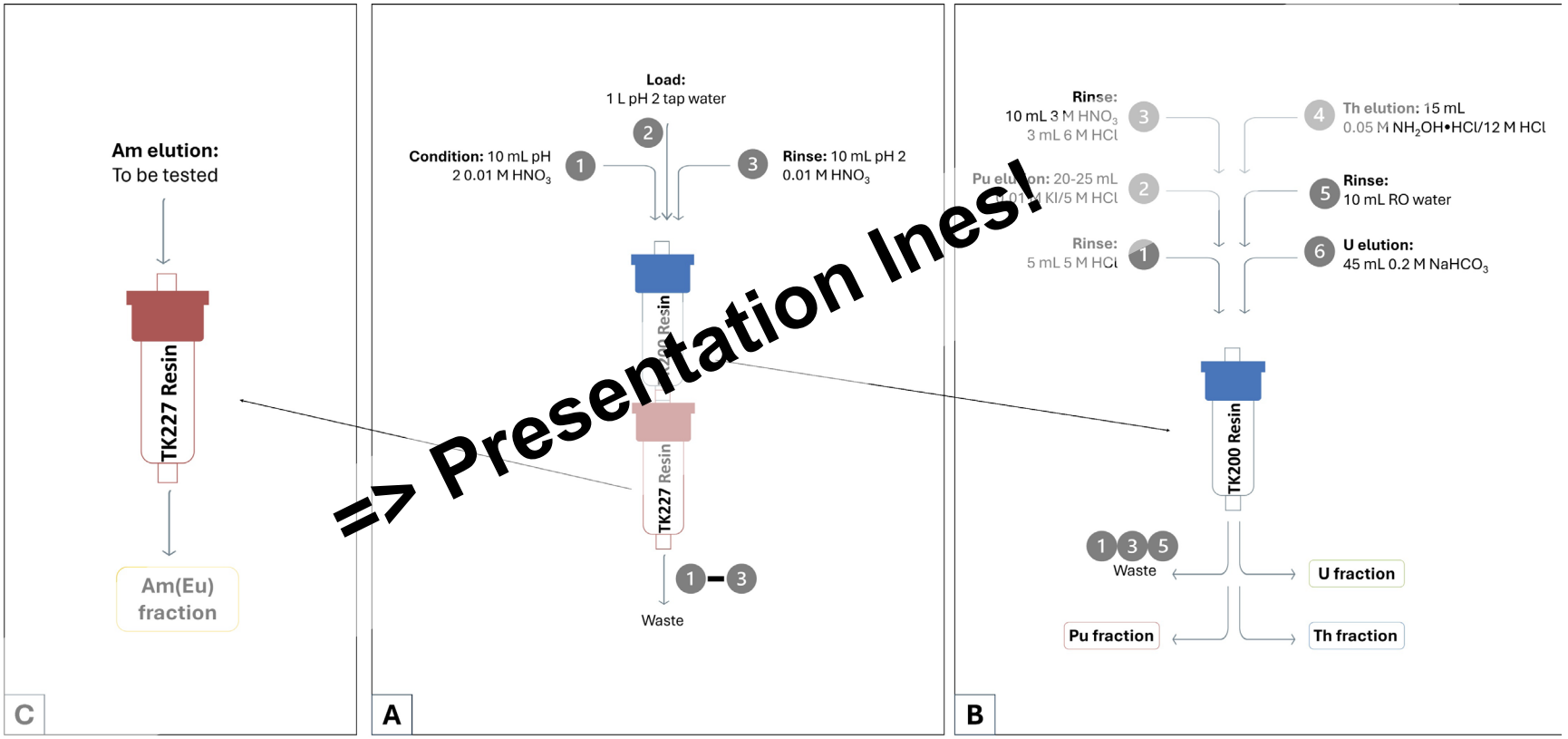






- Data by N. Vajda (RadAnal)
- Method development on-going
- Direct load of U, Th and Pu from acidified water samples (here 900 mL on 2 mL TK200)
- Sequential separation on TK200
- Automatisation & ‘in the field’ preconcentration’?

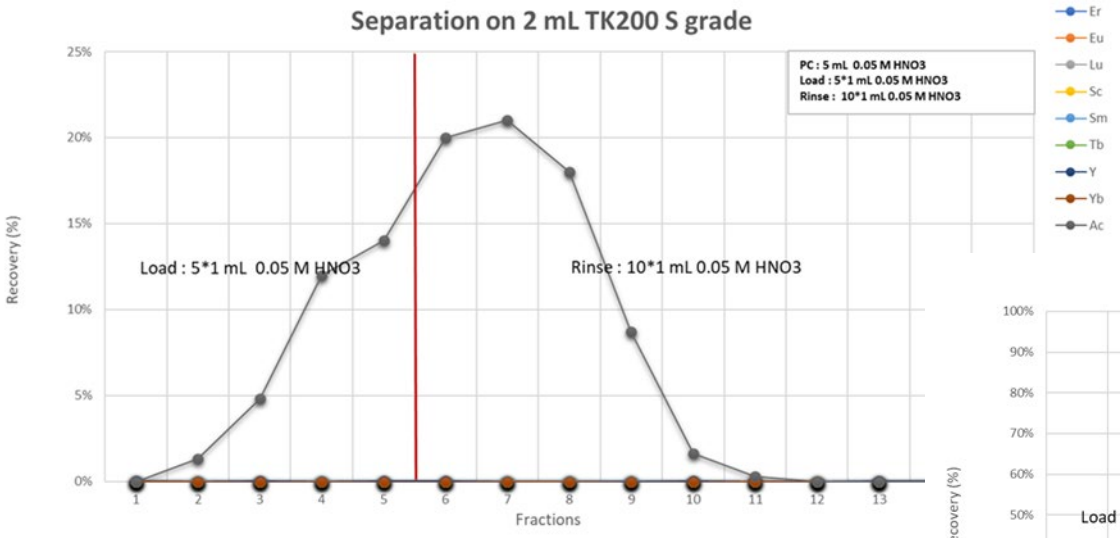
On-going: integration of TK227



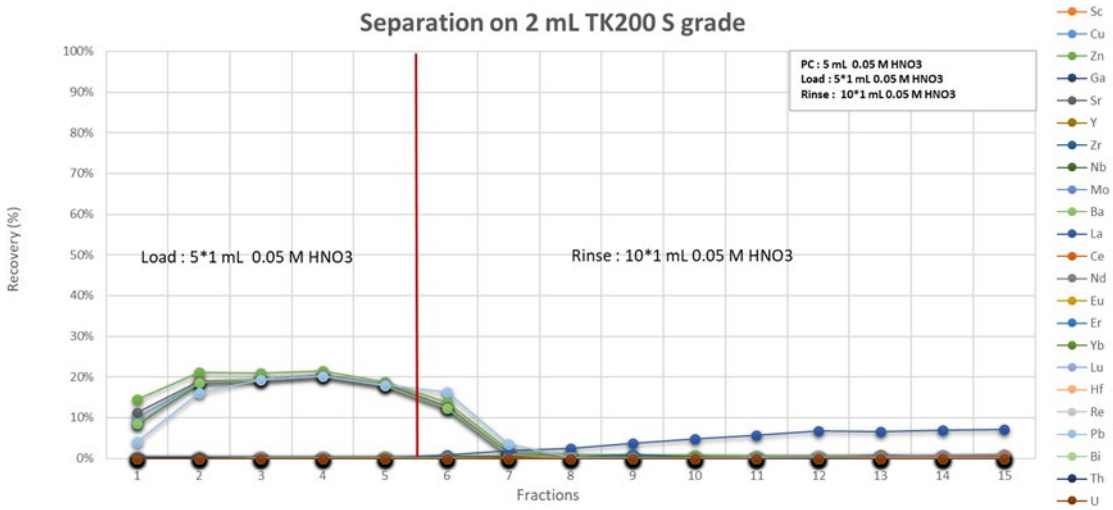
TK200 retains U, Pu, Th from HNO_3 pH 1-2, not Am

TK227 retains Am under these conditions

TK200 Resin – Ac elution studies



Ac data courtesy N. Vajda



Ac not retained in 0.05M HNO_3, U, Th, Bi and lanthanides retained, slow La breakthrough => removal of alpha emitters and lanthanides from Ac-225 in 0.05M HNO_3

Original discussion on TOPO Resin => Am/Ac separation

Most other impurities (Ca, Pb, Fe,… not retained, need to be eliminated upfront)

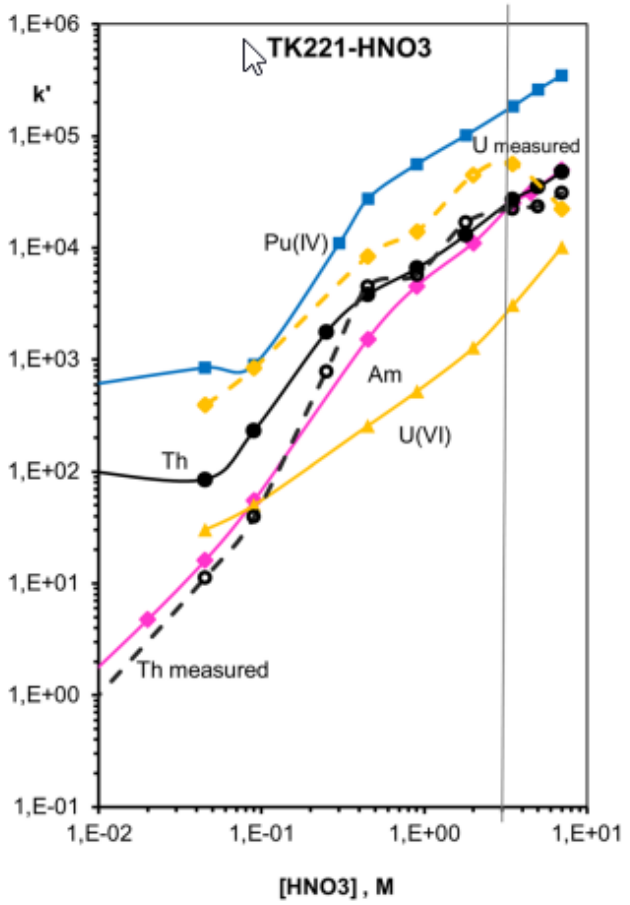
=> Ac-225 QC?

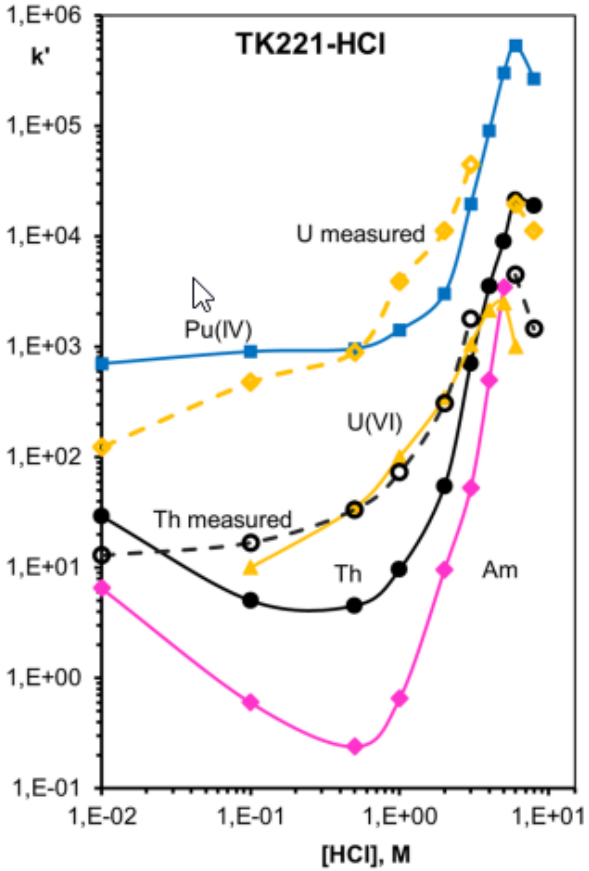
Under testing: TK200 Discs

TK221 Resin

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

- Main applications in RadPharm:
  - Lu, Tb concentration from high acid and elution in small volume of dilute HCl
  - Ac-225 purification
  - Improved radiolysis stability
- Potential use in actinide separations?
  - Synergies between extractants
  - Higher U retention than DGA
  - Higher Am retention than TRU



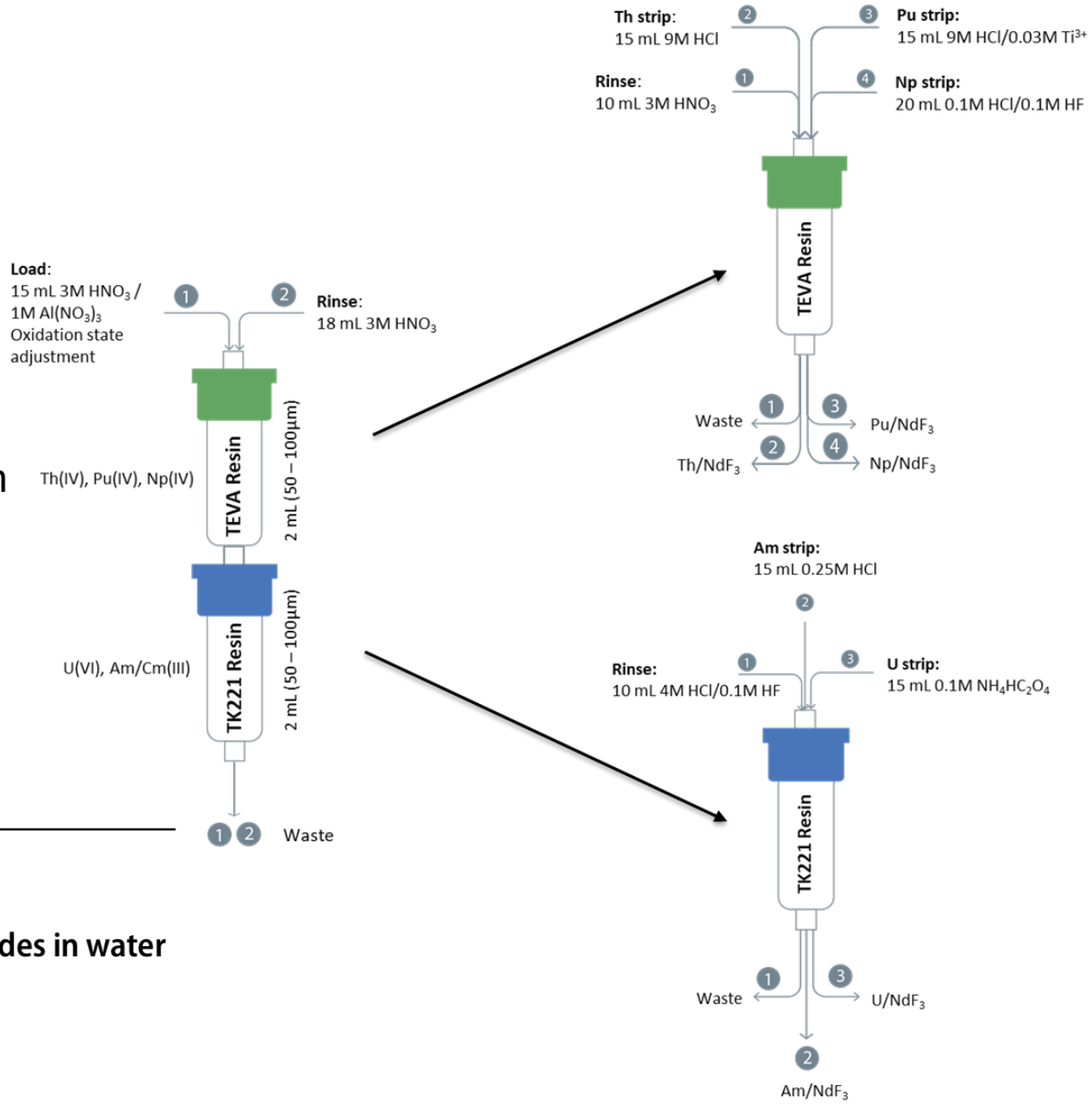


Vajda et al.

TK221 Resin – actinide separation

Cooperation with Nora Vajda
Method development initially for water samples

- TEVA/TK221 method
- Ideally later also soil and decommissioning samples
- Influence of Fe and Ca?
  - N. Vajda: Ca leads to stronger Am retention
- Now trying TK201/TK221 method



Journal of Radioanalytical and Nuclear Chemistry
https://doi.org/10.1007/s10967-022-08389-9

An improved rapid method for the determination of actinides in water

István Papp[1,2] · Nóra Vajda[2,3] · Steffen Happel[4]

Received: 7 April 2022 / Accepted: 27 May 2022
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TK221 Resin

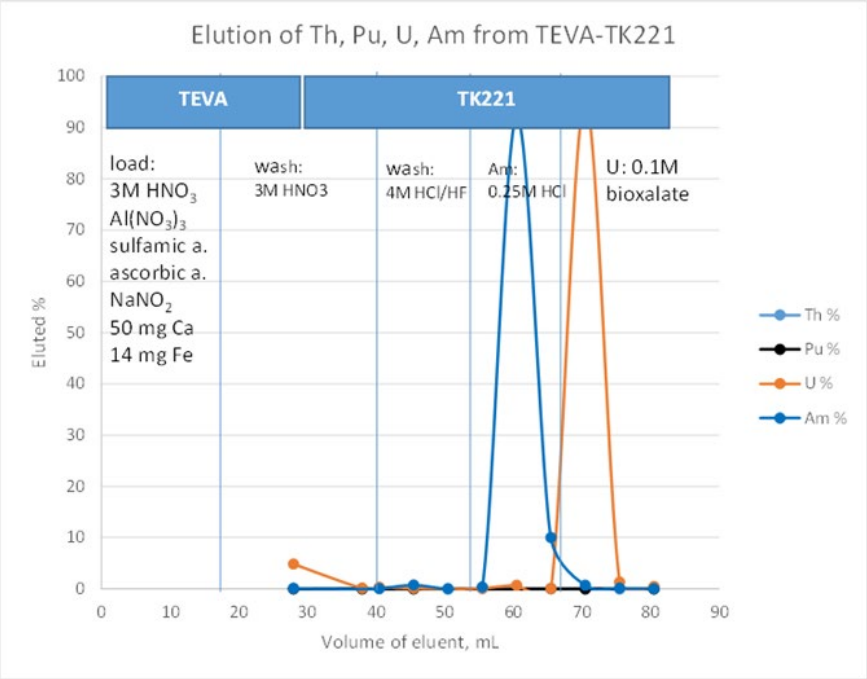


Table 3 Recovery of actinide tracers from spiked water samples

	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

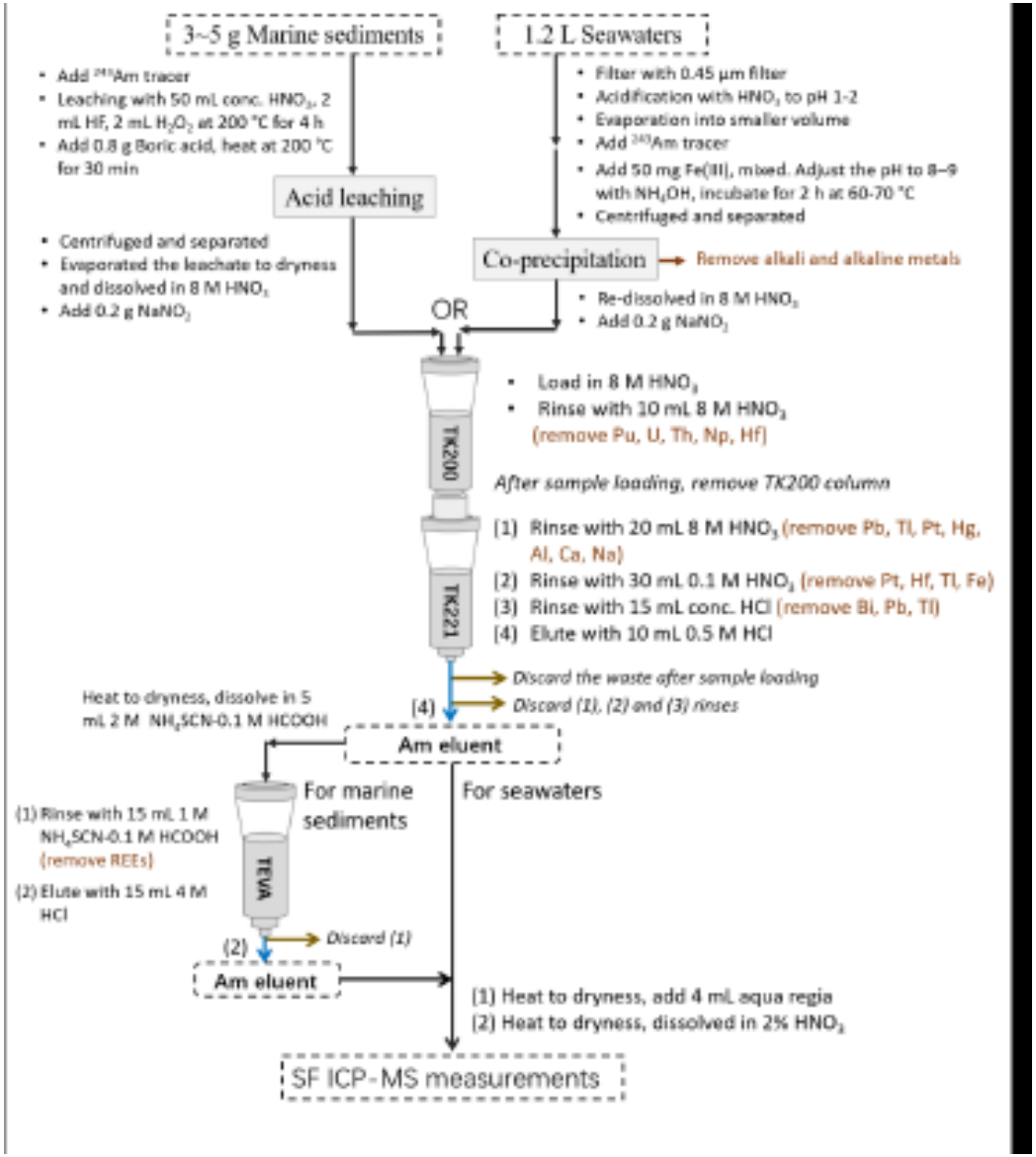
- Th and Pu removed with TEVA.
- Am and U separation on TK221
- Am elution before U => phosphine oxide wins

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
- TK201/TK221, TK200/TK221 methods?

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:

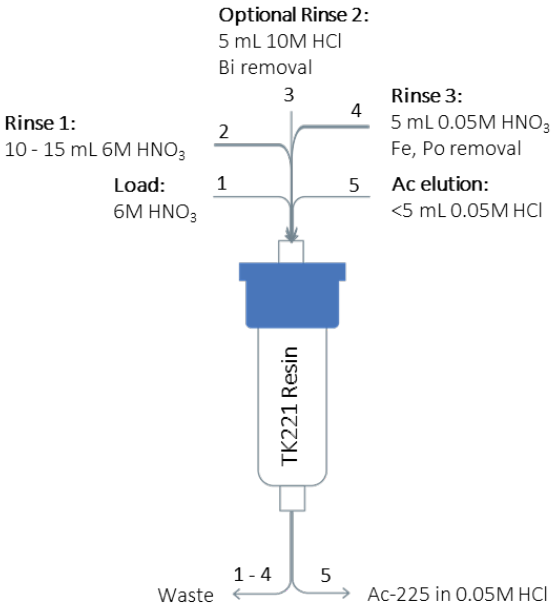
For DGA separation, the decontamination factors (DFs) for Pu, U, and Th were calculated to be (1.8 ± 0.4) × 10^3, (3.0 ± 1.0) × 10^4, and 24±6, respectively.

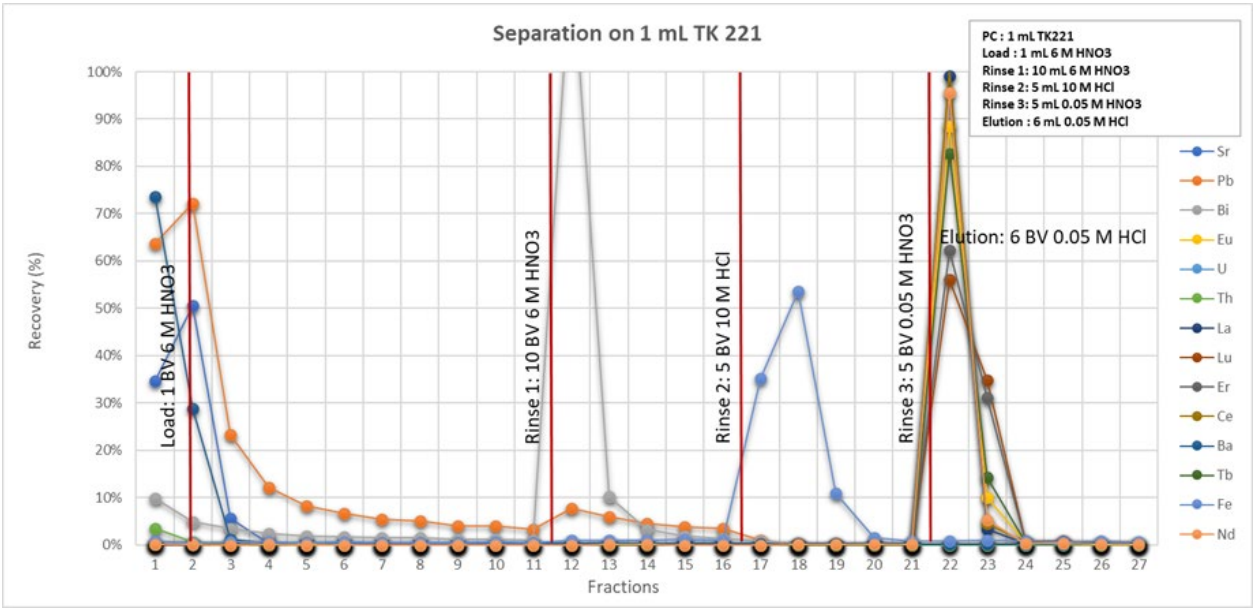
For TK221 separation, the DFs for Pu, U, and Th were (1.5 ± 0.2) × 10^4, (2.1 ± 0.3) × 10^4, and (1.2 ± 0.1) × 10^3, respectively.

