Application of extraction chromatographic resins in the separation of actinides

S. Happel – TrisKem International

SANDA – workshop on actinide target preparation and characterization – the need for radioanalytical chemistry

Geel, 06/12/2023

TRISKEM
Expertise in Separation Chemistry

TrisKem International

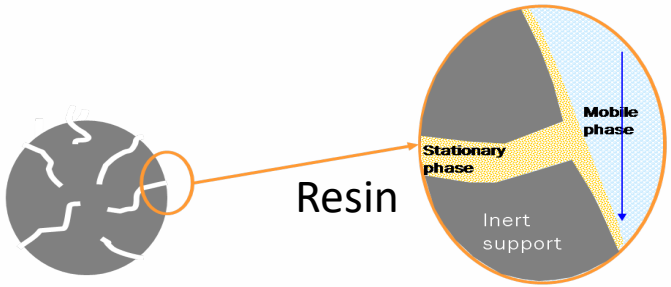
- Based in Rennes (France)
- Independent company since 02/07
  - Formerly part of Eichrom Europe
  - ISO 9001 since 2007
- Main product: extraction chromatographic resins
- Staff : 20
- R&D, QC and TechSupport group:
  - 4 RadChem PhD, 3 Technicians
- R&D: Development of new resins, techniques and applications
- Products used in several domains

Extraction chromatography

Organic extractant impregnated onto inert support

➢ « Supported Solvent Extraction » / « Solvent Impregnated Resins »

- Distribution between two non-miscible phases
- Stationary phase impregnated onto inert support
  - Choice of inert support depending on application
  - Radiolysis stability, plastic scintillators,…
- High density of functional groups
- Fast kinetics/small volumes => rapid separations
- High variety of selectivities:
  - Pure extractants, synergetic mixtures, solid extractants in diluents
  - **Aim: selectivity for analyte(s), no selectivity for matrix/ impurities**
- Combining several cartridges can improve/facilitate separation
- Bleeding might need to be addressed (e.g. Am on TRU)



Extraction chromatography

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Types of Extractants

Acidic e.g. DIPEX (AC Resin)

$$M^{3+} + 3HY \rightleftarrows MY_3 + 3H^+$$

$$M^{3+} + 3(HY)_2 \rightleftarrows M(HY_2)_3 + 3H^+$$

Neutral e.g. CMPO/TBP (TRU Resin), DPPP (UTEVA Resin), TK221, 'TK200'

$$M^{3+} + nE + 3X^- \rightleftarrows ME_n \bullet X_3$$

Basic e.g. Aliquat 336 (TEVA Resin)

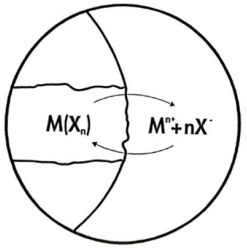
$$R_3N + HX \rightleftarrows R_3NH^+X^-$$

$$R_3NH^+X^- + MX_3 \rightleftarrows R_3NH^+MX_4^-$$

$$X^- = NO_3^-, Cl^-$$

Horwitz et al.

