# Overview and new Developments Radioanalytics

RRMC Workshop 2025

Steffen Happel

03/11/2025

TRISKEM
Expertise in Separation Chemistry

# TrisKem International


- Based in Rennes (France)
- Independent company since 2007 (before part of Eichrom Europe)
- Main product line: extraction chromatographic resins and other separation materials
- Staff : 25
- R&D and TechSupport group:
  - 3 RadChem PhD, 2 Technicians (+ 1 PhD student)
- R&D: Development of new resins, techniques and applications




# Cartridge packing

1mL and 2mL cartridges packed fully automatically

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

Before:


After:

# TK Resin naming

There is some reason…

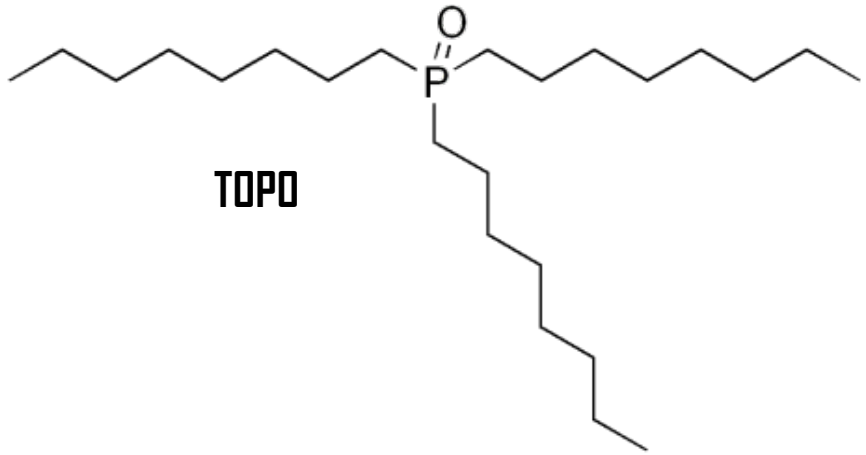
Main domain of application

- 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 => Crown-ether
- TK2**2**1/2/5/7 => DGA
- TK2**1**1/2/3 => « organophosphor » acids

# TK200 Resin




TOPO

Based on TOPO extractant

High retention of actinides

Applications:

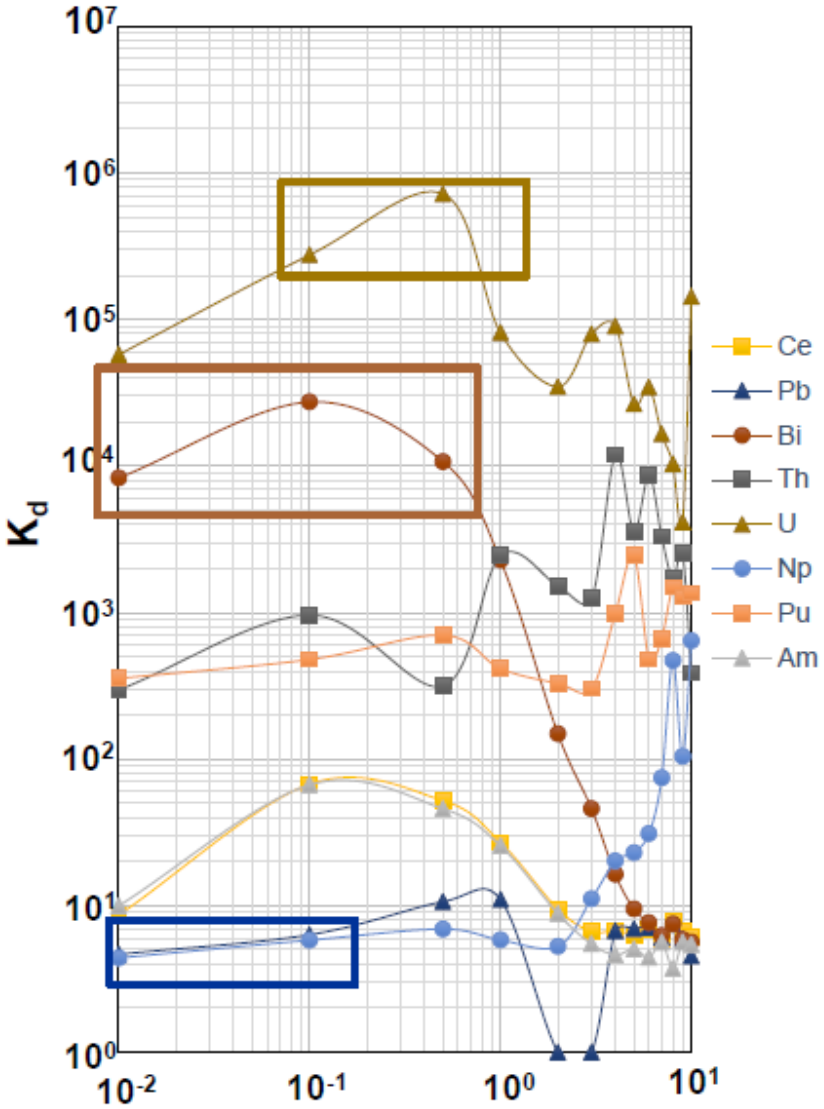
- Use for very efficient U removal from Pu
- Determination of Tc-99 in water samples
- Ga-68 production (in combination with ZR Resin or TK400 Resin)
- Actinide separation from water samples

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

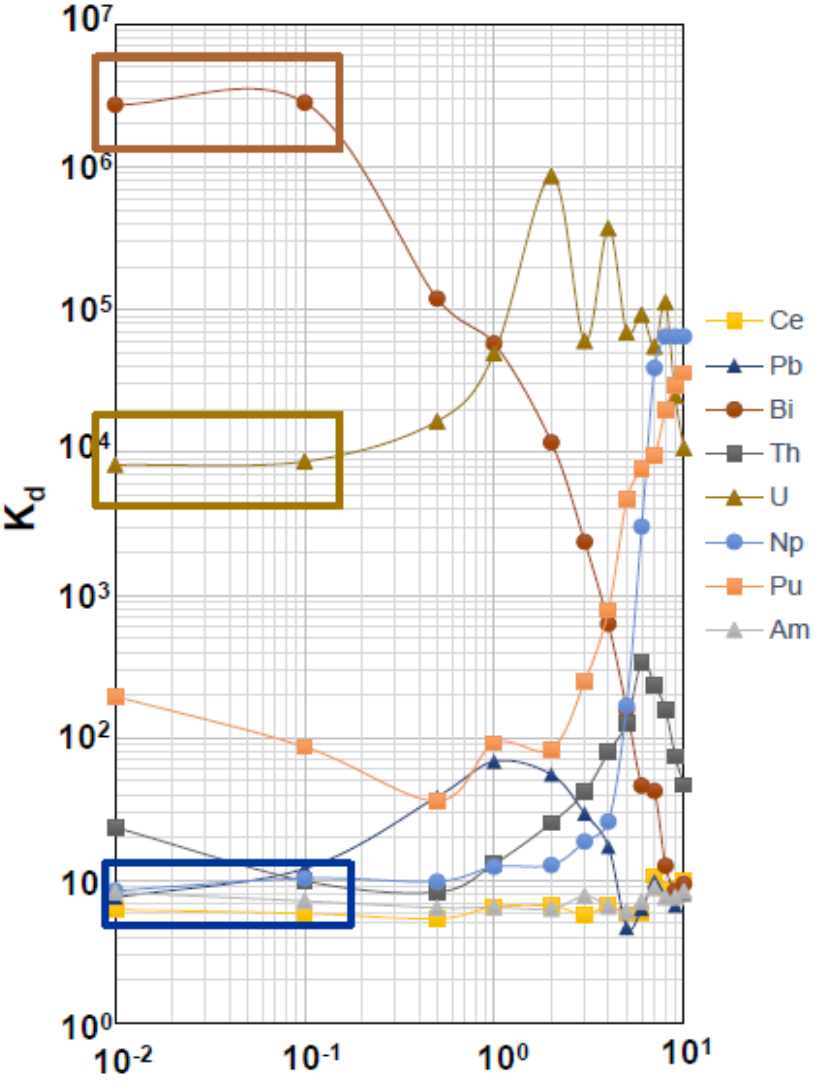
- Preconcentration and purification of selected actinides on same column
- ‘In the field’?

# Actinides on TK200

## (all data Van Es et al.)

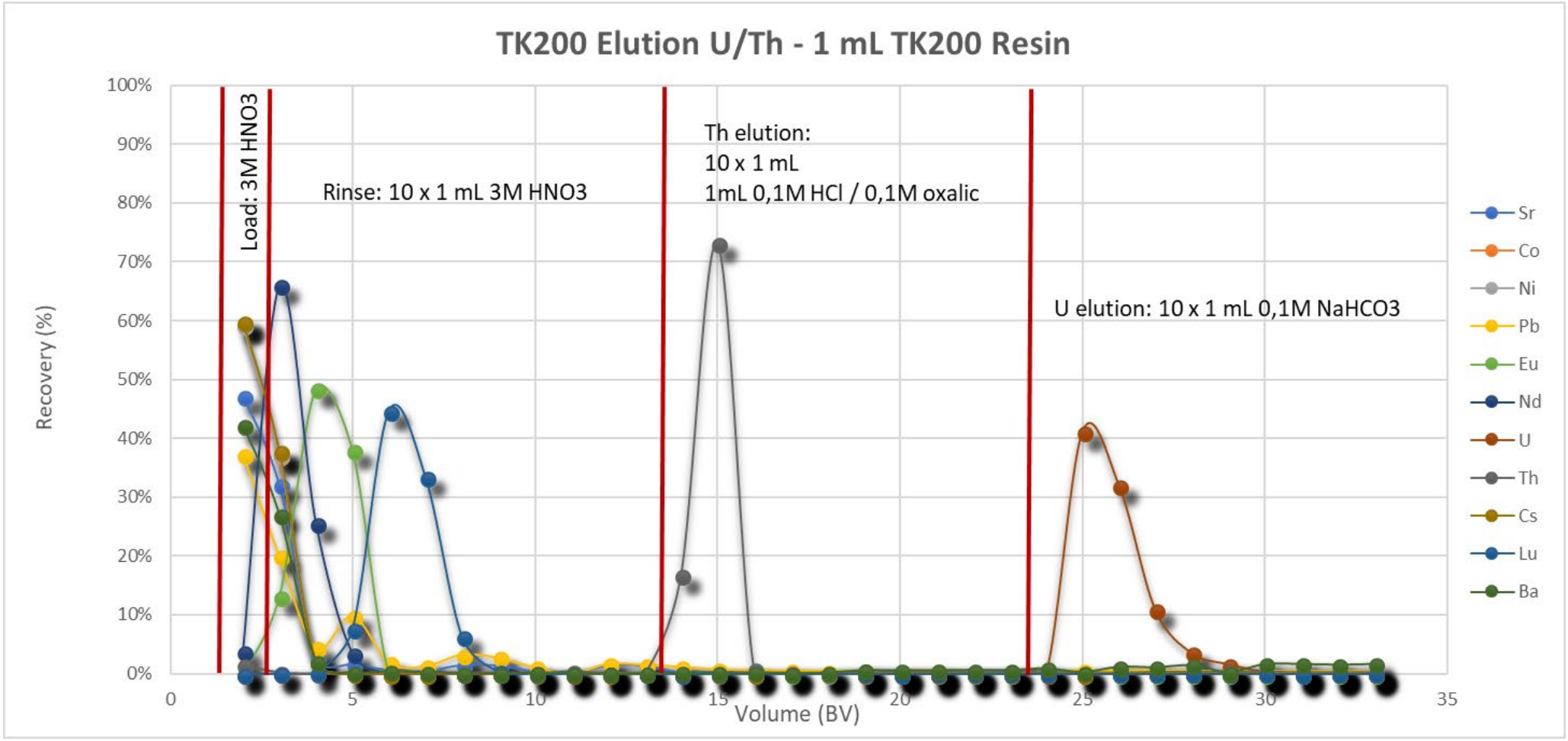



vanEs et al. $[HNO_3]$ M




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

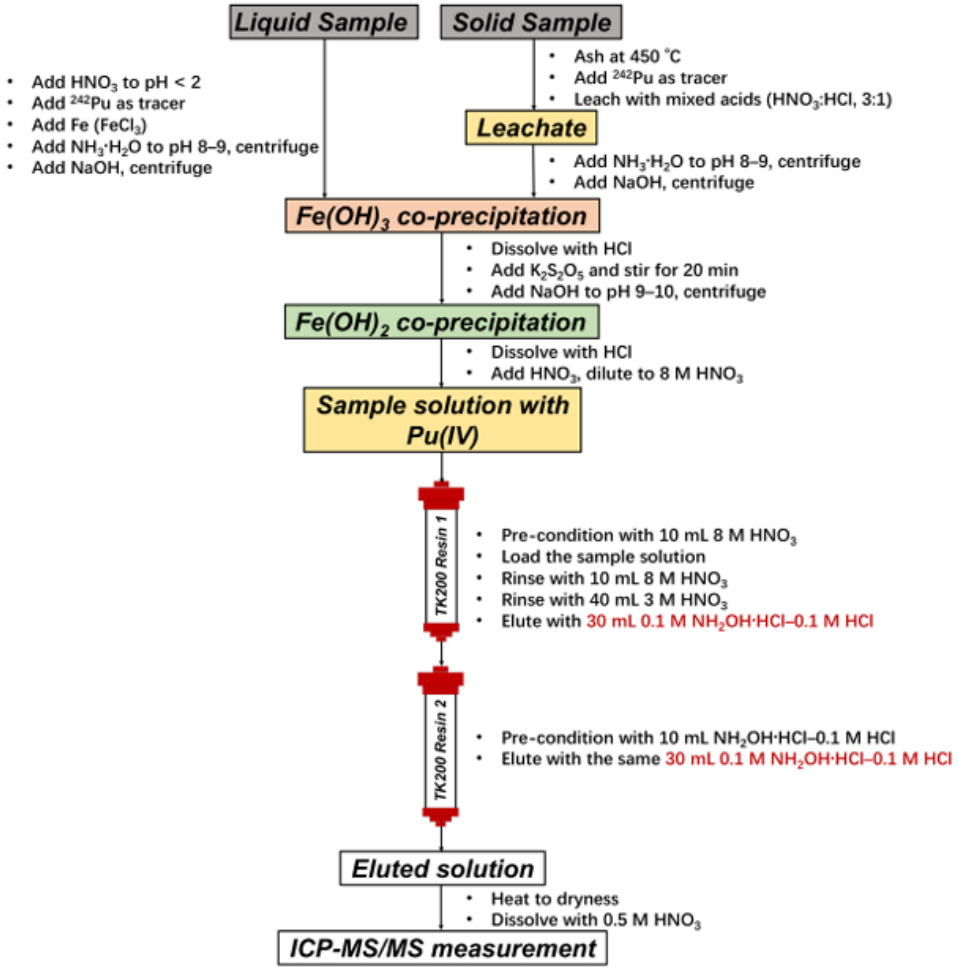



Figure S1. Analytical procedure for determination of plutonium isotopes ($^{238}Pu$, $^{239}Pu$, $^{240}Pu$, $^{241}Pu$)

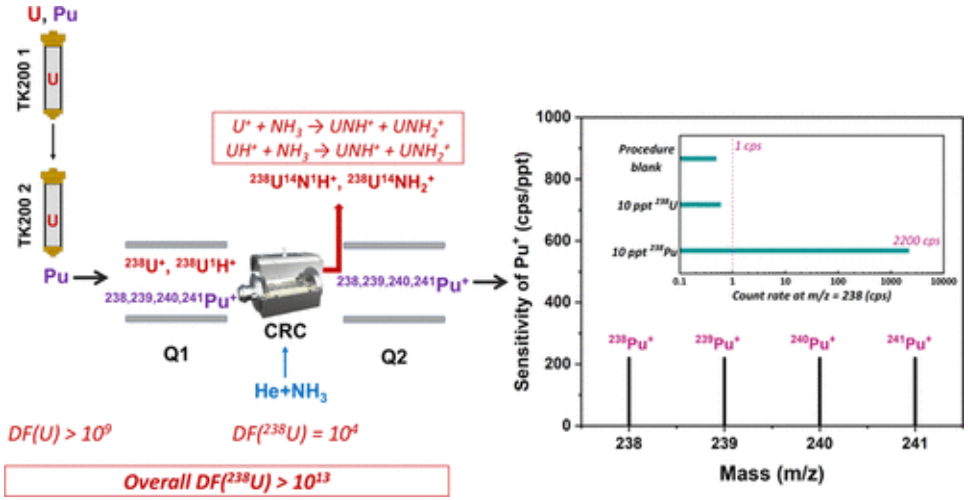
Recent publication by Huang et al.

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

Additional U removal via He+$NH_3$

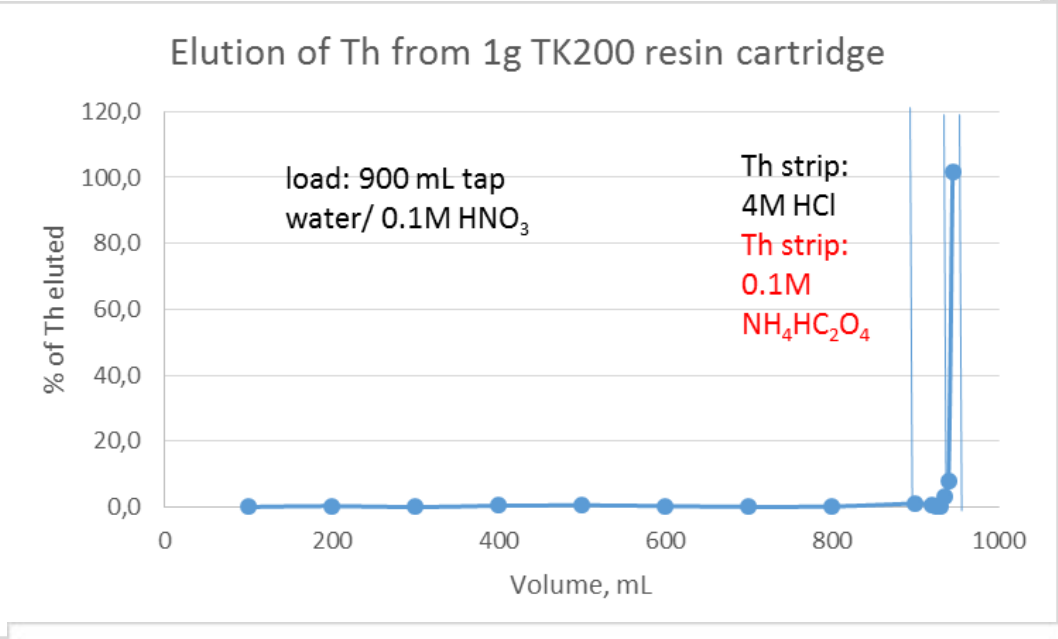
Overall $D_f(U) > 10^{13}$

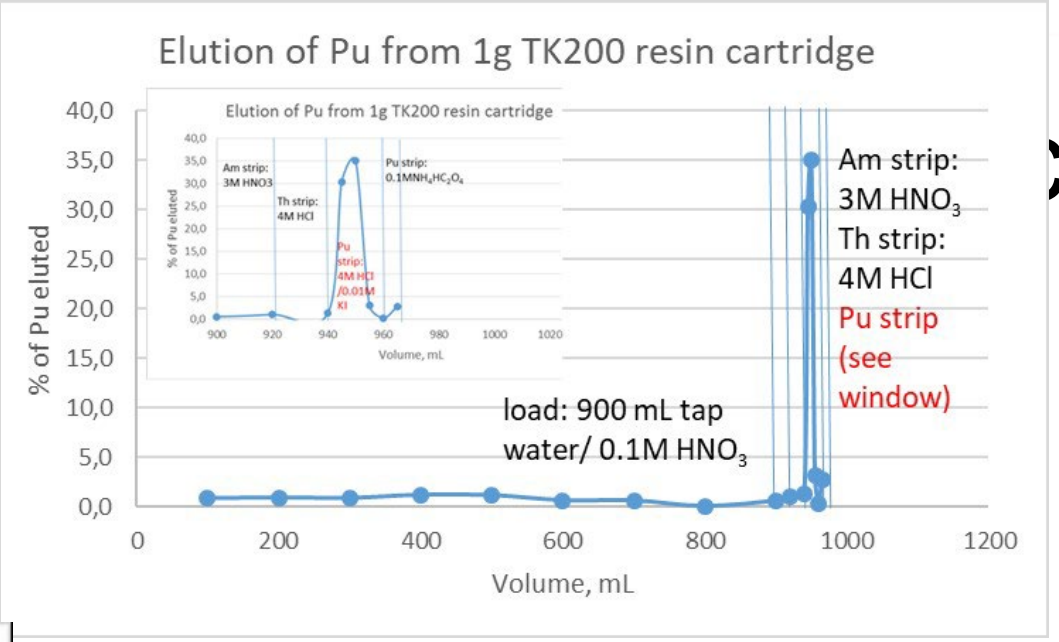
Pu isotopes incl. Pu-238 via ICP-MS/MS

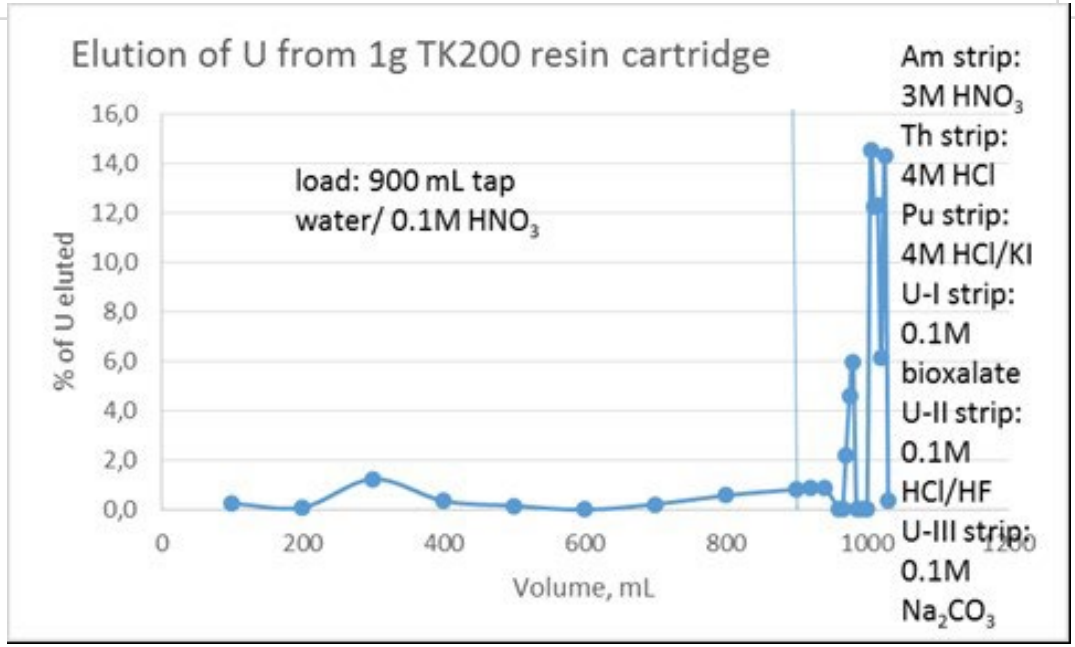



Zhao Huang, Xiaolin Hou, Xue Zhao, Rapid and Simultaneous Determination of 238Pu, 239Pu, 240Pu, and 241Pu in Samples with High-Level Uranium Using ICP-MS/MS and Extraction Chromatography, Anal. Chem. 2023, 95, 34, 12931–12939, https://doi.org/10.1021/acs.analchem.3c02526

# Actinides on TK200 – Application

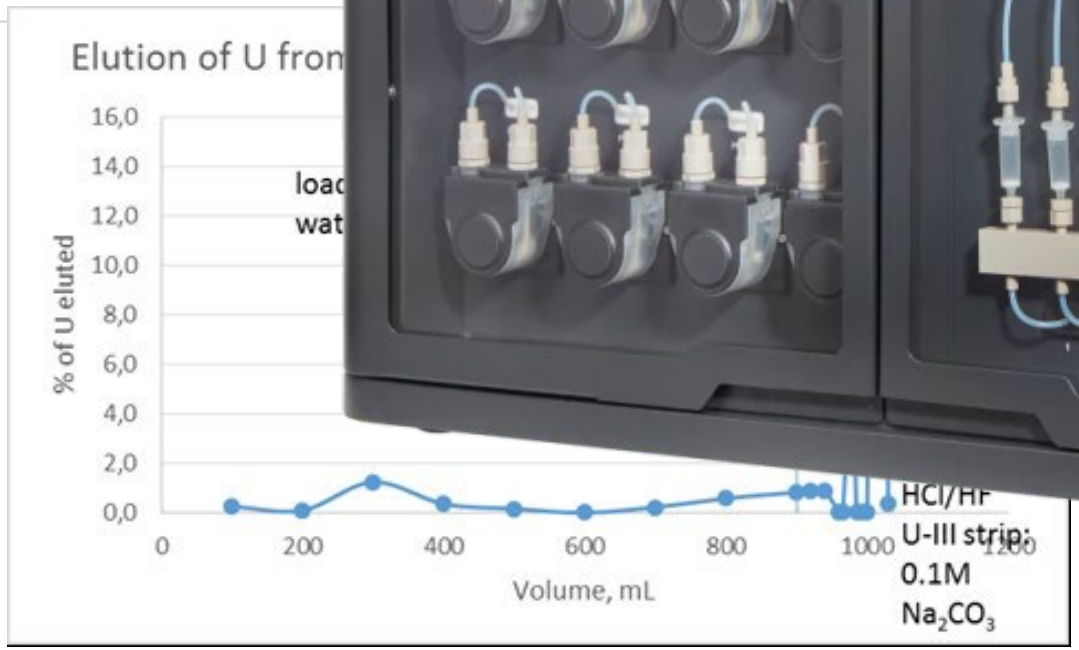



- Data by N. Vajda (RadAnal)
- Method development on-going
- Direct load of U, Th and Pu from acidified water samples (here 900 mL on 2 mL TK200)
- Sequential separation on TK200
- Automatisation & 'in the field' preconcentration'?