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.

=> Higher Th removal, use for Ra-226/8 instead of DGA? => Ines presentation!

TK221 - Ac separation



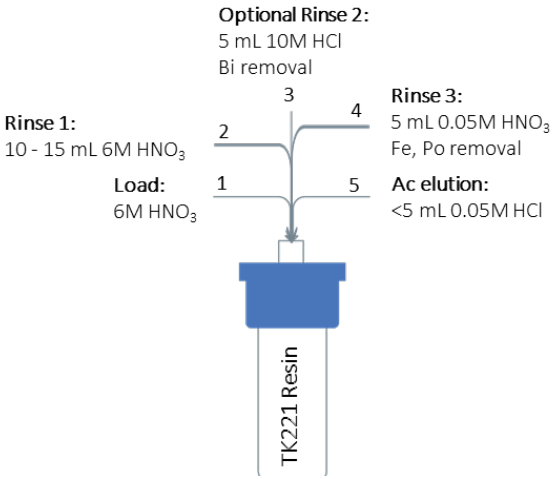


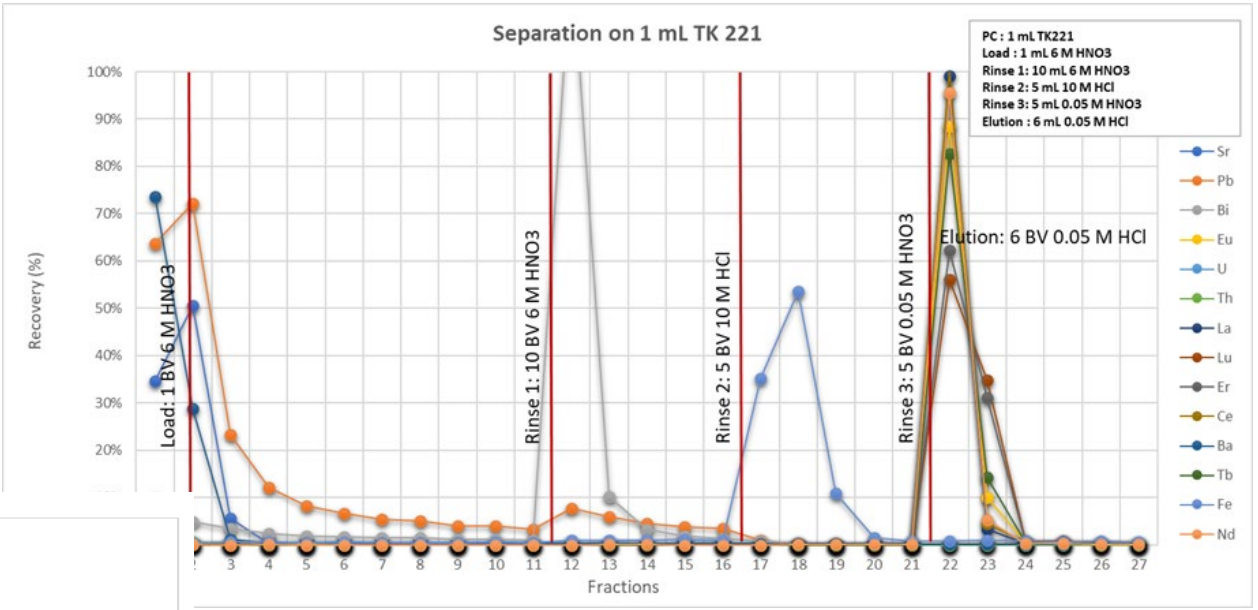
Ac separation from different sources

- Load from 2 – 6M HNO_3
- 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

- Conversion w/o evaporation:
- Load Ac-225 from dilute HNO_3, elute in dilute HCl
  - Additional purification (Fe, Bi,…)
  - Same quality of Ac from different sources
- Analytical questions:
  - Bioassay (e.g. BfS => also testing TK221 Discs) and environment

TK221 - Ac separation





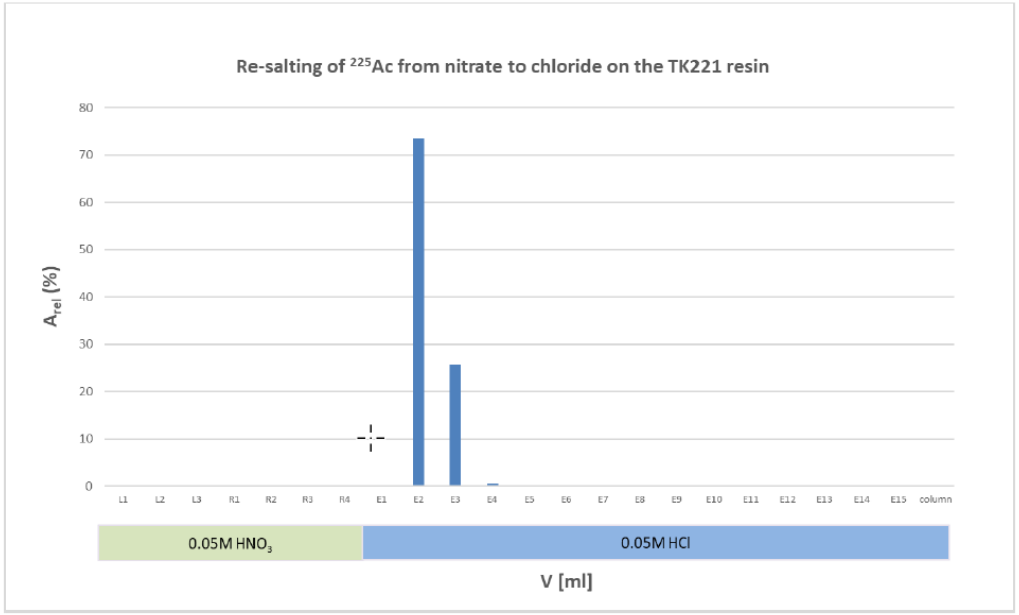
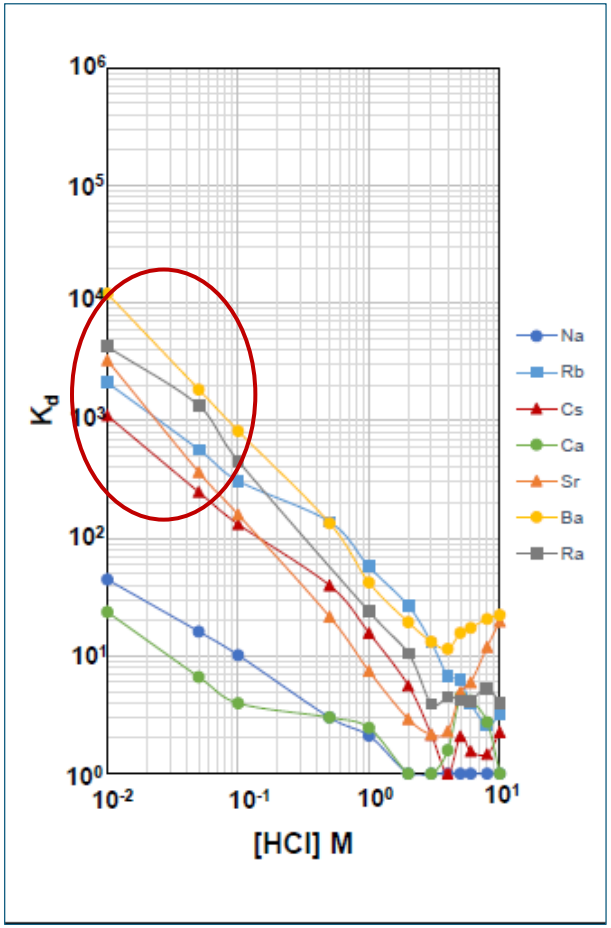
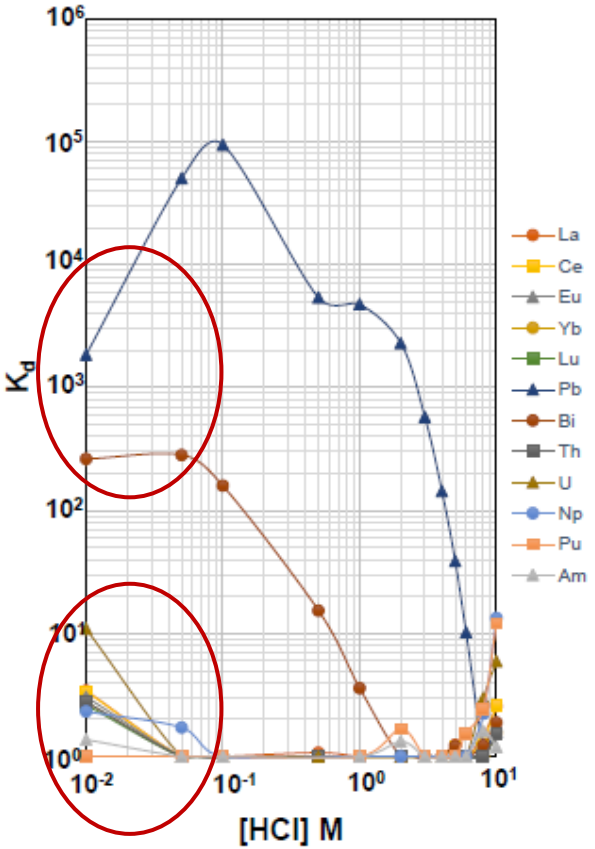


FIG. 5 Re-salting of ^{225}Ac loaded on the TK221 column in 0.05M nitric acid and eluted into 0.05M hydrochloric acid

- Conversion w/o evaporation:
- Load Ac-225 from dilute HNO_3, elute in dilute HCl
  - Additional purification (Fe, Bi,…)
  - Same quality of Ac from different sources
- Analytical questions:
  - Bioassay (e.g. BfS => also testing TK221 Discs) and environment

Optional: TK101 purification step – removal of Ac-225 daughters





Optional:
Ra, Pb, Sr, Ba removal on TK101

Load:
Ac-225 in <5 mL 0.05M HCl

1

2

Rinse:
1 mL 0.05M HCl



Ac-225 in 0.05M HCl
Ra, Pb, Sr remain retained

Data courtesy of B. Russel (NPL)

Optional Pb, Bi, Ra, Sr,... removal step (TK101)
Pass Ac fraction (0.05M HCl) through TK101
Ac passes - Ra, Pb, Sr, Bi,... retained

Reminder: Sr-90 in seawater – 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 – 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.

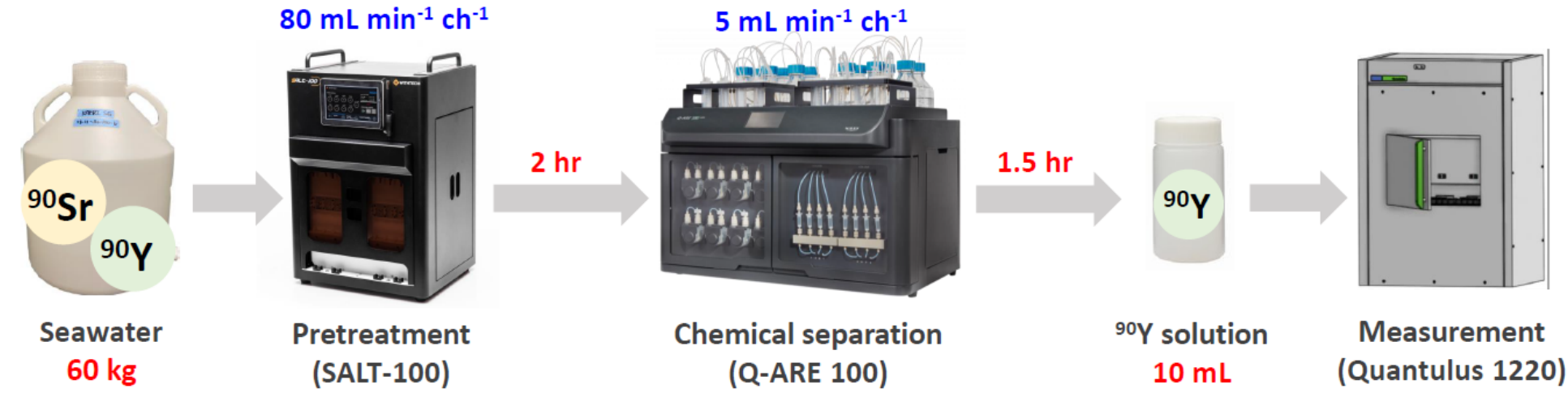
Quick and easy-to-use unattended radionuclide extraction

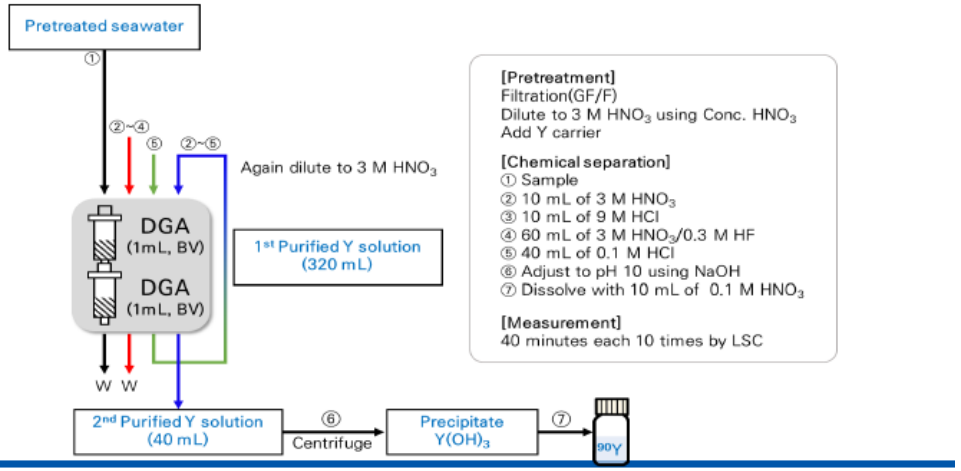
User friendly, intuitive and hassle free.

https://www.hidex.com/

Sr-90 in seawater – KAERI method

^{90}Sr in seawater; procedure





- Separation & sample prep ~4h (w/o measurement)
- Typically >85% yield
- Presentation by Hyuncheol Kim at the TrisKem / Raddec Workshop, 18.04.2024
- Presentation and video available on our website

Sr-90 in seawater – KAERI method

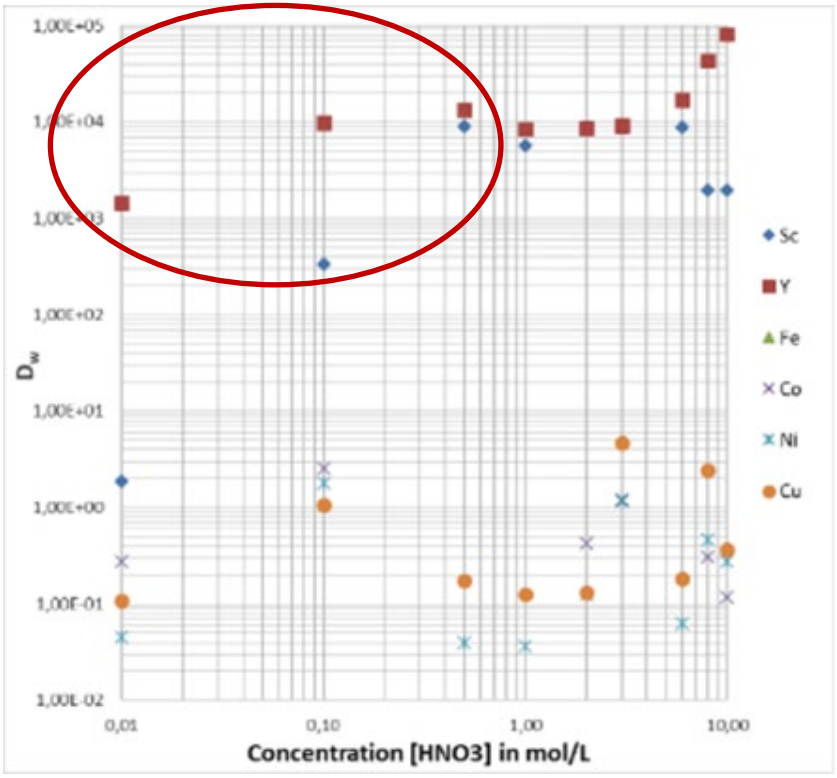
- Rapid automized separation of Y-90 from sea water (60 kg)
  - Aim: determination of Sr-90
  - Faster than standard methods
- Potential drawback: Sample needs to be adjusted to 3M HNO_3 => large amounts of conc. HNO_3
- Discussion: TO-DGA based resin to allow loading from lower HNO_3 ?

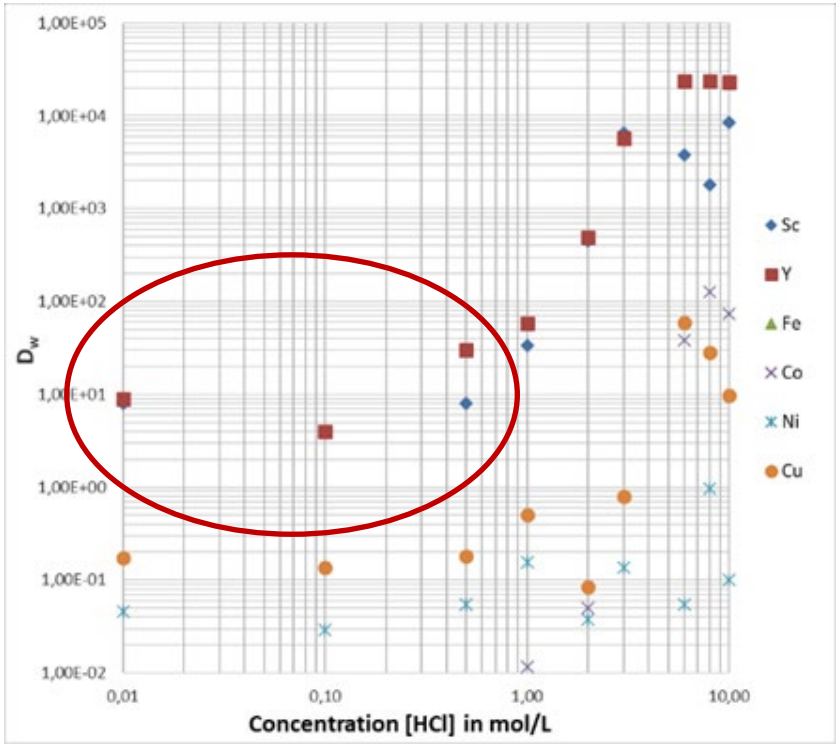
=> 'TK227 Resin'

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

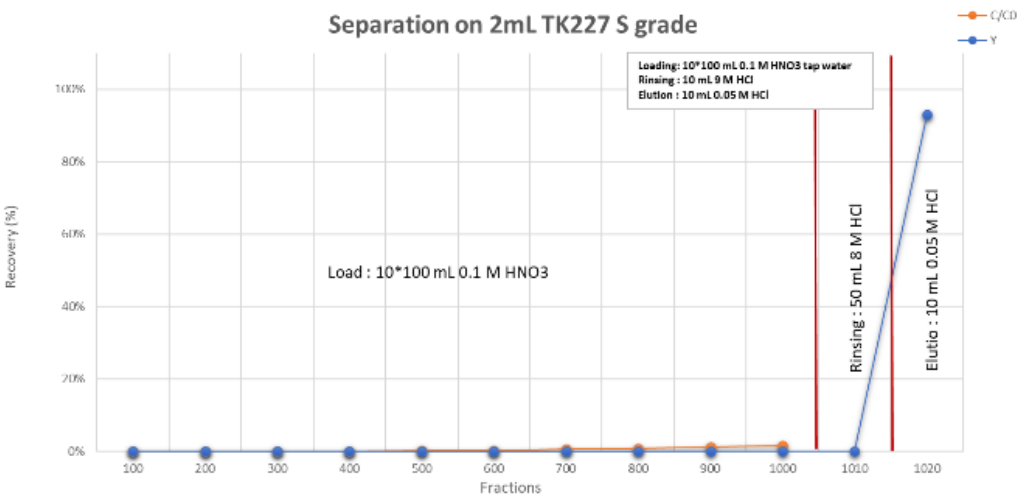
TK227 Resin

- Addition of ionic liquid increased Y retention (idem e.g. lanthanides, especially heavy lanthanides) at lower HNO_3. Further contains phase stabilizer.
  - Remark: too high amounts of IL will lead to low elution yields (=> TK225 – large amount of IL – use in decontamination of effluents from radiolanthanides).
- Important: Separation on TK227 optimized for **mg amounts of Y carrier**!

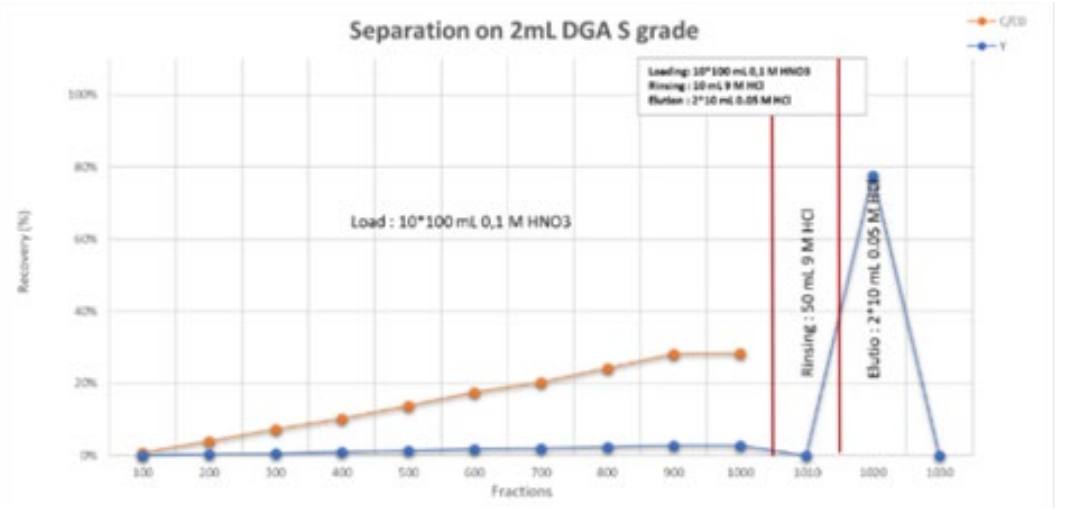




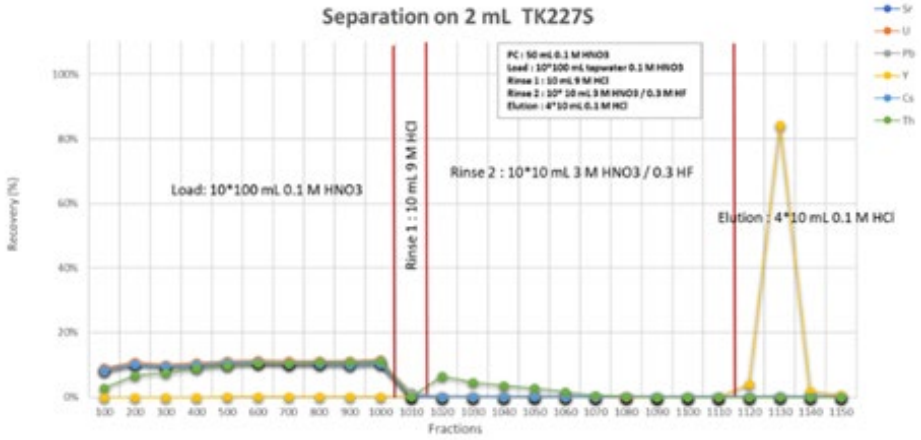
TK227 Resin – drinking water



Elution study, 1L tap water, loading from 0.1M HNO_3, Y separation, 2mL TK227 Resin cartridge



Elution study, 1L tap water, loading from 0.1M HNO_3, Y separation, 2mL DGA,N Resin cartridge



Elution study, 1L tap water, Loading from 0.1M HNO_3, Y separation, 2mL TK227 Resin cartridge, selected elements

Y retention on TK227 from 1L 0.1M HNO_3

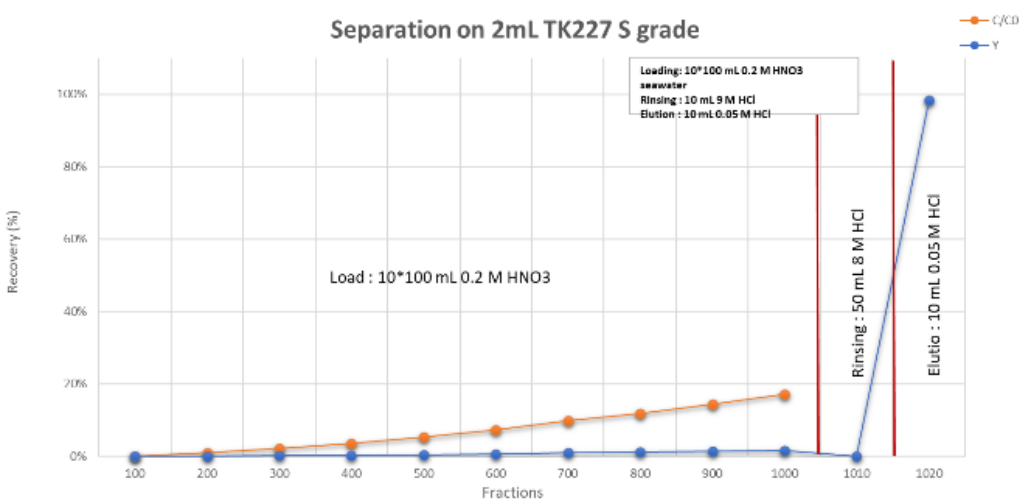
Loading at 10mL/min

Separation from interferences following Kim et al.