Metal Anion Complex Formation

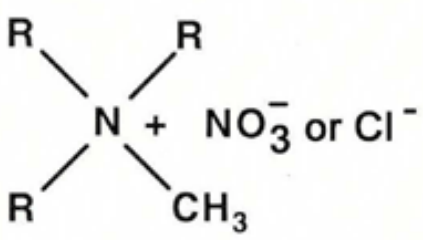


Metal + Anion ⇌ Complex

Complex + Organic ⇌ Extracted

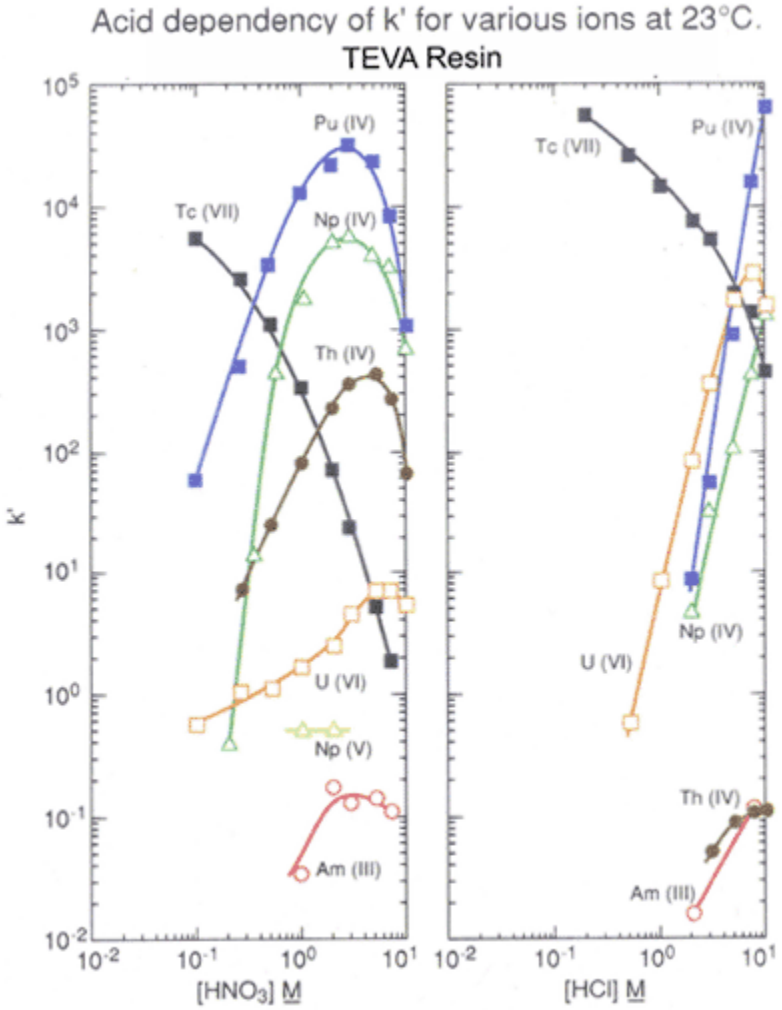
The classics - TEVA Resin

Trialkyl, methylammonium nitrate (or chloride)



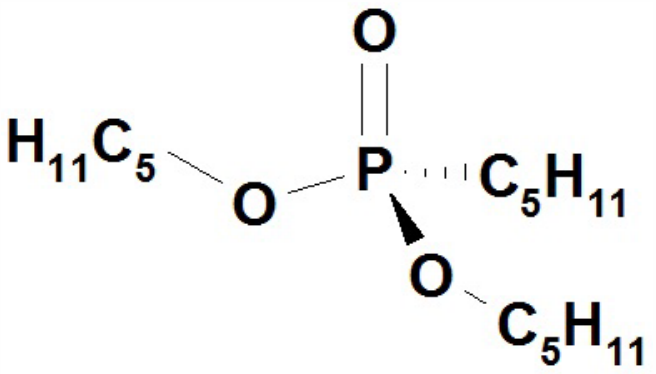
R = C_8H_{17} and $C_{10}H_{21}$

- **Extractant**: Aliquat 336®
- TEVA: **TE**tra**V**alent **A**ctinides
- Pu(IV), Th(IV), Np(IV), Tc(VII),…
- Np/Pu separation
- In HNO_3 no selectivity for U, Am,…
- No selectivity for Fe in HNO_3



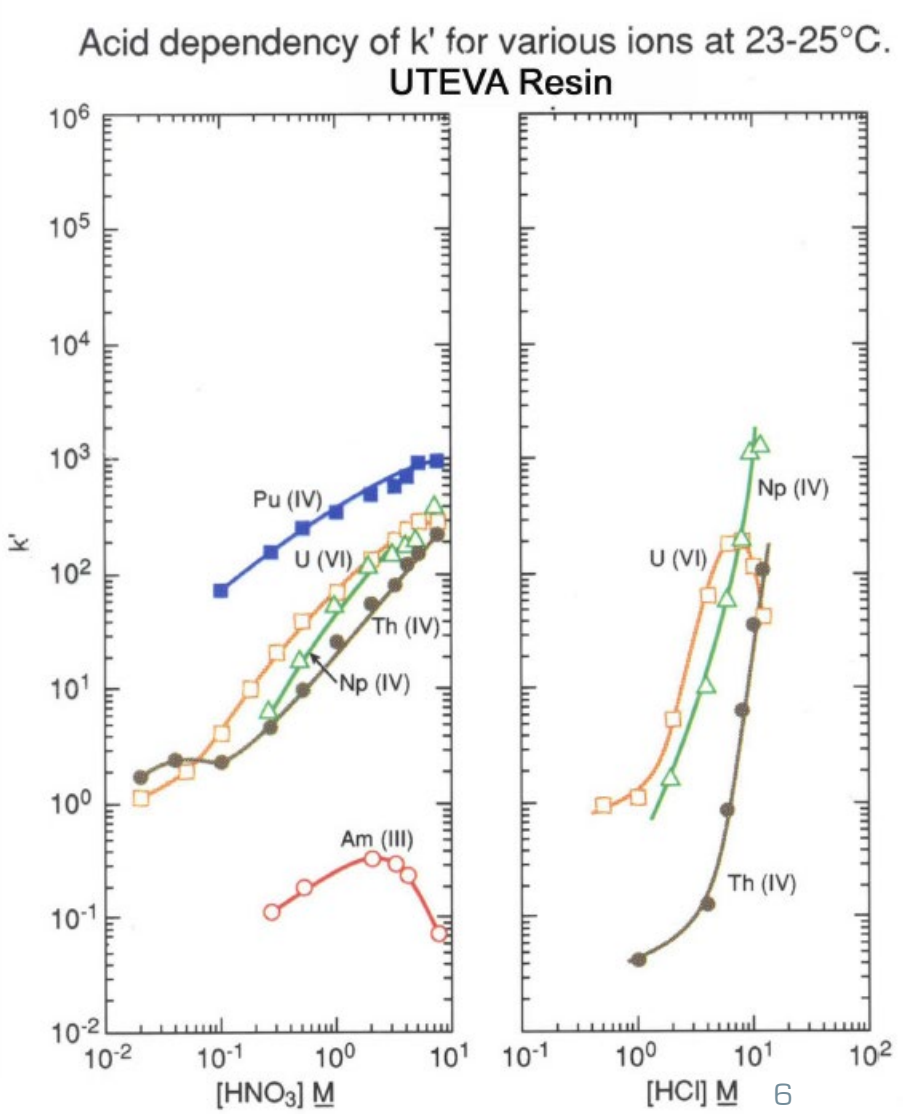
Horwitz, et al. (HP195)