# Actinides on TK200 – Application





- 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

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

LoD:

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

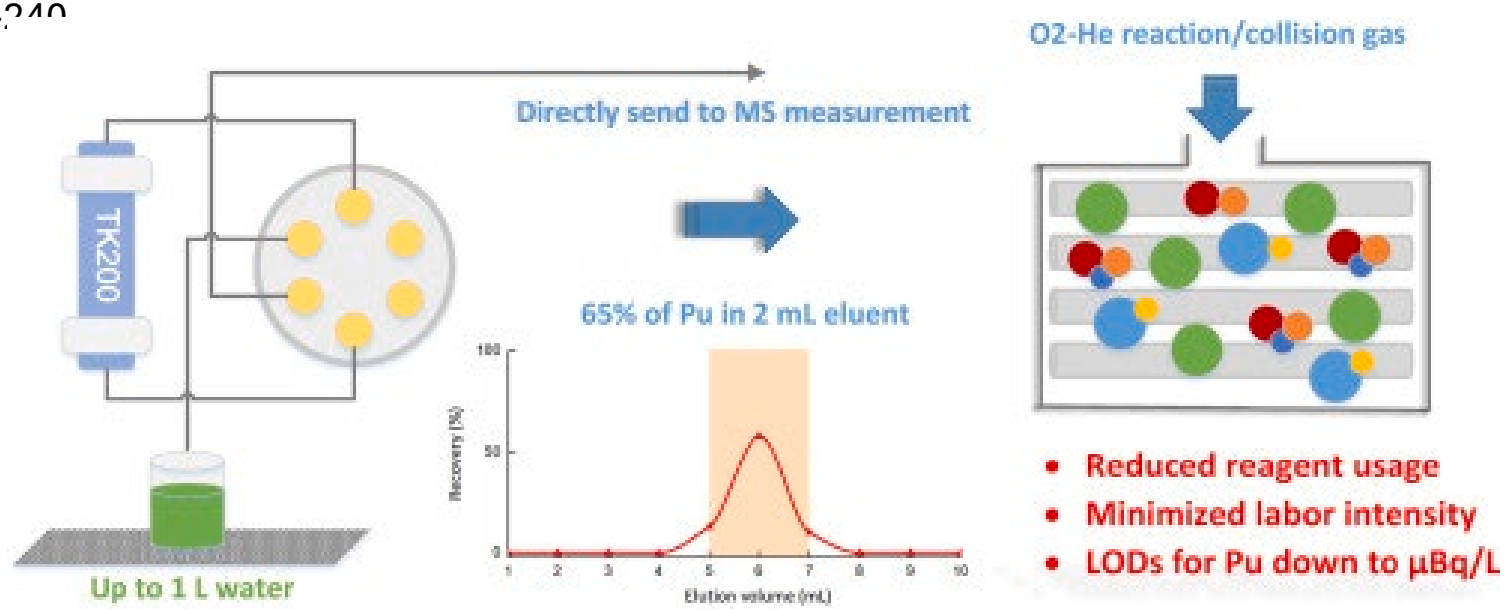
ELSEVIER

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

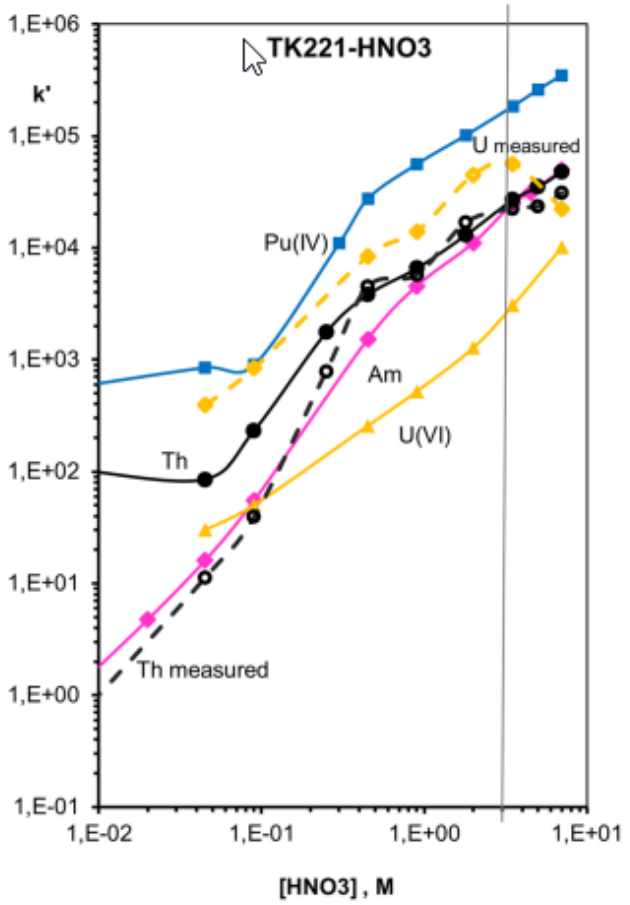
Youyi Ni [a], Wenting Bu [a], Ke Xiong [a], Sheng Hu [a], Chuting Yang [a], Liguo Cao [b]

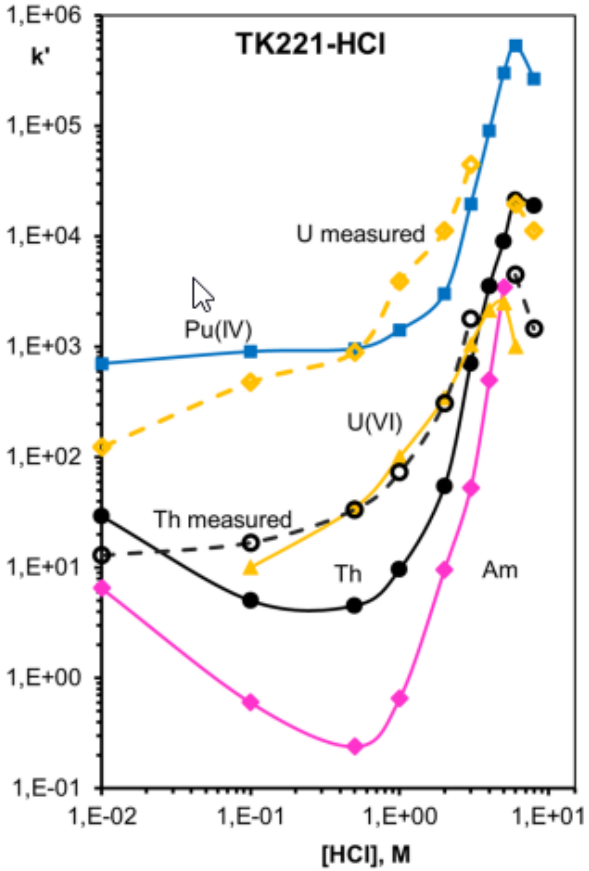


# TK221 Resin

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?




(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)

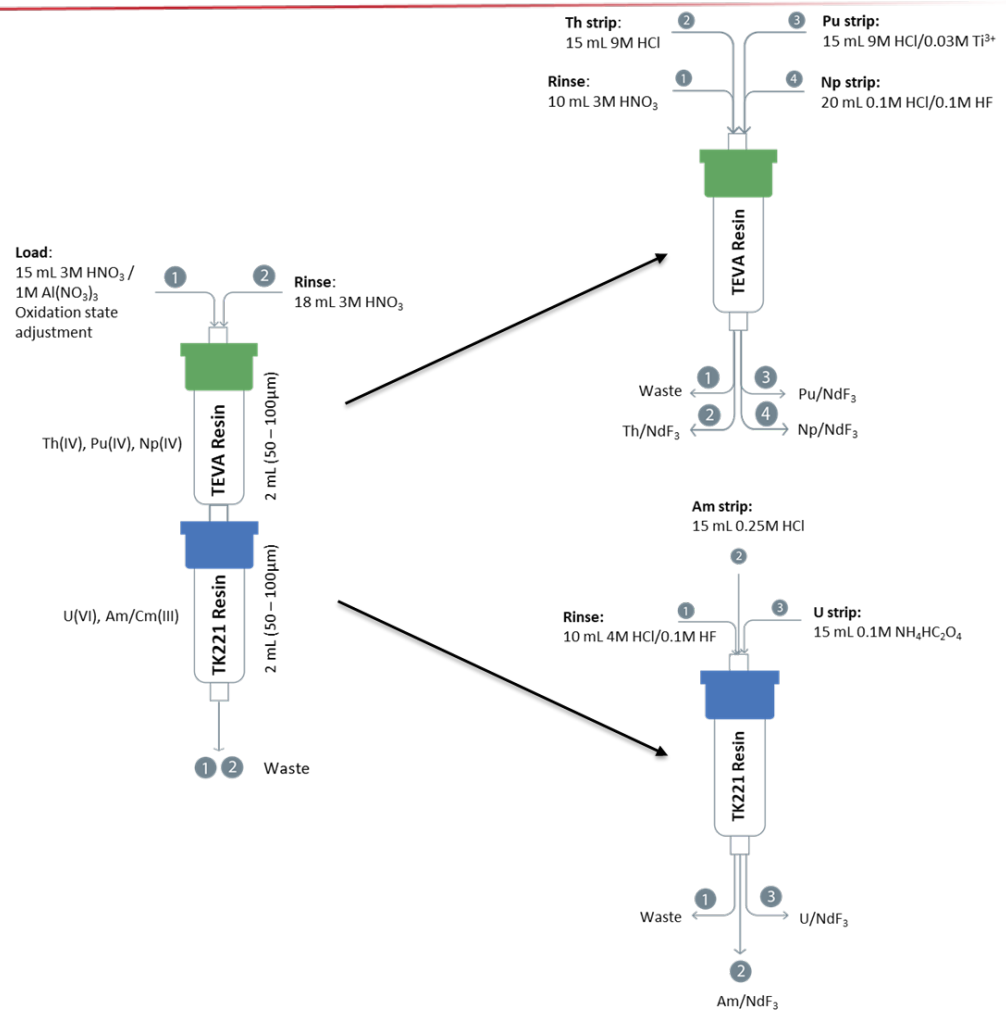
# TK221 Resin – actinide separation

- Synergies between extractants
- Higher U retention than DGA
- Higher Am retention than TRU

Cooperation with Nora Vajda

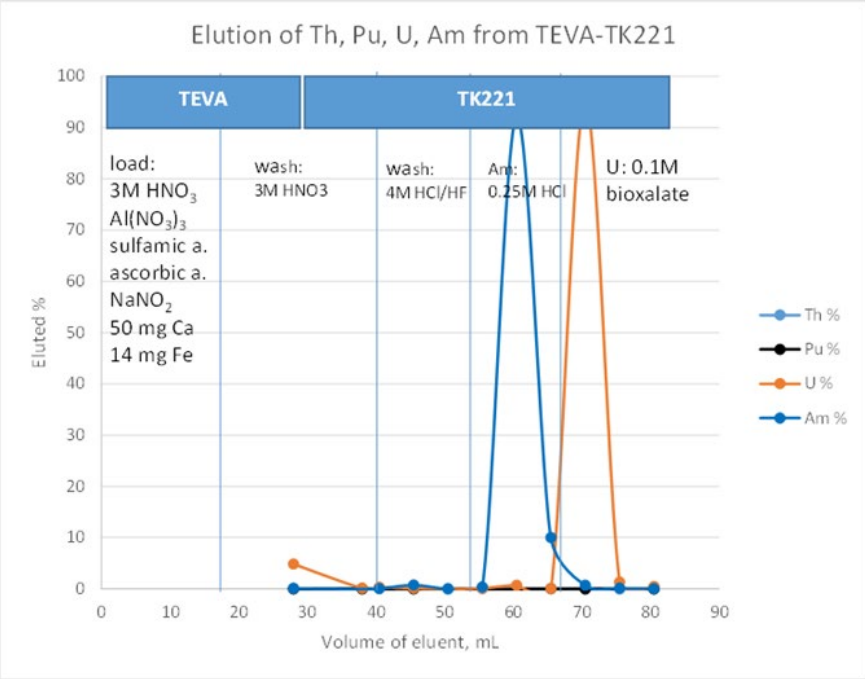
Method development for water samples

- TEVA/TK221 method
- Ideally later also soil and decommissioning samples
- Influence of Fe and Ca?
  - Ca leads to stronger Am retention




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

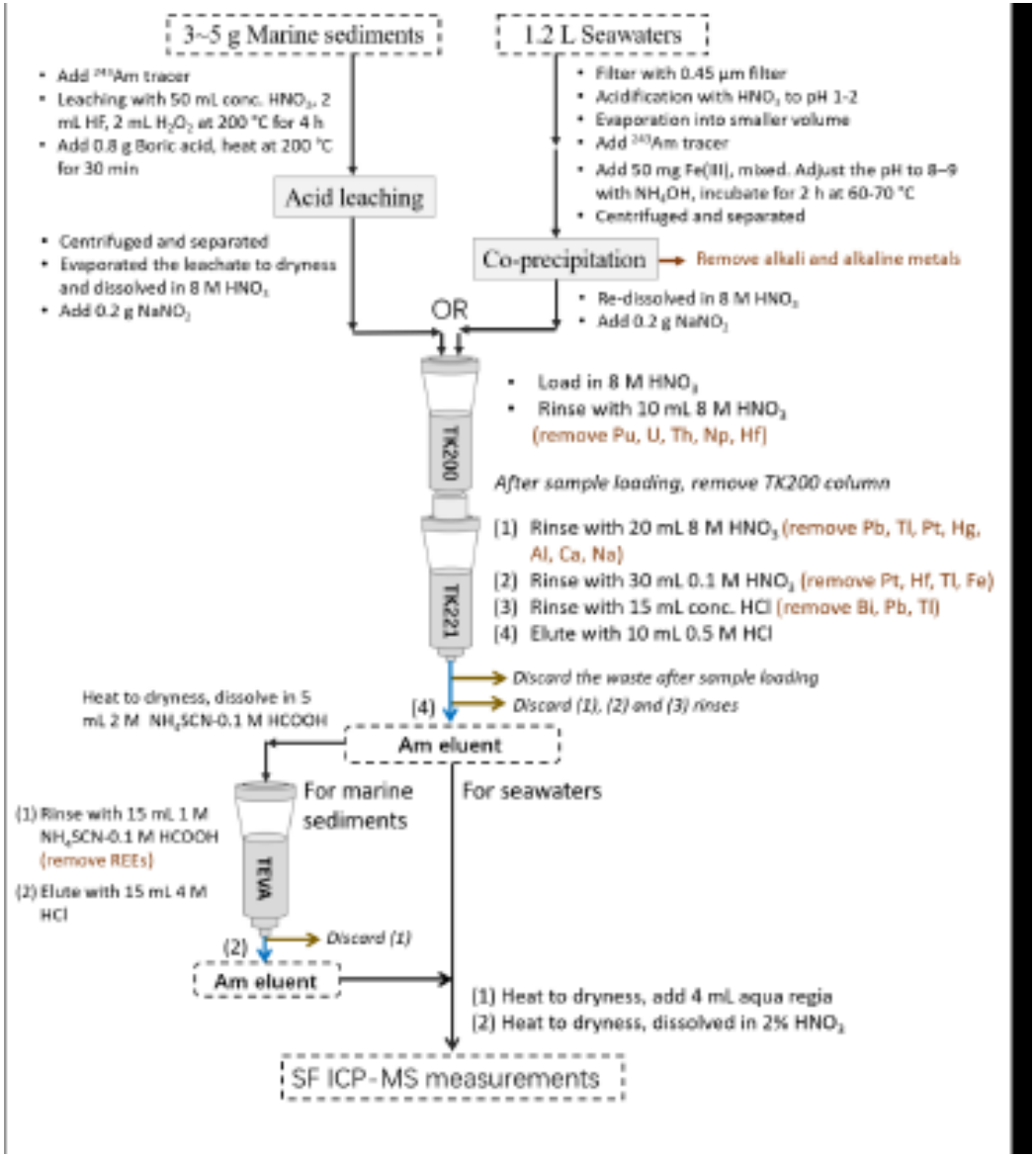
| | Actinides determiantion | |
|---|---|---|
| | Without Np separation | With Np separation |
| | Yield | Yield |
| | % | % |
| TAP water | | |
| $^{230}$Th | 90 ± 8 | 86 ± 7 |
| $^{239}$Pu | 108 ± 7 | 95 ± 7 |
| $^{237}$Np | – | 91 ± 9 |
| $^{241}$Am | 103 ± 7 | 97 ± 6 |
| $^{233}$U | 103 ± 7 | 70 ± 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
- 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:

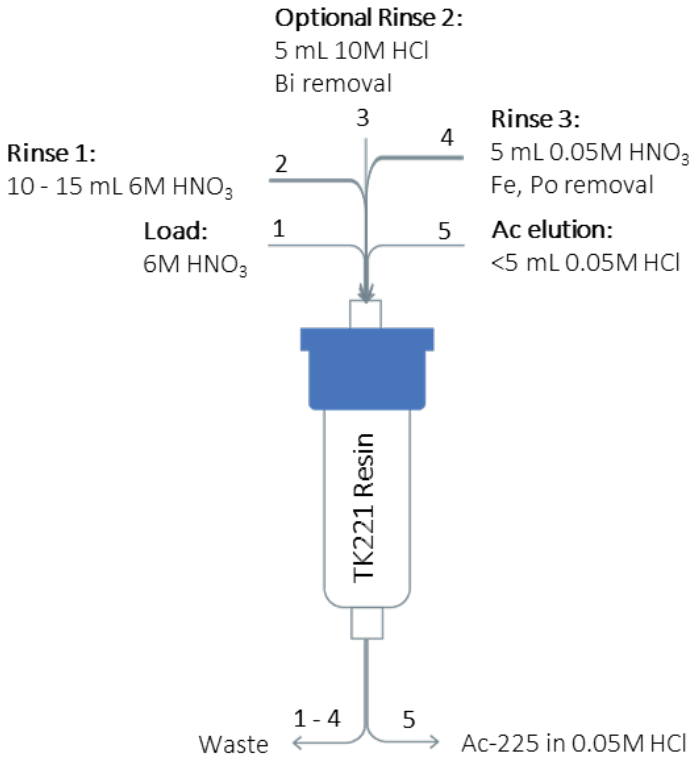
For DGA separation, the decontamination factors (DFs) for Pu, U, and Th were calculated to be $(1.8 \pm 0.4) \times 10^3$, $(3.0 \pm 1.0) \times 10^4$, and 24±6, respectively.

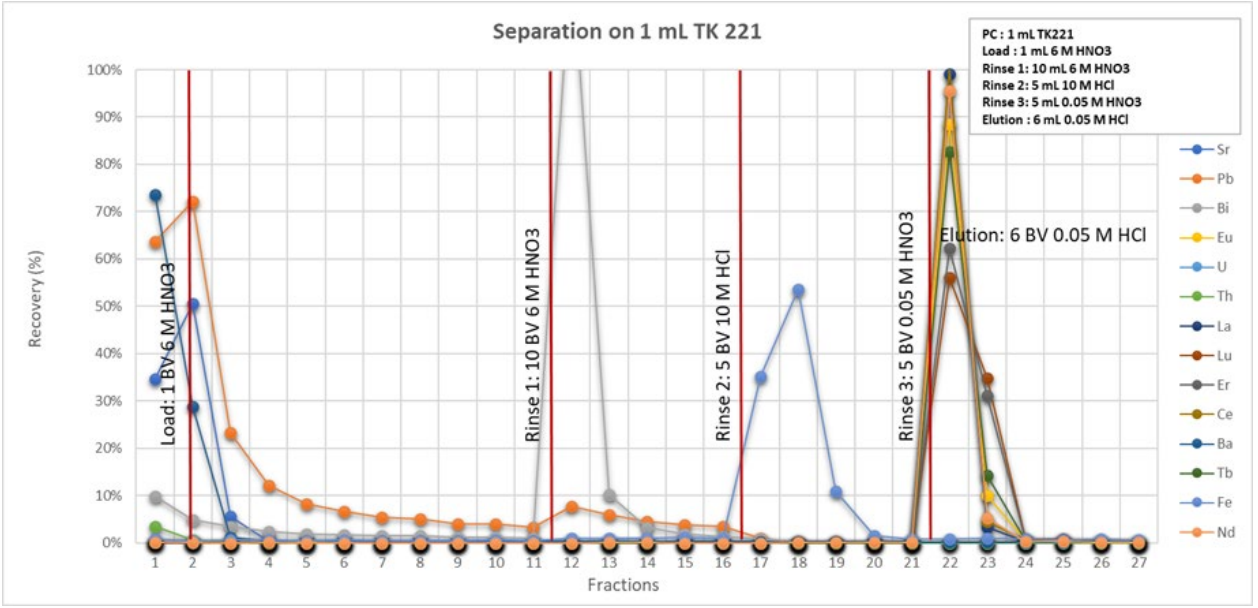
For TK221 separation, the DFs for Pu, U, and Th were $(1.5 \pm 0.2) \times 10^4$, $(2.1 \pm 0.3) \times 10^4$, and $(1.2 \pm 0.1) \times 10^3$, respectively.

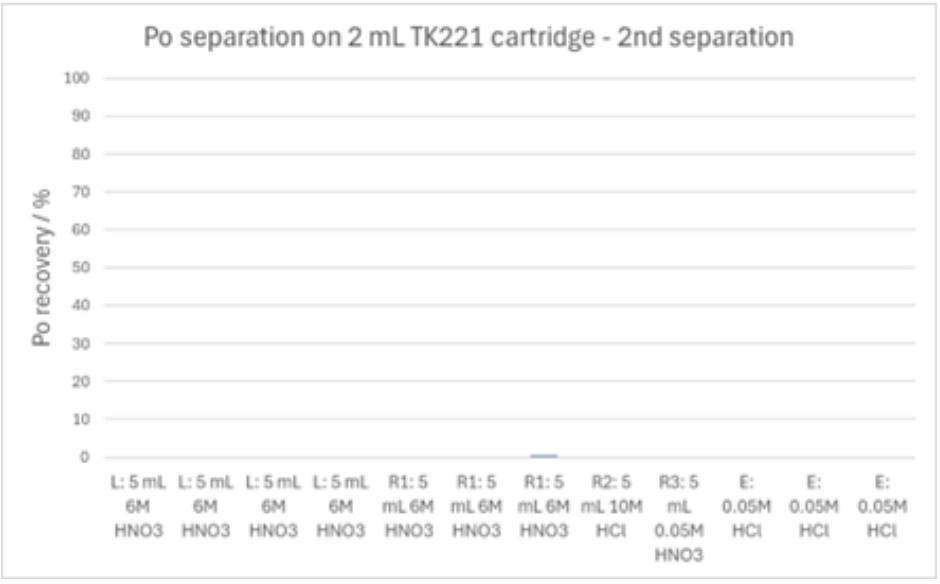
**It can be seen that the TK221 resin displayed remarkably better performance for the removal of Pu and Th than DGA resin, while with an excellent decontamination ability of U, close to DGA.**

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

# Ac separation => RP presentation
# Analytical questions:
# bioassay (e.g. BfS) and environment




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

# 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.

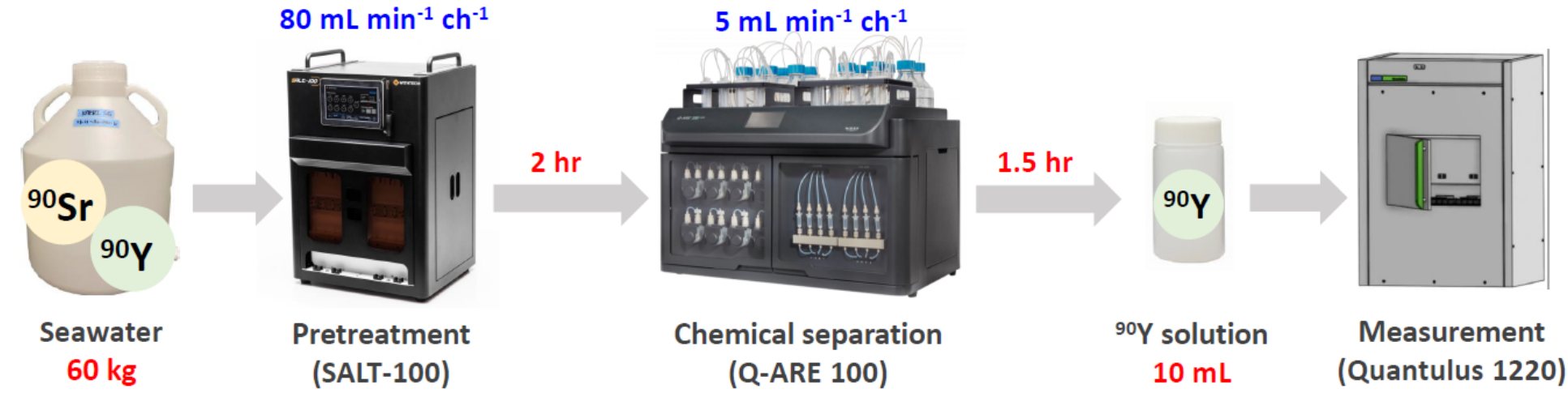
Quick and easy-to-use unattended radionuclide extraction

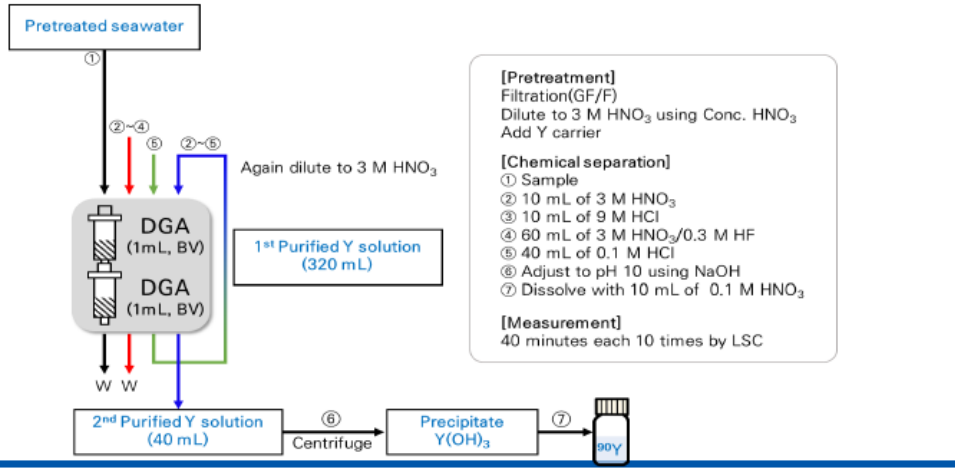
User friendly, intuitive and hassle free.