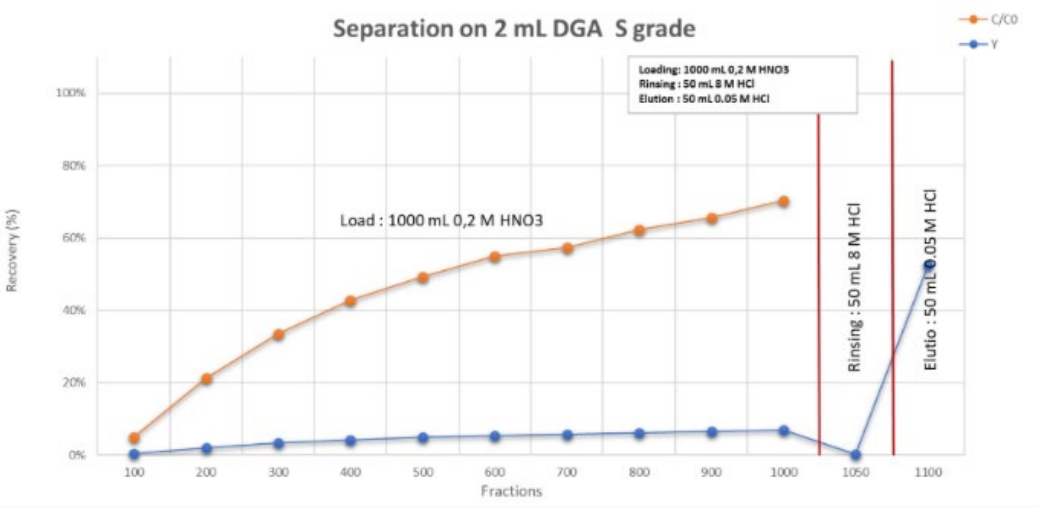
Rapid method for Sr-90 in water?

Use of scintillating beads (PSm, UB)? Disc?

TK227 Resin – sea water



Elution study, 1L sea water, loading from 0.2M HNO_3, Y separation, 2mL TK227 Resin cartridge



Elution study, 1L sea water, loading from 0.2M HNO_3, Y separation, 2mL DGA,N Resin cartridge

- Sea water requires higher HNO_3 concentration for Y retention (min. 0.2M, better higher)
- Loading at 10mL/min
- On TK227 Resin Y breakthrough when loading 1L (<20%) but less than DGA,N (~70%) => higher HNO_3 required to improve yields
- TK227 Resin use in KAERI method showing better yields but acidification to 2M HNO_3 still needed => validation by IEAE-MEL foreseen

On-going: TK227 Disc



20 % EtOH
0,5 M HNO_3

1 L tap water
0,5 M HNO_3

0,5 M HNO_3
9 M HCl

Y elution
20 mL 0,1 M HCl

Use of 47mm TK227 Disc instead of cartridges

Surface waters

Filtration set-up

Load from 0.5M HNO3, 1mh Y carrier

Higher flow rate: 10 – 15mL/min

Y-90 retained

Quantification via:

Cerenkov (Disc in vial + 20mL water)

LSC (Disc in vial + 10mL each water and cocktail or cocktail only)

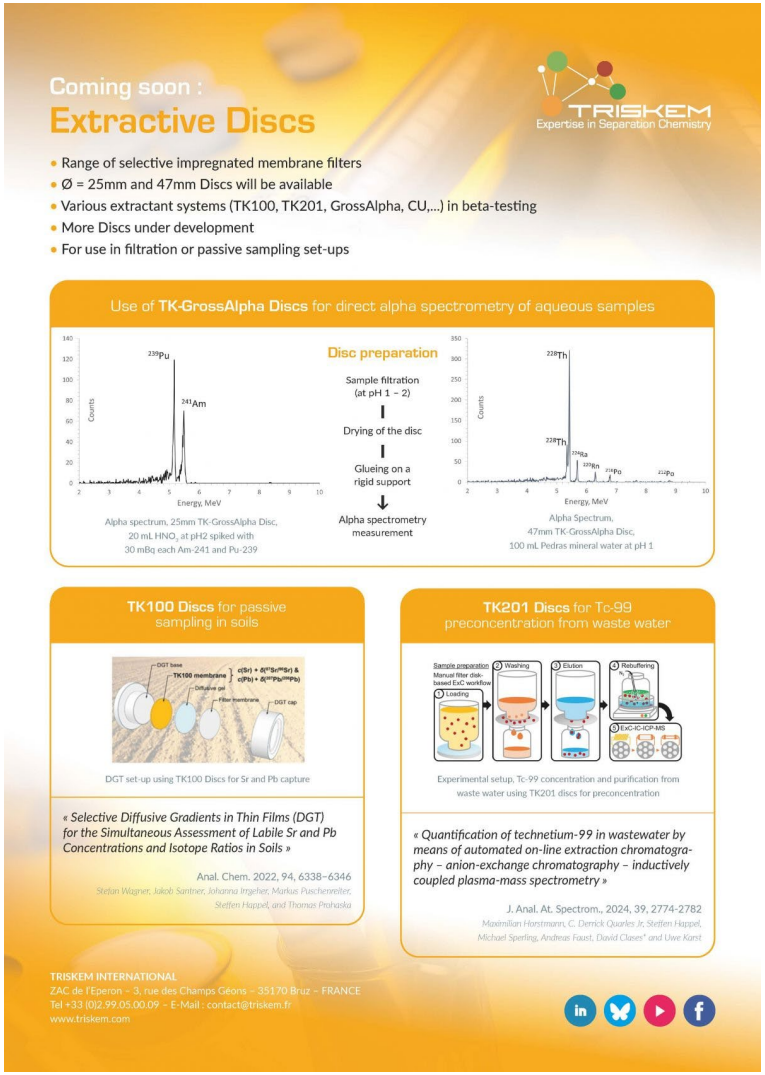
Disc elution with 0.1M HCl (currently 40mL) measurement via Cerenkov or LSC

To be tested: direct measurement of the Disc via GPC

Ines presentation!

New & under development impregnated membrane filters (Discs)

Tesmarac
joint research laboratory



Special membrane filters impregnated with extractant(s)

25mm and 47mm Discs available

Commercialized:

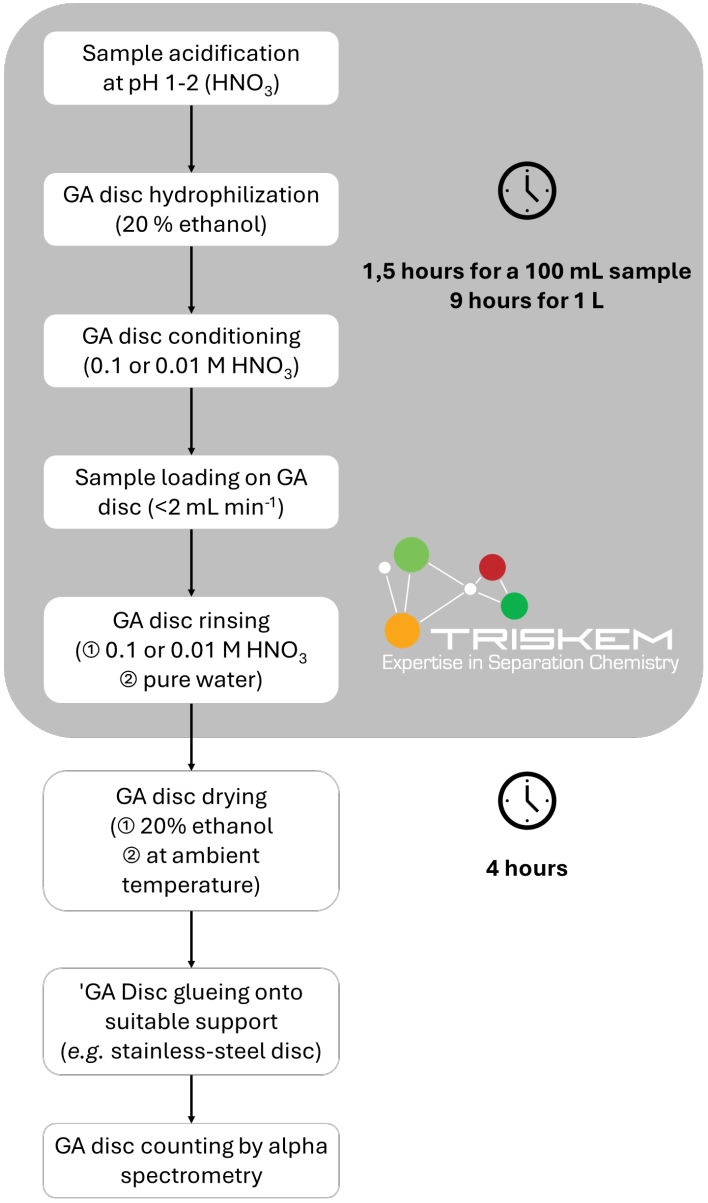
- TK-GA Discs (Gross Actinide)
- ‘Screening tool’

Beta Testing:

- TK100 & TK201 (both published), CU,...
- TK200 (U, Th, Pu) und TK221 (U, Th, Am, Pu) => sequential separation (e.g. TK201 (Pu, Th)) => rapid screening?
- Alphaspec: Retention vs. Retention on the surface (70 - >90%)

New/under development: impregnated membrane filters

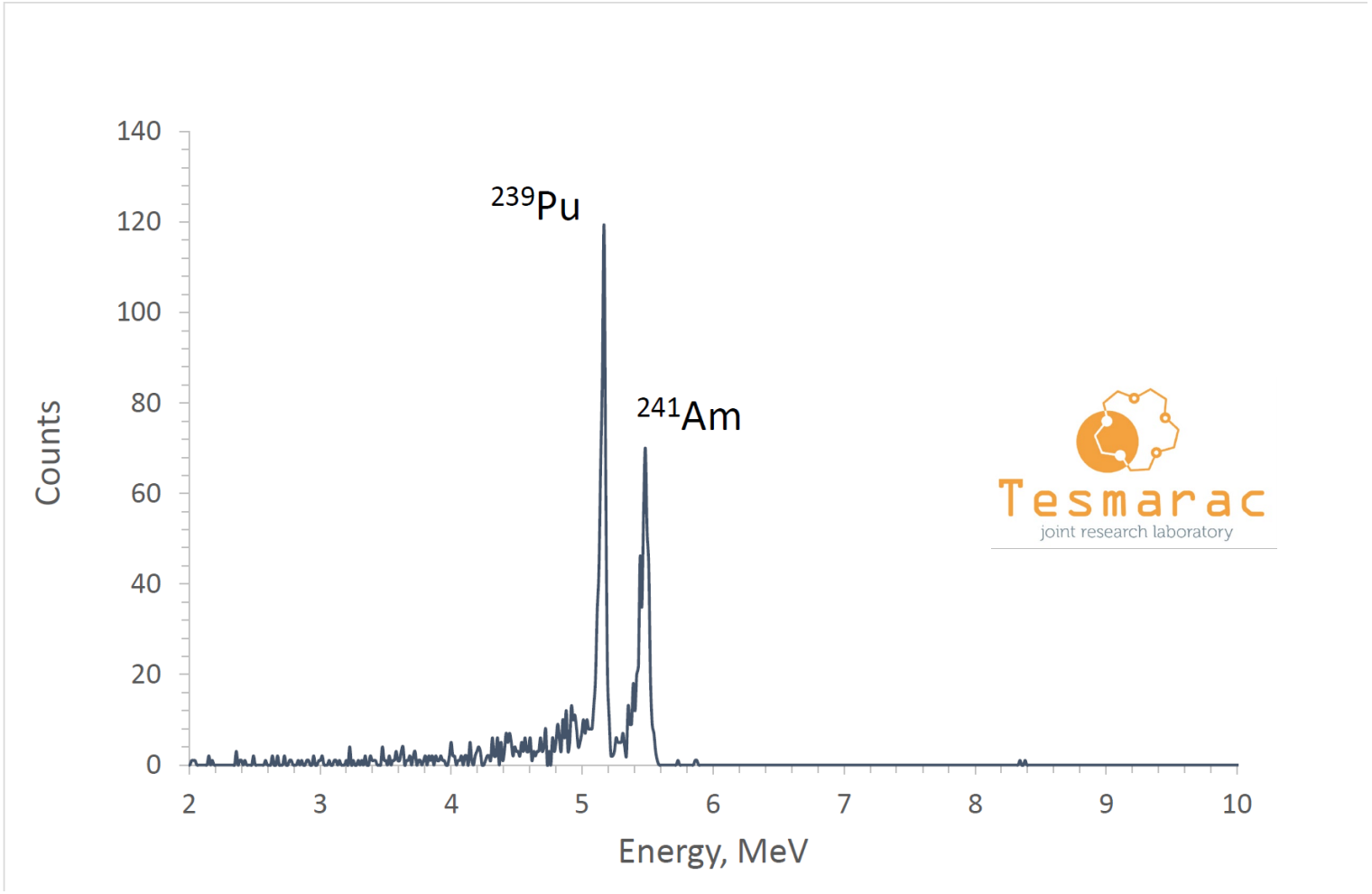
Tesmarac
joint research laboratory



Typical applications of TK-GA Disc:

- pH 1 – 2 (for some actinides up to 3M HNO_3)
- Preconditioning of the disc: 20% EtOH:water, water, then loading medium
- Loading of the sample, flow rate: 1 - 10mL/min,
  - Lower flow rates seem to favor better resolution
- 25 mm Discs typically up to 100mL samples,
- 47 mm Discs typically up to 1L (higher volumes possible depending on extractant system)
- Rinse with water and 20% EtOH:water
- Drying and glueing onto steel disc => alpha spectometry.

TK-GA Disc – Am/Pu in spiked acidified water

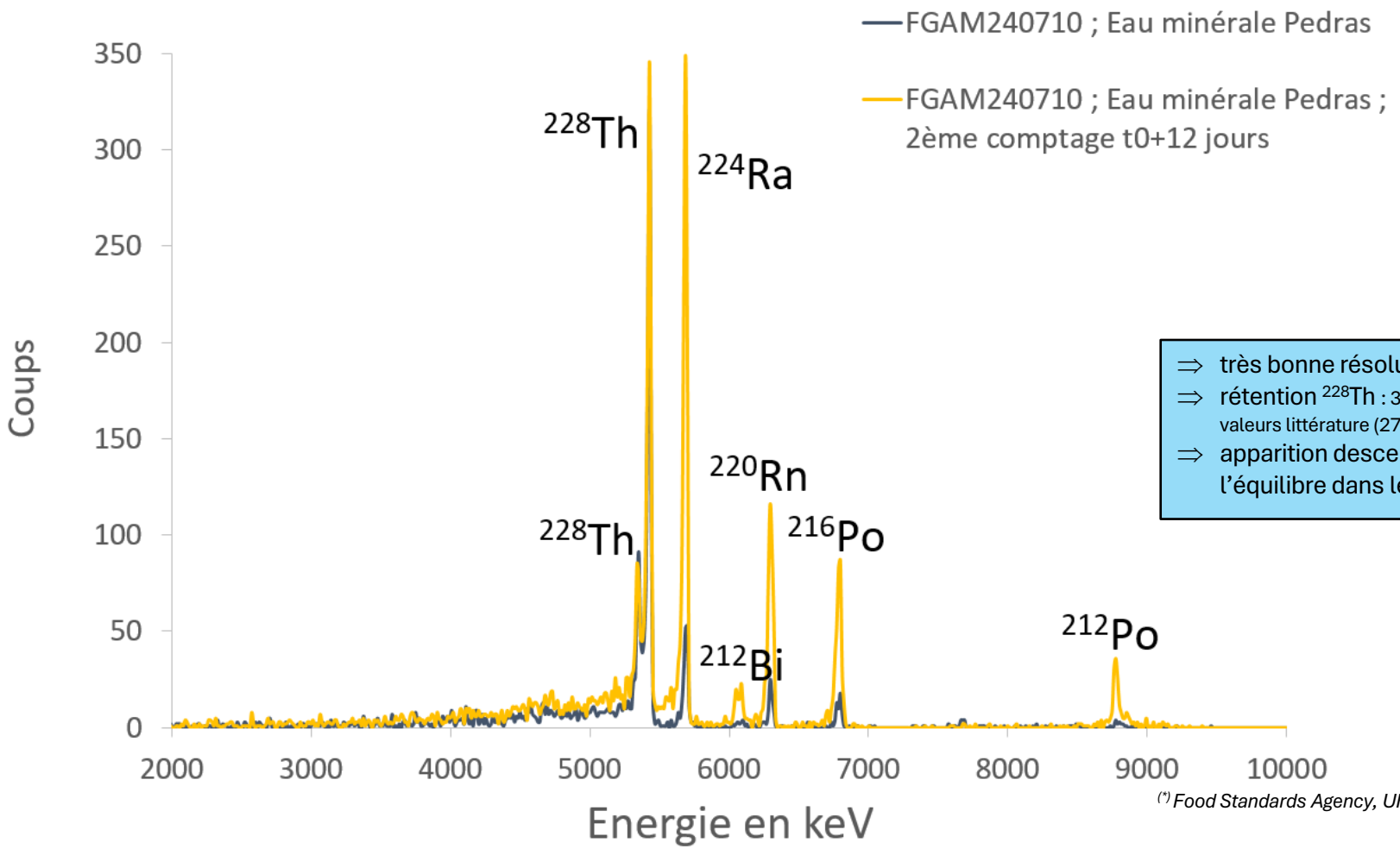


Alpha spectrum, Am-241 & Pu-239, each ~50mBq, 100mL pH2 HNO_3

Tesmarac joint research laboratory

Résultats :

→ Eau minérale naturelle : Pedras (100mL)



⇒ très bonne résolution

⇒ rétention ^{228}Th : 320mBq/L mesuré = cohérent avec valeurs littérature (270mBq/L (*))

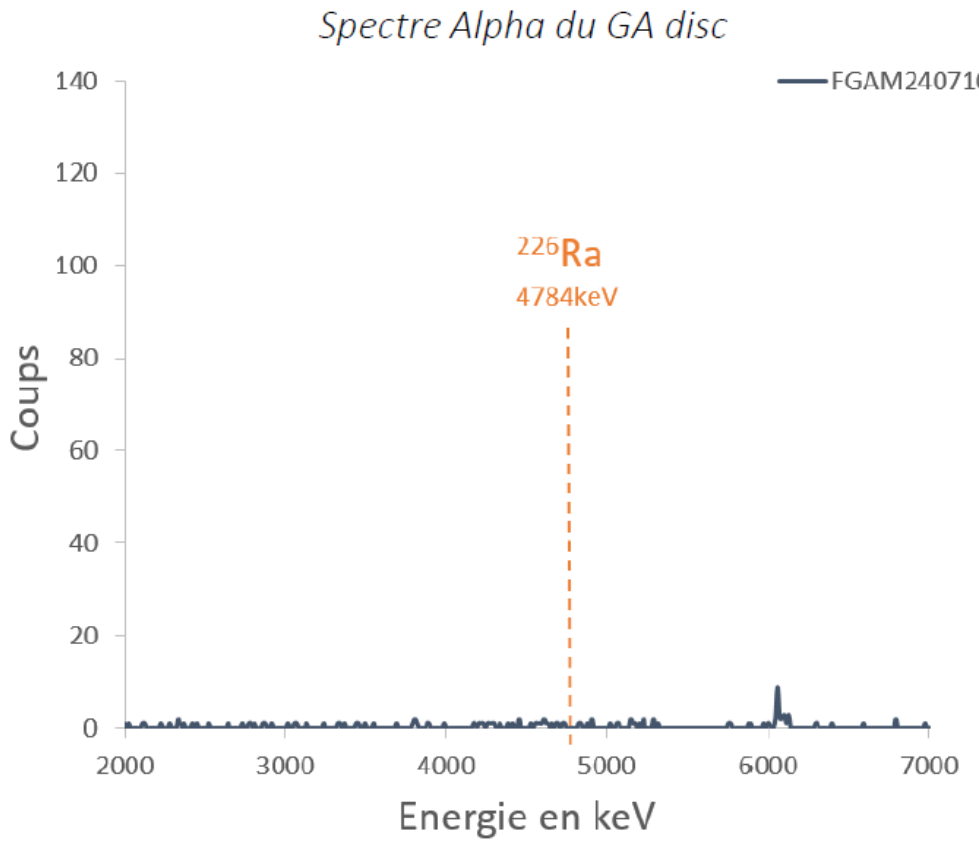
⇒ apparition descendants du ^{228}Th puis mise à l'équilibre dans le temps

(*) *Food Standards Agency, UK, Report 67/04 September 2004*

No Ra Retention in pH1 , Th very well retained. Good resolution

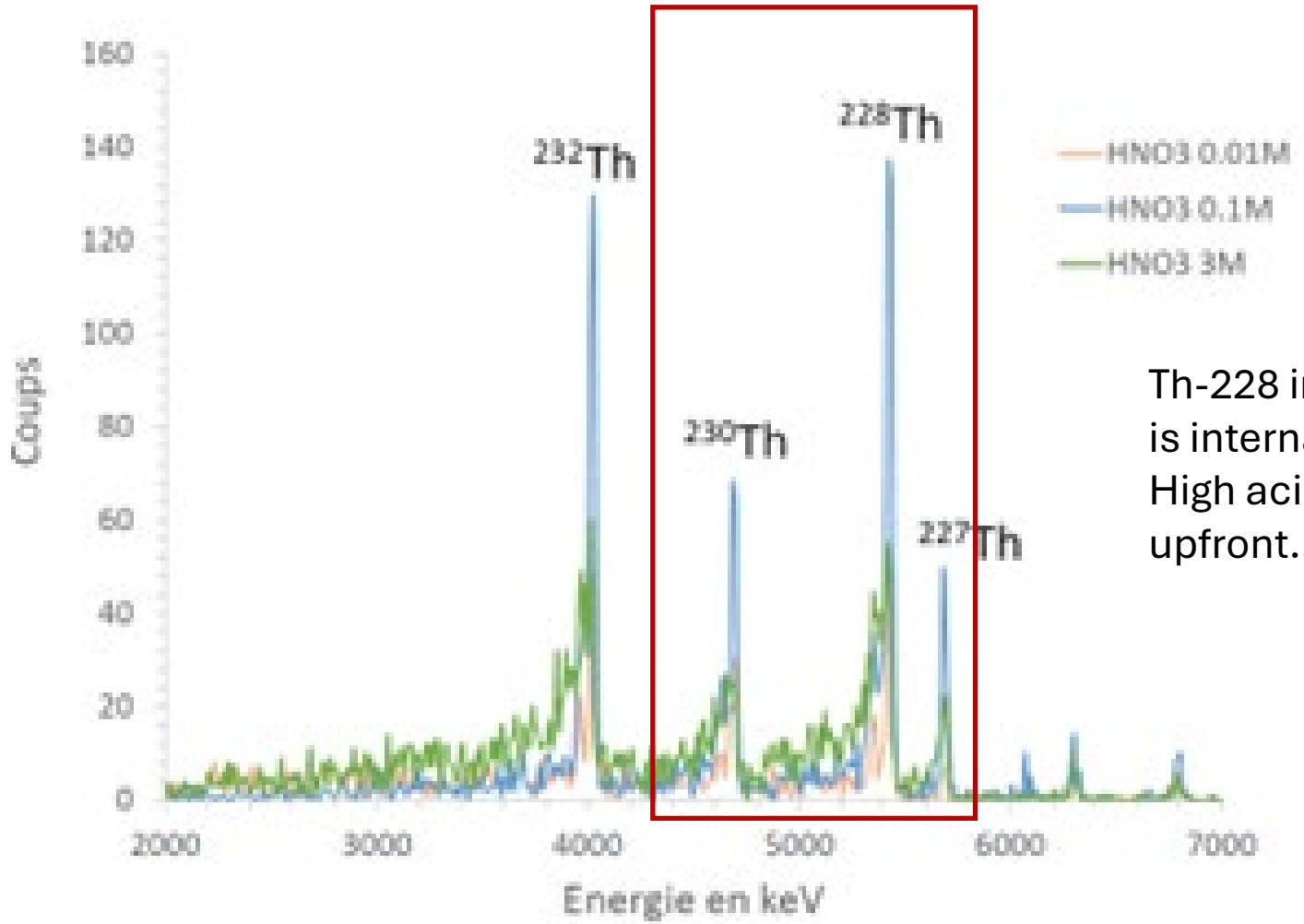
TK-GA Disc – Ra in spiked acidified water

→ Solution synthétique simple HNO_3 (100mL) 0,01M dopée en ^{226}Ra (30mBq soit 0,3Bq/L) *(résultats octobre 2024)*



No Ra retention at Ph 1 and 2. Ra retained at higher pH but no spectrum (TK103 Disc?