The classics - UTEVA Resin

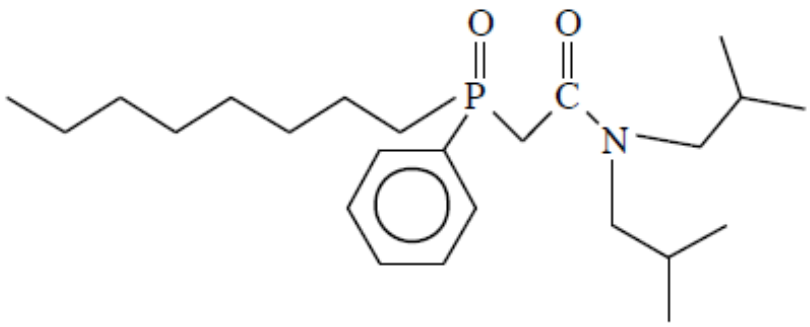


Di-Pentyl-Pentyl-Phosphonate (DPPP)

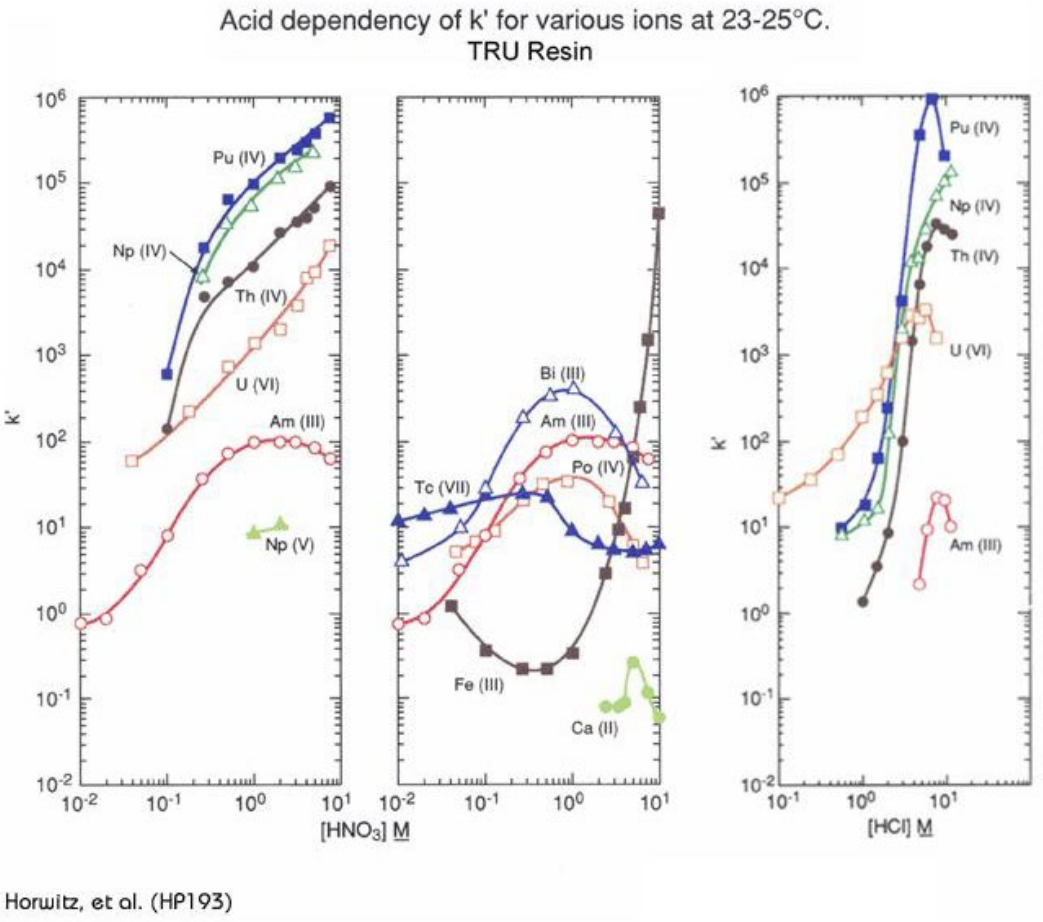
- **Extractant**: DPPP (in literature also called DAAP)
- For **U**ranium and **TE**tra**V**alent **A**ctinides
- Good selectivity but U and Th retention not very high
- No interference by Fe