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. $HNO_3$
- Ongoing: TO-DGA based resin to allow loading from lower $HNO_3$

=> ‘TK227 Resin’

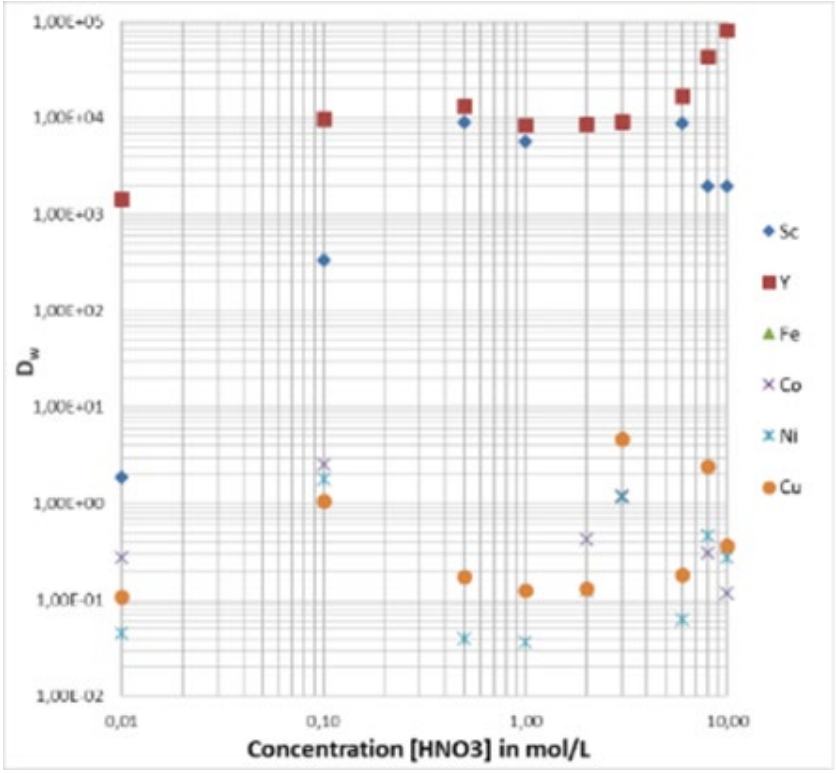
- Similar approach for Am possible?
- SALT / Q-ARE approach also for used Cs-134/7 via AMP-PAN

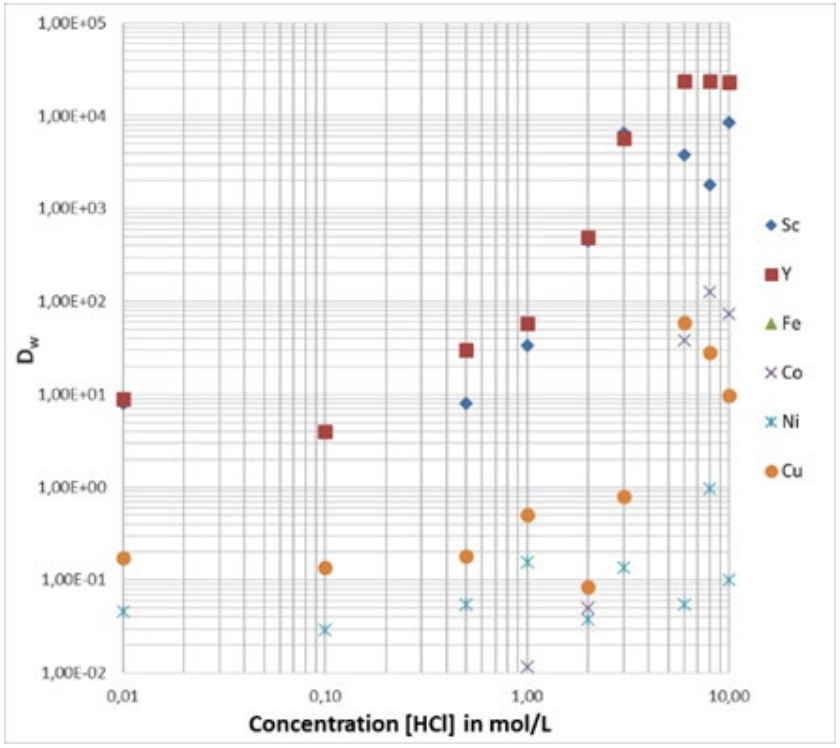
# TK227 Resin

Addition of ionic liquid increased Y retention (idem e.g. lanthanides, especially heavy lanthanides) at lower acid concentrations, especially in $HNO_3$. Also Includes phase stabilizer.

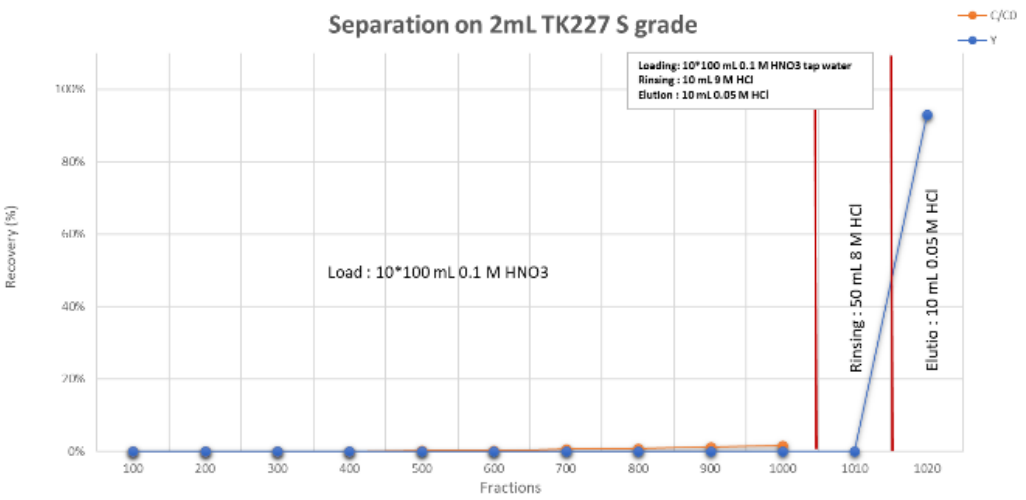
Remark: too high amounts of IL will lead to low elution yields (=> TK225 – large amount of IL – use in decontamination of effluents from radiolanthanides).

Remark: Separation on TK227 optimized for mg amounts of carrier.

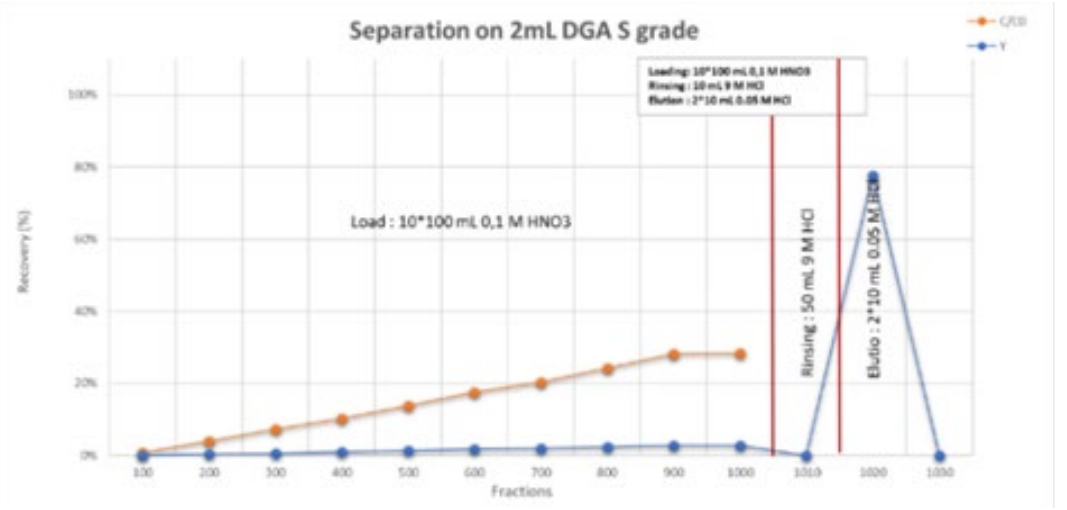


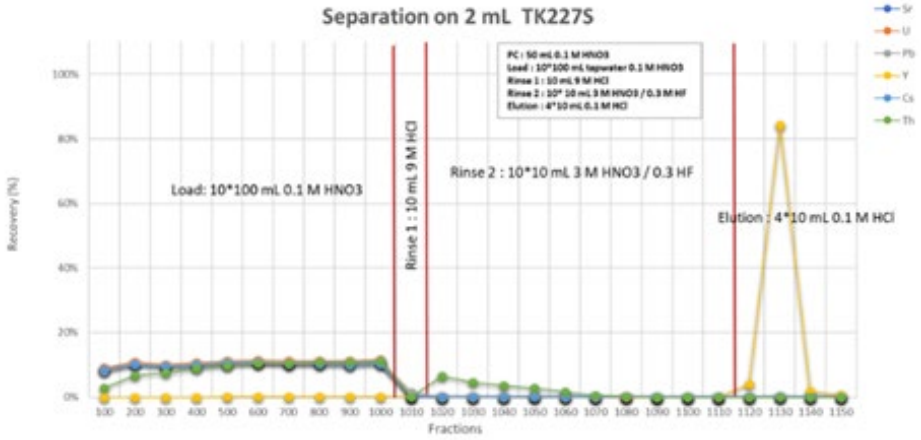
# TK227 Resin – drinking water




**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 $HNO_3$

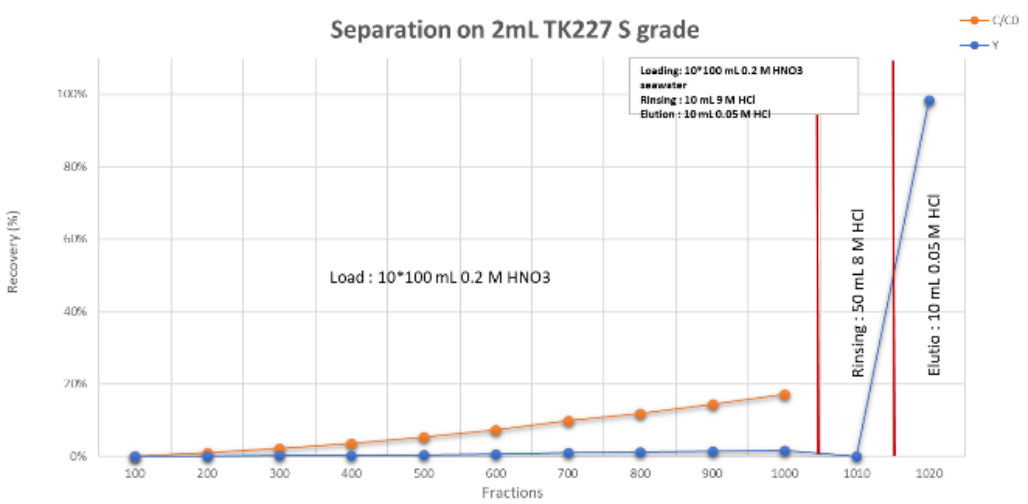
Loading at 10mL/min

Separation from interferences following Kim et al.

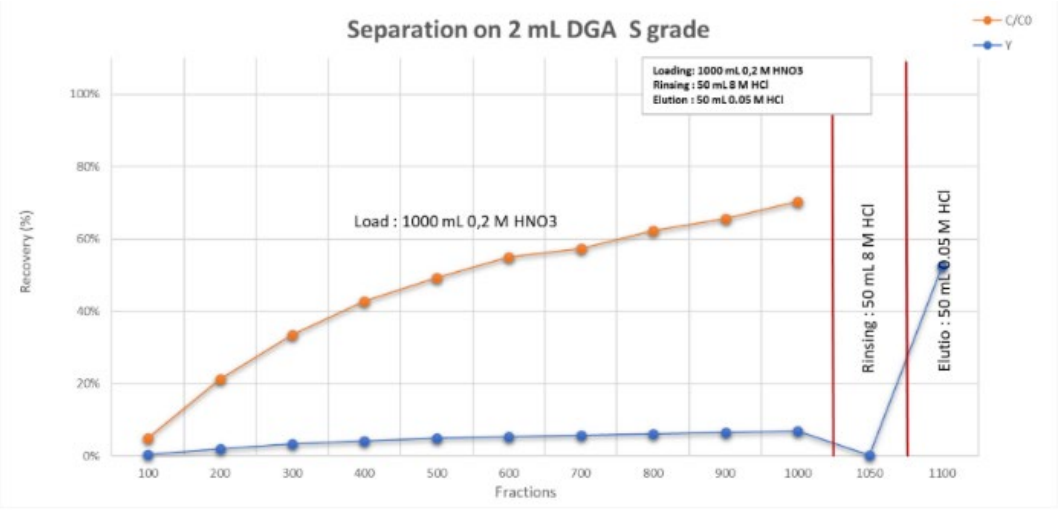
Rapid method for Sr-90 in water?

Use of scintillating beads (PSm)?

# TK227 Resin – sea water




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



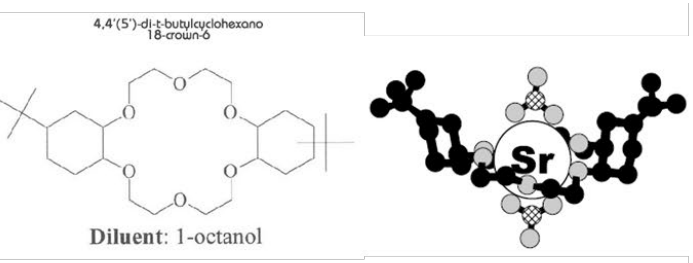

**Elution study, 1L sea water, loading from 0.2M $HNO_3$, Y separation, 2mL DGA,N Resin cartridge**

- Sea water requires high $HNO_3$ concentration for Y retention (at least 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.

# TK100/1 Resins

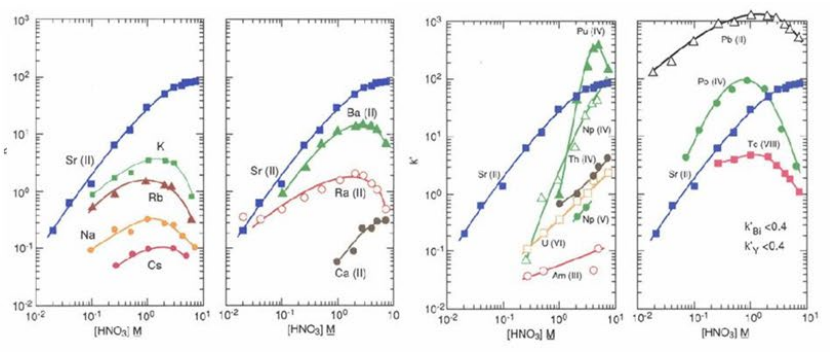
## Based on same crownether as SR Resin

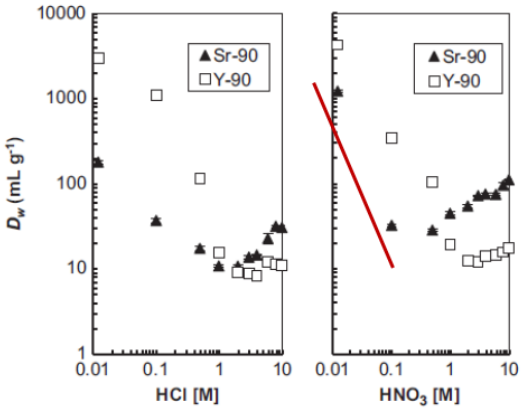
- Different solvents, Sr and Pb uptake also between pH 2 and 7
- Concentration and purification on same column










## 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




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*

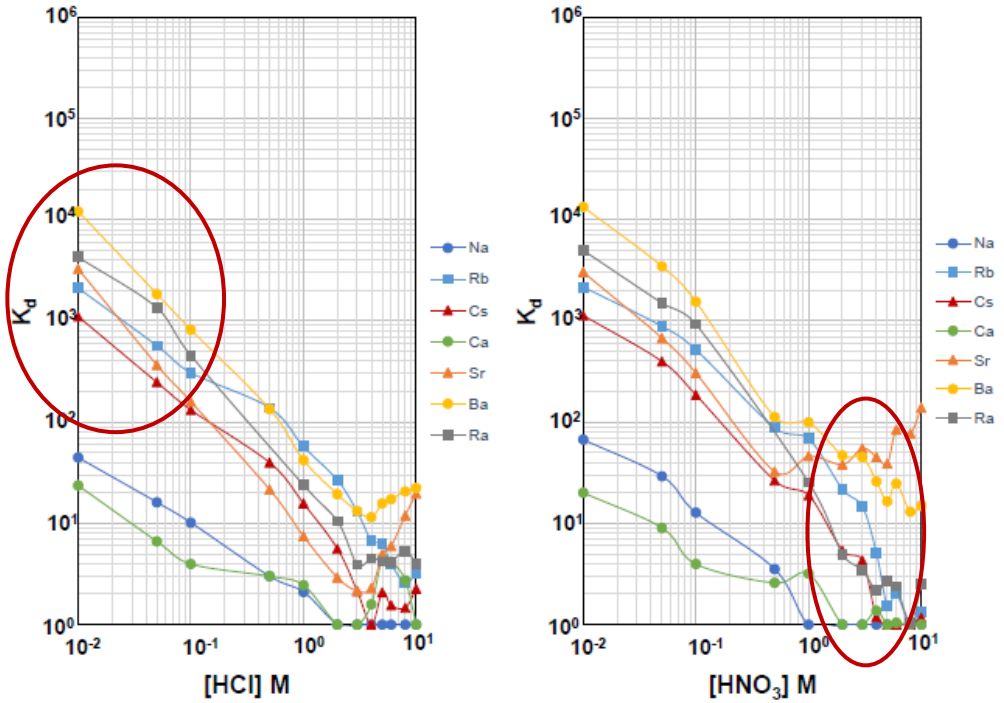

TK100 contains HDEHP

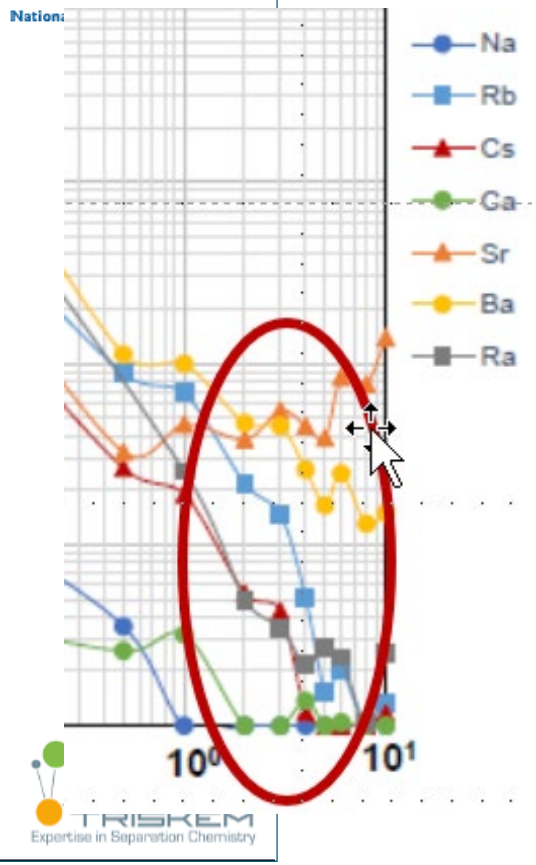
⇒very high Zr retention => high Zr decontamination

⇒ Sr elution in ≥0.5M HCl

# TK101 - Radium

## TK101 Group 1 and 2

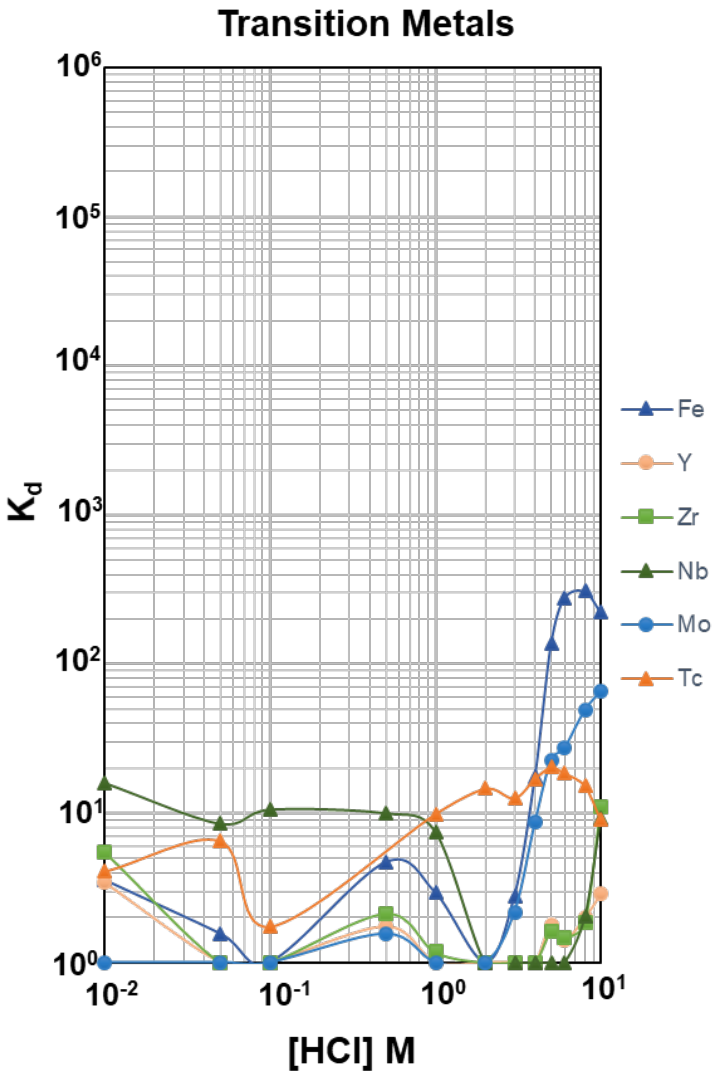


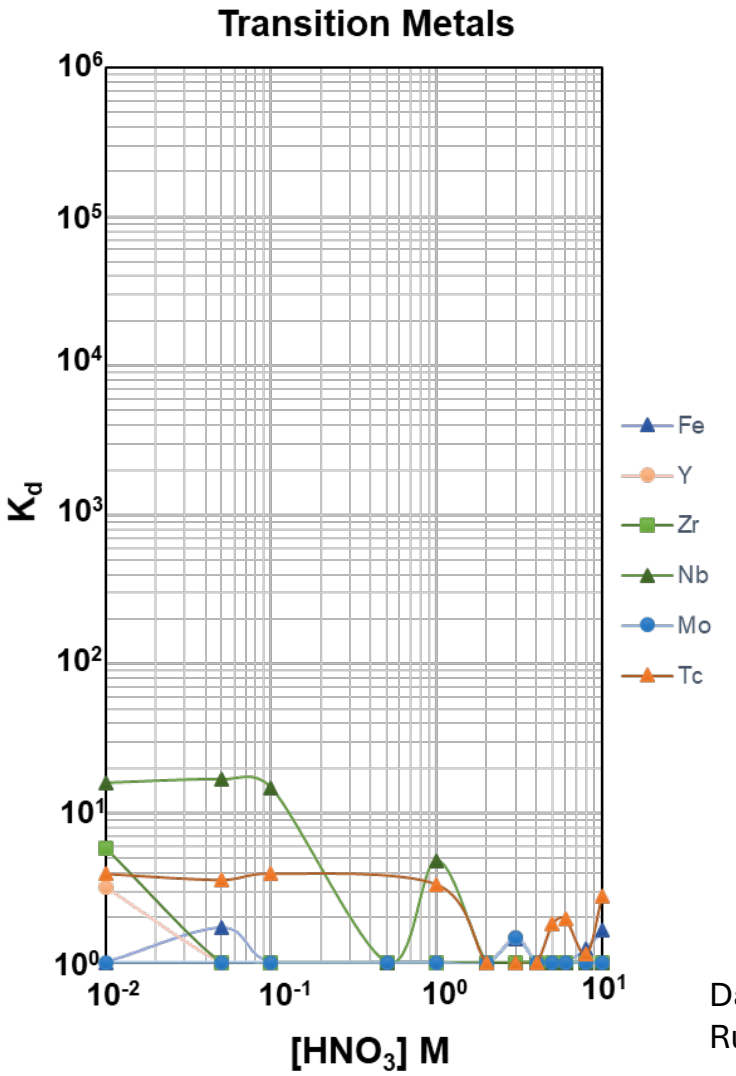




Data provided by Russel et al. (NPL)