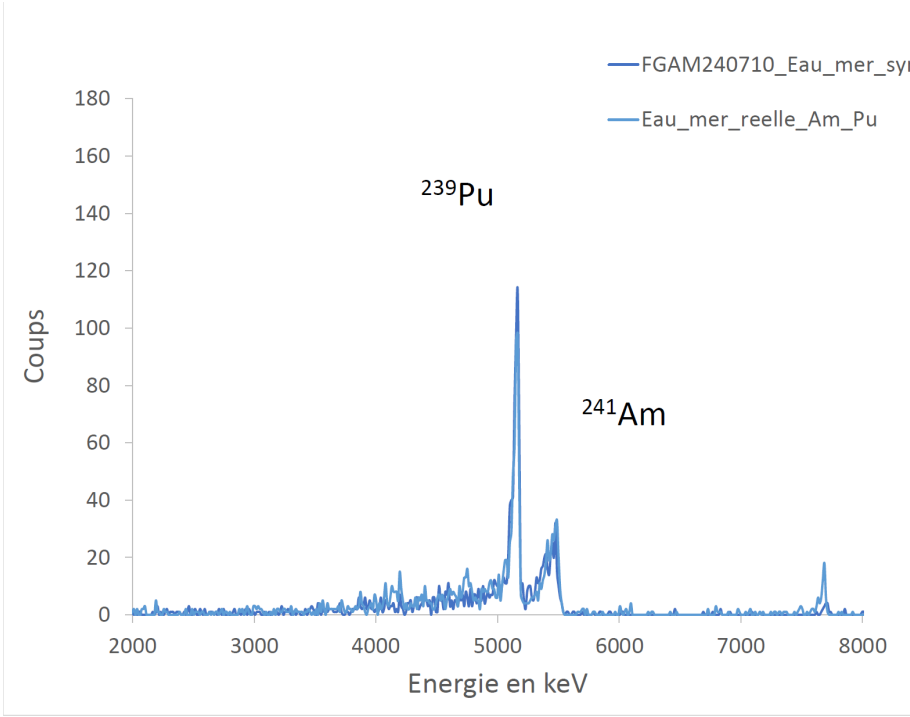
TK-GA Disc – Th retention at varying HNO_3



Th-228 in Pb-212 with Th-230 is internal standard?
High acid or Pb removal upfront…

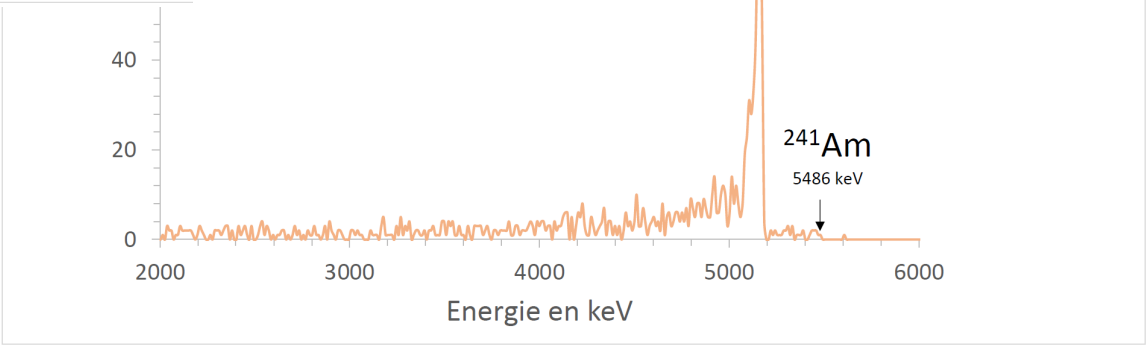
Th retention at varying acid HNO_3 conentrations

TK-GA Disc – Am/Pu - limitations



Alpha spectrum, Am-241 & Pu-239, each ~30mBq, 100mL sea water, pH2 HNO_3

Higher yields for Pu



Alpha spectrum, Am-241 & Pu-239, each ~50mBq, 100mL 3M HNO_3

High yields for Pu, no Am retention => TK221 Discs?

Next steps

TK-GA Discs:

- Publication upcoming
- Other matrices (e.g. primary cooliant) and acid concentrations
- Spectrum deconvolusion => Subatech
- More data on other alpha emitters

TK221 and TK200 Discs in 3M HNO_3

- Stacking for AC screening? => rapid screening methods
- => looks good cold, alpha spectra?

TK103 Discs (Ra) and method optimisation

TK227 Discs? LSC? GPC?

Use in RN QC (Pb-212, Ac-225) e.g. for Th determination? Beta testing

More discs…

Passive sampling

- Wagner et al.
- Passive sampling via DGT (Diffusive Gradiant in Thin films) => ‘bio-availability’
- TK100 Discs for Sr, Pb, Zn and Sr-90
- CU Discs for Cu
- Laser Ablation instead of elution?
    - More homogenous surface compared to resin based films

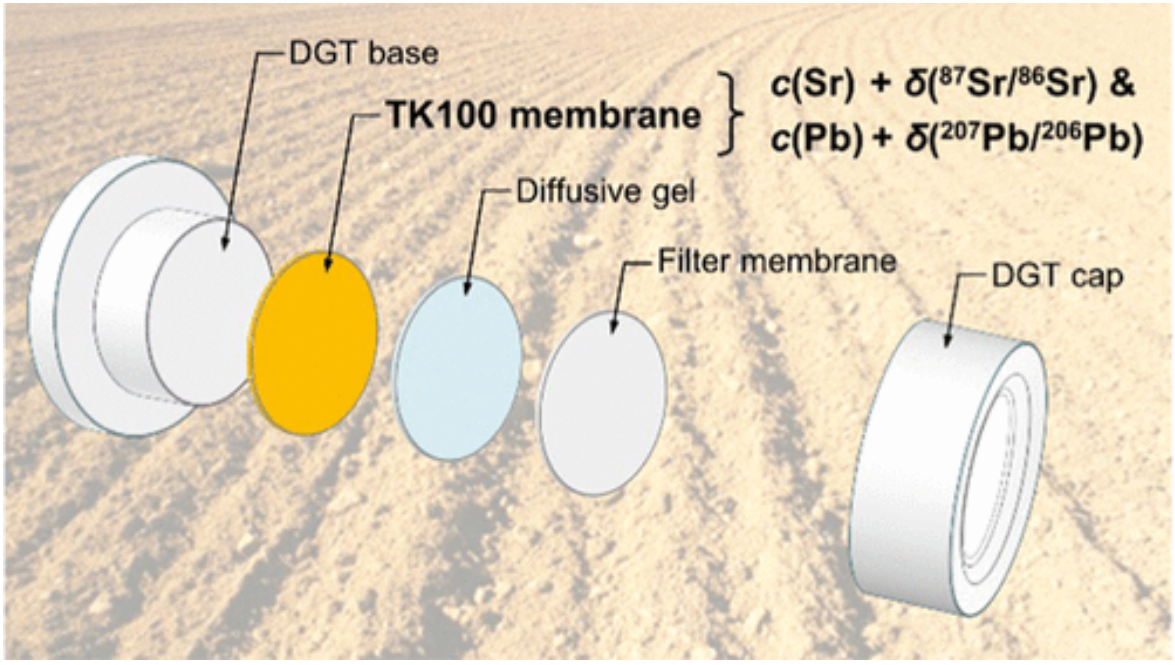
analytical chemistry

pubs.acs.org/ac Article

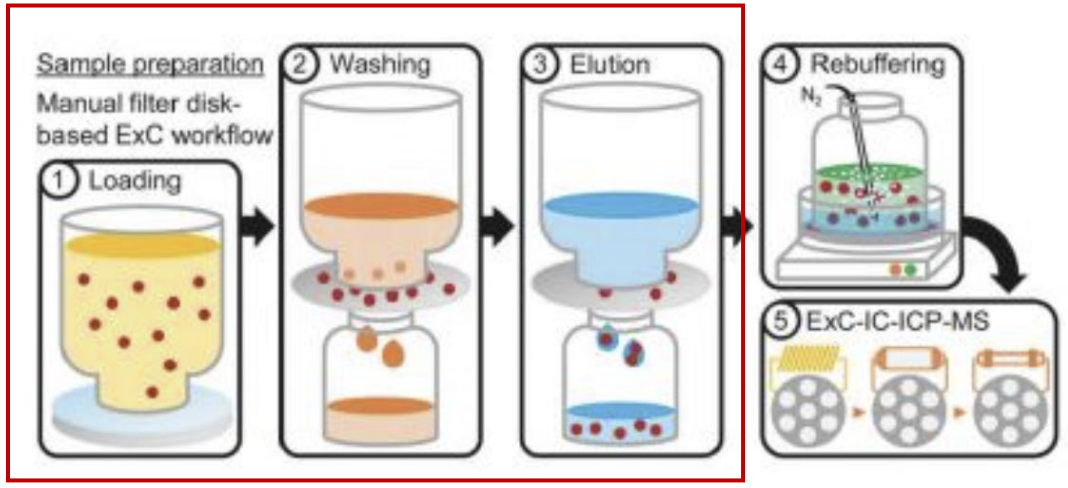
Selective Diffusive Gradients in Thin Films (DGT) for the Simultaneous Assessment of Labile Sr and Pb Concentrations and Isotope Ratios in Soils

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

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



Tc Preconcentration



Experimental setup, Tc-99 concentration and purification from waste water using TK201 discs for preconcentration

- 1L hospital waste water
- Preconcentration on 47mm TK201 Disc
- Elution in 0.5M NH_4OH
- Readjustment of pH to allow loading onto TK201 column (PrepFast)
- Elution in 0.5M NH_4OH concentration/purification step
- Load onto IC column
- Elution in 0.15M NH_4NO_3 in very small volume
- ~100% chemical yield
- LoD < 1fg/kg

« Quantification of technetium-99 in wastewater by means of automated on-line extraction chromatography – anion-exchange chromatography – inductively coupled plasma-mass spectrometry »

J. Anal. At. Spectrom., 2024, 39, 2774-2782

Maximilian Horstmann, C. Derrick Quarles Jr, Steffen Happel, Michael Sperling, Andreas Faust, David Clases* and Uwe Karst

On-going: PhD thesis Eya Abed

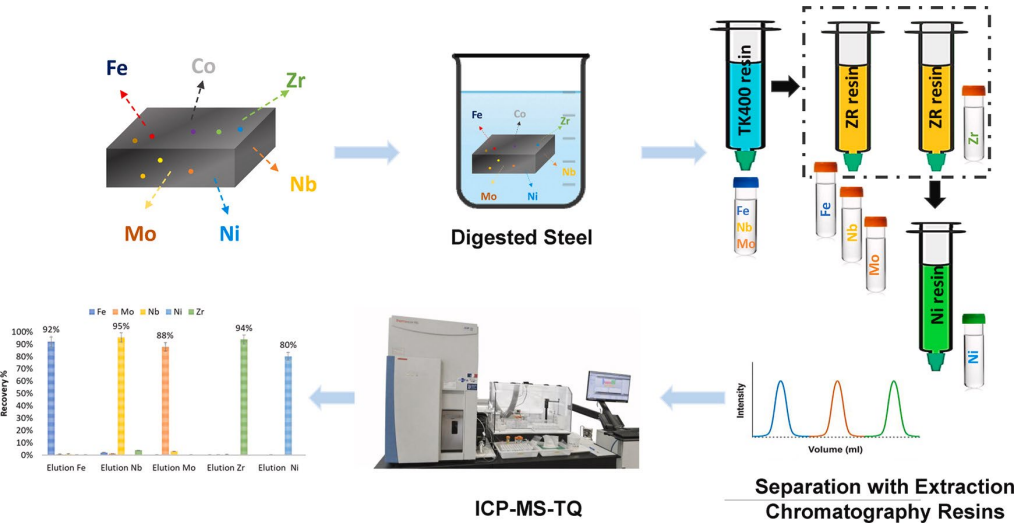
ELSEVIER

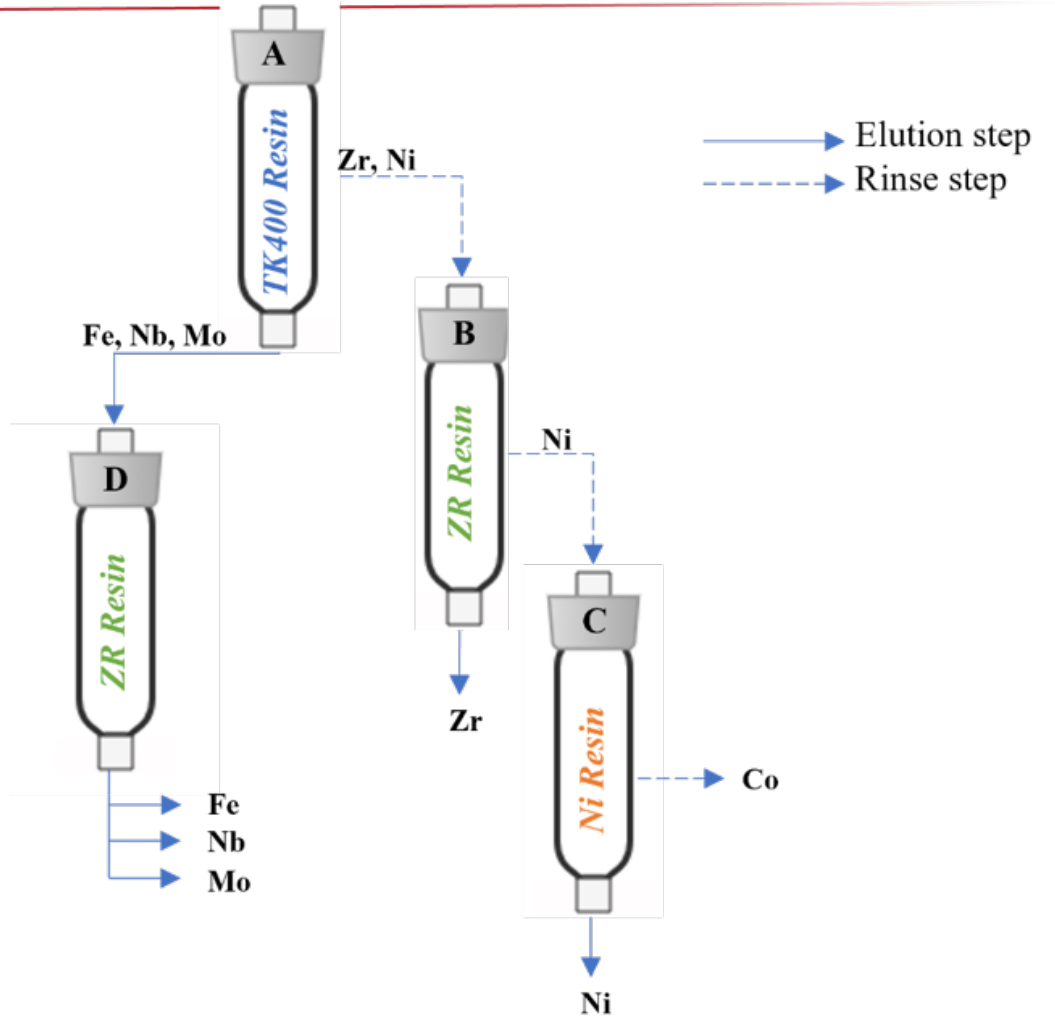
Analytica Chimica Acta

Volume 1419, 15 October 2026, 345891

Optimized single-sample sequential separation for stable elements (Fe, Ni, Mo, Nb, and Zr) at trace levels

Eya Abed [a b], Anne-Laure Nivesse [a], Tomo Suzuki-Muresan [a], Illarion Dovhyi [b], Nicolas Bessaguet [a], Steffen Happel [b], Gilles Montavon [a]

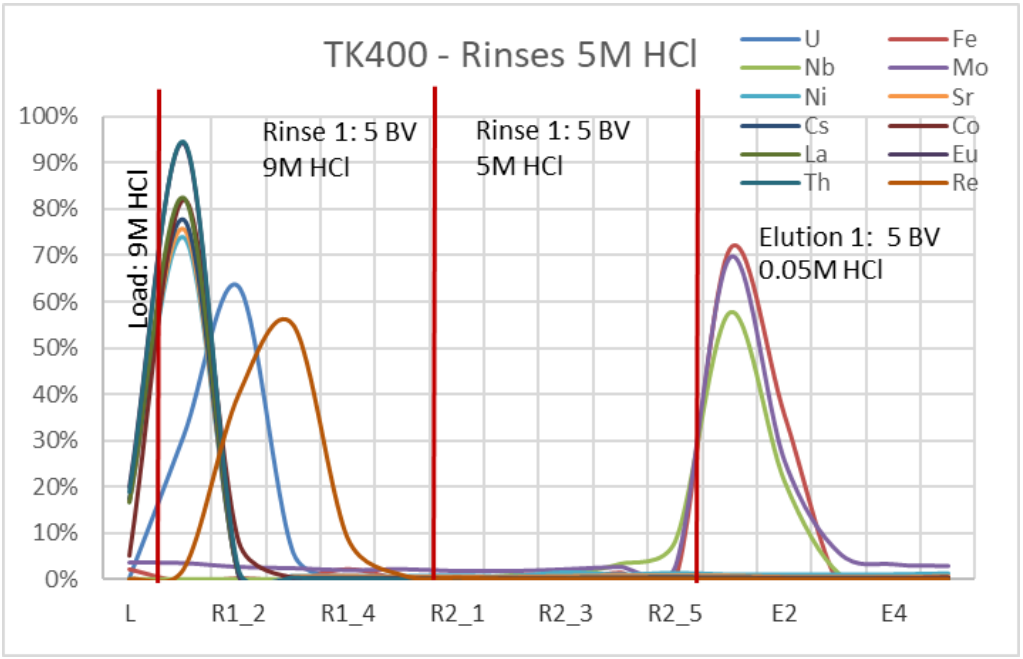


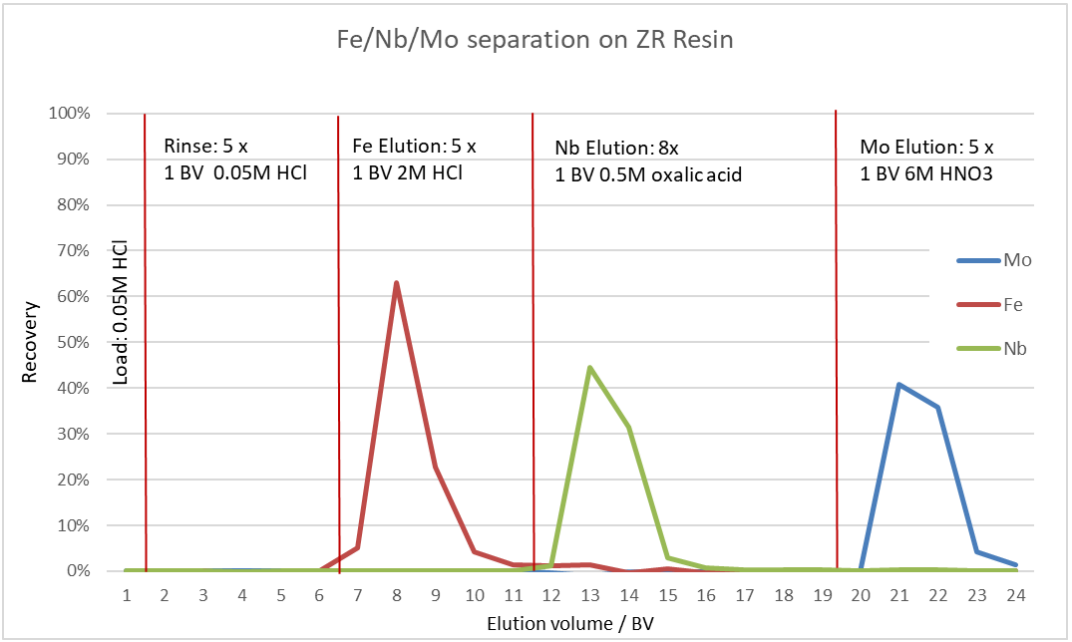


Determination of multiple analytes in decommissioning samples

Ongoing: improved/new NI Resin

Reminder: Fe/Mo/Nb separation

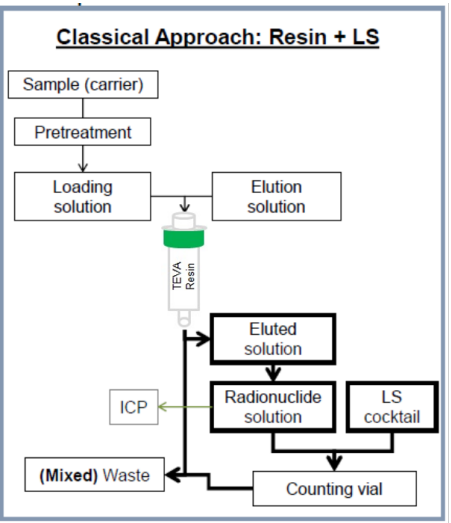


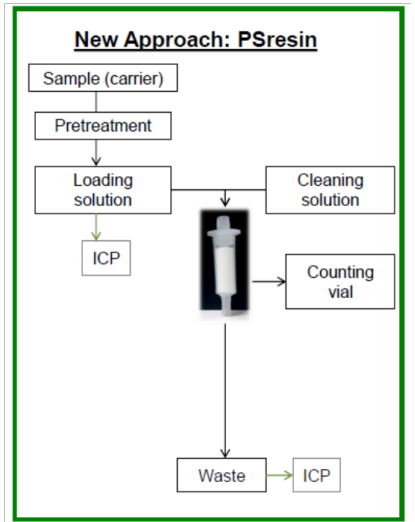


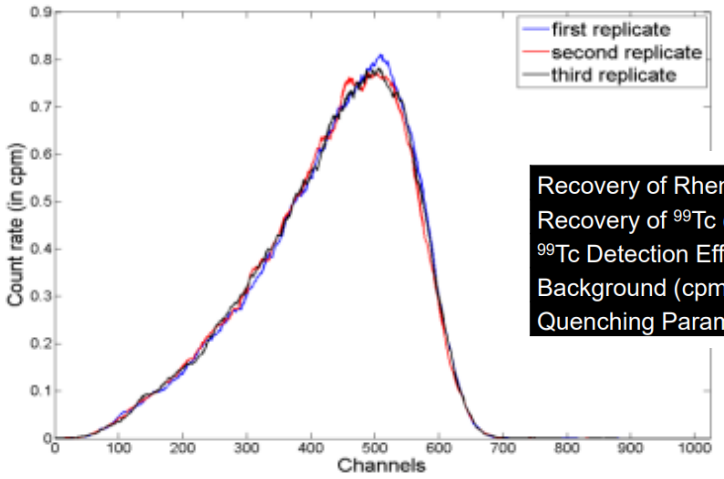
- Part of sequential method for determination of Fe, Ni, Zr, Mo, Nb, Tc in stainless steal (PhD student with Subatech, cooperation with IPHC)
  - Project includes modified NI Resin for improved selectivity (esp. Cu)
- Recovery of Fe/Nb/Mo from high HCl on TK400
- Majority of other elements removed during load and rinses (9M and 5M HCl)
- Fe/Nb and Mo eluted in dilute HCl => separation on ZR Resin

On-going: PhD thesis Eya Abed

- PhD thesis is part of a larger project on RN in stainless steel samples from decommissioing
- Sequentiel method for multi-analyte quantification
- Additional: Tc-99 via TK201 and TK-TcScint
  - TK201: allows for Tc elution in 0.5M NH_4OH (or 3M HNO_3)
  - TK-TcScint, no elution, direct measurement of cartridge
    - Based on impregnated plastic scintillator beads (PSm)
    - Also available TK-SrScint (based on TK102 Resin extractant)







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)

Cl-36 via ICP-MS/MS

Analytica Chimica Acta 1410 (2026) 345611

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

« S » free elution of Cl-36 to avoid isobaric interference

Allows for Cl-36 analysis via ICP-MS/MS

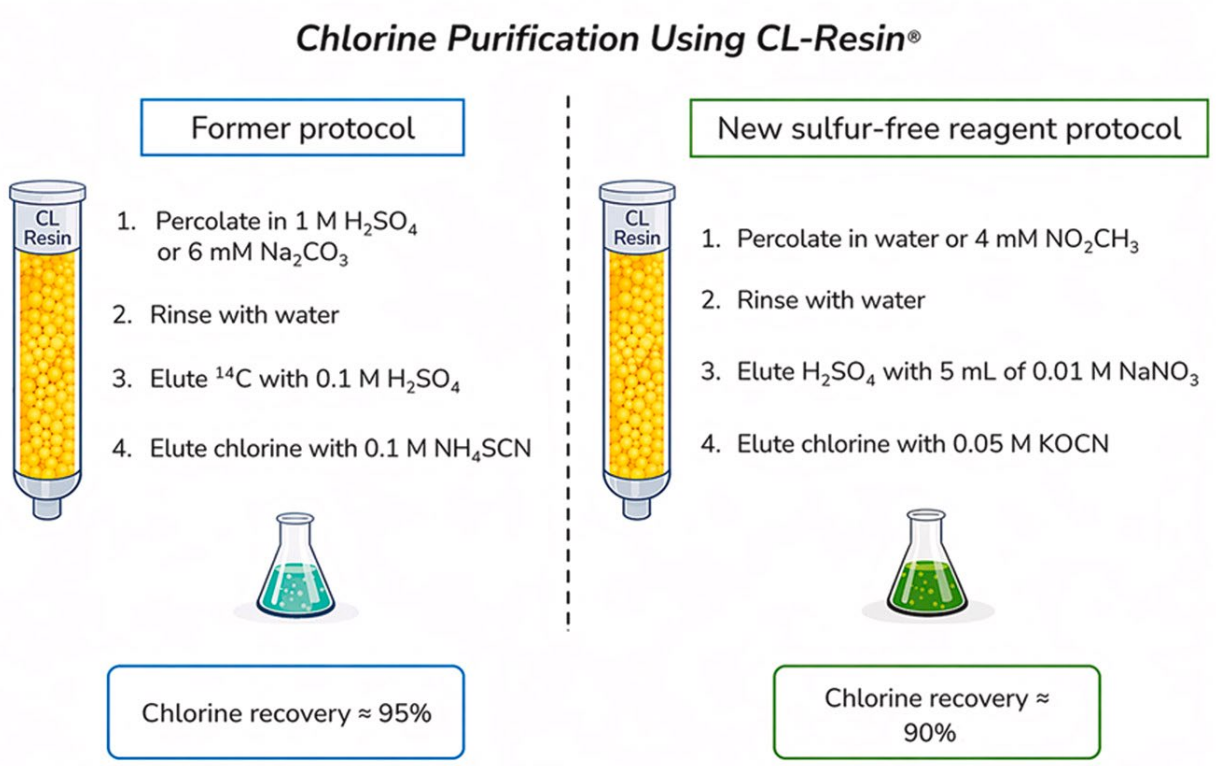
Investigation of the CL-resin® properties for a sulfur-free content molecule protocol

Amayès Gaston-Bellegarde [a,b,*], Azza Habibi [b], Pascal Fichet [c]

[a] Sorbone University, Paris, France
[b] The French Authority for Nuclear Safety and Radiation Protection, Le Vésinet, France
[c] The French Alternative Energies and Atomic Energy Commission, Saclay, France

Table 1. Solubility product constant (K_{sp}) and calculated solubility (s) of silver compounds.