The classics - TRU Resin



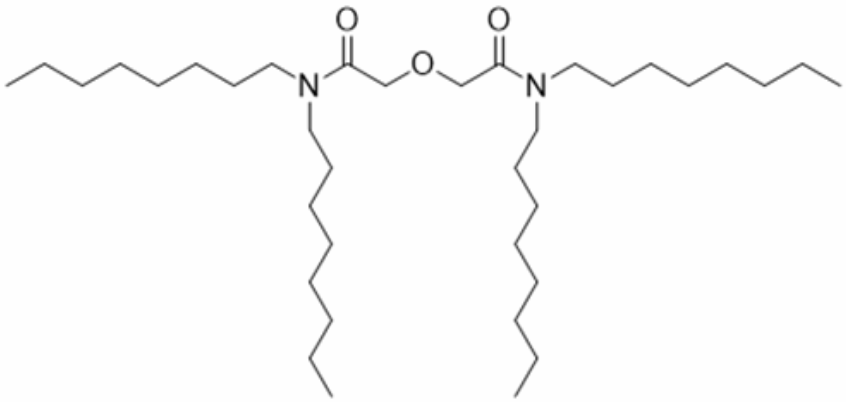
octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide



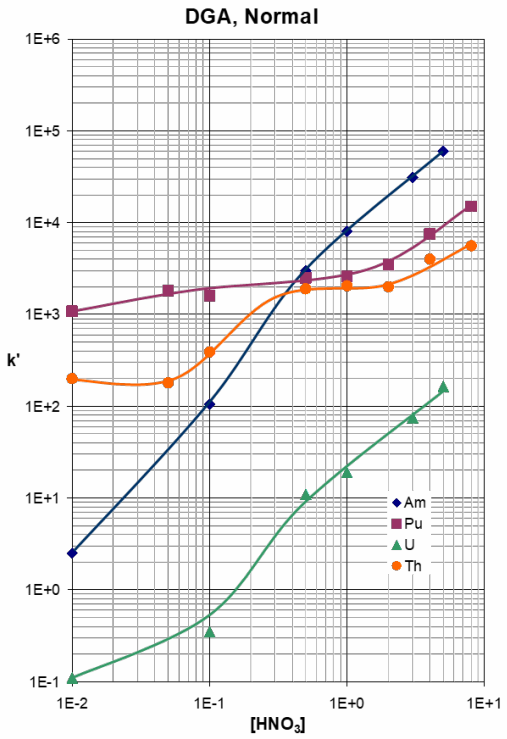
Horwitz, et al. (HP193)

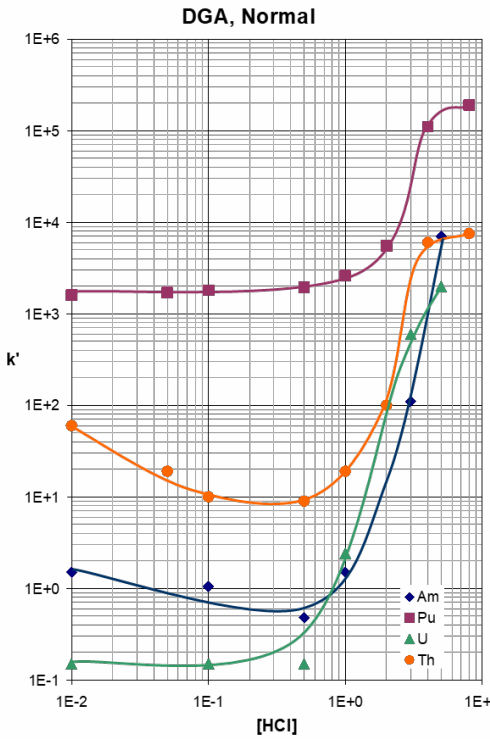
- **Extractant**: CMPO in TBP
- **TR**ans**U**ranium elements
- Am/Cm, U, Pu,…
- Am retention interfered by Fe(III)