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

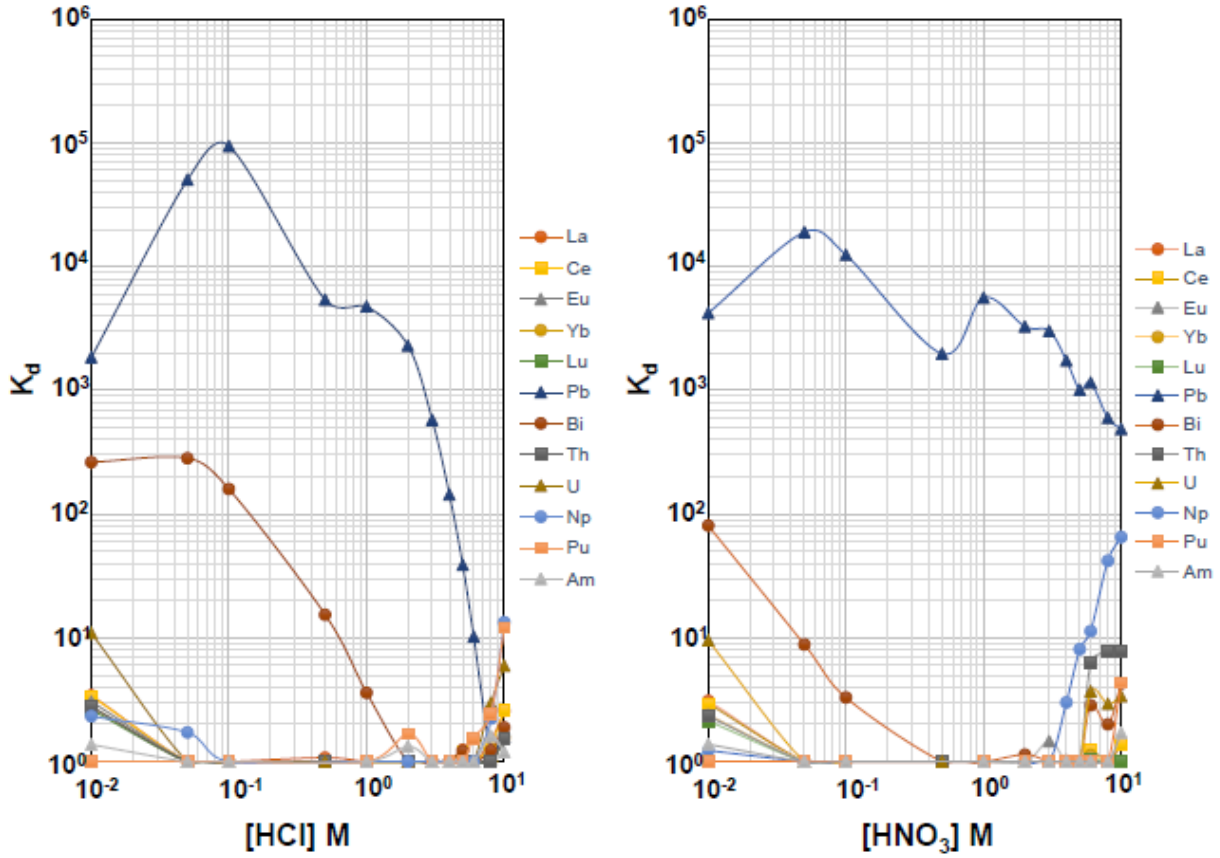
# TK101 Transition Metals




Data provided by Russel et al. (NPL)

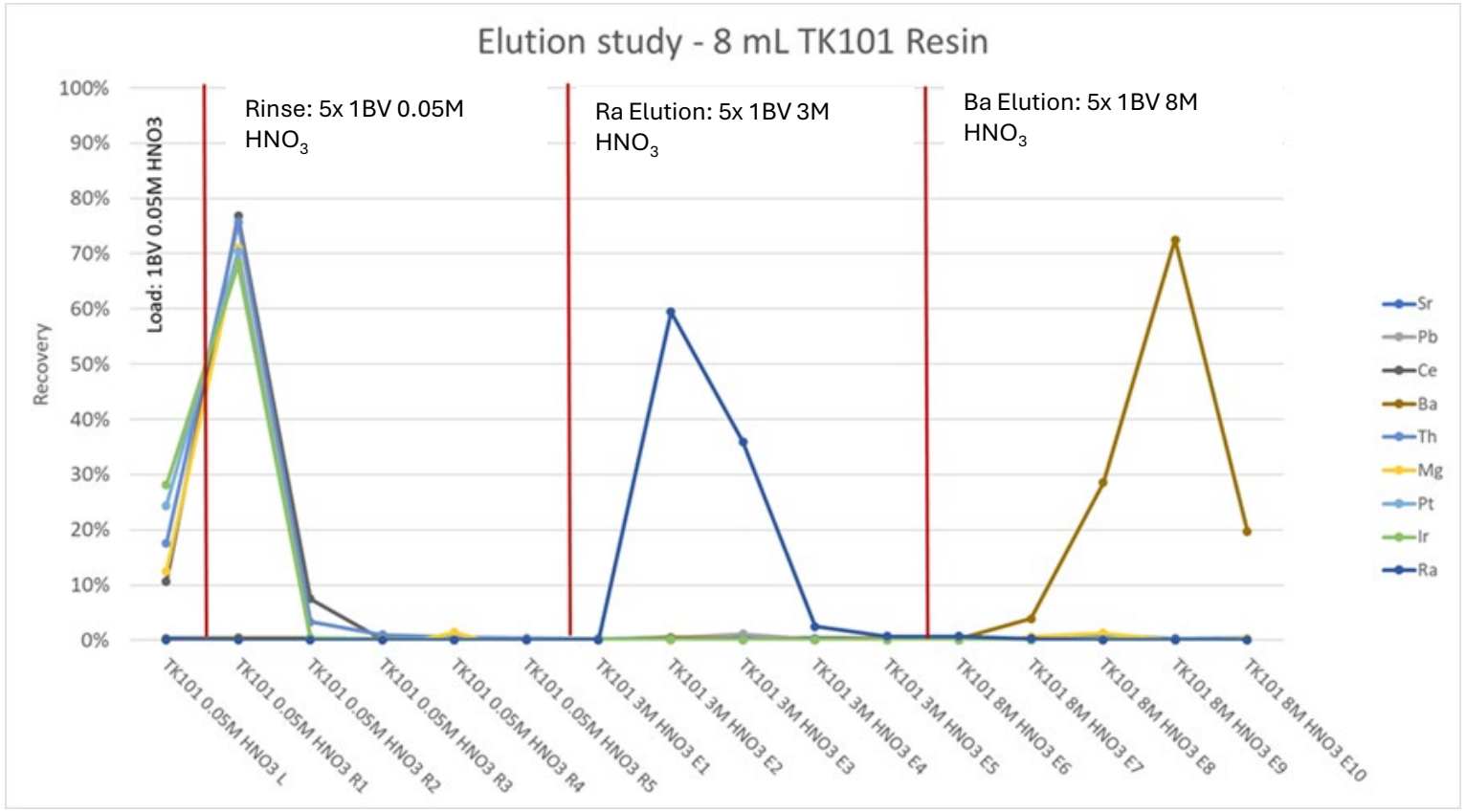
# TK101 - Ra




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 – up to 300mL per 2mL cartridge

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

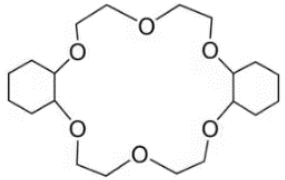
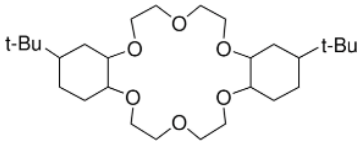
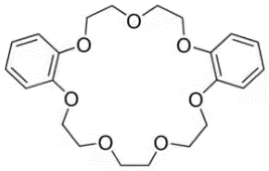
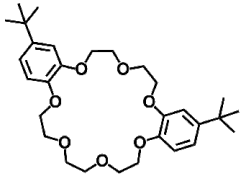
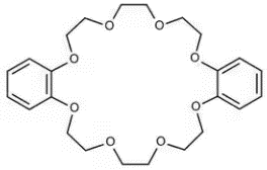
Further Ba removal via TK102 possible

Ra/Ba co-eluted in 8M $HNO_3$

No retention of U, Th, Pt, Ir,…

# 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 |

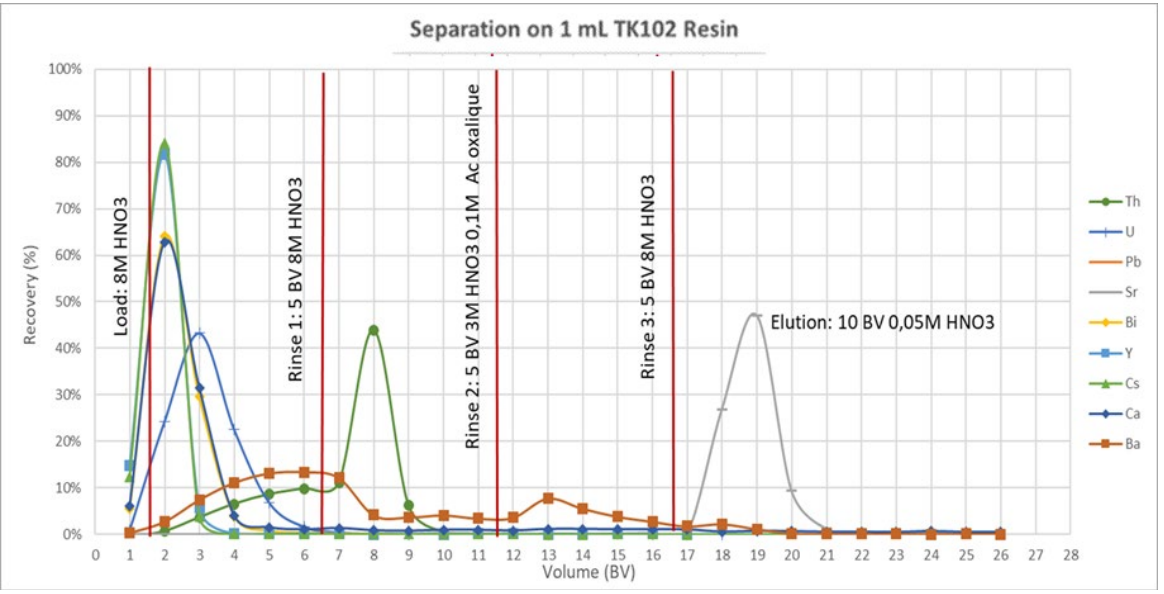
- Obtained data => Modelisation
- Upcoming: Ra Workgroup with research groups
  - Environment/medical
  - Modelisation
  - Synthesis labs

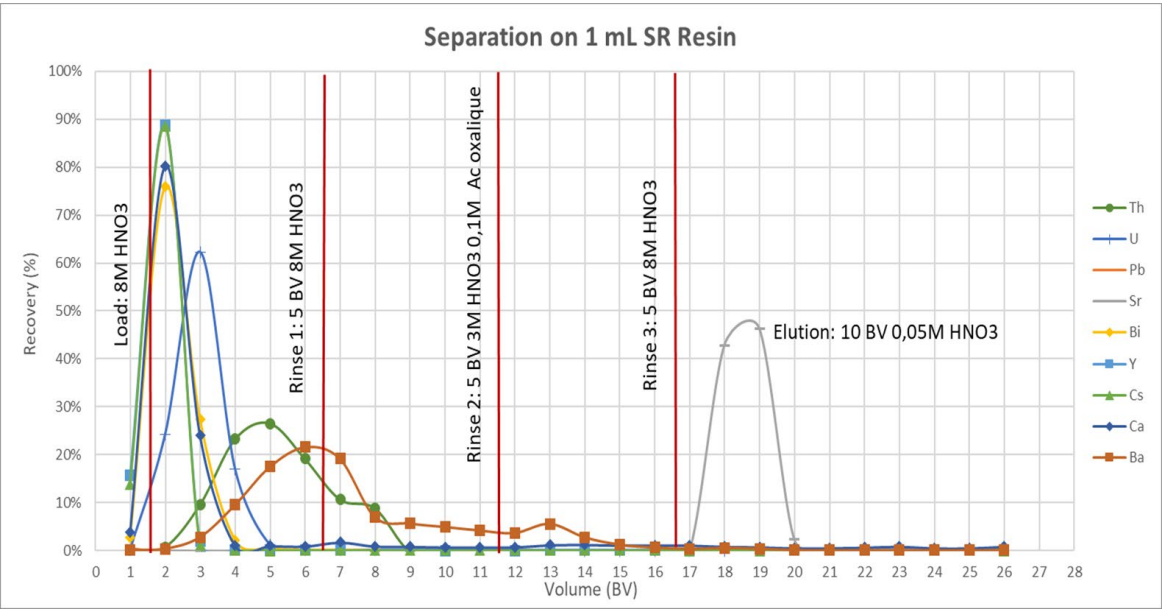
**Presentation I. Dovhyi at NRC10**

# 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
  - Generally higher $D_W$ and capacity for Sr, Pb and Ba
- Work by Illarion Dohvyi (Poster during ERA14), Marine Bas, Soumaya Khalfallah, Nora Vajda, Steffen Happel
- Optimized for Ra/Ba separation => main use
- Under testing: use in Sr isotope ratios via TIMS (less bleeding) and decommissioning samples

# TK102 Resin – Elution curves comparison vs SR Resin - Sr separation

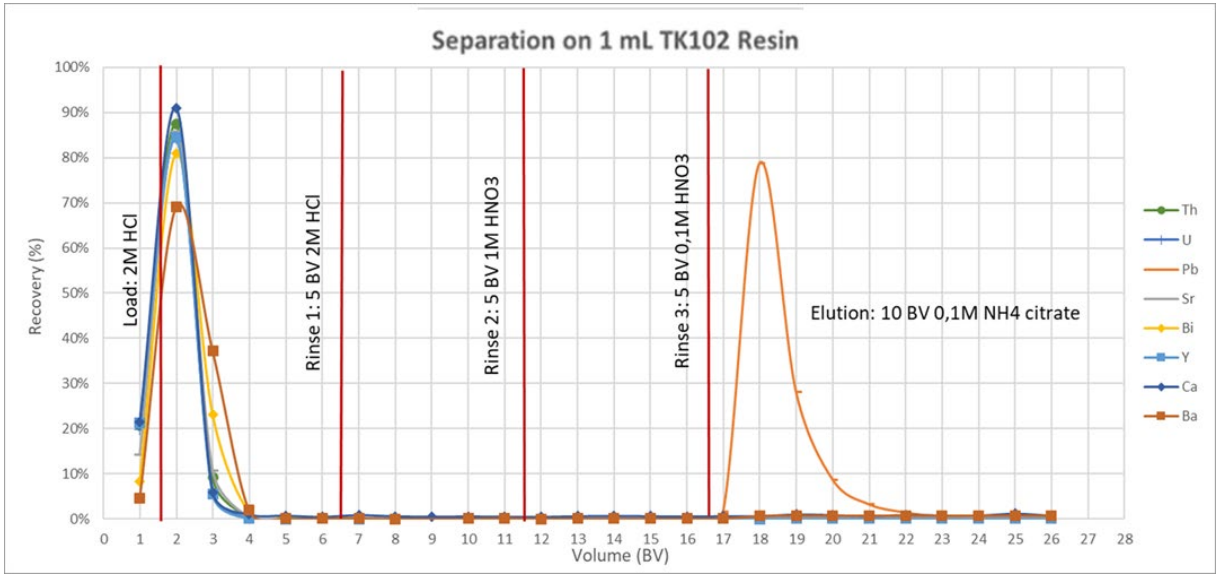


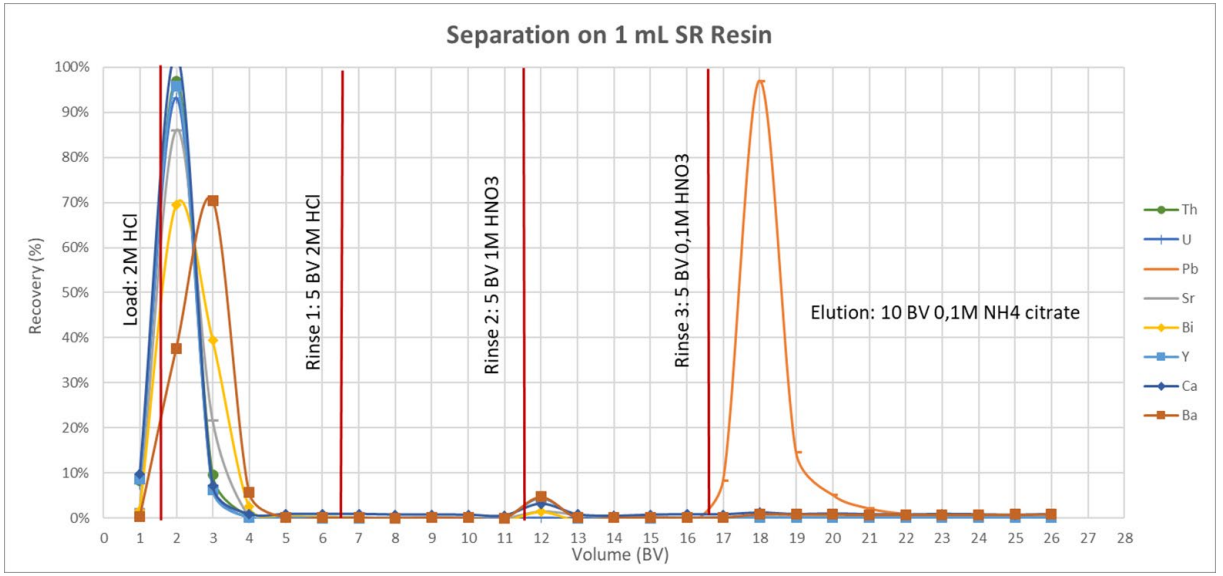




TK102 Resin vs SR resin:
Sr elution study in 8M $HNO_3$ load medium

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

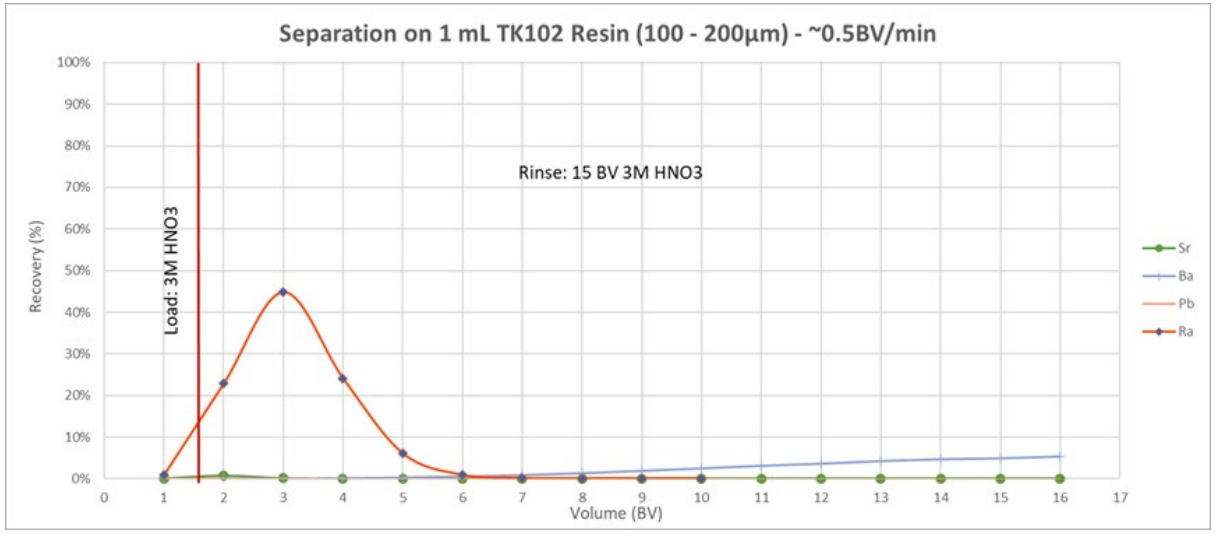


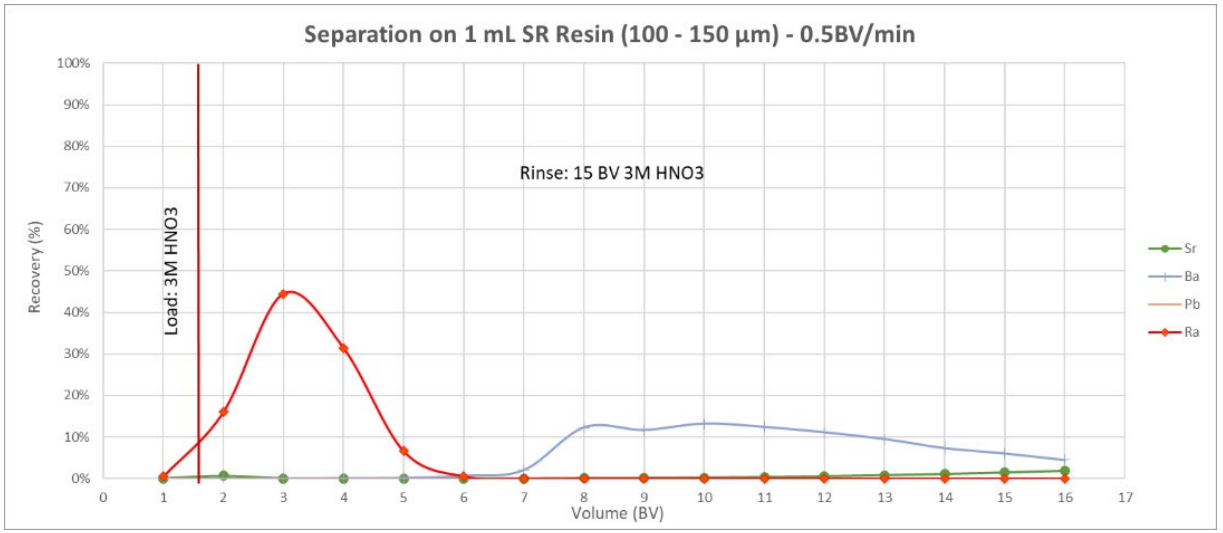




TK102 Resin vs SR resin:
Pb elution study with 2M HCl loading medium

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

➢ Other options

TK201 Resin

TK202 Resin

TK200 Resin

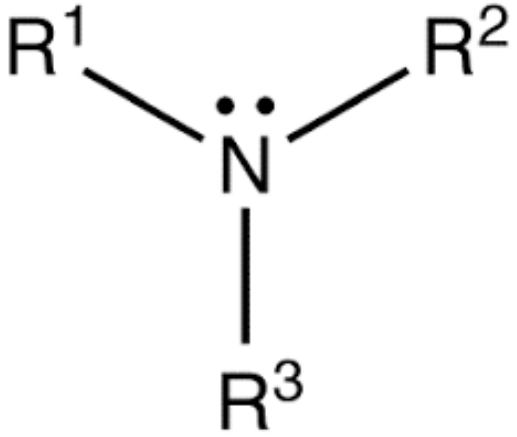
TK-TcScint

# TK201 Resin

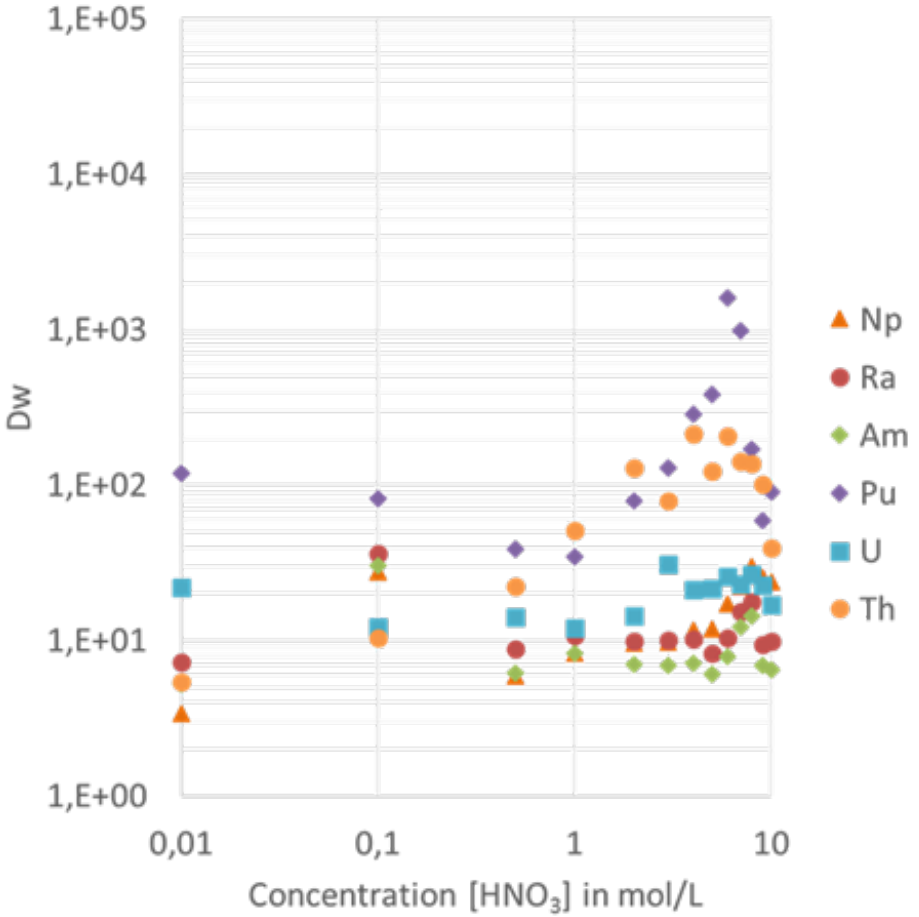
Based on tertiary amine (weak Anion Exchanger) impregnated on inert support