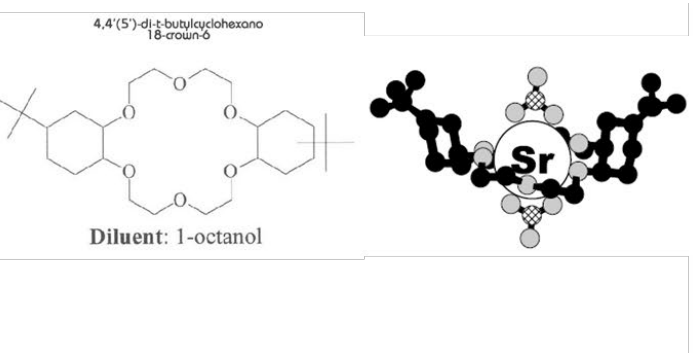
Compound	K_{sp}	Solubility (s) mol.L^{-1}	References
AgCl	1.77×10^{-10}	1.33×10^{-5}	[3]
Ag_2CO_3	8.46×10^{-12}	1.28×10^{-4}	[3]
AgOCN	2.3×10^{-7}	4.8×10^{-4}	[14]
AgSCN	1.03×10^{-12}	1.01×10^{-6}	[3]
Ag_2SO_4	1.20×10^{-5}	1.44×10^{-2}	[3]
AgCN	5.97×10^{-17}	1.10×10^{-8}	[3]
Ag_2SO_3	1.50×10^{-14}	1.55×10^{-5}	[3]

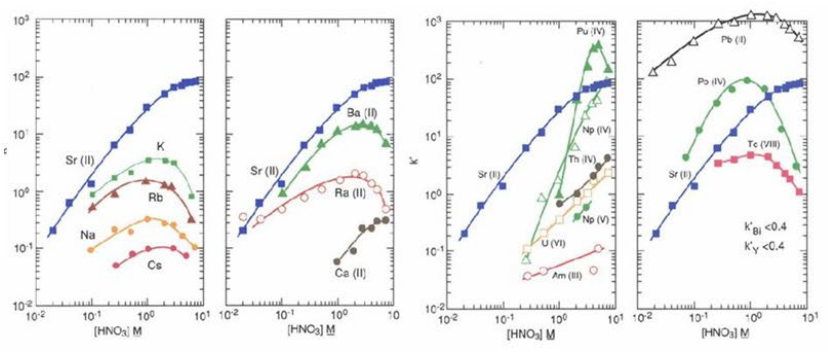


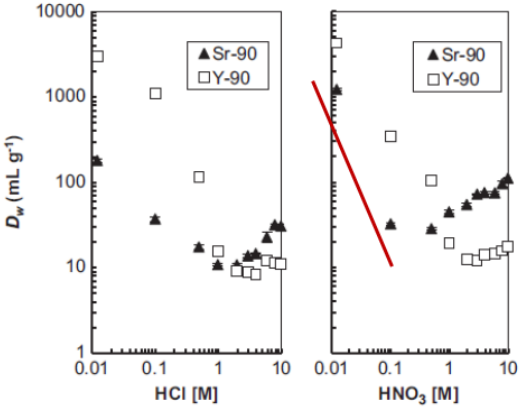
Reminder: TK100/1 Resins

Based on same crownether as SR Resin

- Different diluent (HDEHP), Sr and Pb uptake also between pH 2 and 7
- Original application: passive sampling
- 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, van Es paper (Ra in ground water)

Radium-
Reminder 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

Ben Russell[1], Elsje May van Es[1,2], Glenn Woods[3], David Read[1,2]

1. National Physical Laboratory, Teddington, UK

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



Applied Radiation and Isotopes 126 (2017) 35–39

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

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

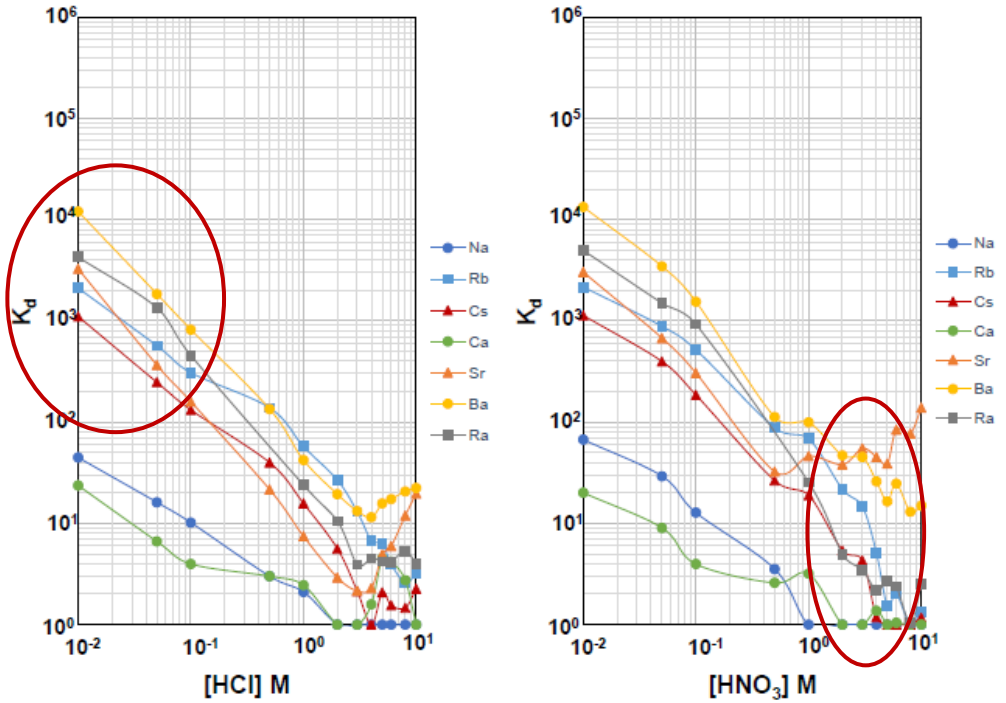
TK100 retains Ra from 1L groundwater (pH 1 – 2) on 2mL cartridge

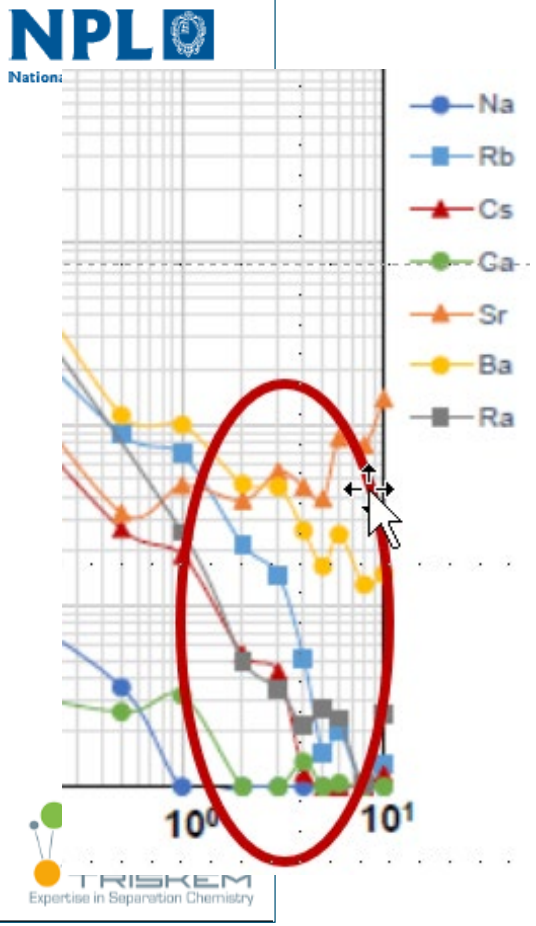
TK100 contains HDEHP => wide range of éléments retained (incl. U, Th,…)

Problematic for Ra separation

TK101 - Radium

TK101 Group 1 and 2

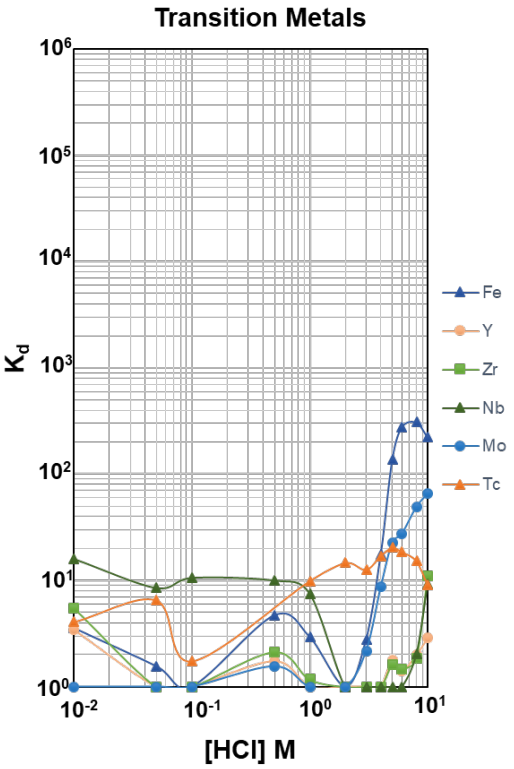


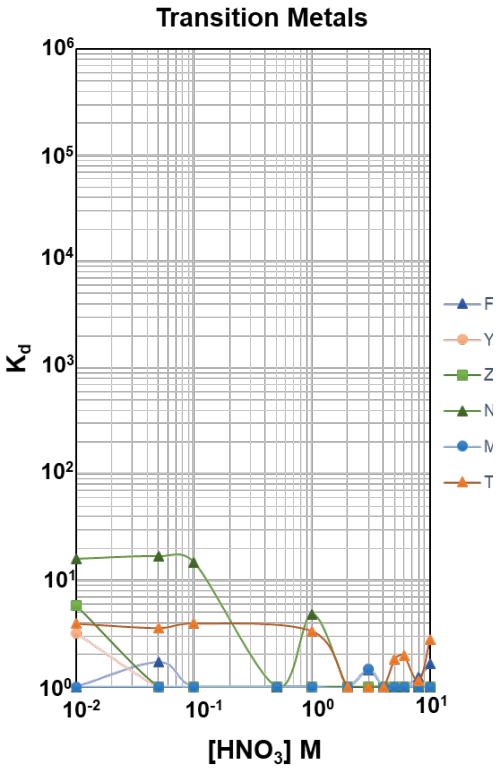


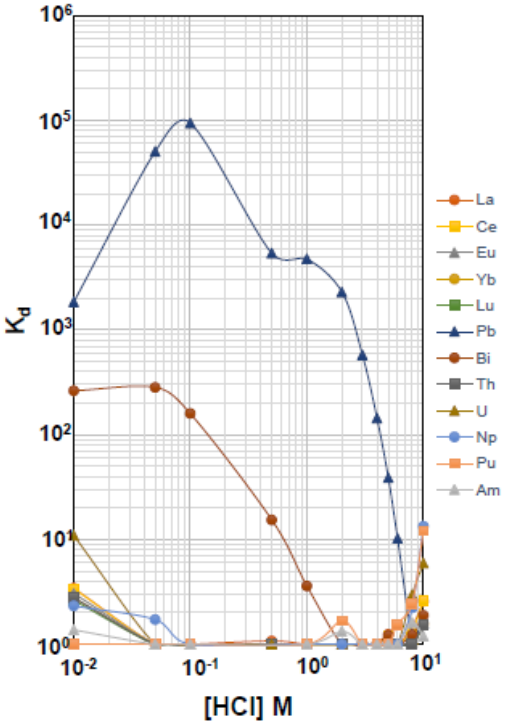
Data provided by Russel et al. (NPL)

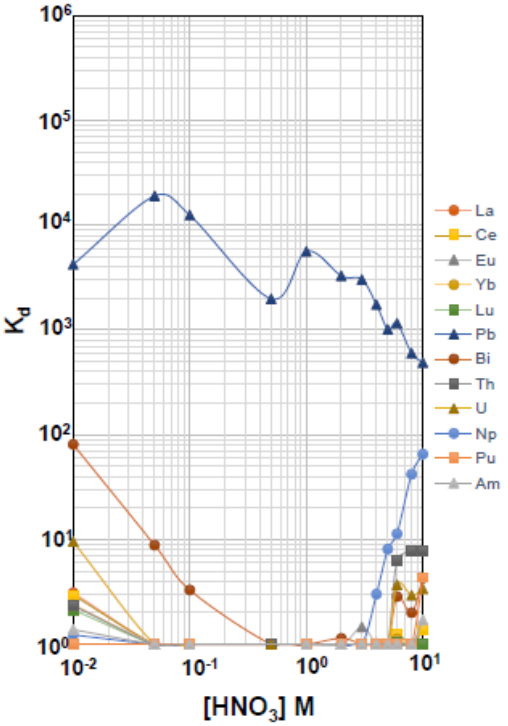
- TK101 => IL instead of HDEHP, better selectivity
- Ra retention from water/dilute acid up to ~0.5M HNO_3/HCl
- At higher conc. selectivity closer to SR Resin/TK102 Resin

TK101 Resin





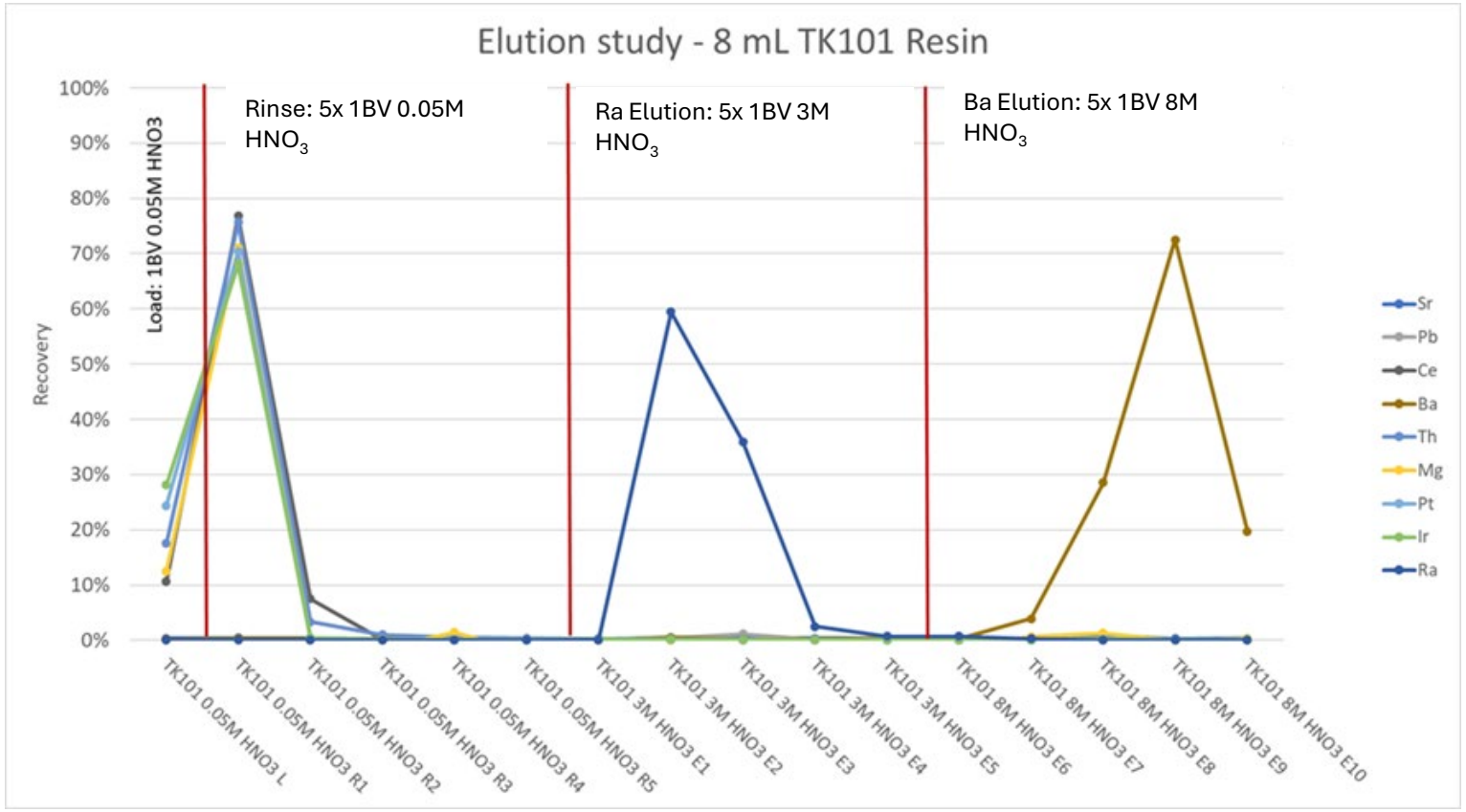




- No / very low selectivity for Th/U and TMs
- Very strong Pb retention => elution in high HCl or citrate

Data provided by Russel et al. (NPL)

Ra separation on TK101



Good Ra separation when loading **from dilute HNO_3/HCl**

Only up to 300mL per 2mL cartridge!

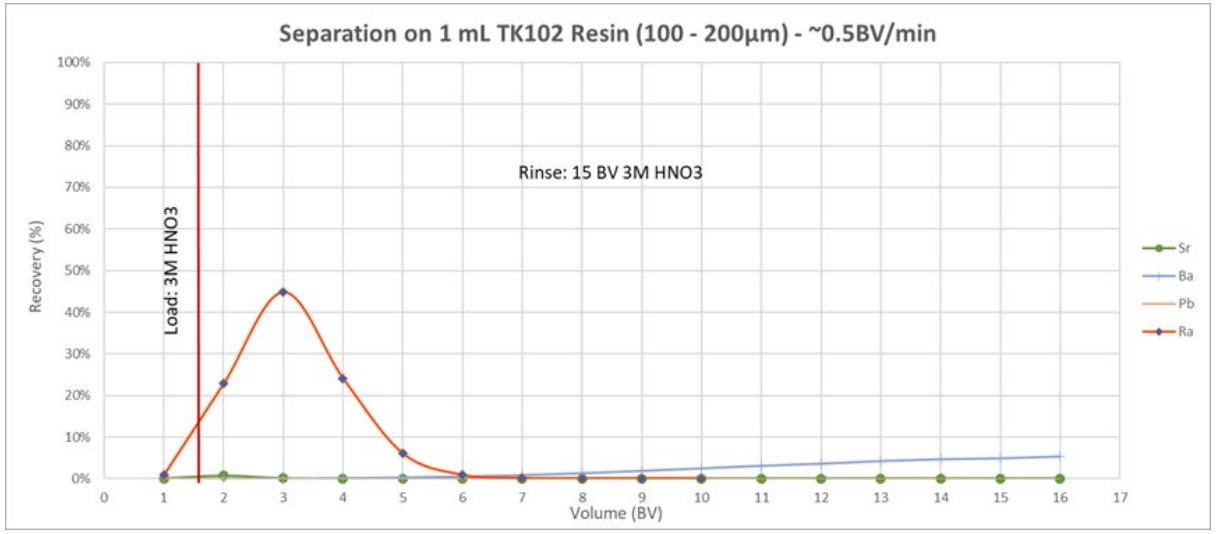
No retention of U, Th, Pt, Ir,…

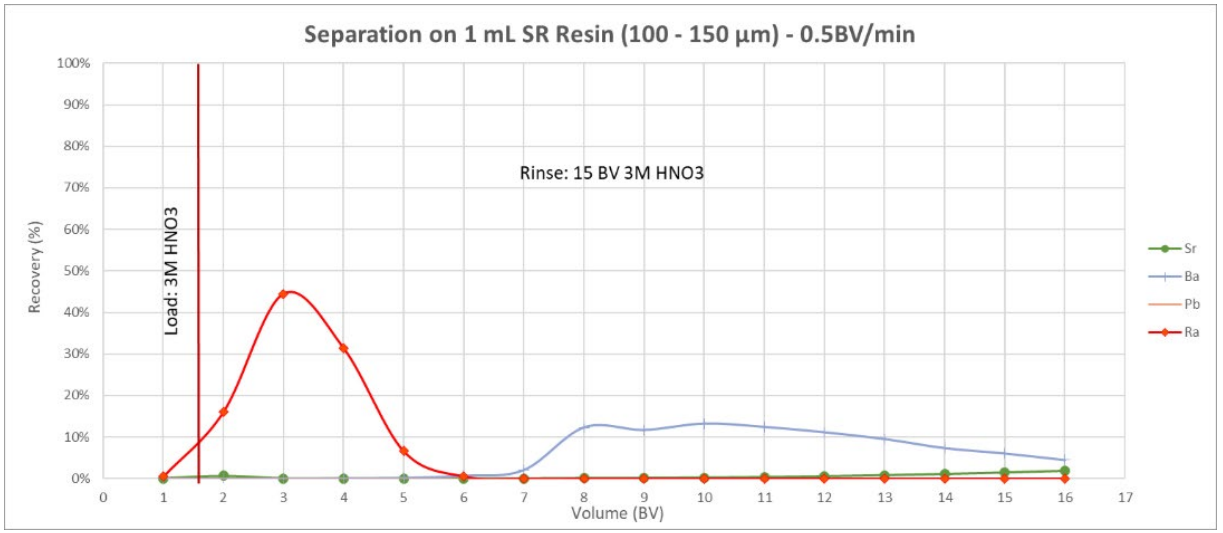
When eluting Ra in 3M HNO_3, Ba, Pb, Sr remain retained

Further Ba removal via TK102 possible

Ra/Ba can be co-eluted in 8M HNO_3

Ra/Ba separation – TK102



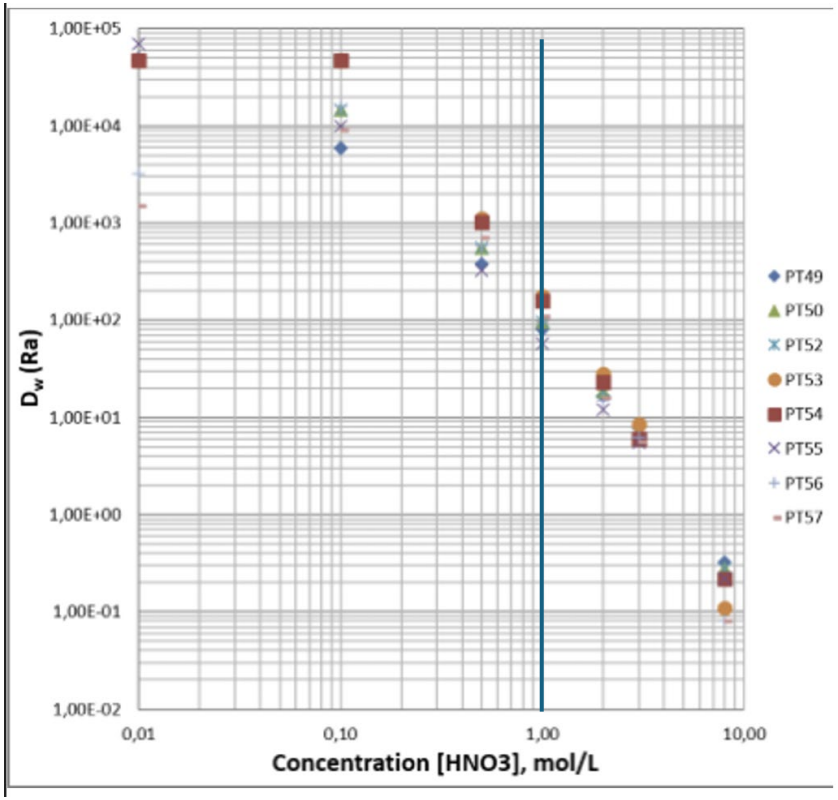


- TK102: higher D_W for Sr, Ba, Pb,…
- Based on same CE than SR Resin
- TK102 Resin: significantly lower Ba breakthrough than SR
- Suitable for Ba removal from Ra at 3M HNO_3