The classics - DGA Resin



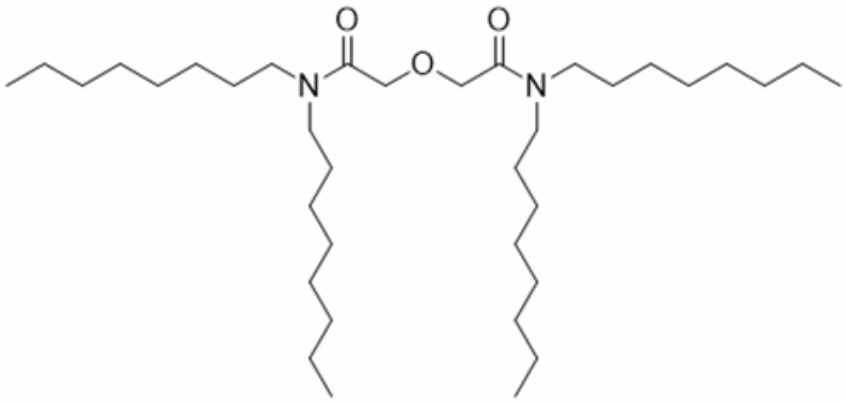
N,N,N',N'-tetra-n-octyl-diglycolamide



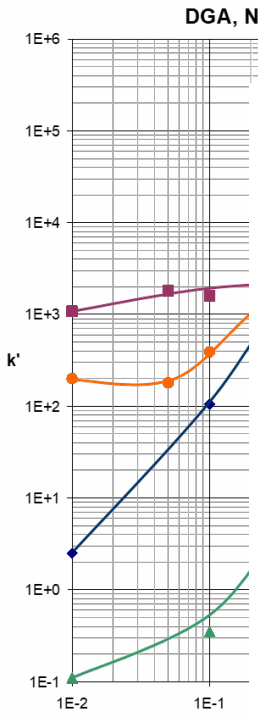


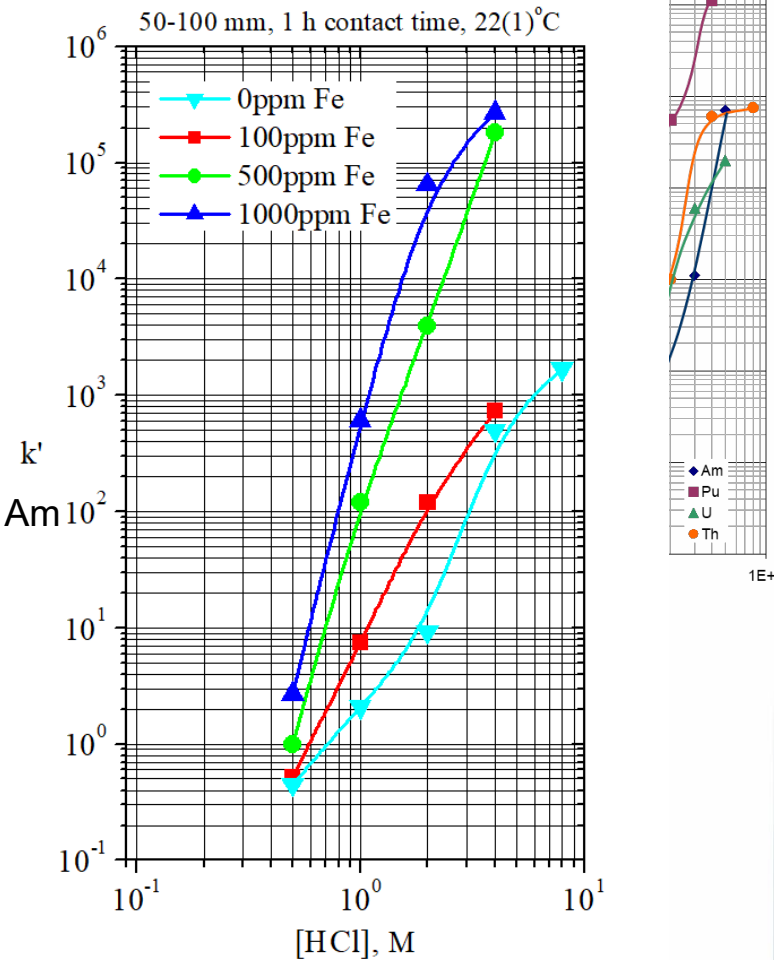
- Extractant:
  - **DGA, Normal** (N,N,N',N'-tetra-n-octyldiglycolamide) = DN
  - Generally used in analytical applications
  - DGA, Branched (N,N,N',N'-tetrakis-2-ethylhexyldiglycolamide) = DB
- Actinides, especially Am
- Robust against Fe interference, often used for soil samples