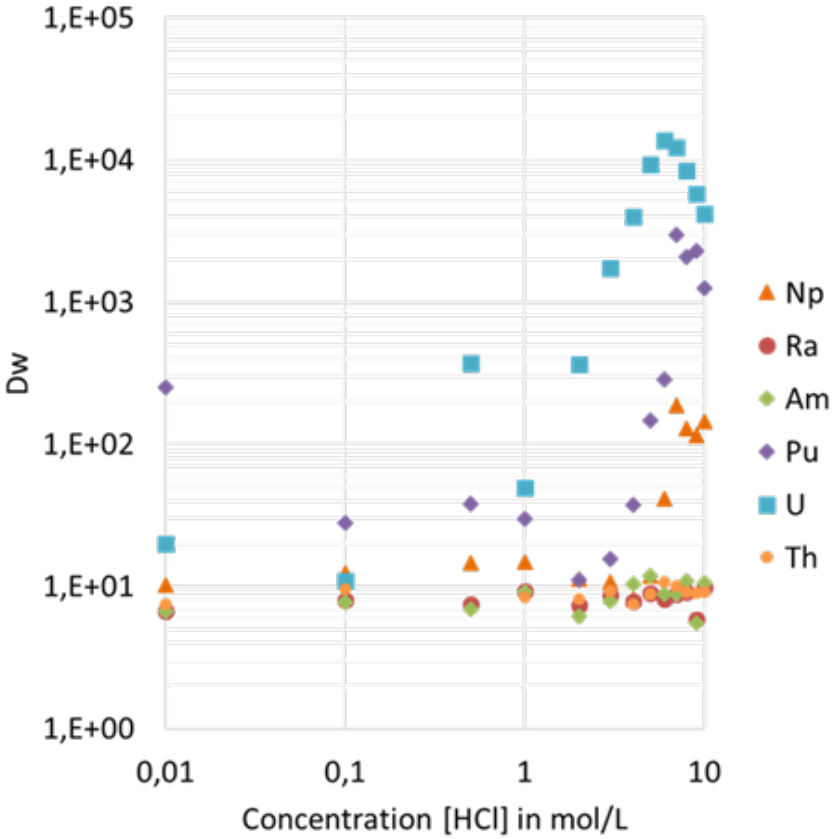
Main applications:

- Tc separation
  - Environmental monitoring
  - Decommissioning
  - Easier to elute
    - Use of $NH_4OH$ or 3M $HNO_3$
- Cu separation
  - Cu-61/4 from Ni targets
- Zn, Fe separation
  - Geochemistry



# TK201 – Actinides



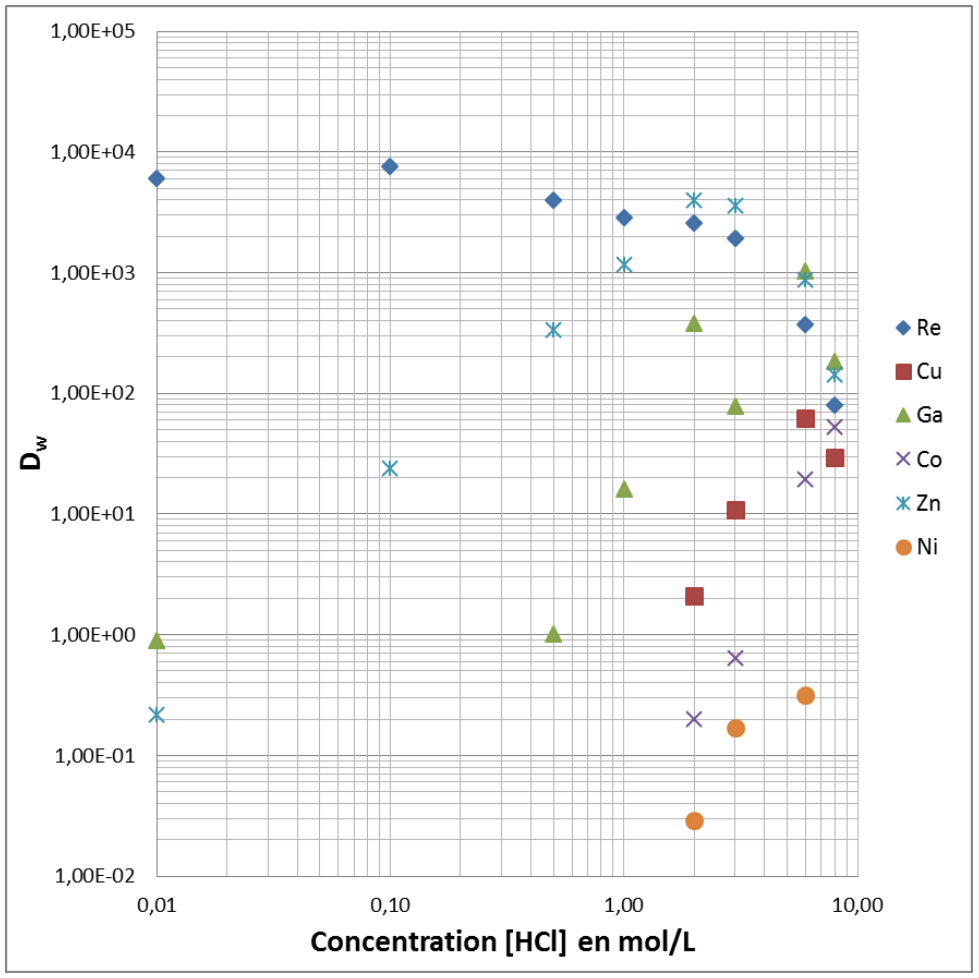



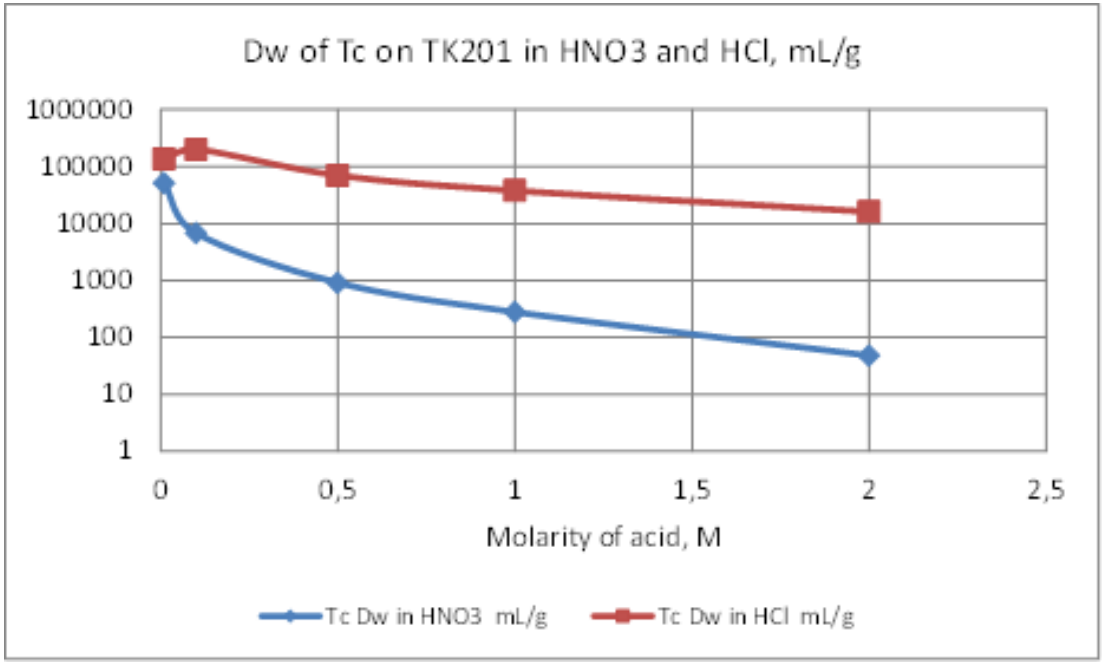

- Re uptake between pH 2 – 5M HCl
- In $HNO_3$ medium, Re fixed at pH 1-2

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

Data Russel et al. NPL

# TK201 – Dw values




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

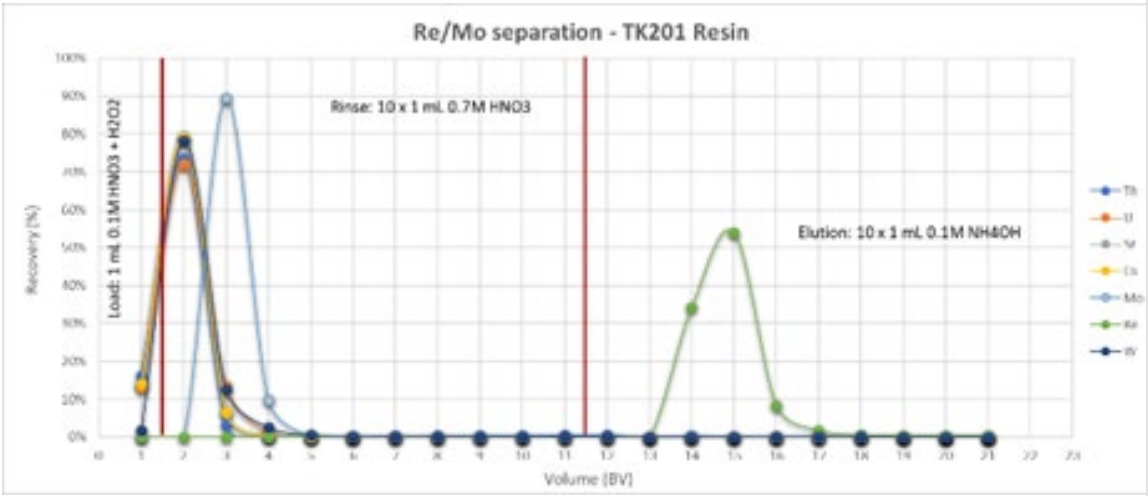
Load of sample at pH 1-2 to retain Re & Tc

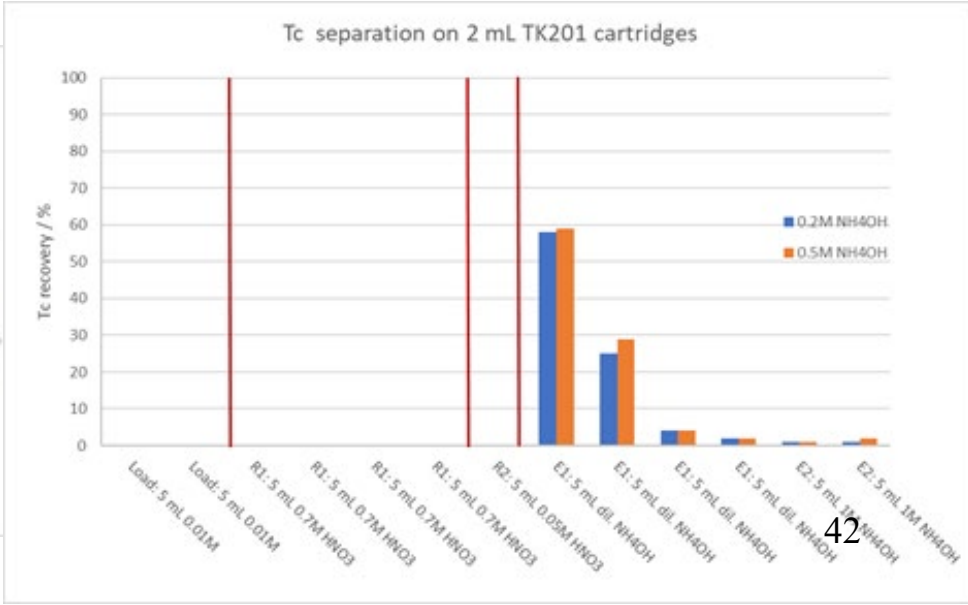
Interferences removed during load/rinse

Mo elution at 0.7M $HNO_3$

Tc/Re elution in 3M $HNO_3$

Preferable eluton option: ≥ 0.5M $NH_4OH$



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Article

# Online Solid-Phase Extraction–Inductively Coupled Plasma–Quadrupole Mass Spectrometry with Oxygen Dynamic Reaction for Quantification of Technetium-99

Makoto Matsueda,* Kayo Yanagisawa, Kazuma Koarai, Motoki Terashima, Kenso Fujiwara, Hironobu Abe, Akihiro Kitamura, and Yoshitaka Takagai*

Cite This: *ACS Omega* 2021, 6, 19281–19290

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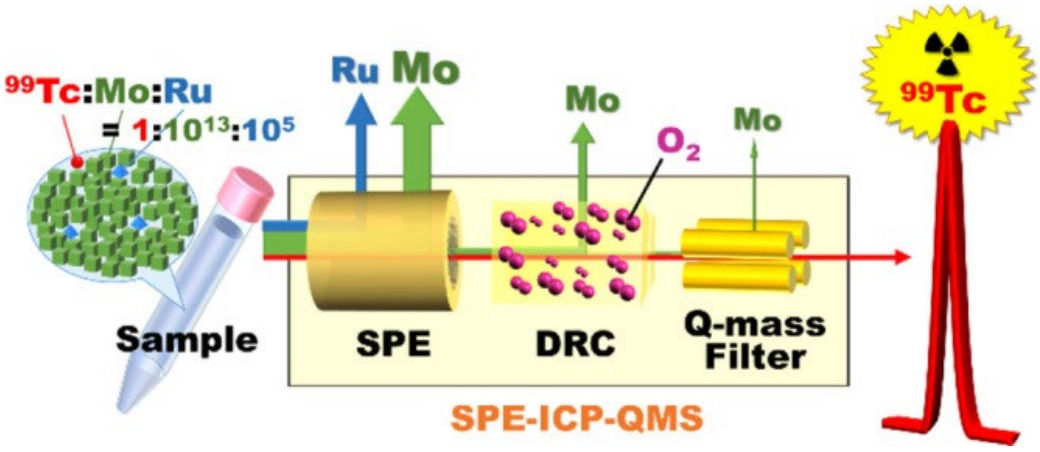


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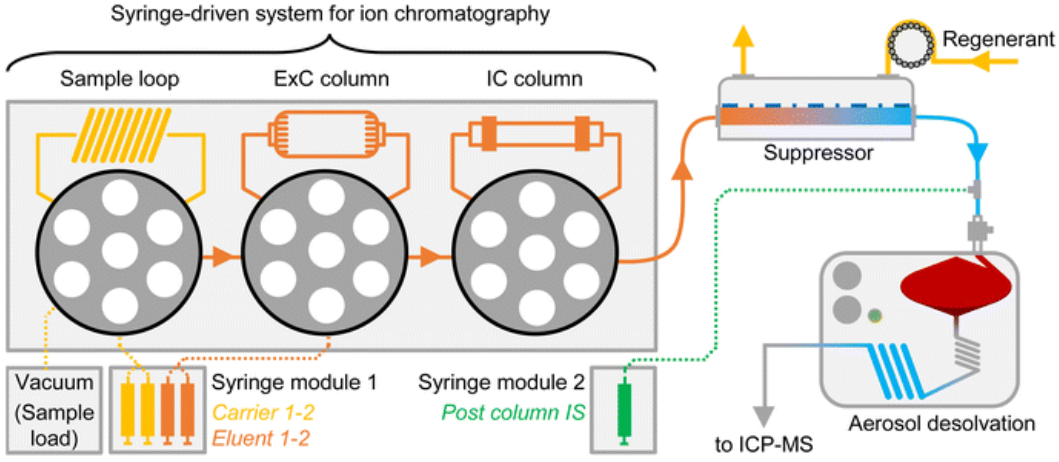
Cite this: *J. Anal. At. Spectrom.*, 2024, 39, 2774

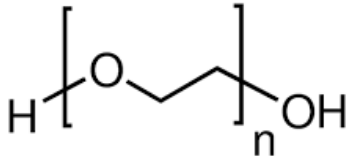
# Quantification of technetium-99 in wastewater by means of automated on-line extraction chromatography – anion-exchange chromatography – inductively coupled plasma-mass spectrometry†

Maximilian Horstmann, [a] C. Derrick Quarles, Jr, [b] Steffen Happel,[c] Michael Sperling, [d] Andreas Faust, [e] David Clases [*f] and Uwe Karst [*a]




Second publication including TK201 Discs for higher sample load => better LoD

# TK202 Resin

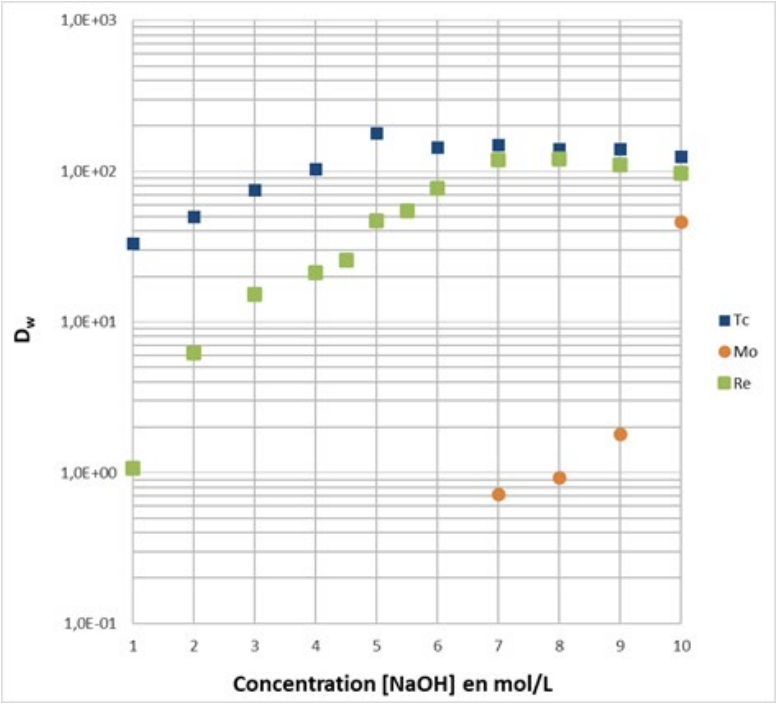



Polyethylene Glycol (PEG) grafted on inert support

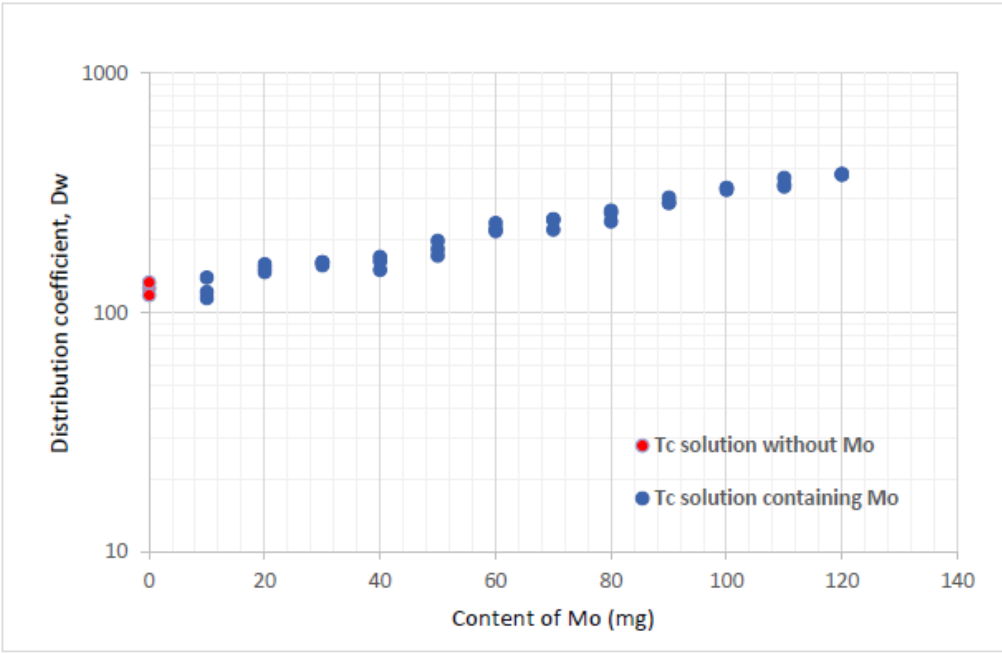
Retention of chaotropic anions e.g; $TcO_4^-$ in the presence of kosmotropic anions ($SO_4^{2-}$, $CO_3^{2-}$, $OH^-$, $MoO_4^{2-}$,…)

For samples rich in Mo: Tc yield > 90% for 6 – 8g Mo per g TK202

Analytical application: e.g. Tc-99 in concrete samples




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

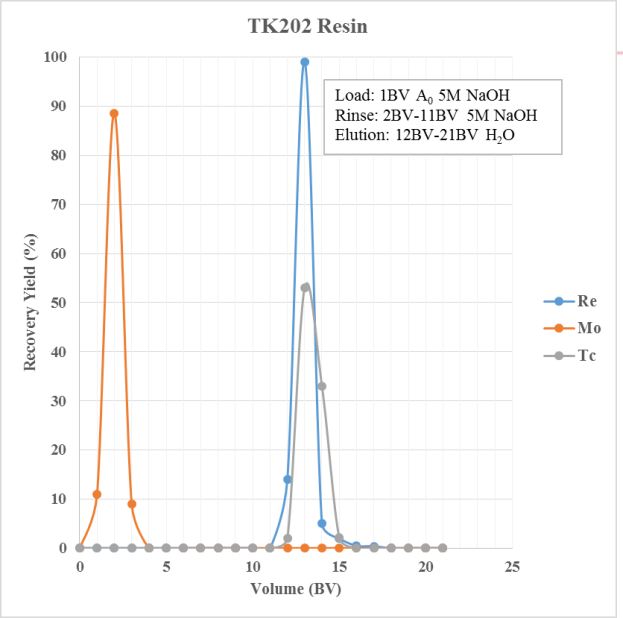
Retention of Tc from concentrated NaOH medium (5 - 7M)

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

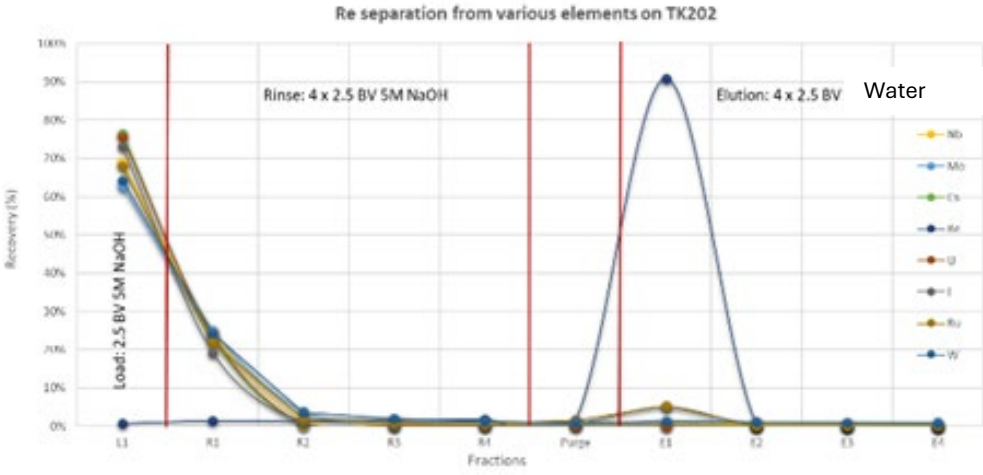
Re can be used as internal standard

Elution in a small volume of water

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




Re/Tc separation from Mo on TK202 Resin



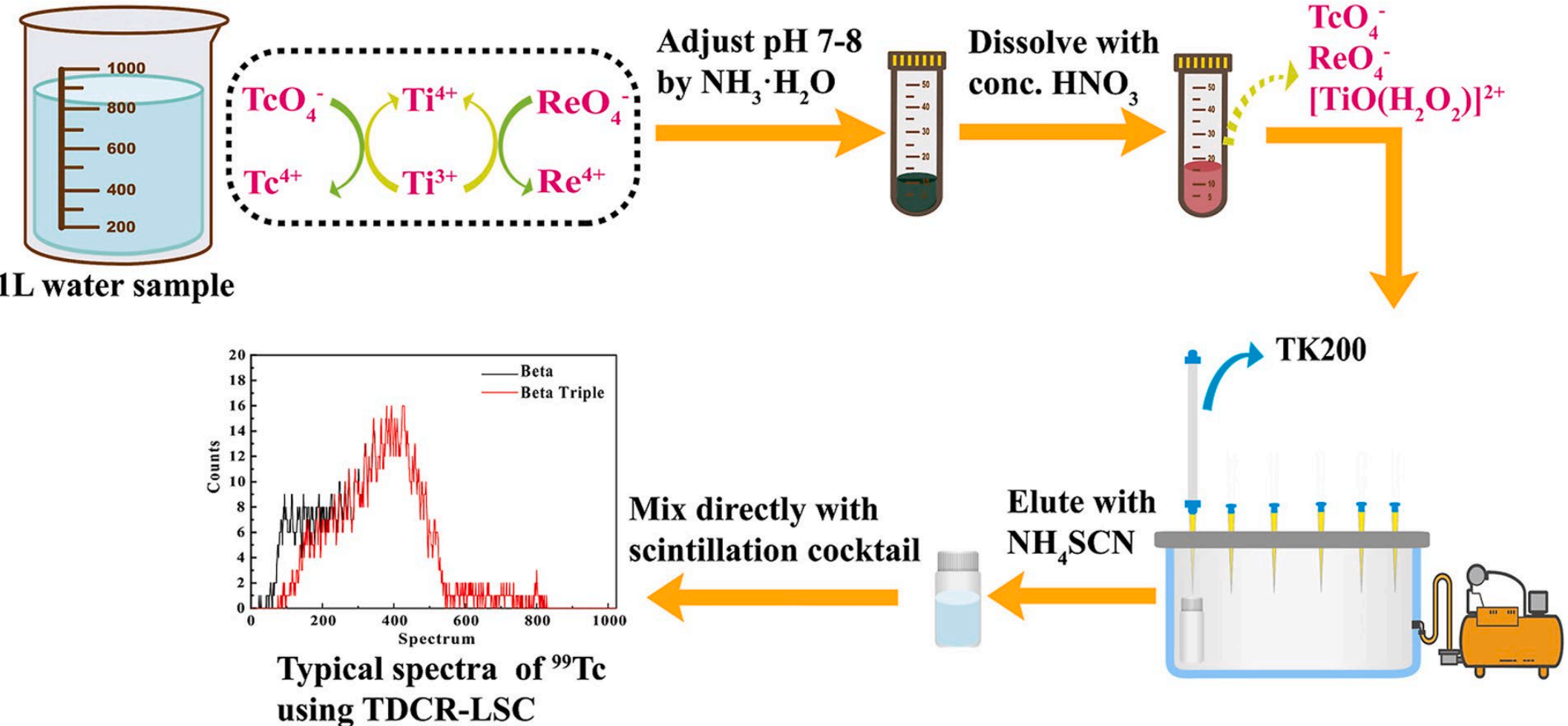

Re separation from selected elements on 2 mL TK202 Resin cartridge, load and rinse at 1 BV/min, elution at 0.25 BV/min.