Ongoing: TK103 Resin

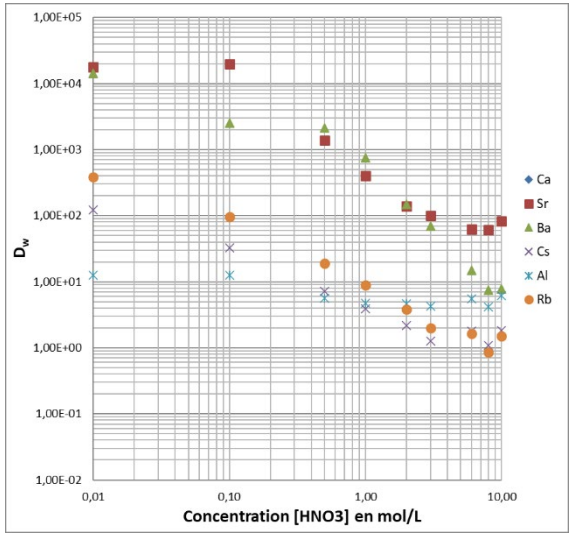
- TK101 shows good selectivity for Ra, but retention from low acid only, max. 300mL load onto 2mL cartridge
- TK100 allows for loading 1L of sampler through 2mL cartridge in low acid but retains numerous other éléments.
- Potential alternative: TK103 Resin
- Also based on crown ether but different diluent system
- 2 PT under beta testing (PT 52 and 56), one containing a fluorinated compound (PFAS….), the other does not
- Very similar selectivity

Under beta testing: TK103 Resin

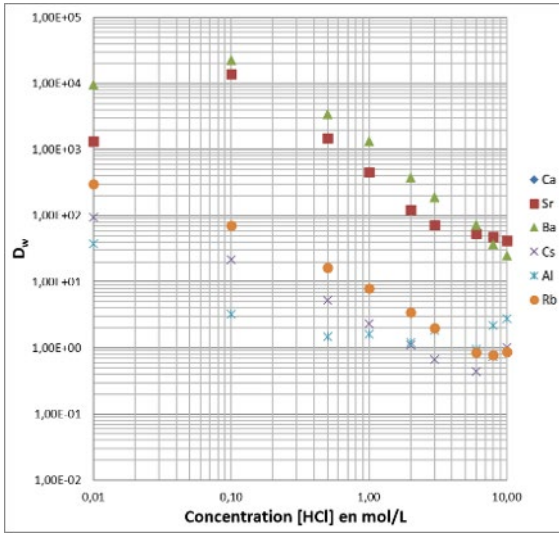


Ra Dw values PT under testing, HNO_3

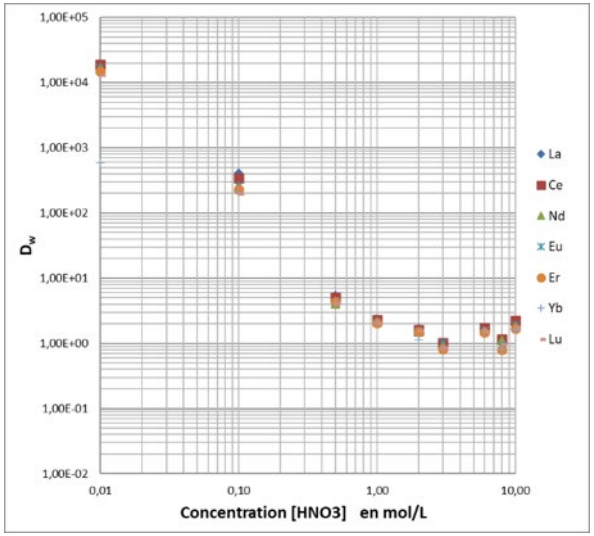
Improved Ra retention at 1M HNO_3 compared to TK101 Resin



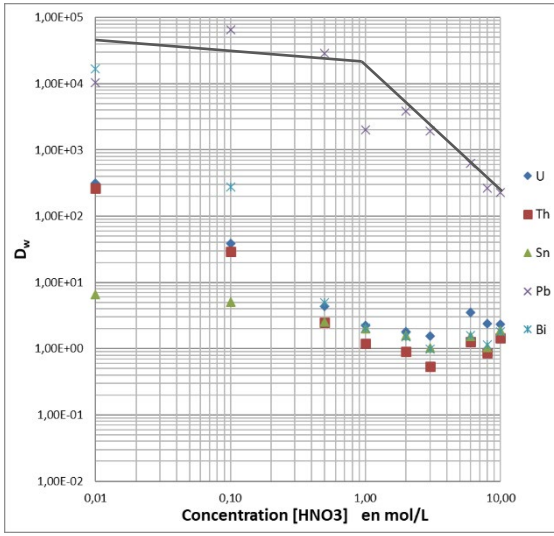
Dw values PT52, HNO_3



Dw values PT52, HCl

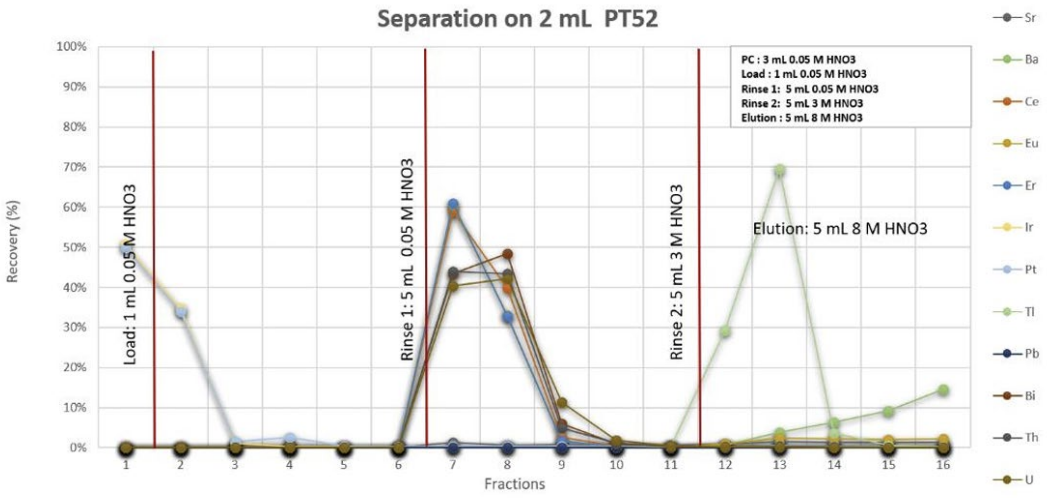


Dw values PT52, HNO_3

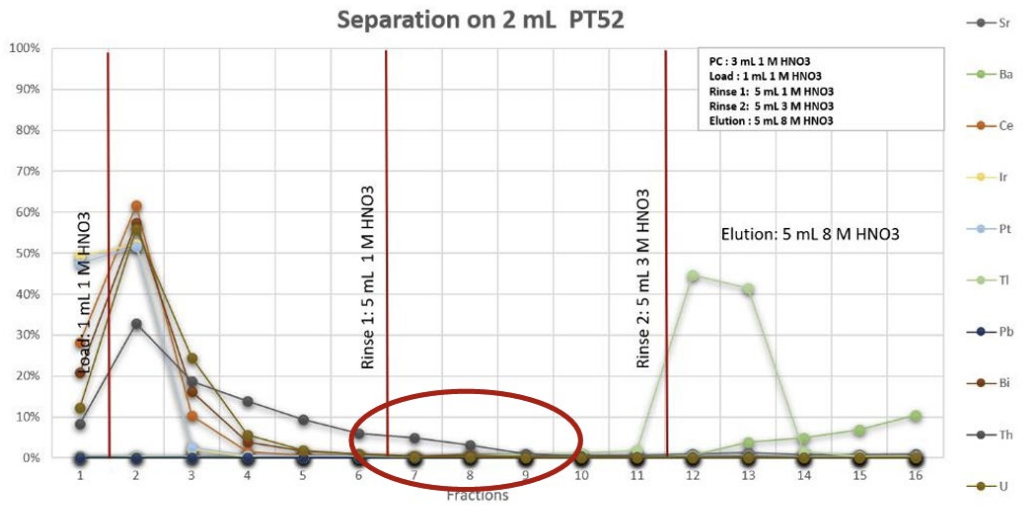


Dw values PT52, HNO_3

TK103 Resin – elutions studies

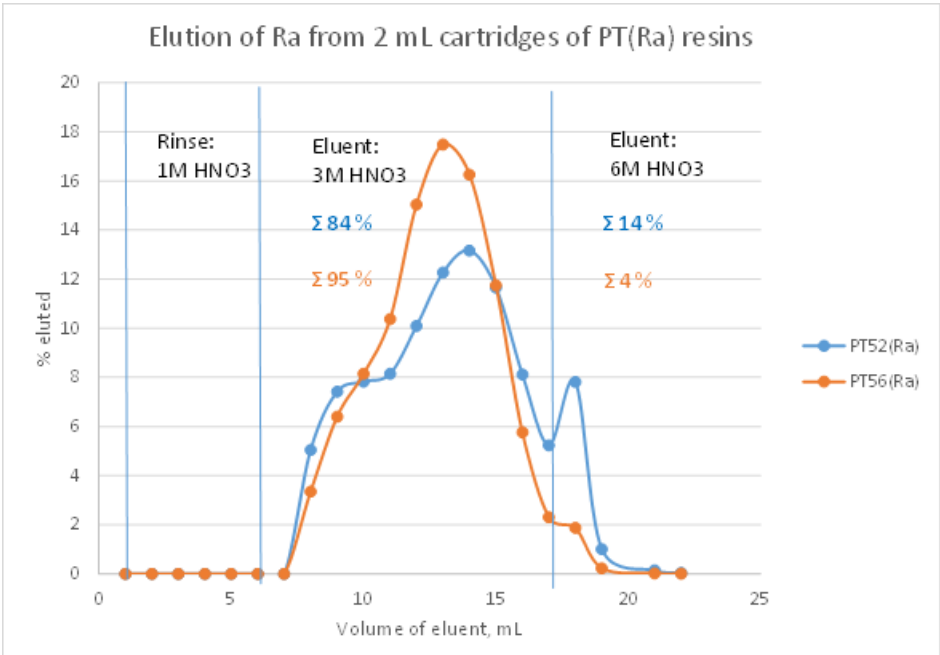


PT52

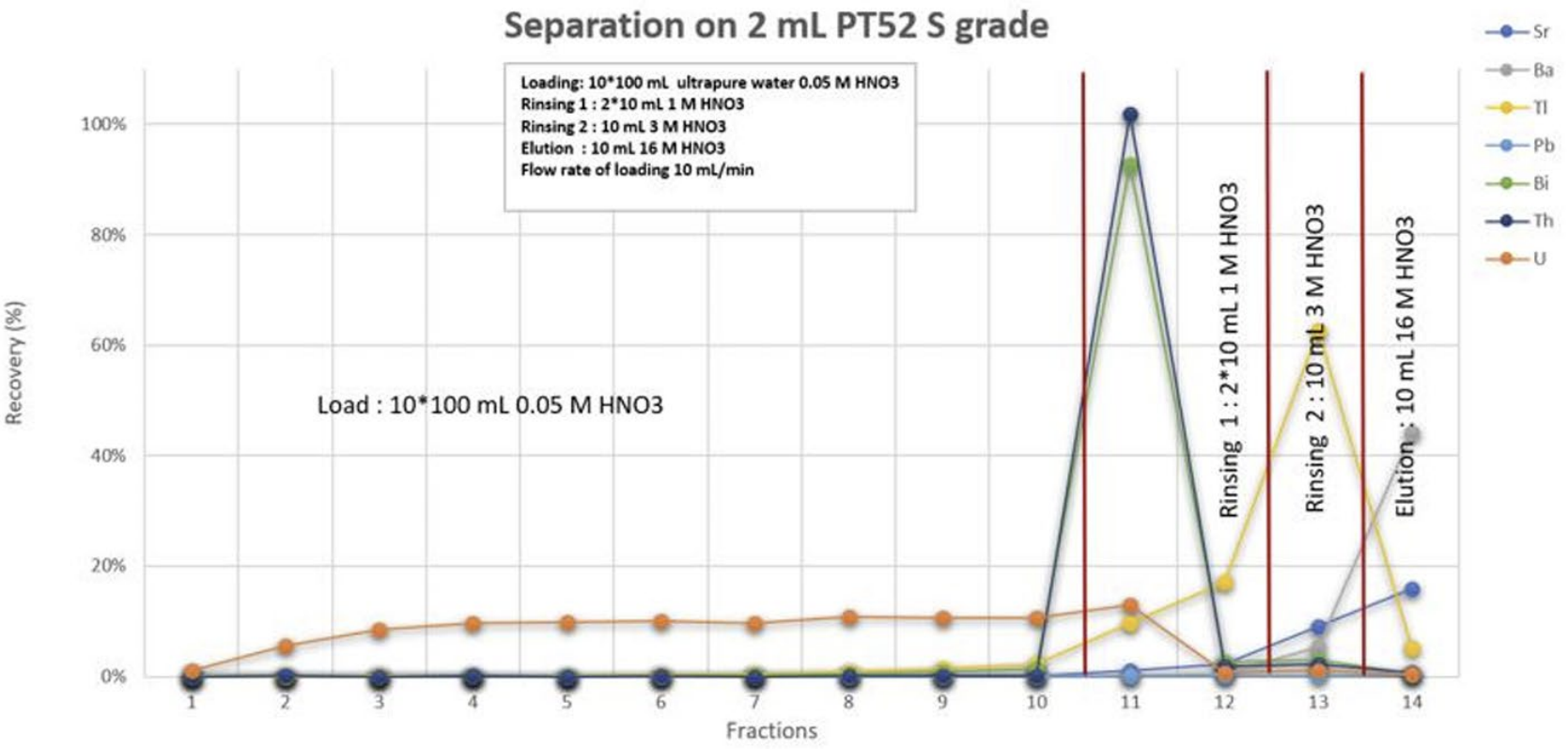


PT52

- Load from 0.05M HNO_3: large number of analytes retained incl. Ra, Ba, Sr, Pb,…
- Rinsing step with 1M HNO_3 required to remove most RN.
- Special attention to Th, requires larger rinse. Ra, Ba, Sr, Pb remain retained
- Ra elution in 3M HNO_3
- Slightly smaller elution volume for PT56



TK103 Resin – 1L samples



Both allow for loading 1L of 0.05 HNO_3 samples through a 2mL cartridge.

Original test: Ba, confirmed for Ra (N. Vajda)

Ongoing: optimisation of rinsing/elution volumes

Pure Ra fraction / Ra/Ba co-elution (e.g. Ba-133 internal standard)? Ba elution difficult

Ongoing: TK103 Resin

- Choice between 2 PT, probably PT w/o fluorinated compound
  - No significant difference in selectivity
  - With fluorinated compound better Ra retention in 1M HNO_3 => PFAS…
  - But elution in 3M HNO_3 less sharp
- Good Ra uptake from dilute acid to 1M HNO_3
  - Current beta testing: Radiopharma: Ra-226 purification / recycling
- In dilute acid: loading of 1L of sample through a 2mL cartridge
  - Including phosphoric acid => recovery of Ra from phosphate matrix?
  - Several RN retained, 1M HNO_3 for RN removal (special attention to Th)
- Ra elution in 10 - 15mL 3M HNO_3 (sharper in higher HNO_3)
- Ba elution probably complexing agent (e.g. citric, NTA, EDTA)
  - Impact on microprecipitation, use of Ba-133
- Next step: TK103 Disc and beta testing / real samples

On-going: TK104 Resin

Request from Radiopharmaceutical customers (Pb-212):

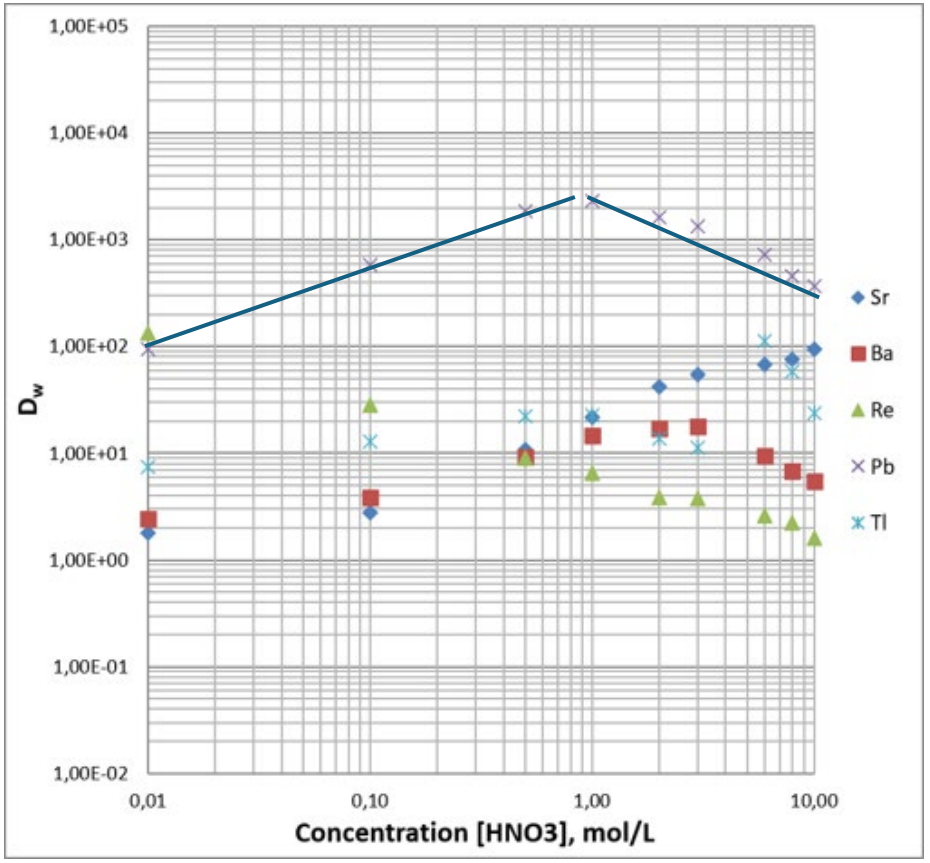
Smaller elution volume with acetate buffer or (even better) water

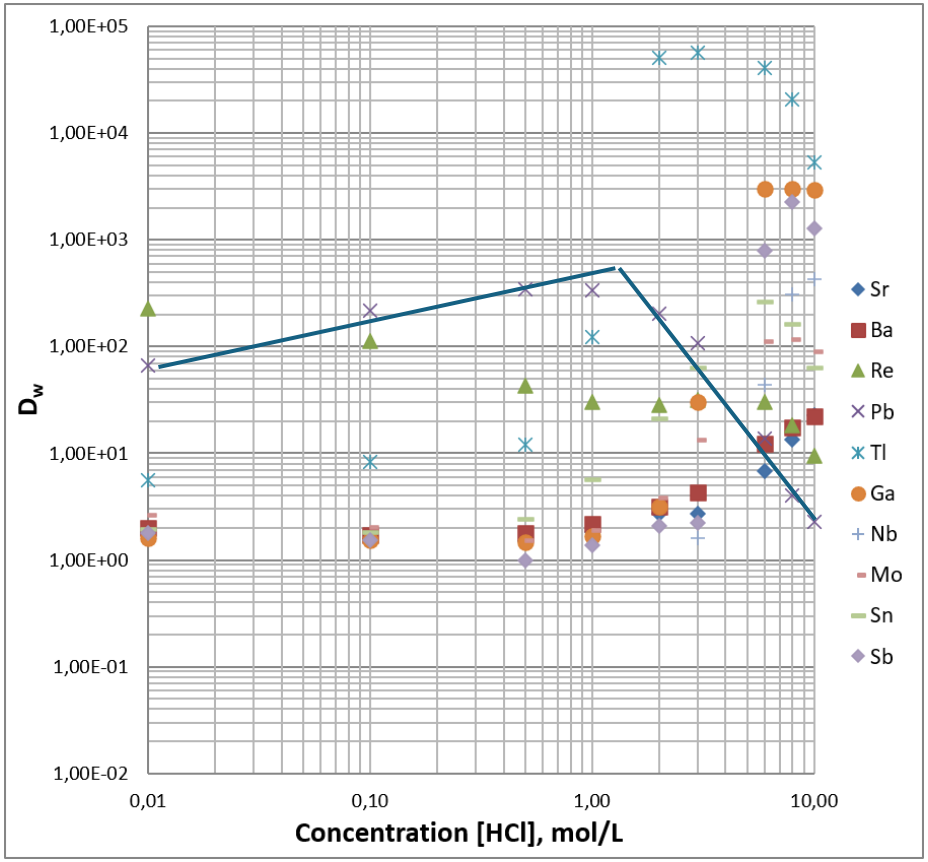
Also based on CE (need to keep away from TK201: patent, 1M HNO_3)

Optimisation of organic phase to facilitate Pb elution while keeping retention in 1M HNO_3 and 2M HCl high enough

First samples out for beta testing

TK104 Resin – D_w values





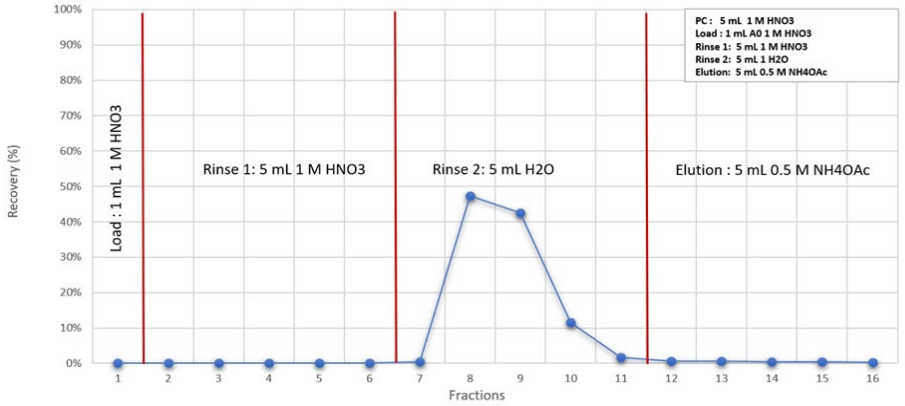
Dw Pb > 1000 at 1M HNO_3 and >300 in 2M HCl

Low retention of earth-alcalines in HNO_3 and HCl

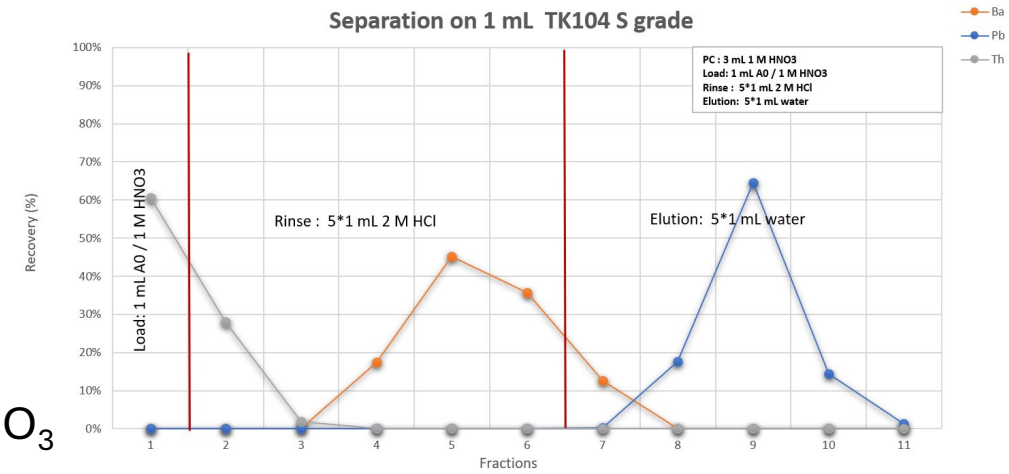
Several elements retained in high HCl

On-going: TK104 Resin

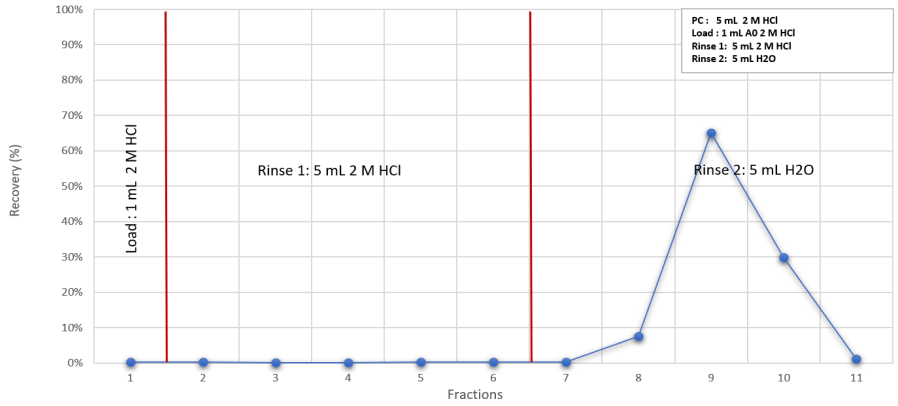
Elution studies



Elution on 1 mL TK104, load and rinse: 1M HNO_3
elution: water



Elution on 1 mL TK104, load: 1M HNO_3,
rinse: 2M HCl, elution: water, Th, Ba, Pb



Elution on 1 mL TK104, load and rinse: 2M HCl
elution: water

Pb retained from 1M HNO_3 and 2M HCl

Pb elution in 3-4 BV water

Beta testing on-going

Calixarene based resin for Cs separation – TK300 Resin

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
- Matrix load => MS measurment (e.g. Cs-135)