The classics - DGA Resin



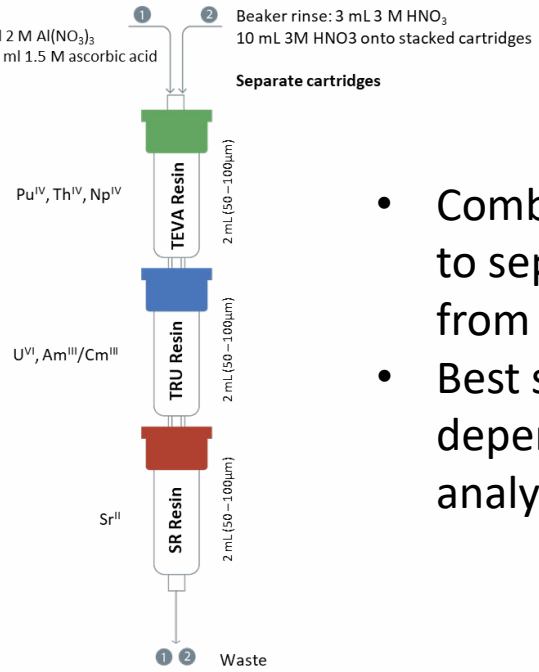
N,N,N',N'-tetra-n-octyl-diglycolamide



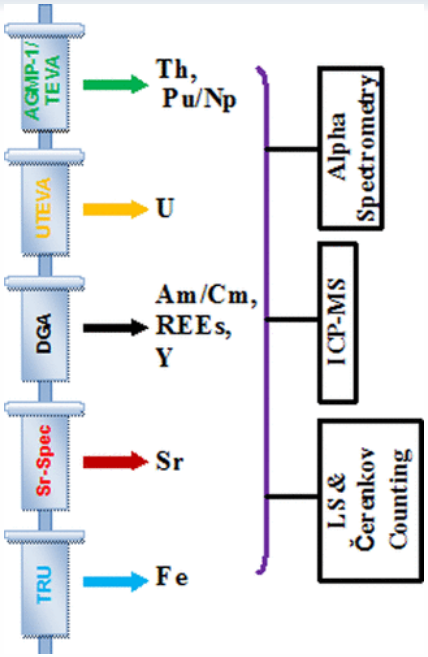


- Extractant:
  - **DGA, Normal** (N,N,N',N'-tetra-n-octyldiglycolar
  - Generally used in analytical applications
  - DGA, Branched (N,N,N',N'-tetrakis-2-ethylhexyl
- Actinides, especially Am
- Robust against Fe interference, often used

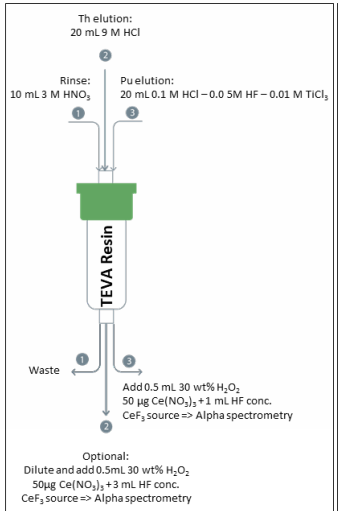
Stacked cartridges

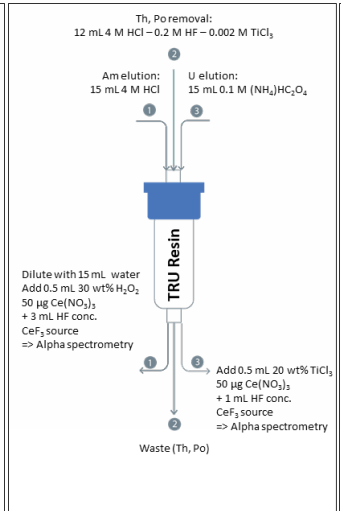


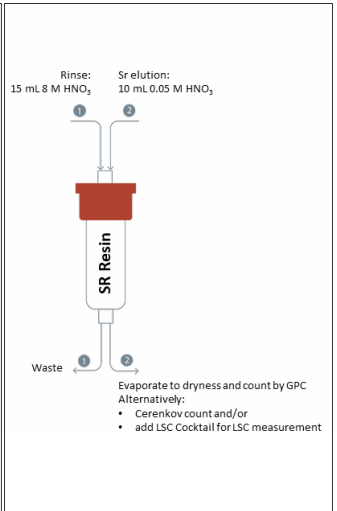
- Combination of several resins to separate several analytes from one sample
- Best suitable combination depends on matrix (Fe,…) analytes (Am, Np/Pu)

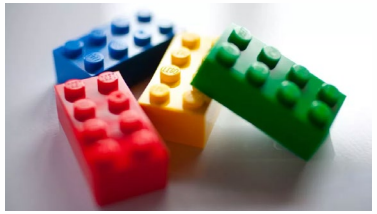


•Xiongxin Dai, Sheila Kramer-Tremblay, Anal. Chem. 2014, 86, 11, 5441–5447, Publication Date:May 6, 2014, https://doi.org/10.1021/ac500572g