# 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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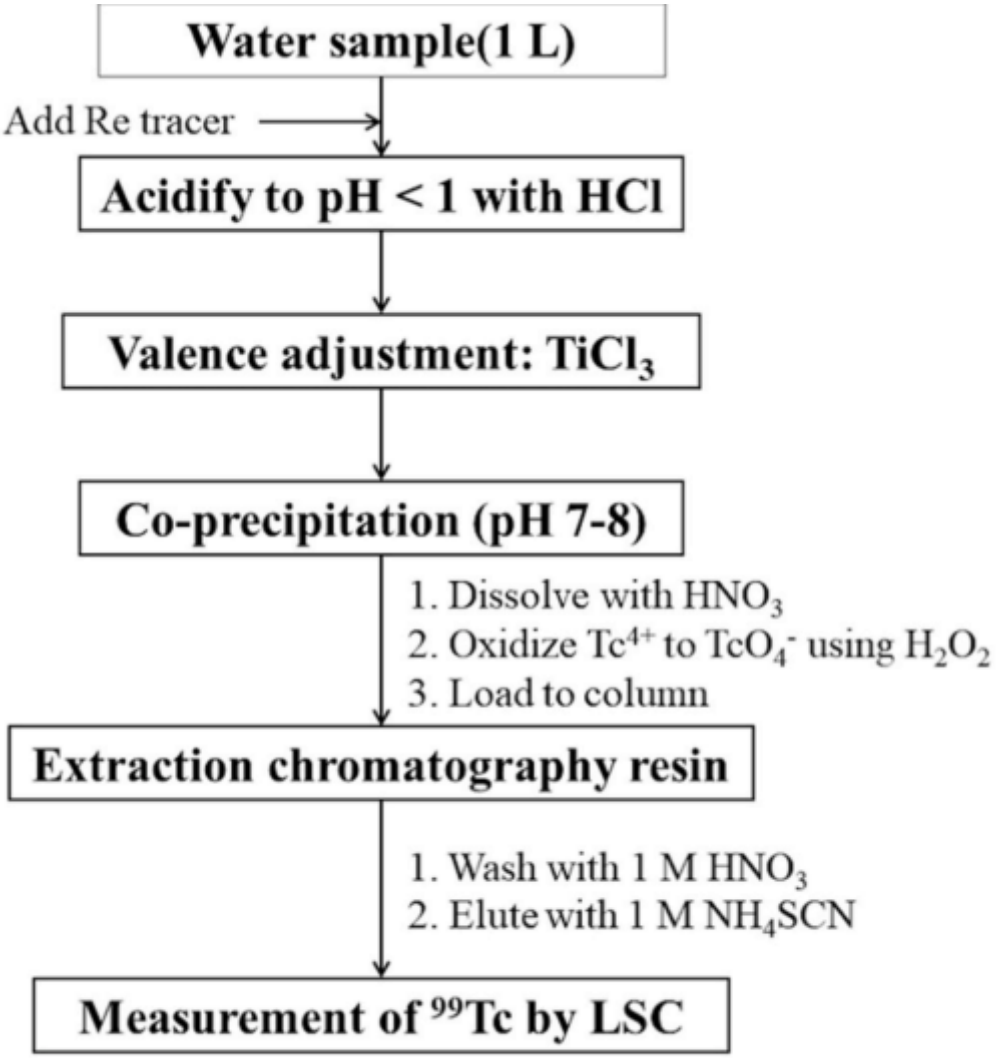
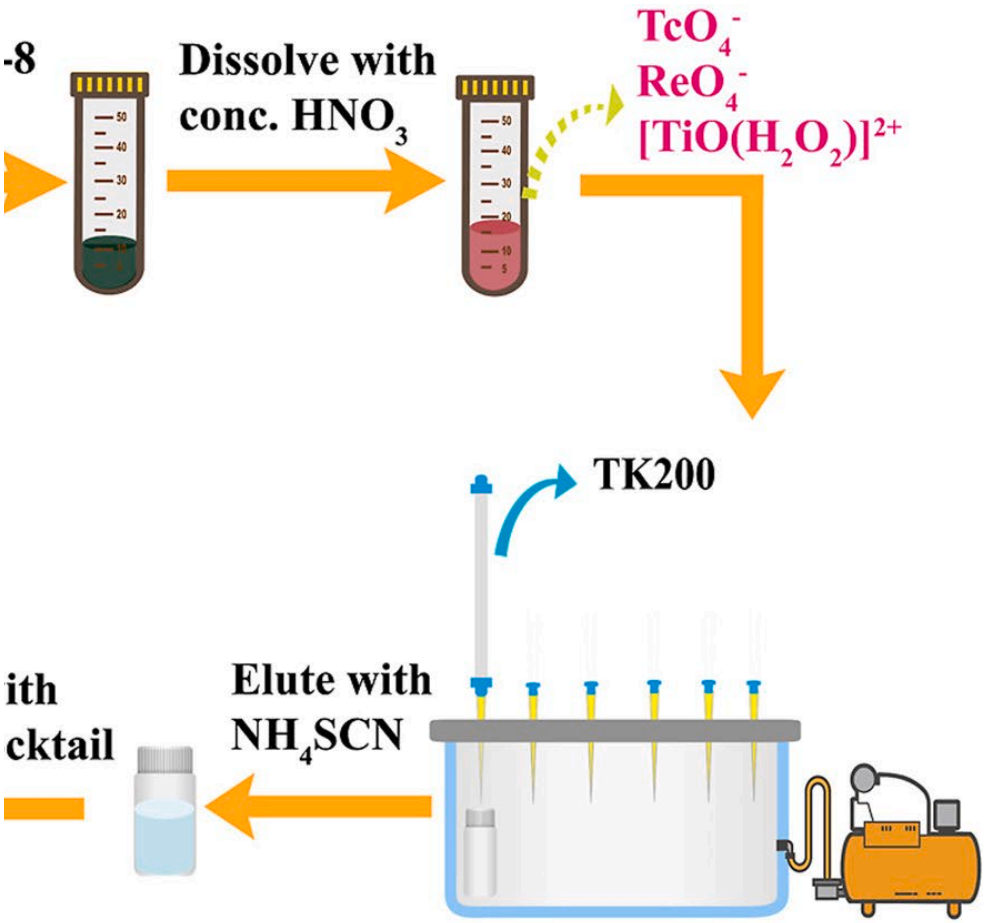



**Fig. 1.** Schematic diagram of the chemical procedure for separating $^{99}Tc$ from the water sample.




using TDCR-LSC

# TK-TcScint

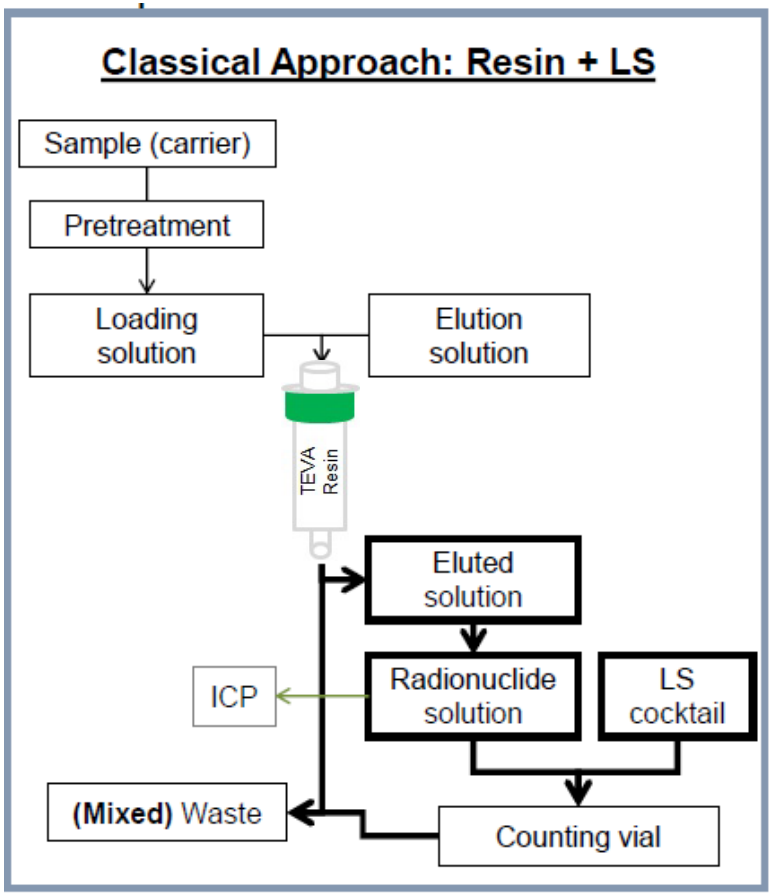
Plastic scintillating beads impregnated with selective extractant

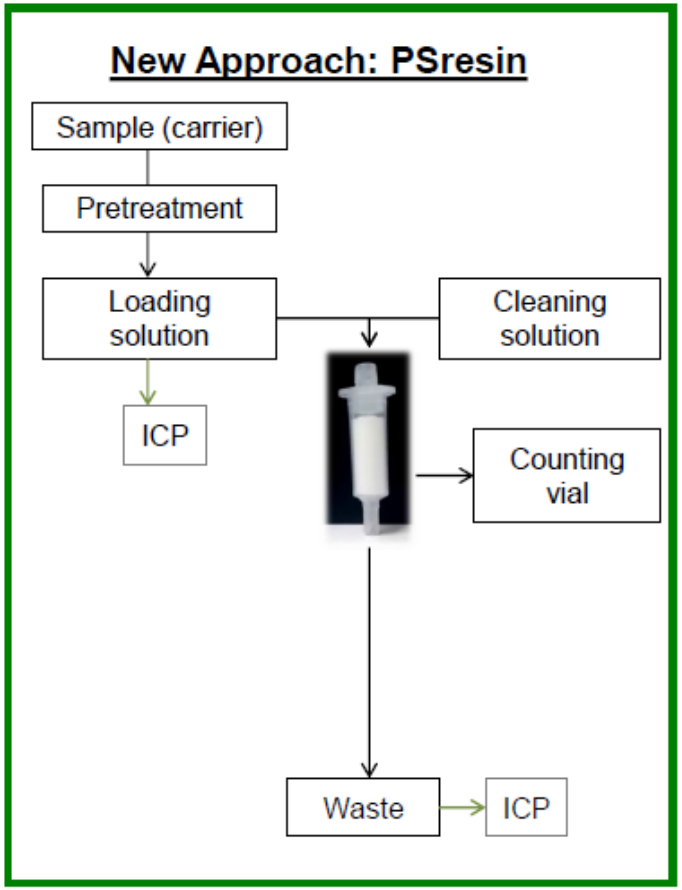
Developped by University of Barcelona

- 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
  - New: TK-SrScint
    - Sr and Pb
  - More products under development:
  - gross alpha(/TK-GA), DGA(/TK227), TK101 (Pb, Ra,..),...

# 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

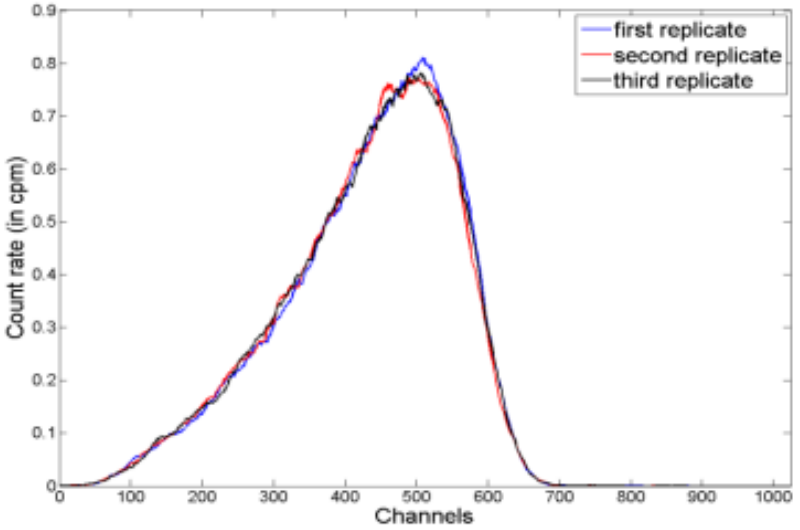
Precondition with 2ml 0.1M HCl

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) |



# TK-SrScint

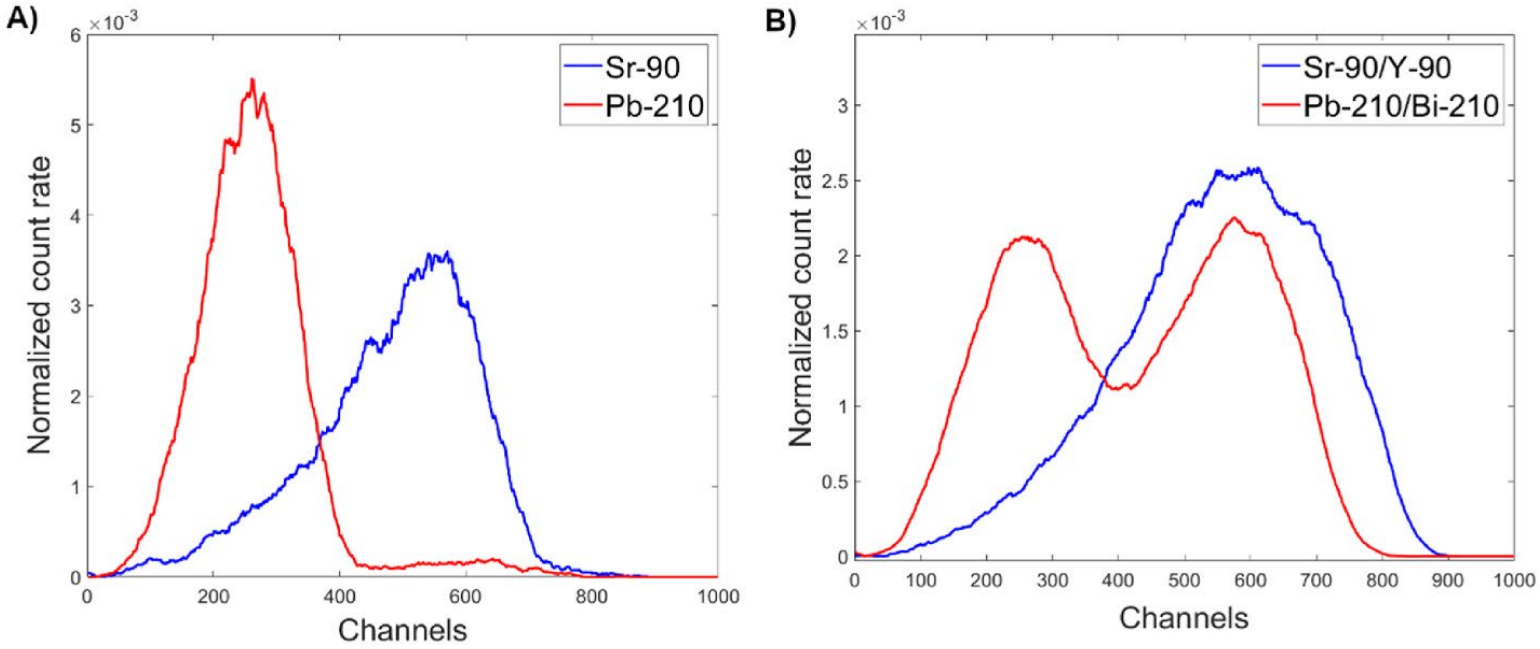
Impregnated plastic scintillation beads (PSm)

TK102 extractanten system (better loading volumen, capacity)

Crown ether + fluorinated alcohol

Sr and Pb retention => chemical yield typically Sr or Pb carrier in eluate via ICP

Detection efficiency for Sr-90: >90%, after Y-90 ingrowth >190%




Normalized LSC spectra Sr-90/Y-90 (blue) and Pb-210/Bi-210 (red)
on TK-SrScint at t= 0 (A) and after ingrowth of the daughters at t >21 Tagen (B).

# TK-SrScint

Well suitable for decommissioning samples (no presence of Pb-210)

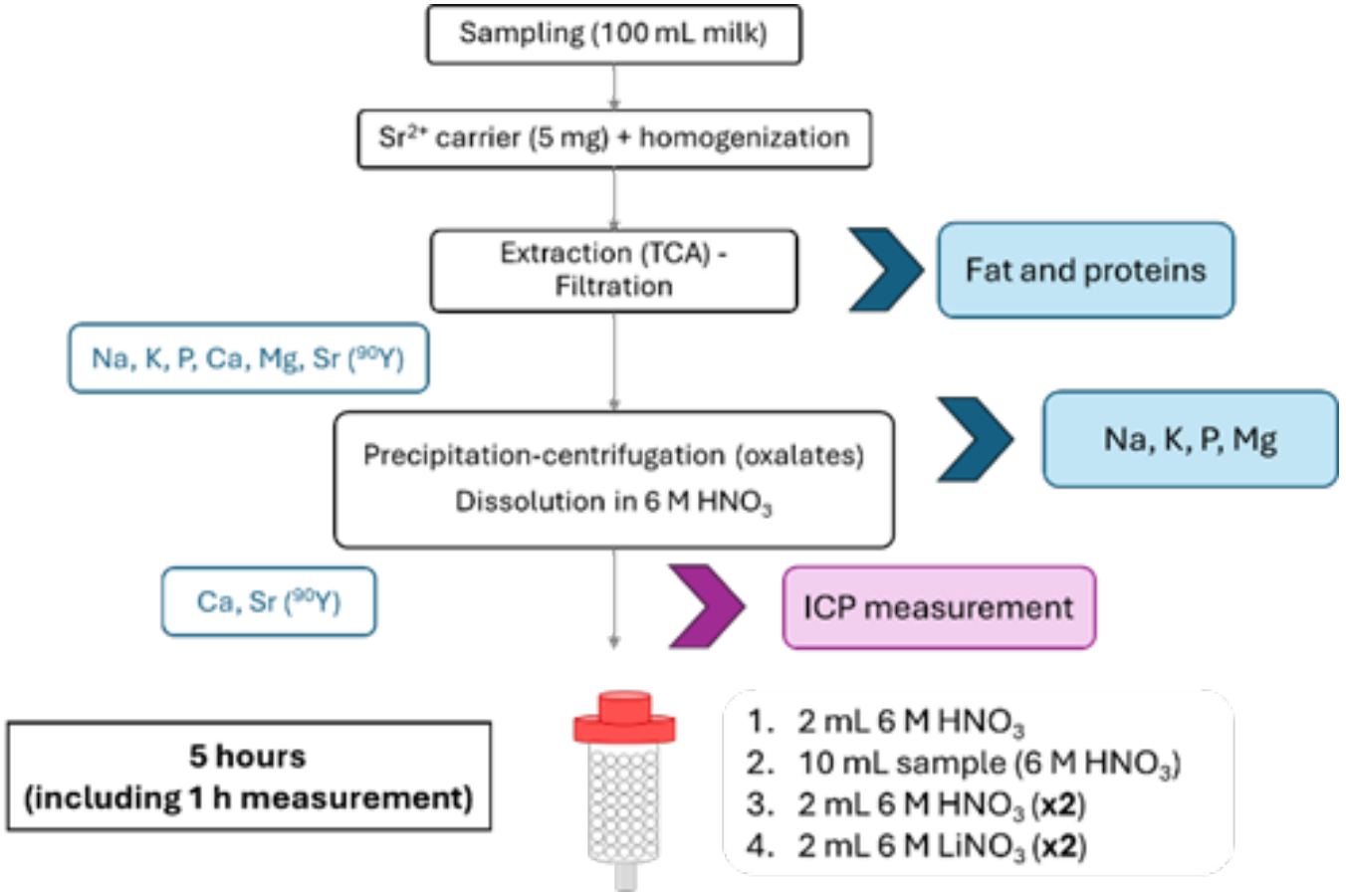
Environmental samples, potential for false positives through Pb-210 (and Bi-210)

- No Sr elution, Pb and Sr remain on the resin, Y-90 and Bi-210 ingrowth
- Tarancon et al. Pb-210 removal through co-precipitation with iodate in presence of Ca at ΔT. Sr remains in solution
- Sr co-precipitation with Ca-Phosphate
- Dissolution in 8 M $HNO_3$
- Load onto TK-SrScint
- Rinse with 8M $HNO_3$, followed by 6M $HNO_3$ and 6M $LiNO_3$ (acid removal)

For 1L Wasserproben: additional preconcentration via carbonate co precipitation

=> Chemical yield for full process between 63 % and 81 %

# TK-SrScint – Rapid method Sr-90 in milk




Sr-90 determination using TK-SrScint

# TK400 Resin

Long chained alcohol

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

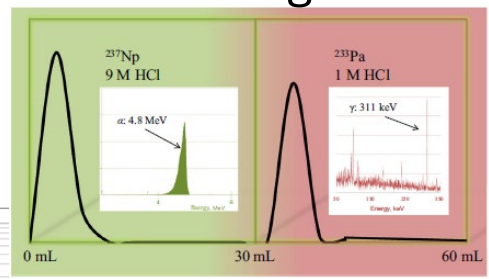
Retention only at high HCl concentration (>6M HCl), elution in low HCl, water,…

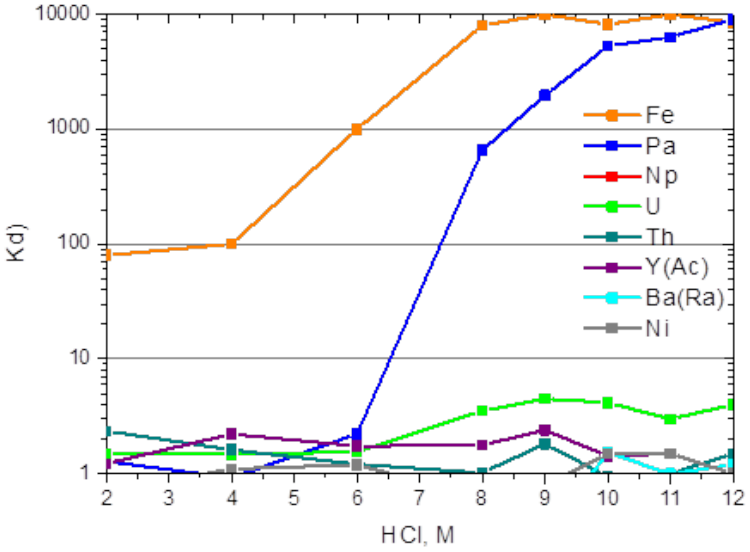
Main application: Pa separation & Ga-68 production

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

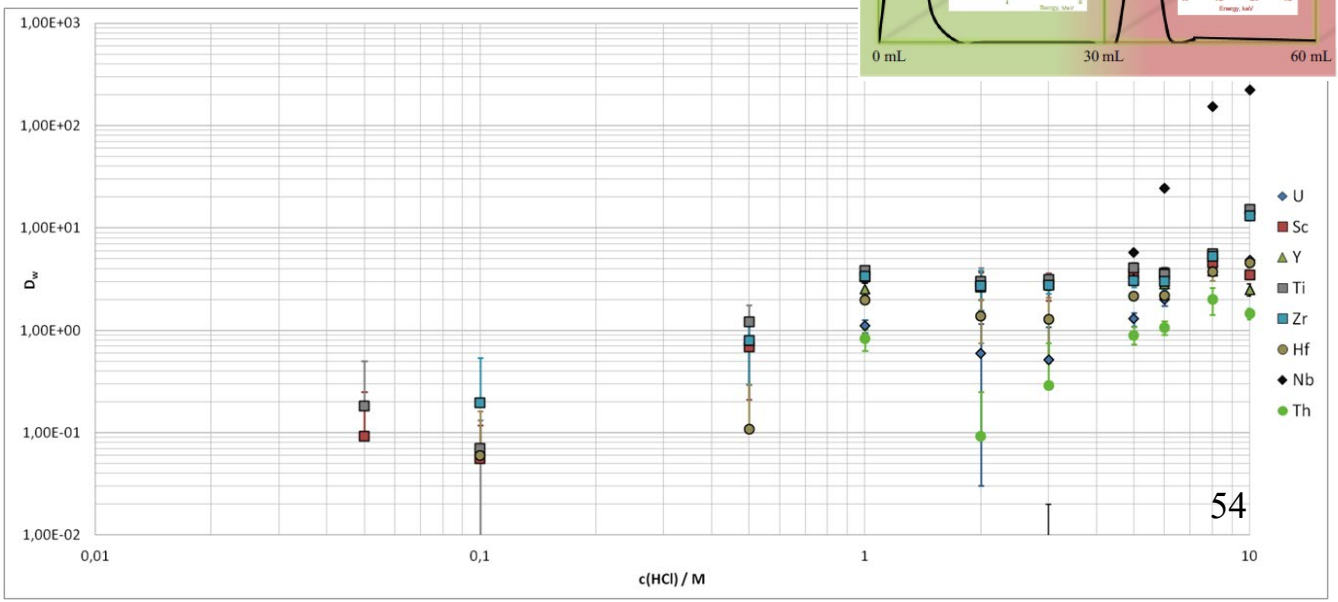
Higher Fe capacity than e.g. TRU Resin (~15mg Fe/g TK400)

Knight et al.