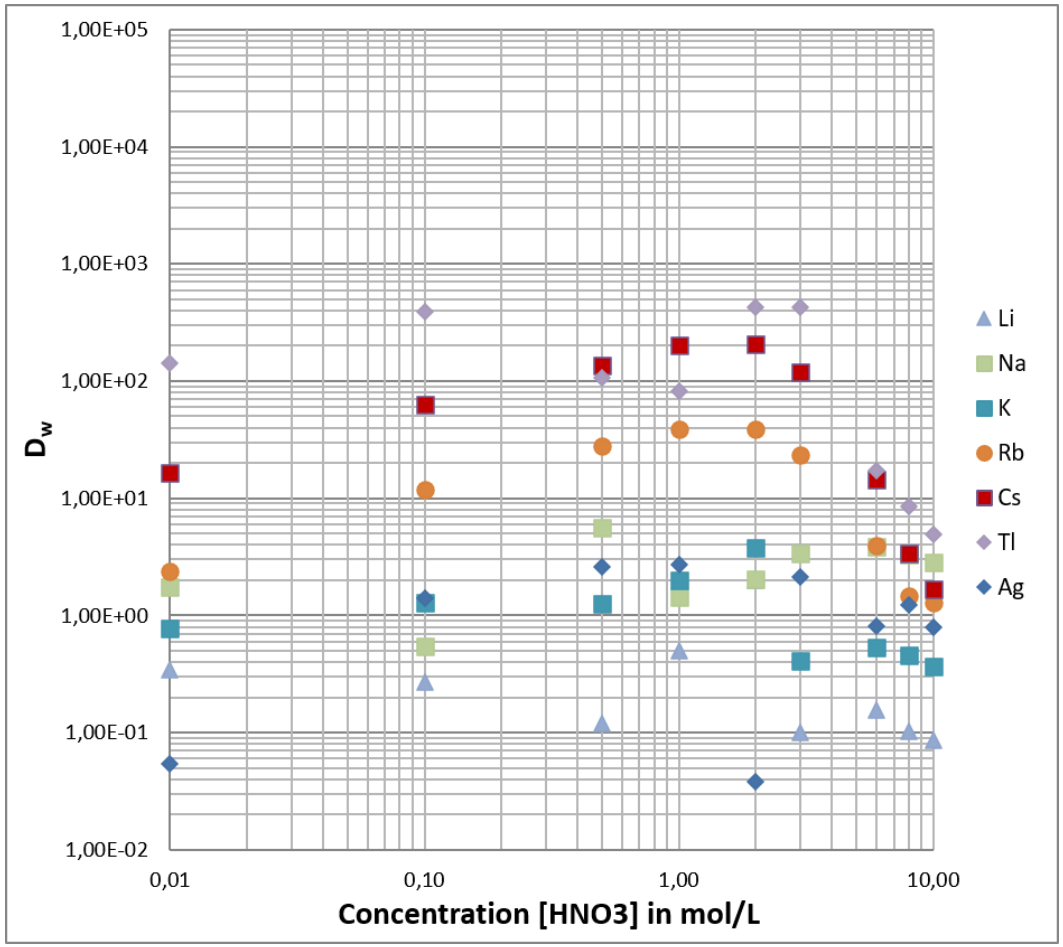
Use of calixarene based resins instead => pricing…

Original TK300 Resin work

- High Cs/Ba selectivity
- Load at up to 1-2M HNO_3
- Elution in water not possible, NH_4 salts or very strong HNO_3
- Home made calixarene => upscale too difficult

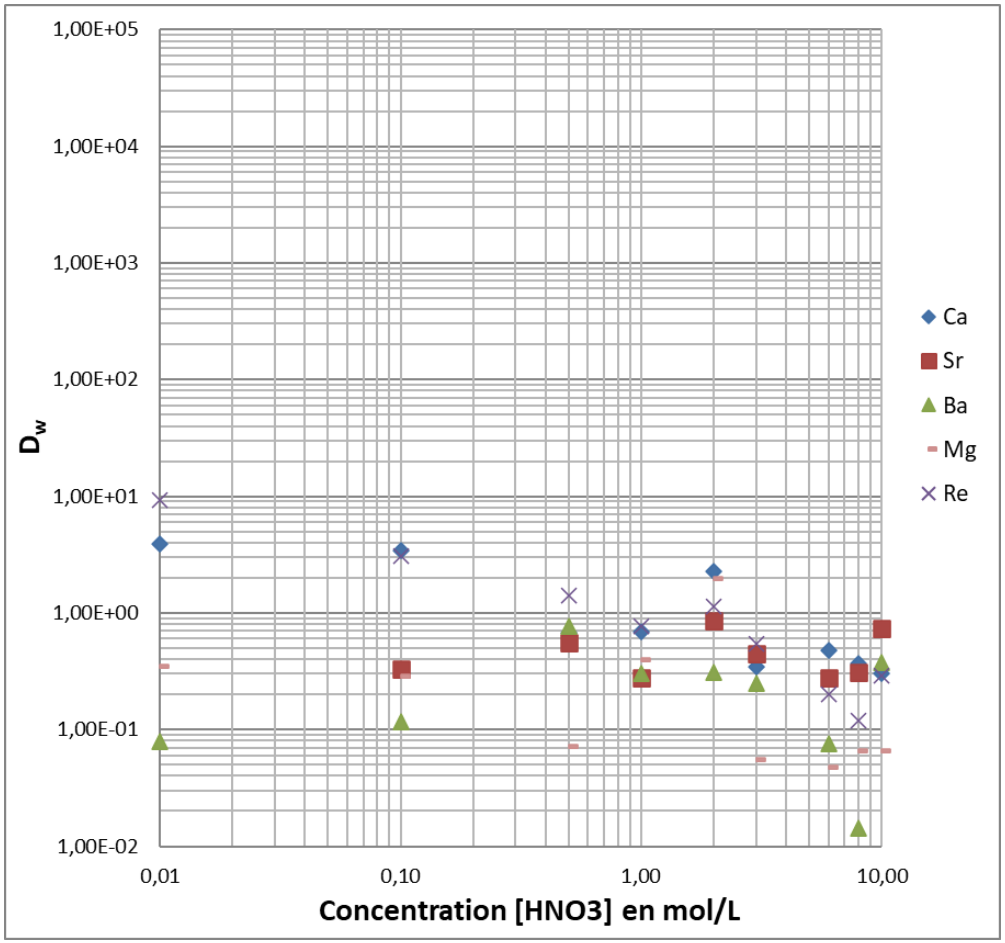
  => Use of commercially available Calixarens

Dw values TK300 Resin



Distribution coefficients of selected elements on TK300 Resin in HNO_3

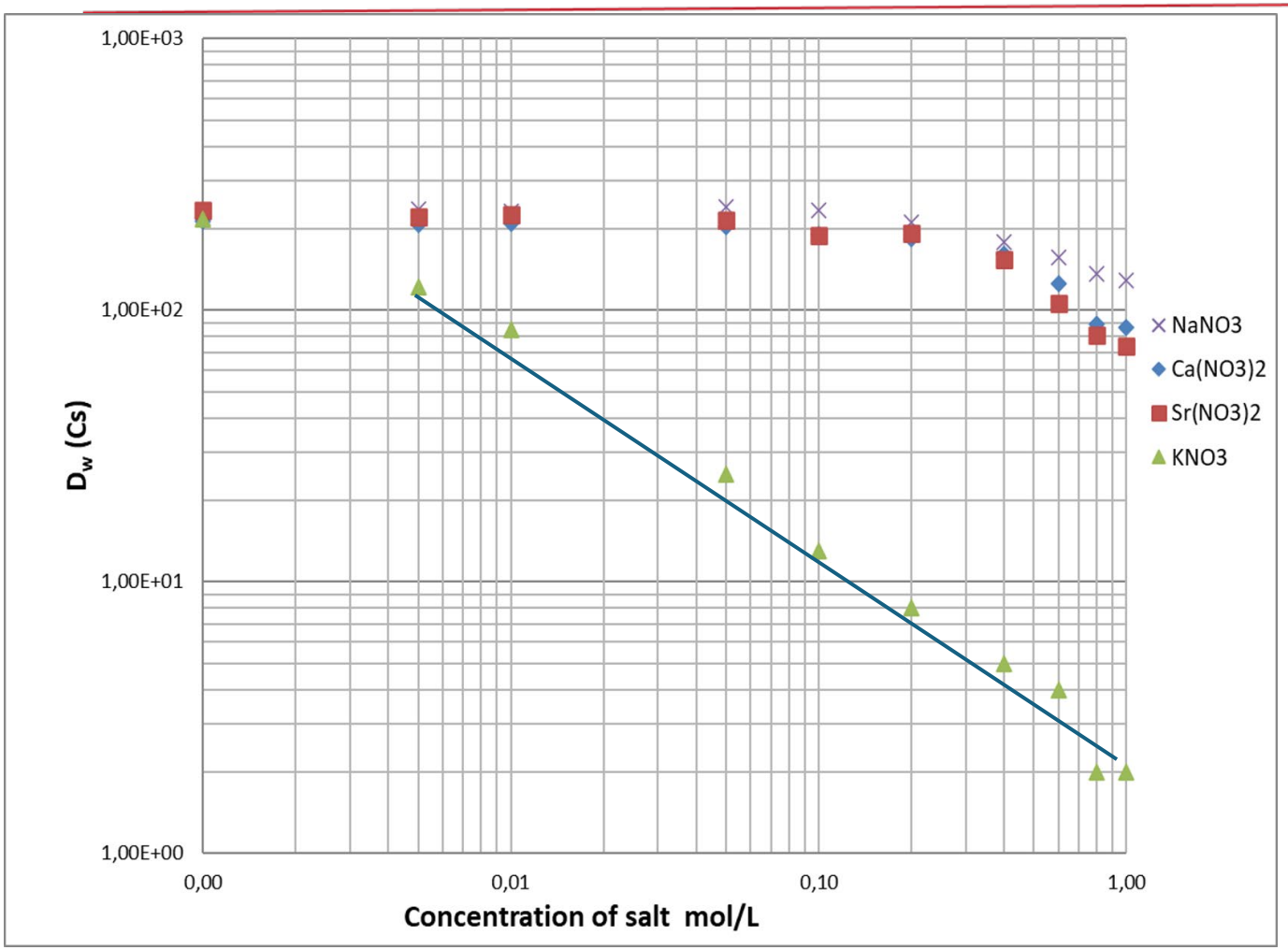
► Rb, Cs and Tl show retention in HNO_3



Distribution coefficients of selected elements on TK300 Resin in HNO_3

► low retention of alkaline earth elements

Influence of matrix elements



Distribution coefficients of Cs on TK300 Resin in 2M HNO_3 / salt

► good Cs retention in presence of elevated concentration of Na, Ca, Sr

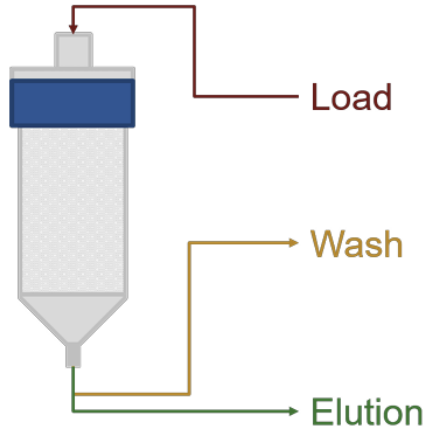
►strong decrease of Dw in the presence of elevated concentration of K

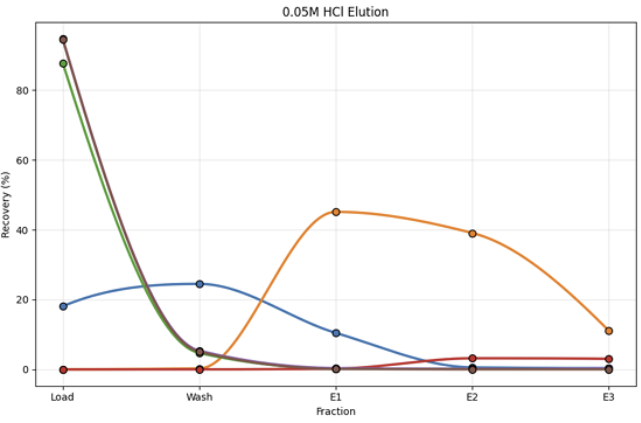
► Not suitable for environmental samples

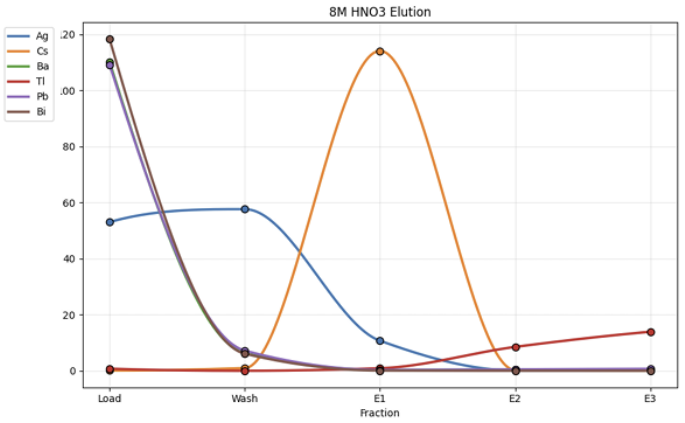
TK300 Resin

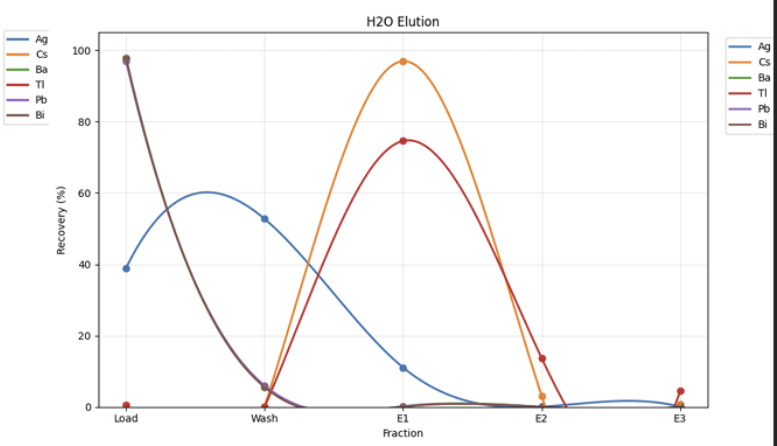
Elution profiles

- Automated separator
- Conditions
  - Load in 10ml 1M HNO3
  - Wash with 10ml 1M HNO3
  - Elution with 3 x 10ml of elution condition
- For elements with Kd >10^2
- Tl and Ag show some retention to column
  - Tl eluted out using H2O



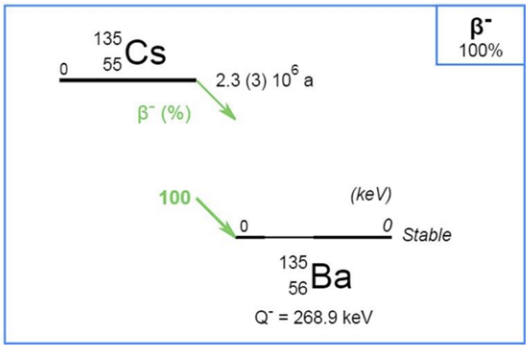




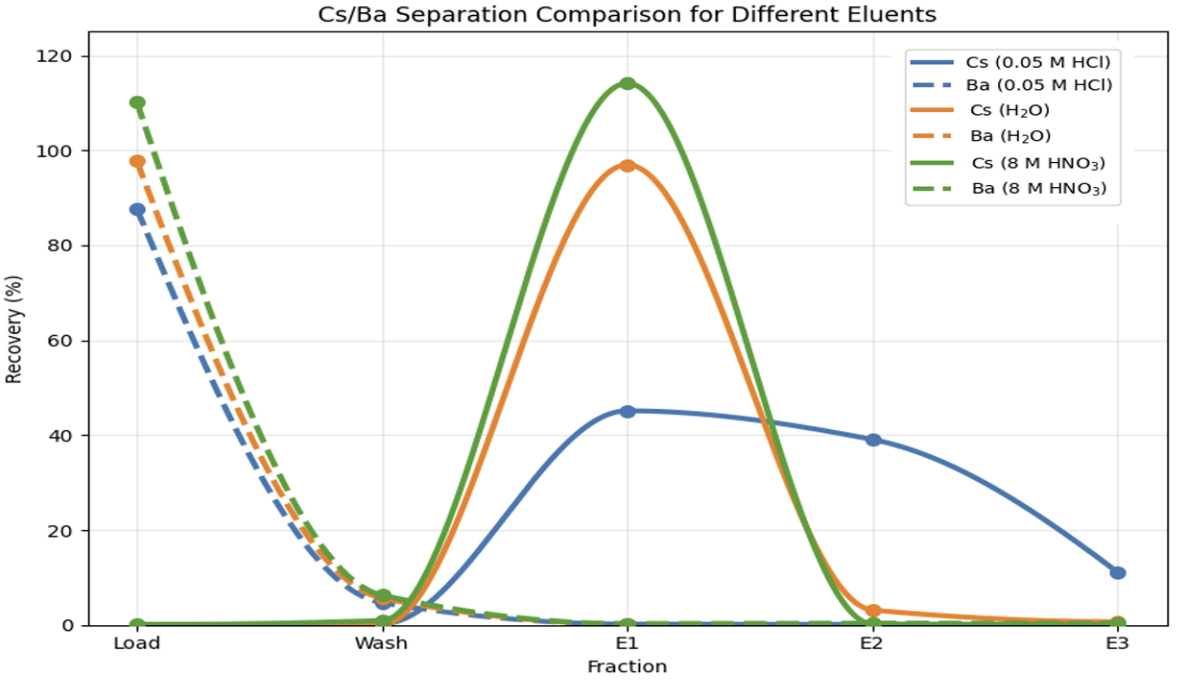


TK300 Resin

Cs/Ba separation



- Comparison of Cs/Ba from previous elution profile
- Ba consistently coming off in Load - clean separation
- Good support for mass spec measurements of Cs-135/137 isotopic ratios



TK300 Resin

- Design fix, beta testing on-going
- Decommissioning samples, not suitable for environmental samples
  - Strong interference by K, low Cs capacity
    - High capacity version: TK305 => pricing…
  - Cs below 0.5 mg recommended
- Resin is very hydrophobic, precondition with 20% EtOH necessary
- Cs load from dilute acid to 2M HNO_3
  - Preferably >0.5M HNO_3 => improved Tc removal
- Good selectivity for Cs over Ba
- Attention to Ag, Tl
- Several option for Cs elution
  - Prefered water or 8M HNO_3

TK430 Resin

Following multiple requests…

NOBIAS type of resin

- IDA / EDTA type of functional groups covalently bound on polymer support

NOBIAS widely used in hydrogeology for concentration of ‘heavy metals’ from water + matrix removal => SeaFAST

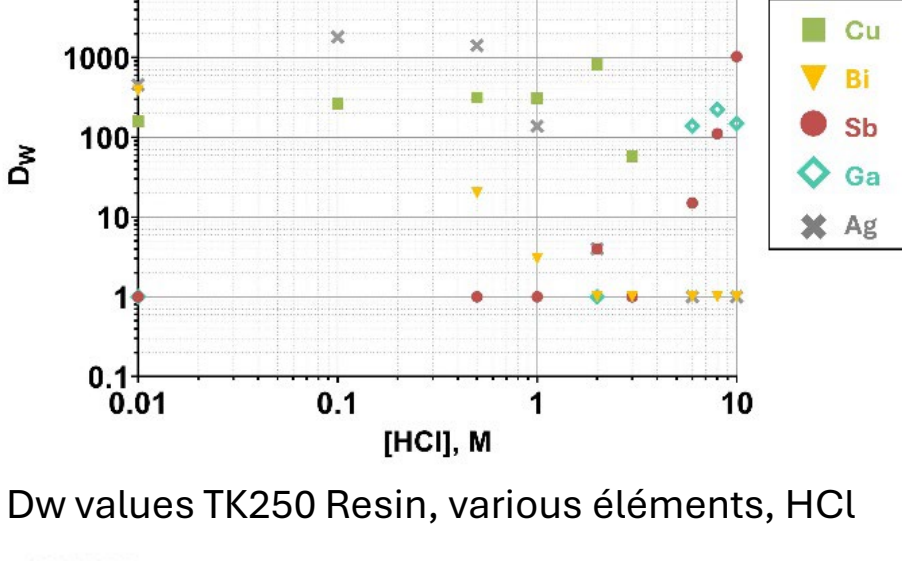
Resin production stopped

Request to re-establish supply

Production upscale on-going, first beta testing samples sent

Upcoming: TK250 Resin

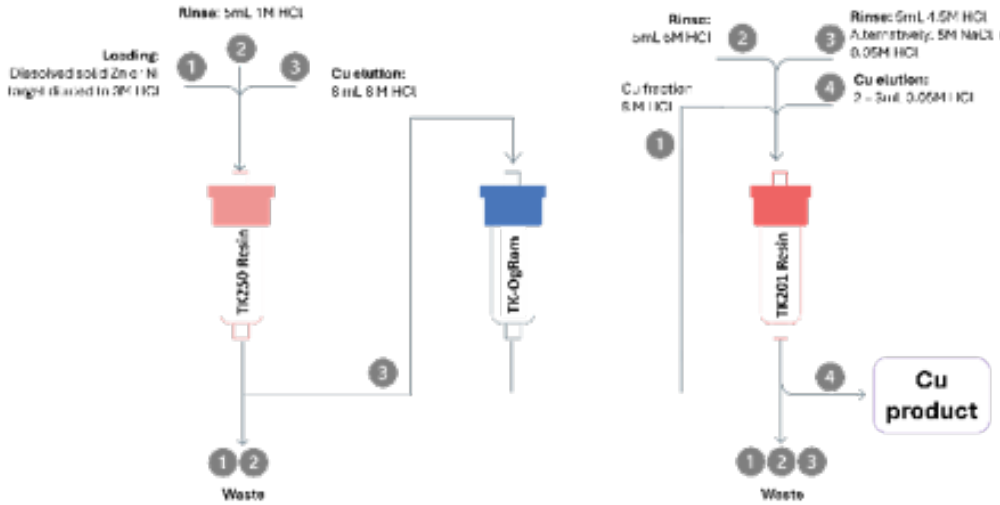
- CU Resin high selectivity for Cu over Zn but loading from pH >2 required
- TK201 good for solid Ni targets but not Zn
- Upcoming TK250 Resin:
  - Cu retention from up to 3M HCl and 1M HNO_3
  - Rather low Cu capacaity (~0.2mg/g)
  - No selectivity for Ni **and Zn**
    - Tested up to 300mg each
  - Cu elution in 8M HCl
  - 8M HCl to low HCl on TK201 Resin
  - D_f typically >10^3 - 10^4
  - Important: TK-OgRem for organics removal
- Next steps:
  - Integration in sequential separation of Cu and Ga from Zn targets e.g. with TBP Resin (Ga)

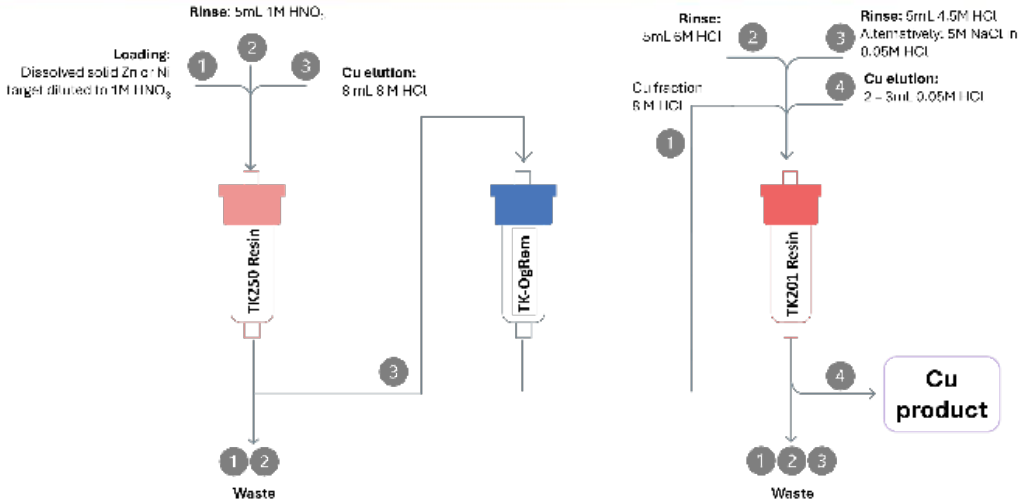


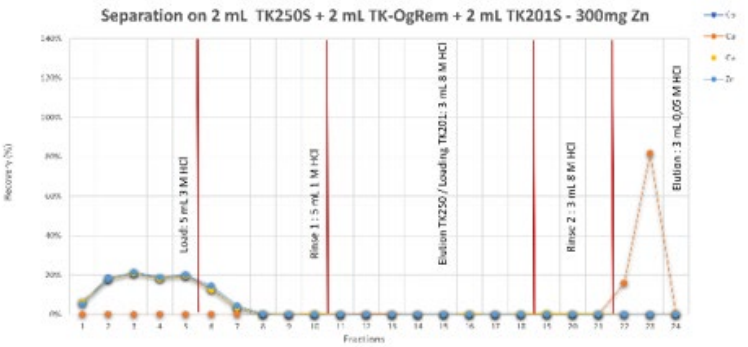
Dw values TK250 Resin, various éléments, HCl