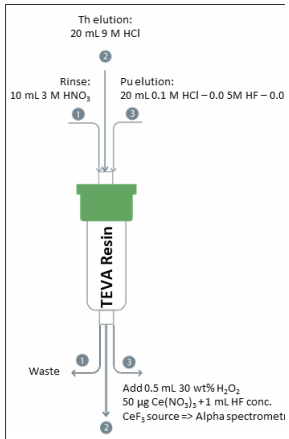


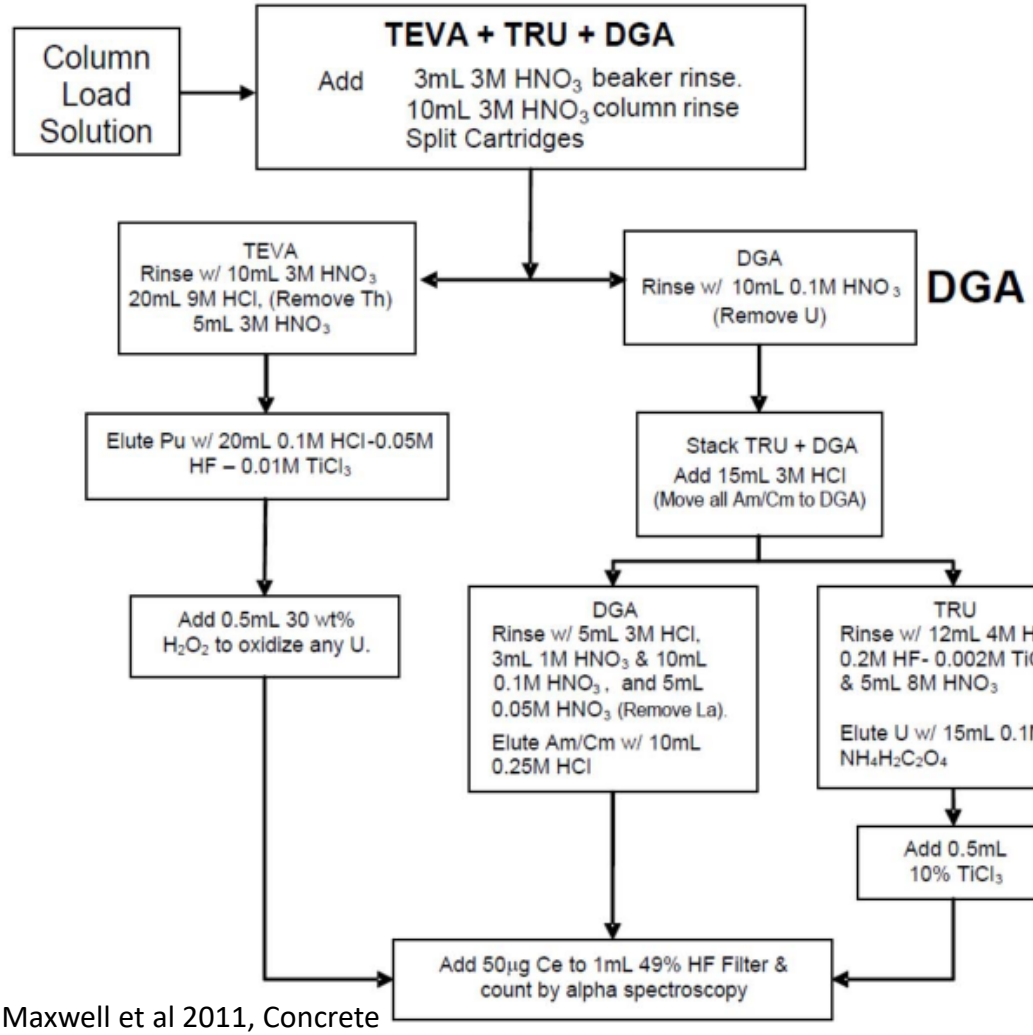
Taken from: Rösch, Frank. Volume 1+2 [Set Rösch: Nuclear- And Radiochemistry, Vol 1+2, De Gruyter, 2023. Referring to Maxwell et al. 2017

Stacked cartridges

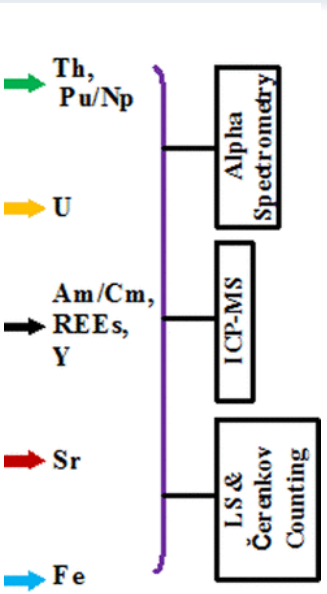
Acid digestion
1) Redissolve in 6 ml 6 M HNO_3 and 6 ml 2 M $Al(NO_3)_3$
2) Add 0.5 ml 1.5 M sulfamic acid + 1.25 ml 1.5 M ascorbic acid
3) Add 1.25 ml 3.5 M sodium nitrate

1 2 Beaker rinse: 3 mL 3 M HNO_3
10 mL 3M HNO3 onto stacked cartridges





Maxwell et al 2011, Concrete and brick samples



-Tremblay, Anal. Chem. 2014, 86, 11,
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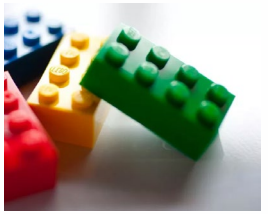
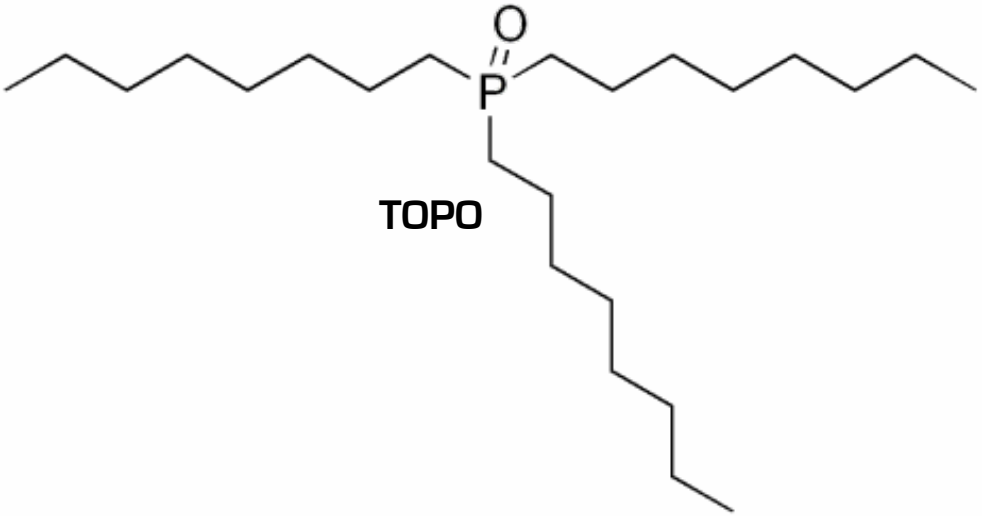