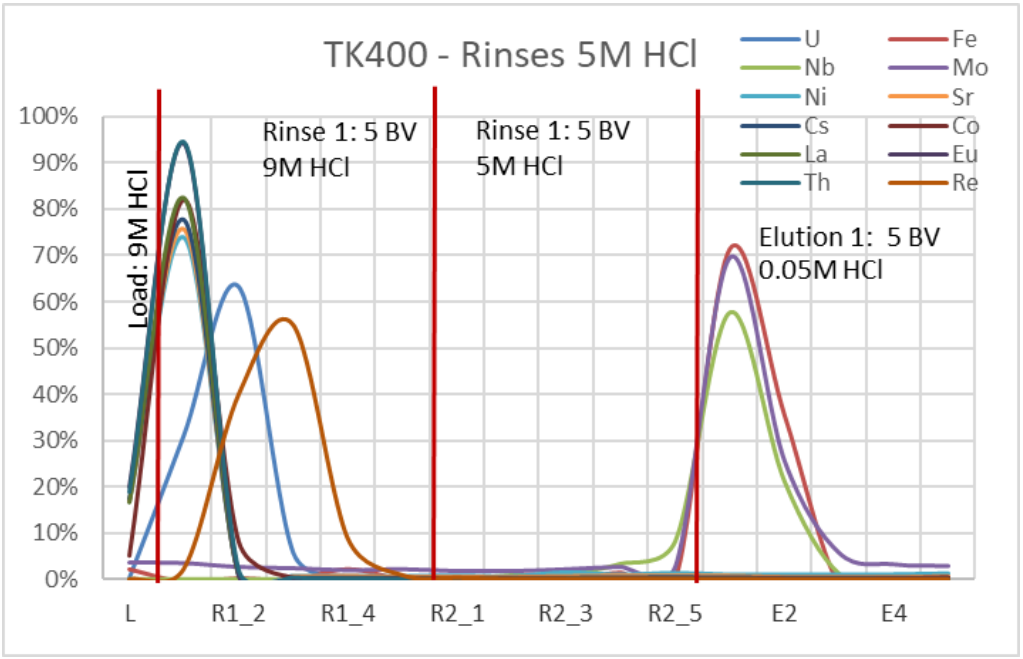


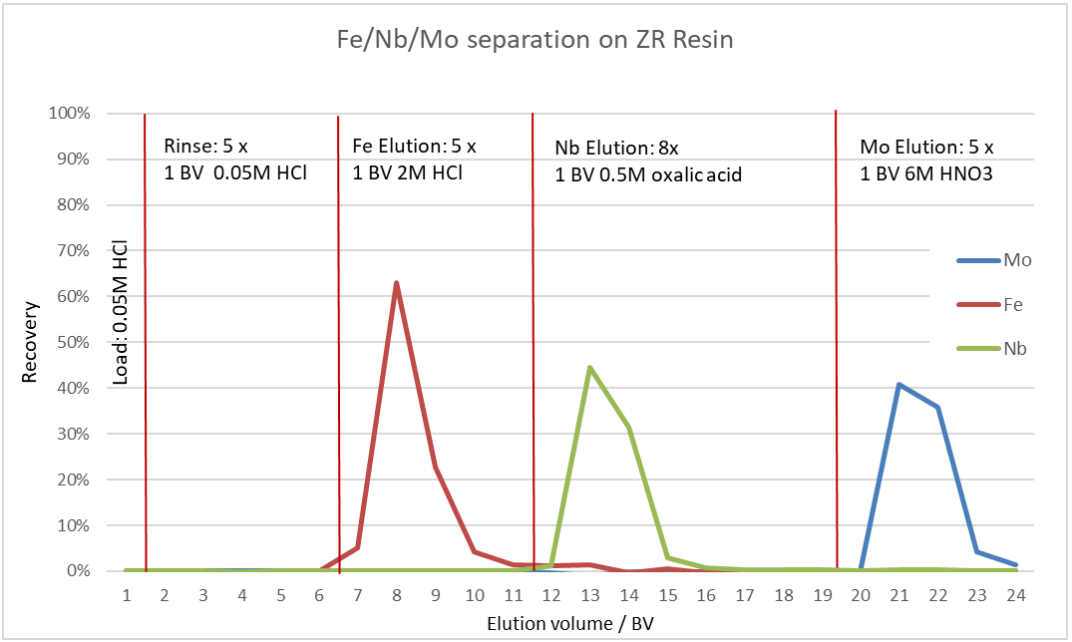




Data provided y B. Russel (NPL)



# 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

# 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 and vice versa
- Use of ionic liquids or short-chained alcohols,… as diluents

Preparation of >15 test resins (PR) based on commercially available calixarenes

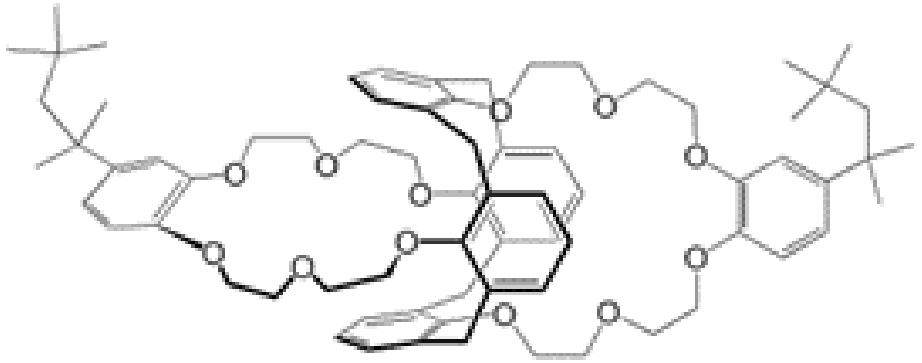
Characterisation of these resins

- $D_W$ 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

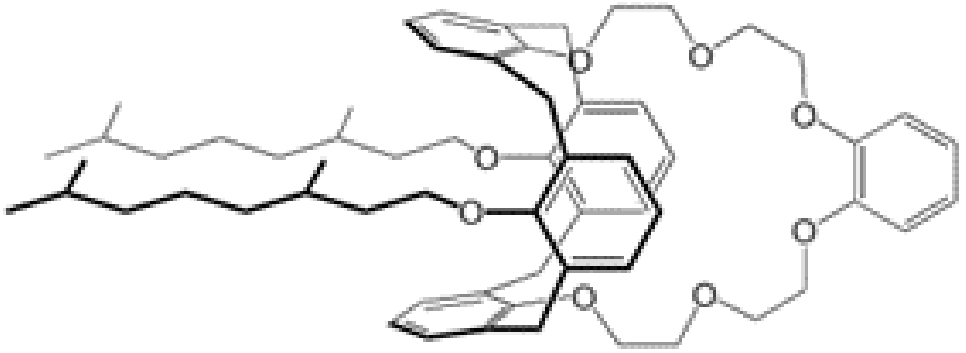
Work performed by Illarion Dovhyi, presented at last TKI/Raddec Workshop (18.04.2024) => visit our website for more data

Decision on which resins will be fabricated end of this year => beta testing

# Tested Calixarenes



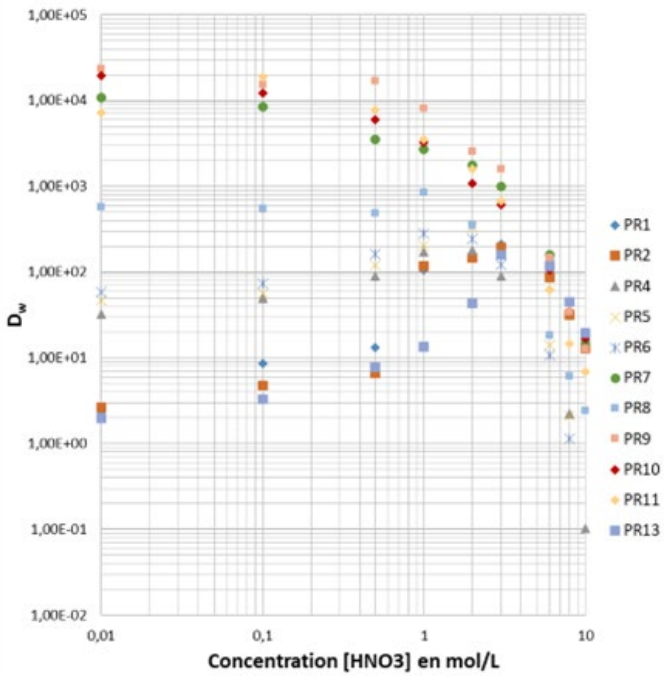
Calix[4]arene-bis(tert-octylbenzocrown-6, $C_{72}H_{92}O_{12}$ (BOBCalix)



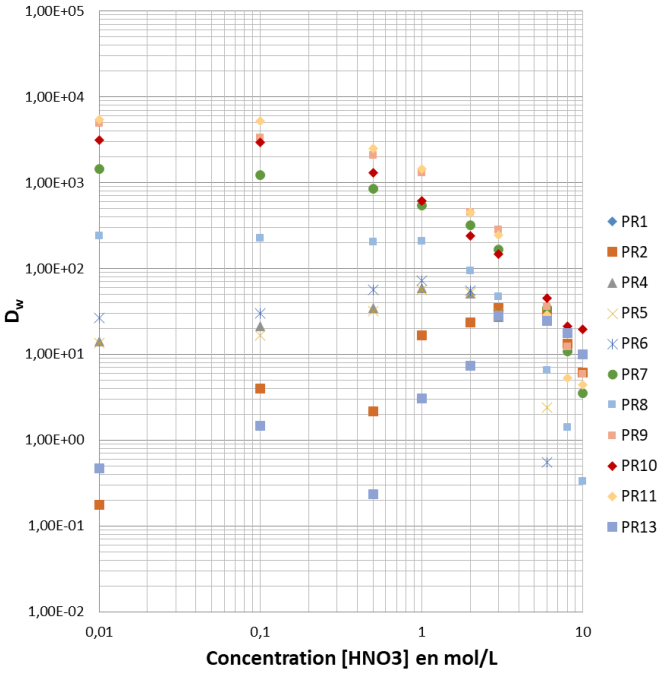
1,3-alt-25,27-Bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6, $C_{62}H_{82}O_8$ (MAXCalix)

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

# $D_W$ values of selected cations in $HNO_3$



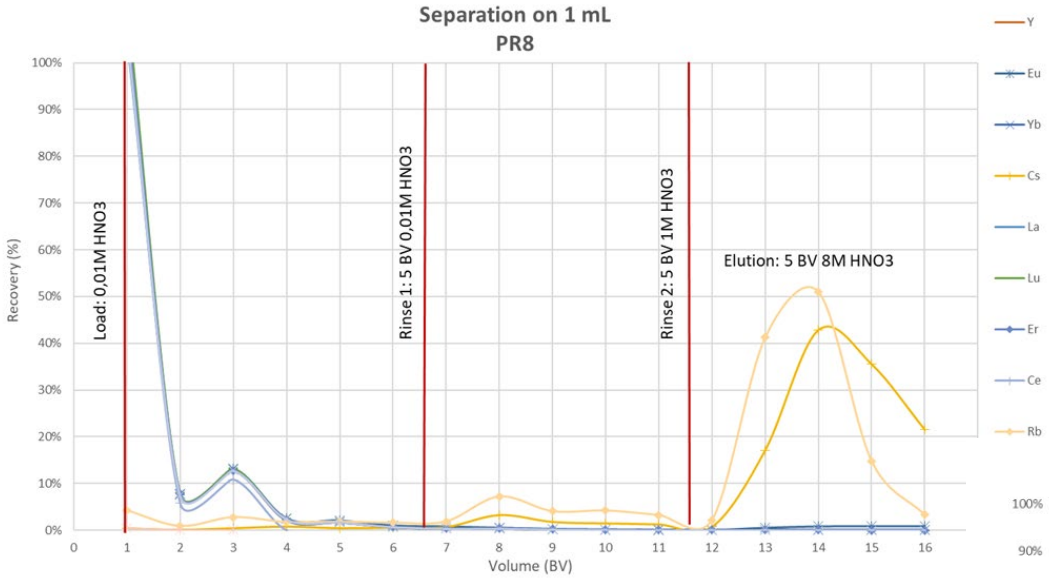

Acid dependency of $D_W$ for $Cs^+$ on PR1-13 in $HNO_3$




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

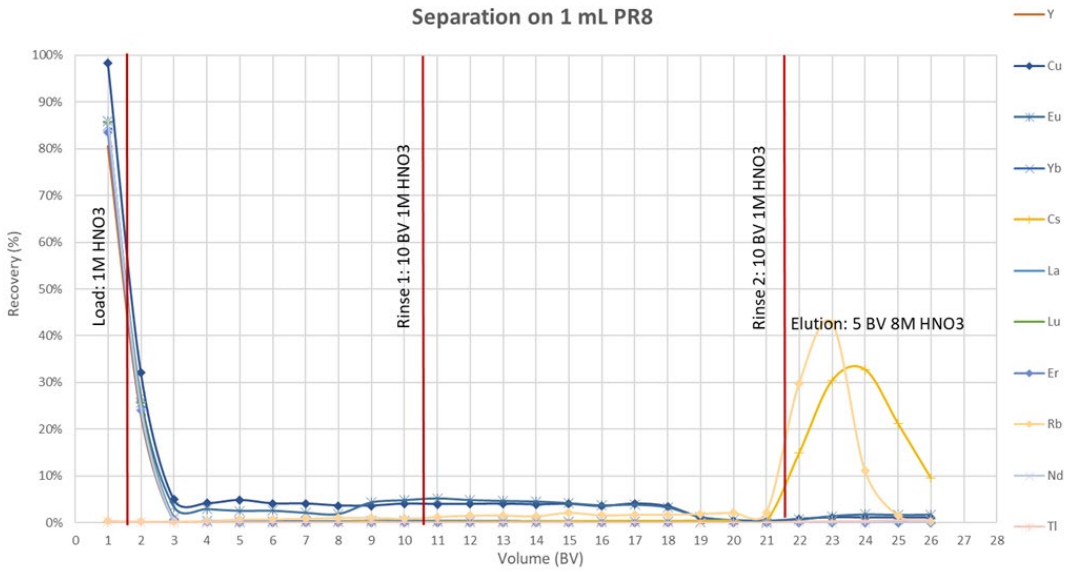
- Generally, $D_W$ Cs > Dw Rb, other elements (Ag, Al, Ba, Bi, Ce, Co, Cu, Er, Eu, Ga, Hf, La, Lu, Mo, Nb, Nd, Ni, Pb, Re, Sb, Sc, Sn, Sr, Th, U, Y, Yb, Zn, Zr) not retained from $HNO_3$
- Ionic liquid based resins: very high $D_W$ from 0.01M to ≥1M $HNO_3$
- Other test resins (non IL) low Cs/Rb extraction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

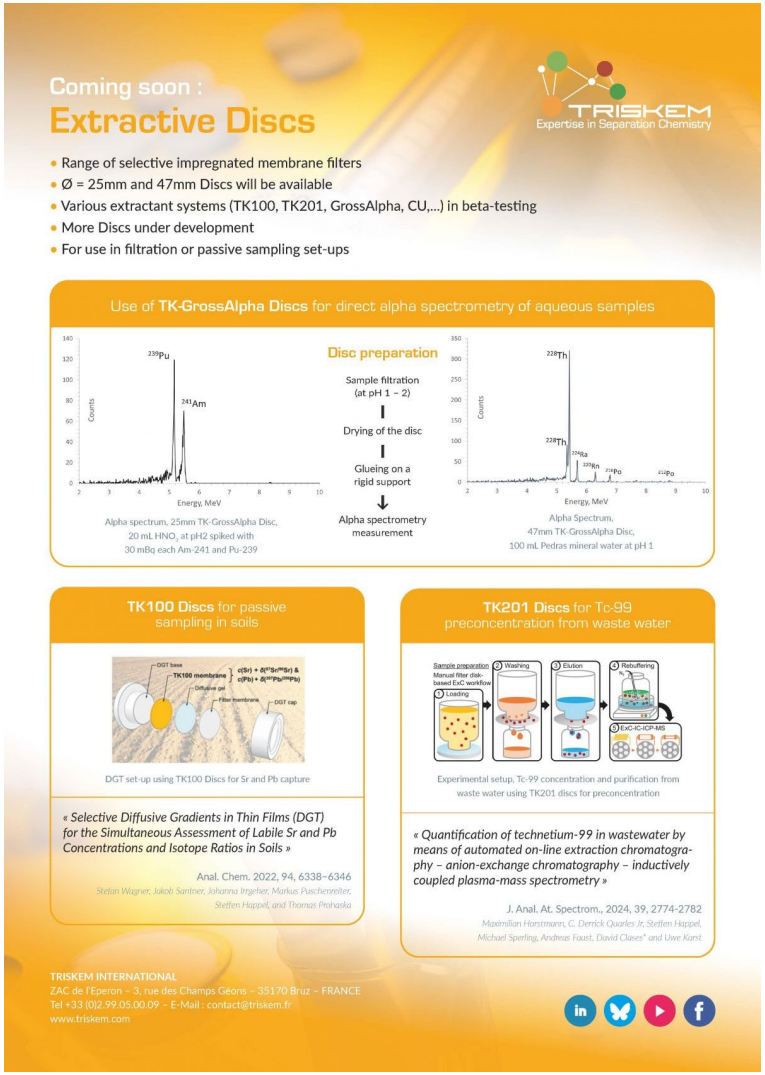
- Generally high selectivity for Cs and Rb, interferents well removed
- Cs elution required >5 BV 8M $HNO_3$




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

# New/under development impregnated membrane filters

Tesmarac
joint research laboratory




Special membrane filters impregnated with extractant(s)

25mm and 47mm Discs available

Commercialized:

- TK-GA Discs (Gross Actinide)

Beta Testing:

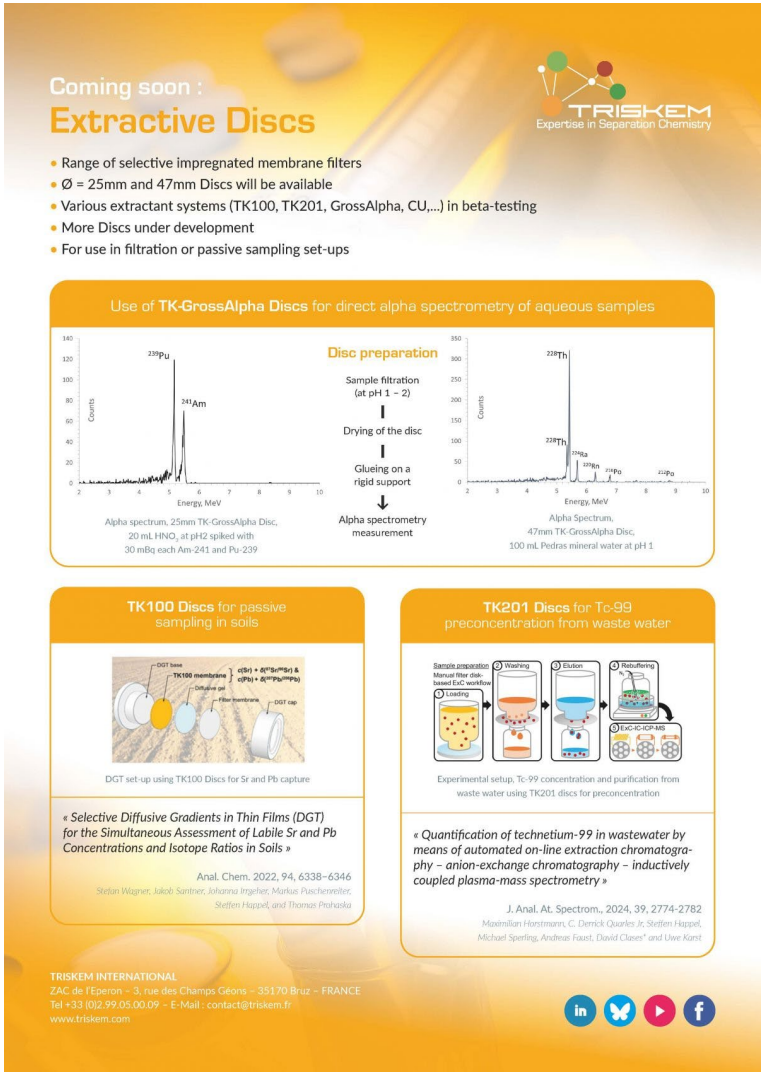
- TK100 & TK201 (both published), CU,...
- TK200 (U, Th, Pu) und TK221 (U, Th, Am, Pu) => sequentila separation (evtl. TK201 (Pu, Th)) => rapid screening?
- Alphaspec: Retention vs. Retention on the surface (70 - >90%)

Under development:

- TK102/TK227 - Rapid methods for Sr, TK101 (Pb, Ra),...