Dw values TK250 Resin, various éléments, HNO3

Upcoming: TK250 Resin

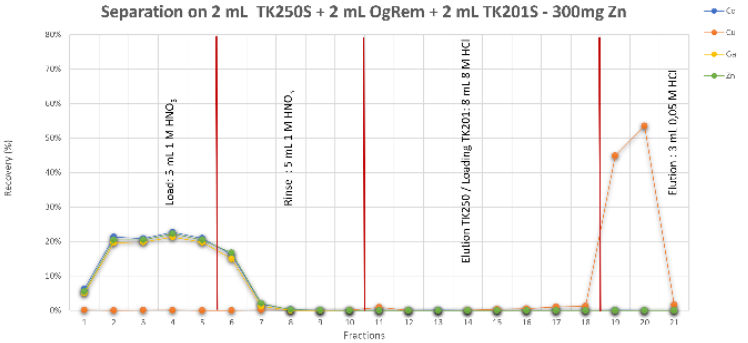






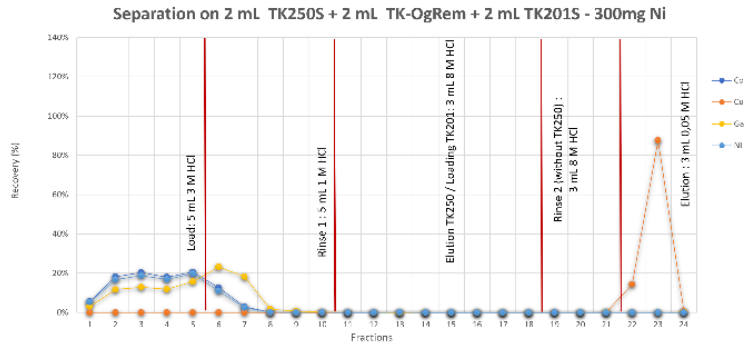
1 – 3M HCl

300mg Zn

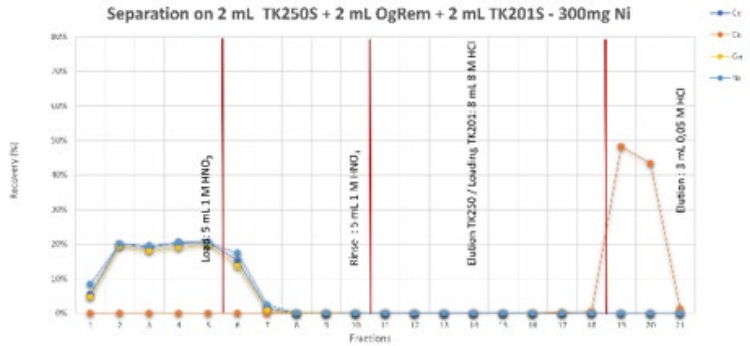


1 M HNO_3

300mg Zn



300mg Ni



300mg Ni

TK230 Resin

Already selling it…

Originally on demand production, making it more widely available

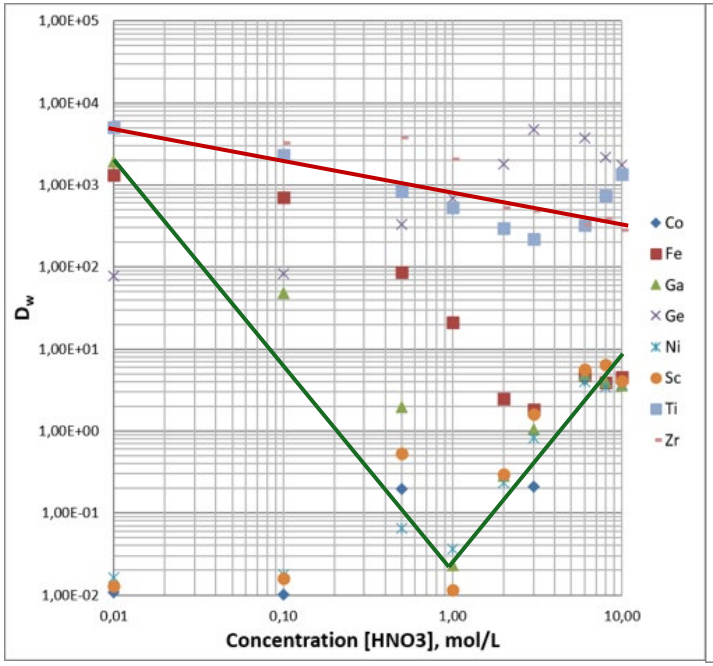
Production upscale on-going…

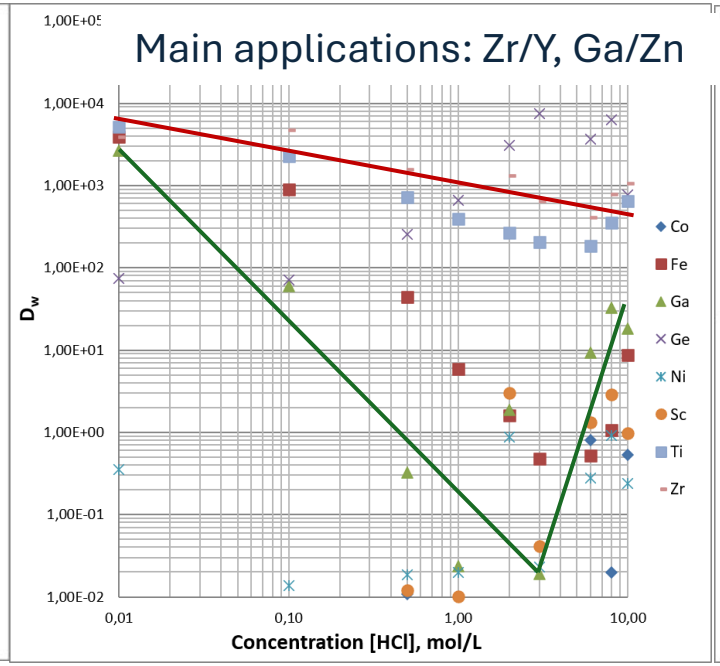
Covalently bound hydroxamate

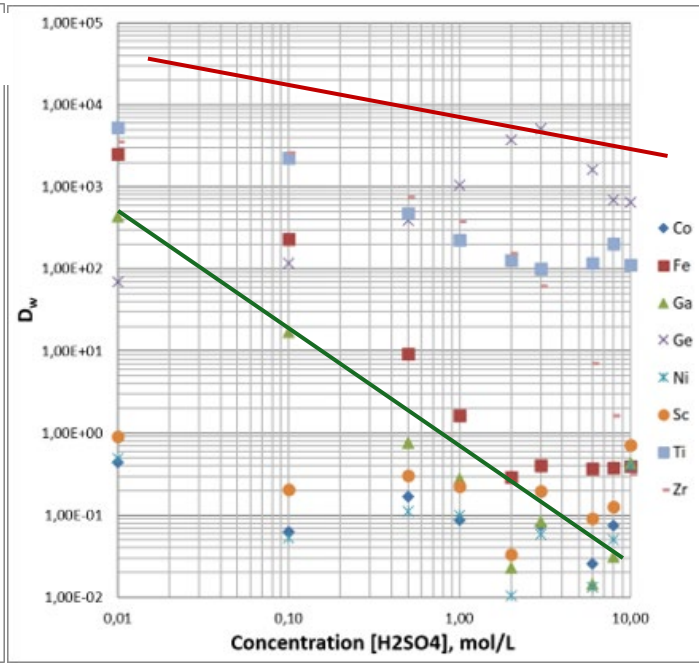
Main applications:

Ga-68 (use with CUBCX => existing patent) and Zr-89, testing for Ge and Ti ongoing

TK230 Resin – D_W values







High Zr Retention in all three acids over the whole acid range, will require 1M oxalic for elution

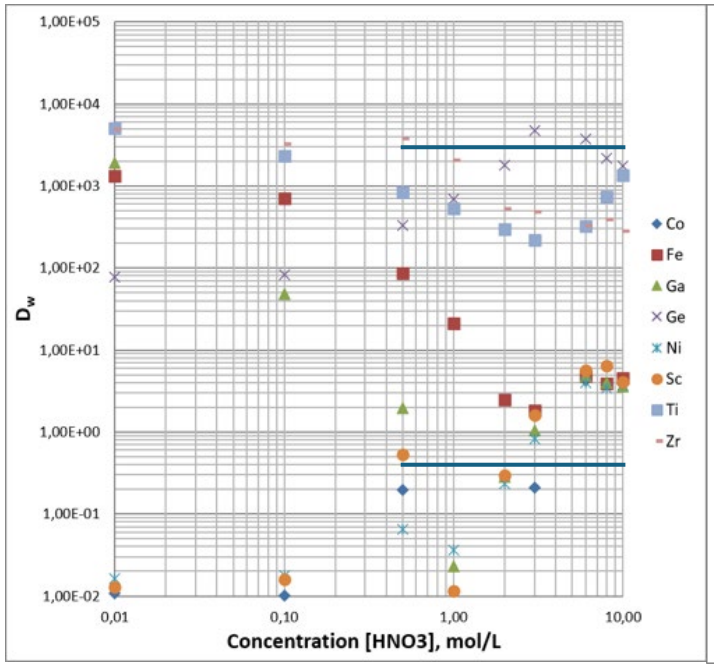
D_W Y below 10^{-2} throughout

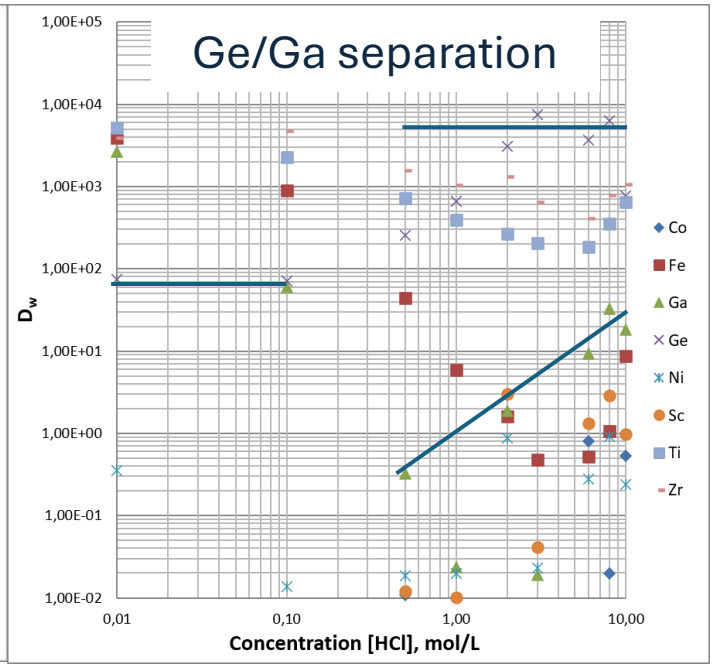
High Ga retention in dilute HNO_3, HCl and H_2SO_4, some retention in high HCl (lower than ZR Resin)

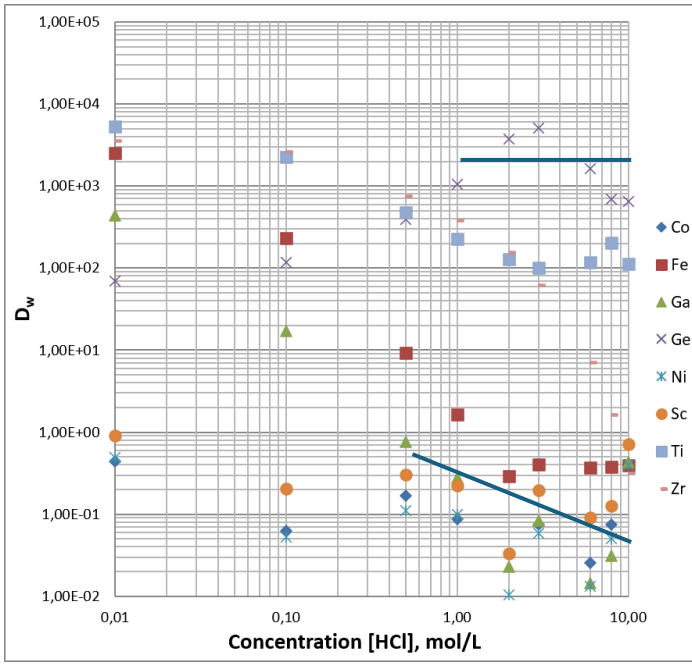
D_W Zn below 10^{-2} throughout

Fe requires attention => Ga/Fe separation possible

TK230 Resin – D_W values

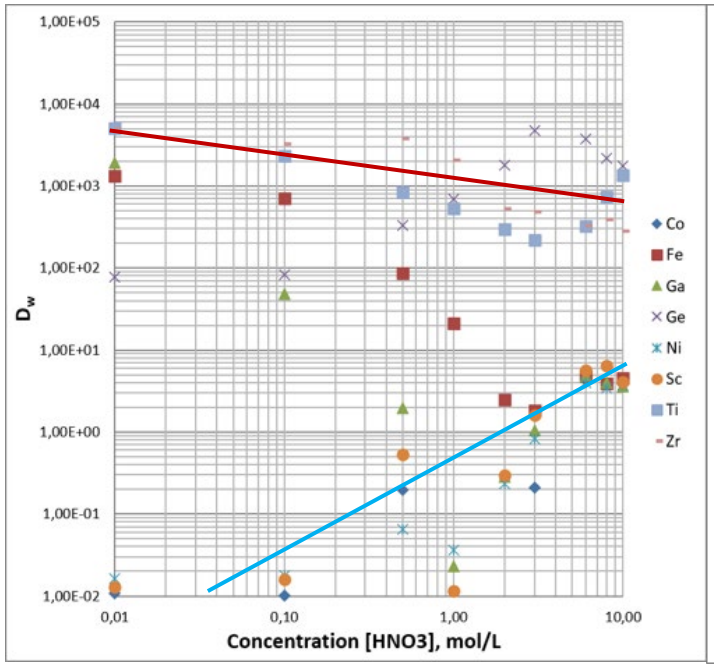


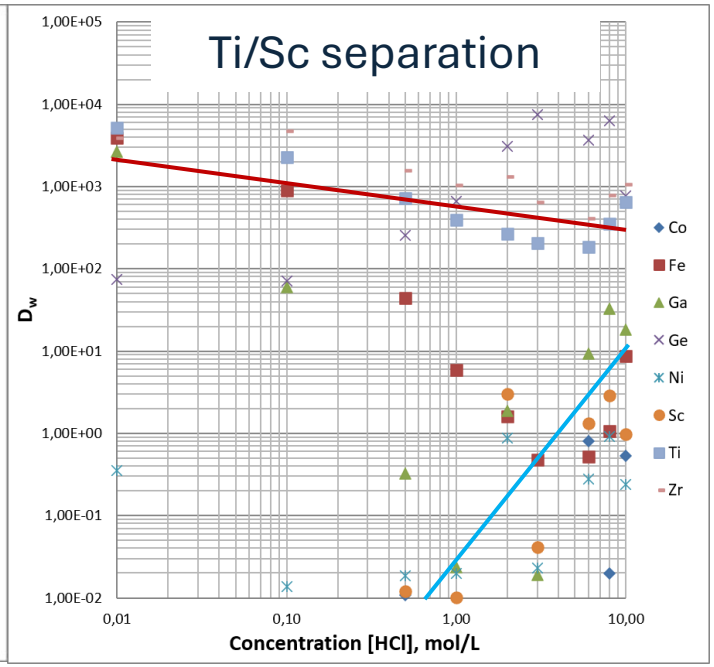


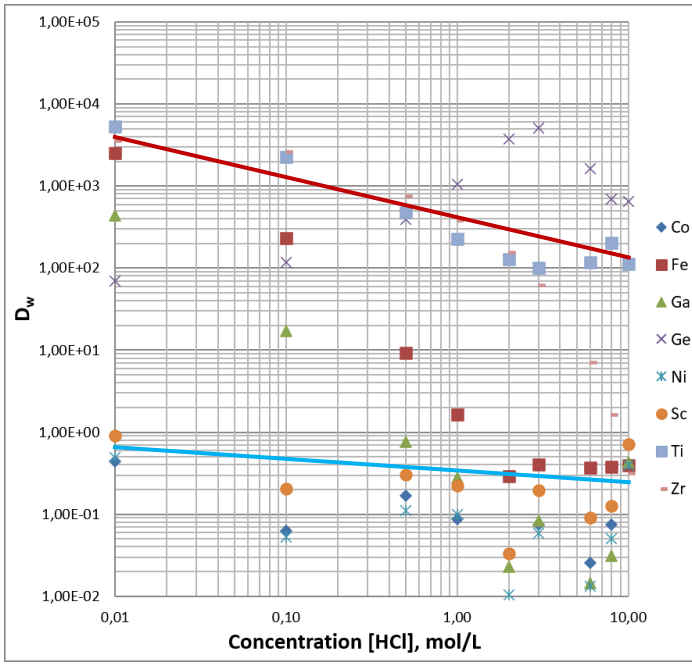


- Generally high selectivity for Ge over Ga,, Ni, Co in high HNO_3, HCl, H_2SO_4
- TK230 more stable in high HNO_3 than ZR Resin
- No Ge elution in dilute HCl, probably requires complexing agents => ZR Resin

TK230 Resin – D_W values







- Overall high selectivity for Ti over Sc
- Slight increase of Sc retention at elevated HNO_3, HCl
- No Ti elution in dilute HCl
- Elution via H2O2 or oxalic acid => ZR Resin
- Use as Ti/Sc generator? Literature…

At-211

- Requests for cartridge based separation of At from Bi targets in HNO_3. Resin approach already used by Burns et al. (3-octanone)
- Eriksen et al. showed At separation from Bi possible in HNO_3 via LLX using Octanol (=> TK400 Resin)
- Tereshatov et al. tested several extraction chromatographic resins for At separation from Bi incl. TK400 and TK200
    - => At elution possible via alcohol (removal of org. phase + At from resin)
- => several projects to identify other options
- TK400 and 4 additional resins currently being tested (“TK401” - “TK404”)
    - Another option: Gagnon et al. PEG Resin (=> TK202)?
- Elution via NaOH possible? Other reagents?
- At still active in labelling reactions?
- Currently shipping samples
- Also working on resins for Rn-211/At-211 generator
    - Rn retention on resin, At elution. Po retention?

Production of « industrial » extraction chromatographic resins

Hydrometallurgy, some decontamination work

- Valorisation / critical metals from ‘waste’
- Decontamination / valorisation of wastes, effluents or decontamination agents (e.g. acid)
  - Example: Am-241 for isotope batteries
- Number of cycles

Range of different resins being fabricated and tested

Bigger particle size support: ~300 – 800µm

Higher amount of resins requested

- Challenge: supply of raw materials
- Pricing

Increase of production capacity for these resins

Sheets

TO-DGA (normal DGA) and TEH-DGA (branched DGA) impregnated Whatman TLC paper

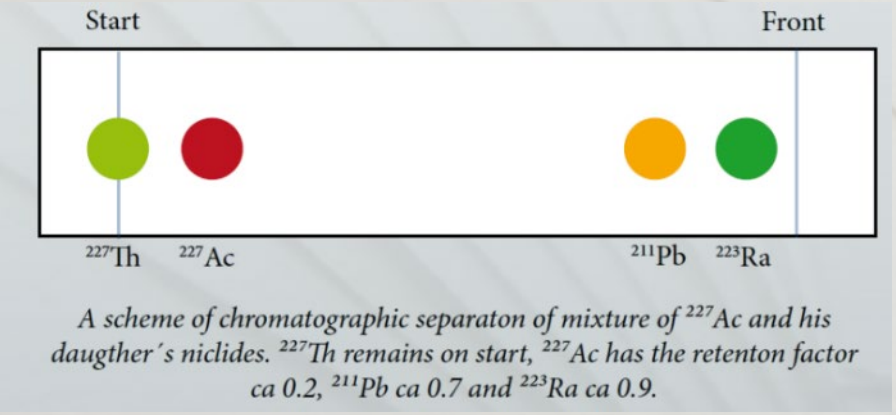
- Developed at CVUT (Kozempel et al.)
- Now also iTLC based (iSheets), incl. CU iSheets

QC of radionuclides and generator eluents (p.ex. Ra-223, Ac-225/Bi-213, Pb-212,…)

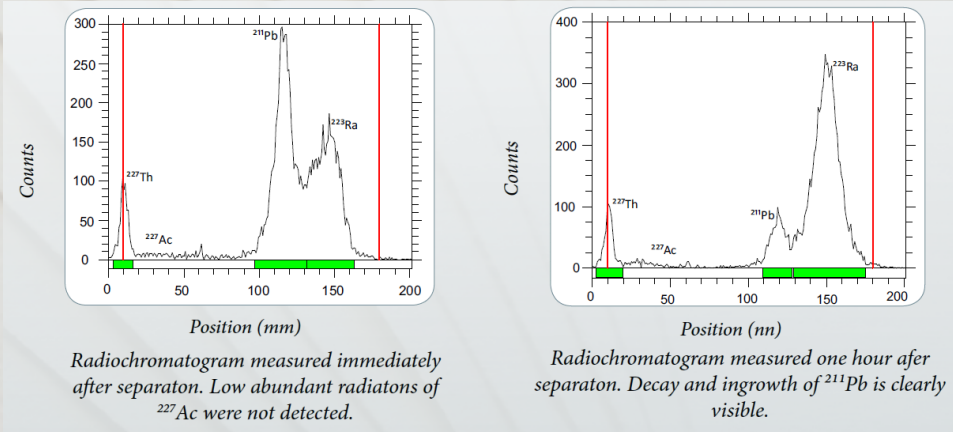
- TLC scanner or radiometer/LSC or HPGe after cutting

Run under acidic conditions => radionuclidic purity

Run at i.e. more neutral conditions labelled vs non-labelled (e.g. Ra-macropa, CU Sheets)



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.



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.

More types of sheets under development (selectivities, geometry, support)

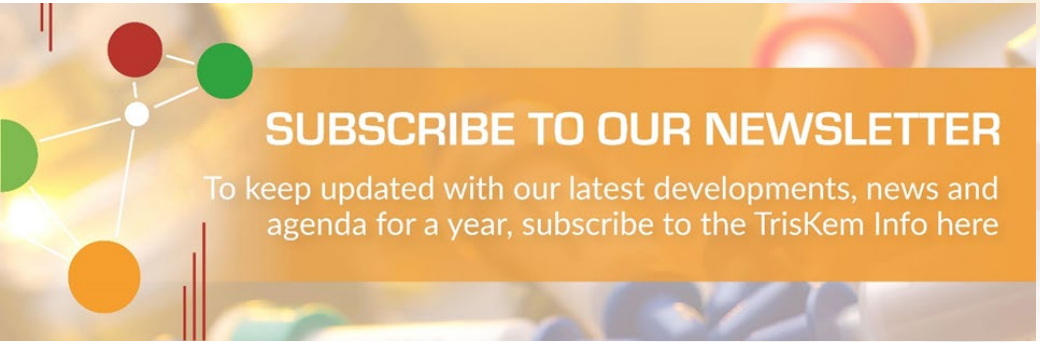
- TK213, ZR, TK201,...
- 2D TLC for radionuclide screening ?

Some other on-going projects

- Upscale Lu-177/Tb-161 separation
  - Lu-177: 1g Yb routine (commercial equipment available and another under development), upscale to 4 – 5g Yb on-going
  - Tb-161: Upscaled to 5g Gd, next 10 – 15g, commercial units under development/validation
  - 20µm particle size (TK212, TK211)
  - Radiation stability (25 -200 kGy)
- Additional TLC supports for RN QC in nuclear medicine
  - DGA, CU, upcoming TK213,…
  - Rapid test for RN in decomm samples? 2D TLC?
- Decontamination of effluents
- Removal of free RN from reaction mixtures
- Auger emitters…
- Rapid tests (Triage)
  - More impregnated PSm resins
  - Range of ‘Test sticks’
- Fate’ of RN in the environment + bioassay
  - Mainly longer lived RN (=> therapy)
- In-field preconcentration
  - Impregnated membranes
  - Cartridges
  - Transport supports to the lab…
- Other ’geometries’ &

‘Non-resin’ separation materials incl. microfluidics

Thank you for your attention!



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