# New/under development: impregnated membrane filters

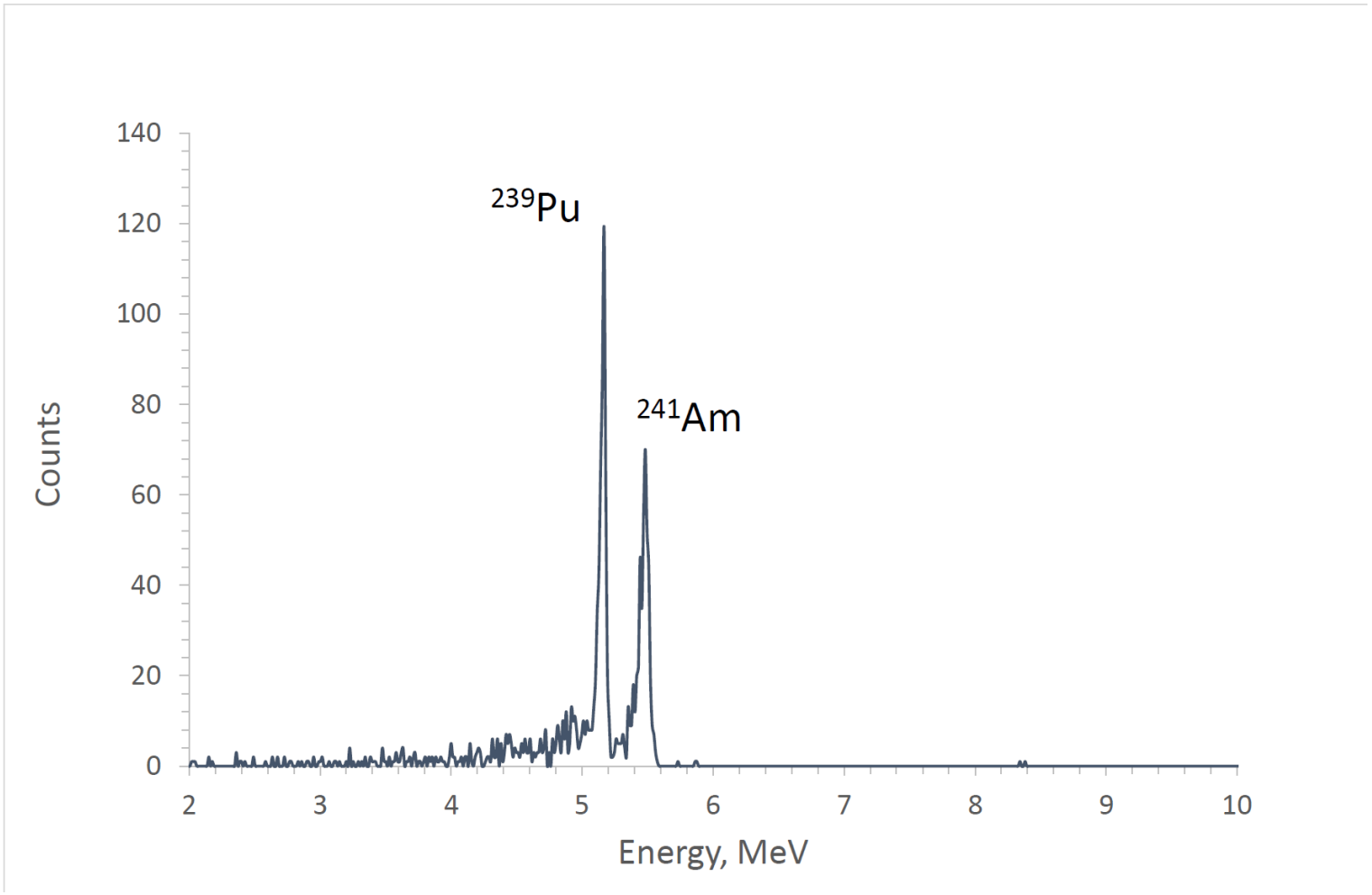
Tesmarac
joint research laboratory




## 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.
- Optional: subsequent Alpha/Beta via LSC

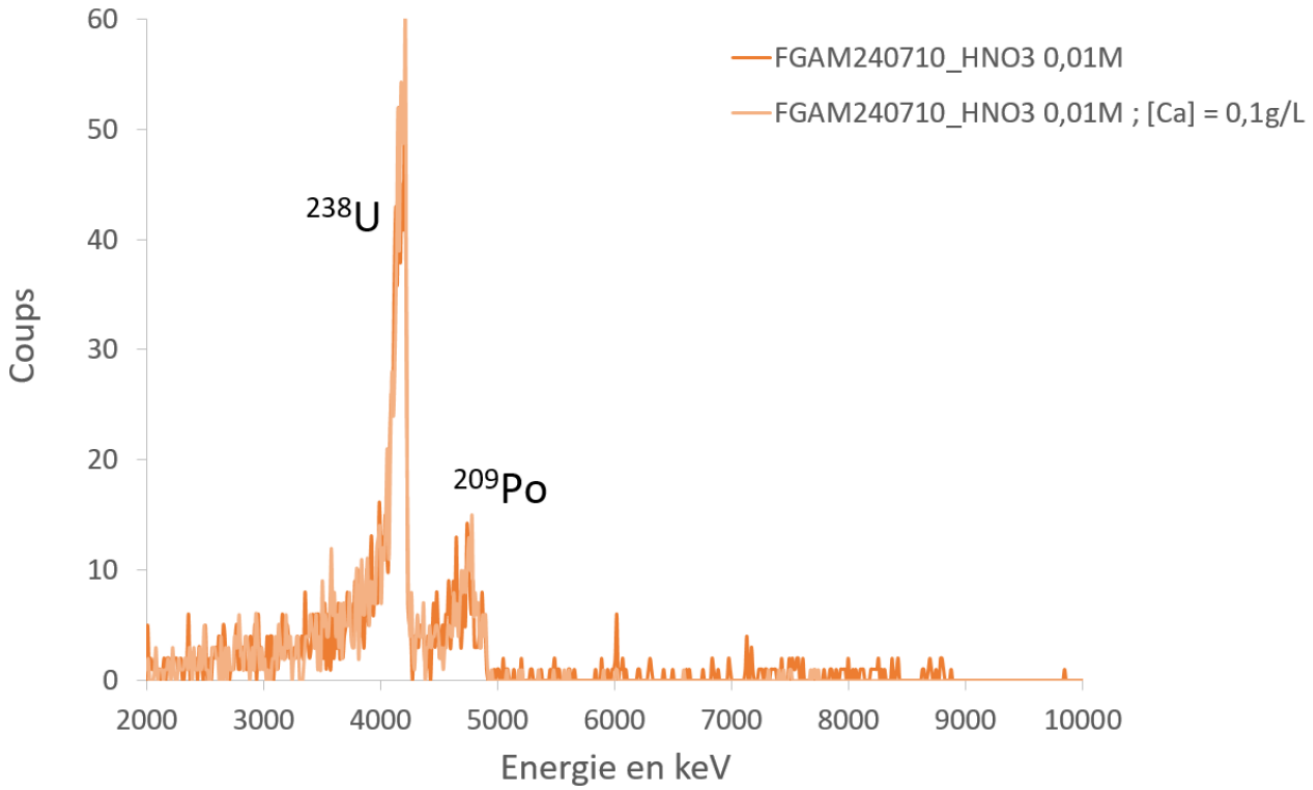
# TK-GA Disc – Am/Pu in spiked acidified water




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

# TK-GA Disc – U/Po in spiked acidified water

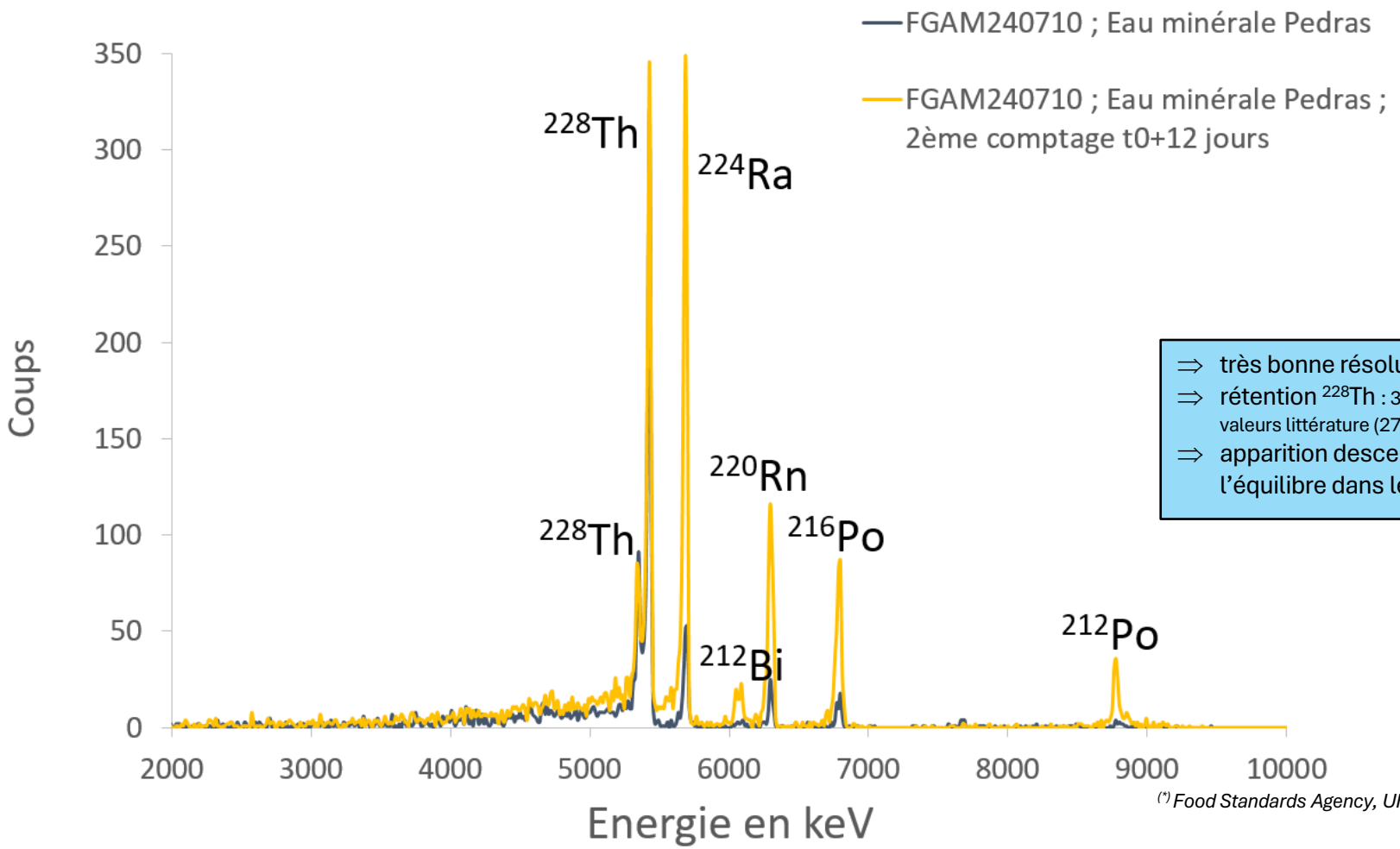
→ Solution synthétique simple dopée en $^{238}U$ et $^{209}Po$
(100mL $HNO_3$ 0,01M ; sans ou avec Ca à 0,1g/L ; 30mBq soit <u>0,3Bq/L</u>)



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 (*))

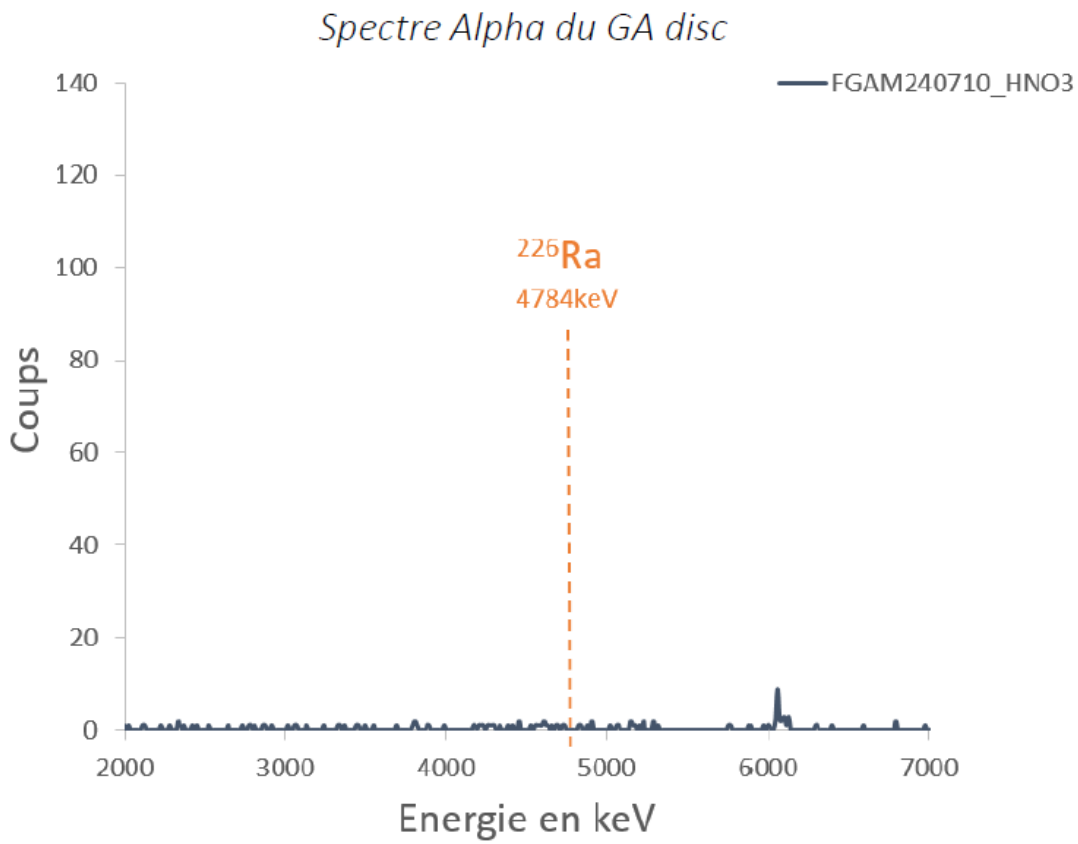
⇒ apparition descendants du $^{228}$Th puis mise à l'équilibre dans le temps

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

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

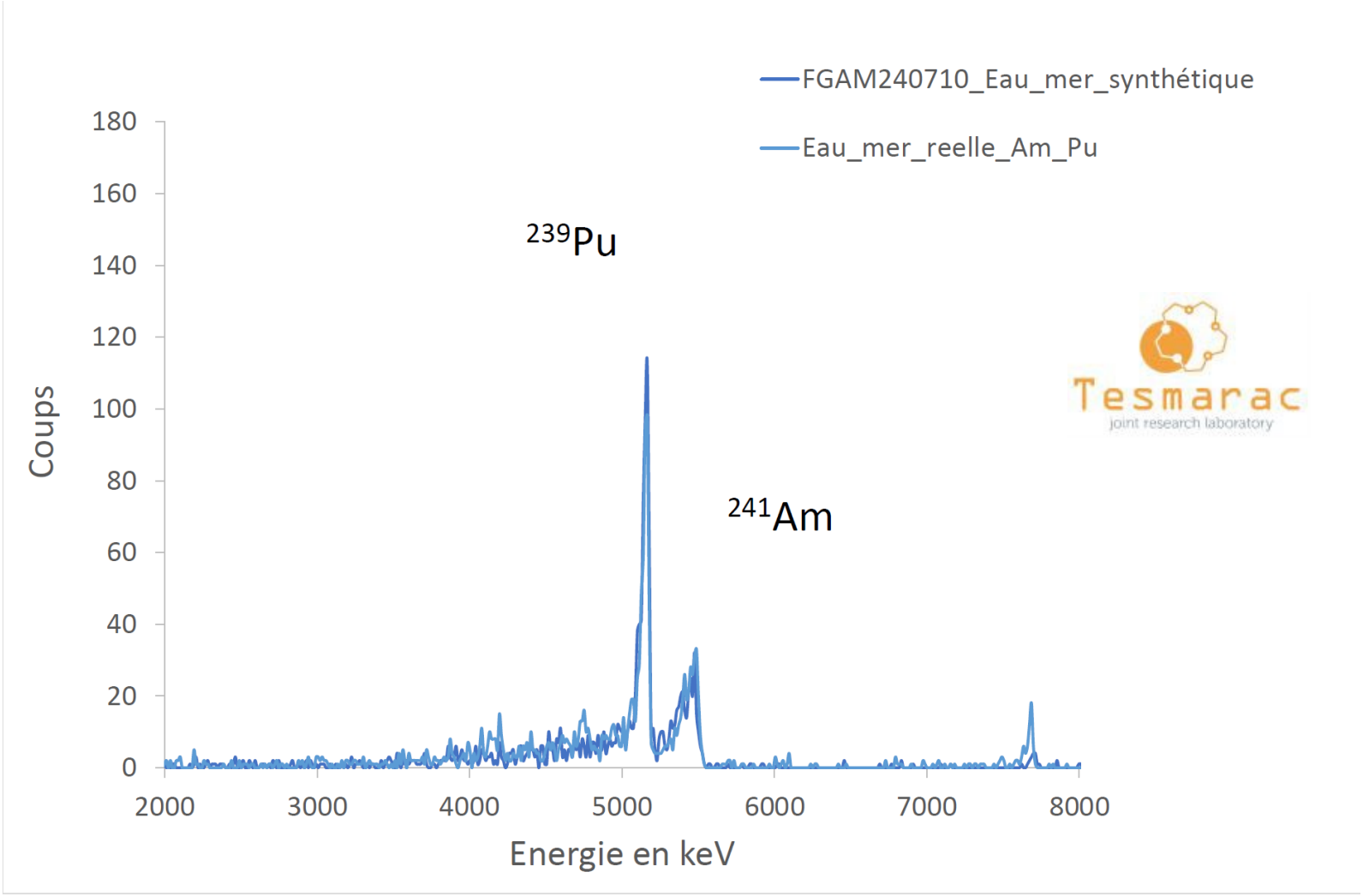
# TK-GA Disc – Ra in spiked acidified water

→ 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

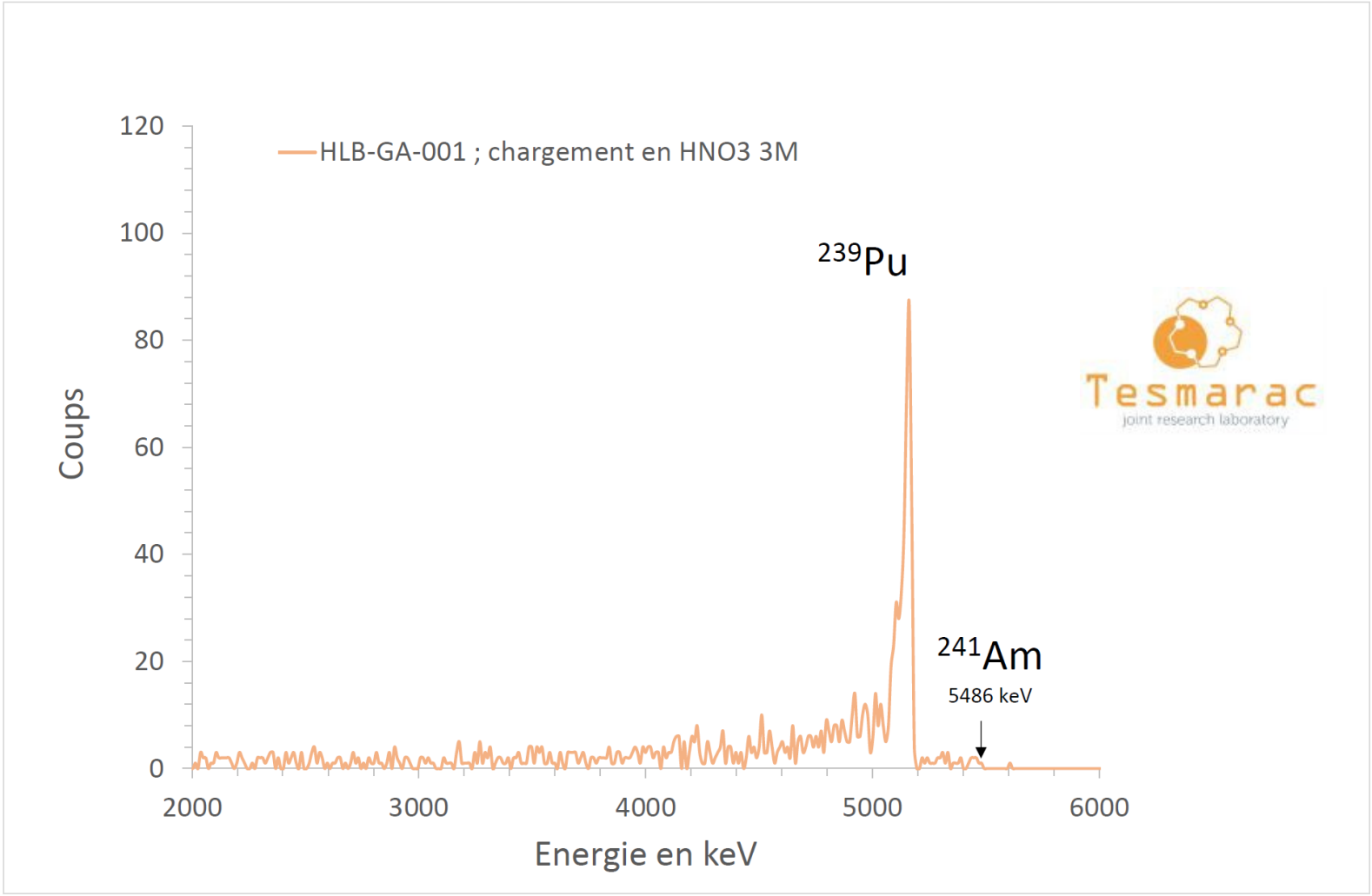
# TK-GA Disc – Am/Pu in sea water




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

Higher yields for Pu

# TK-GA Disc – Am/Pu in 3M $HNO_3$




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

High yields for Pu, no Am retention

# 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
- Behaviour of Ra
  - Retention at pH3-4 but no alpha spectrum
  - Migration into the disc?

TK221 and TK200 Discs in 3M $HNO_3$

- Stacking for AC screening? => rapid screening methods
- Will require 6M $NaNO_3$ rinse before drying for acid removal…
- => looks good cold, alpha spectra?

TK201 and TK101 Discs and methods optimisation

Sr via TK102 and/or TK227 Discs? LSC? GPC?

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

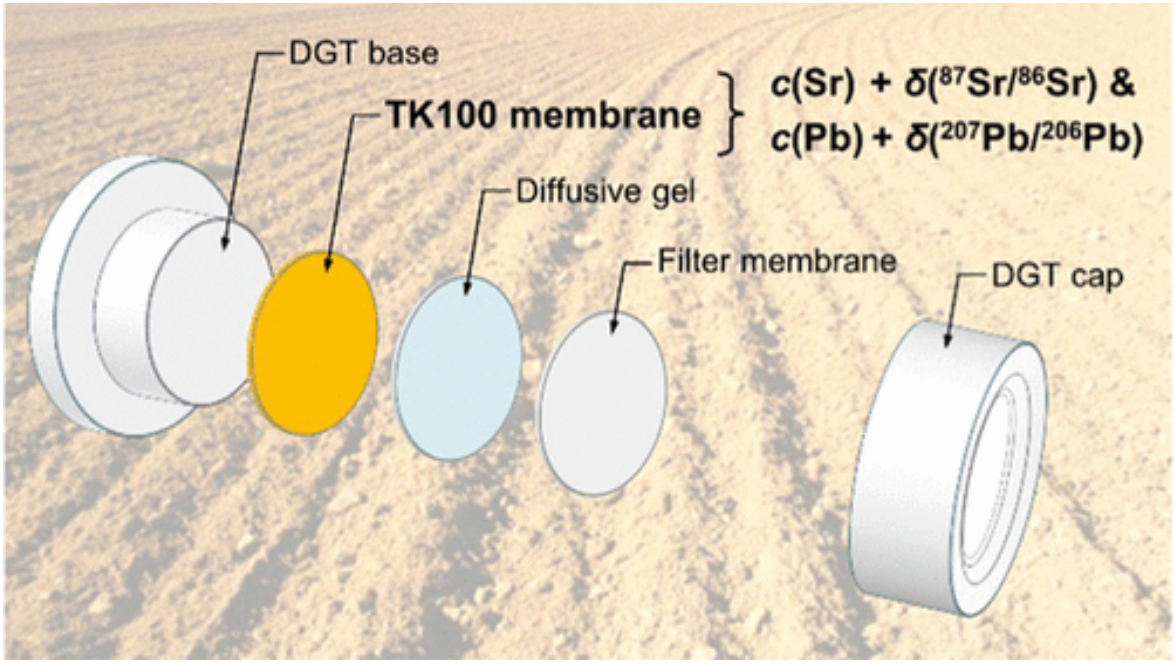
analytical chemistry

pubs.acs.org/ac Article

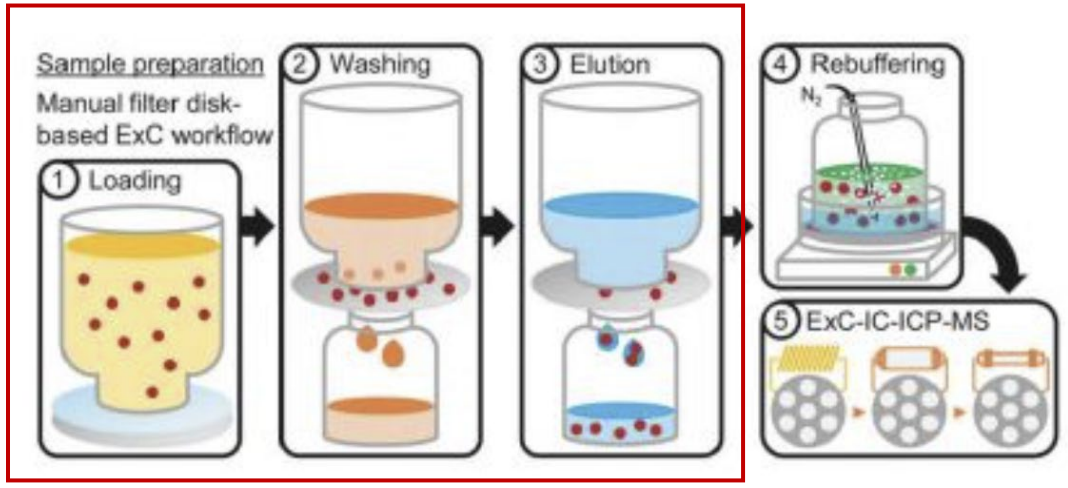
**Selective Diffusive Gradients in Thin Films (DGT) for the Simultaneous Assessment of Labile Sr and Pb Concentrations and Isotope Ratios in Soils**

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

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



# Tc Reconcentration




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 $NH_4NO3$ 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*

# 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 reuses

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

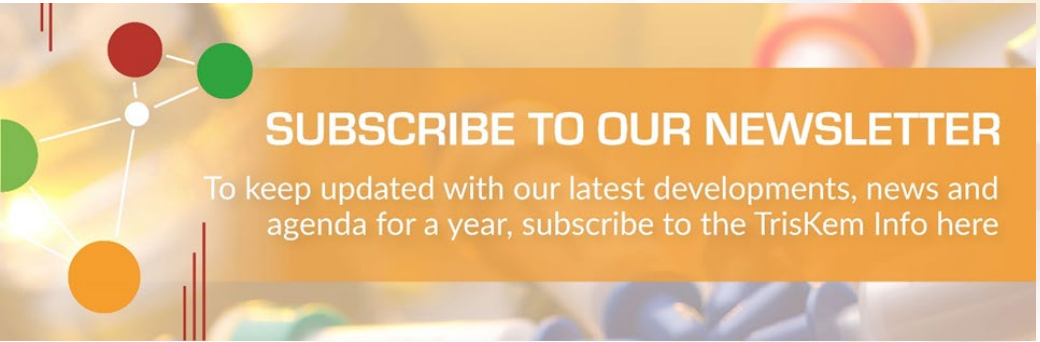
Increase of production capacity for these resins

# Some other on-going projects

- Rapid tests
  - Impregnated PSm resins
  - Range of 'Test sticks'
    - Suitable impregnated support
    - UM => rapide isotope ratio analysis by MS (metallomics): Cu, Ca, Zn,…
    - NPL
    - Uni Barcelona
- Passive sampling (DGT)
- Separation of DTM
  - SE Resin => Ines presentation
  - Zr-93, Fe, Mo, Nb,…
- Fate' of RN in the environment + bioassay
  - 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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