et al. 2017

‘New’ resins - TK200 Resin



- Based on TOPO extractant
- High retention of actinides
  - U, Th higher than on UTEVA
  - In HNO_3 some retention of trivalents
- Extracts actinides even at pH 1 - 2 (nitric acid)
  - Preconcentration and purification of selected actinides on same column
  - ‘In the field’?

Actinides on TK200 – HNO_3
(all data N. Vajda et al)

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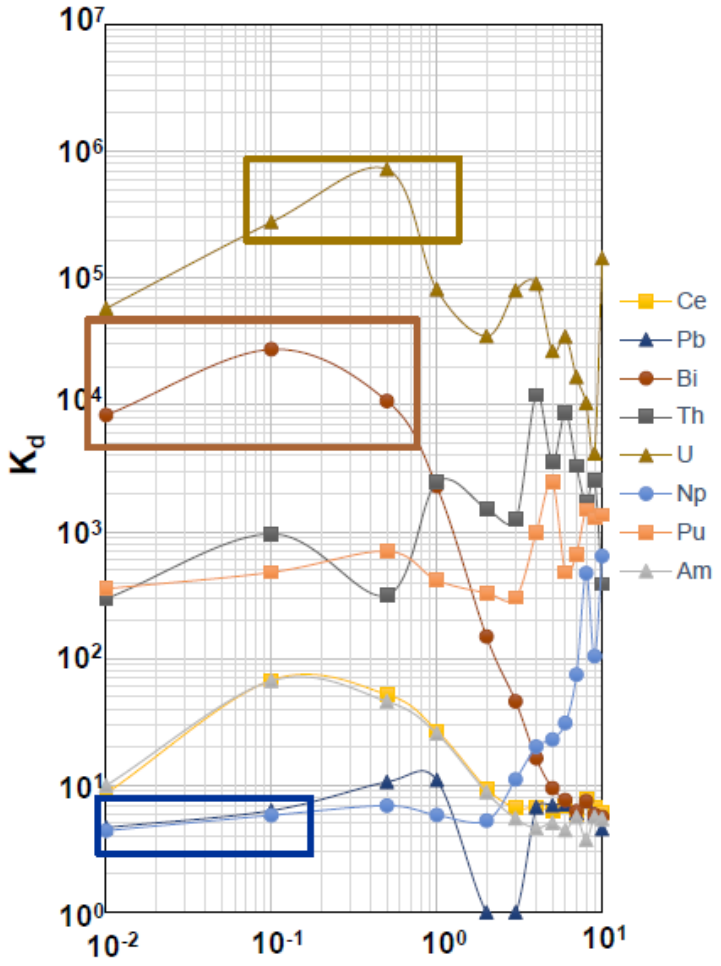
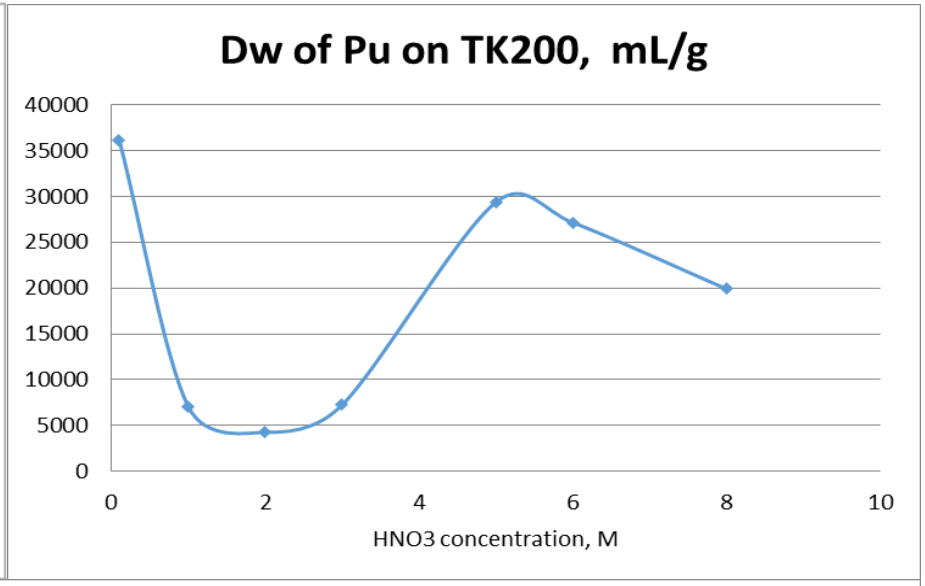
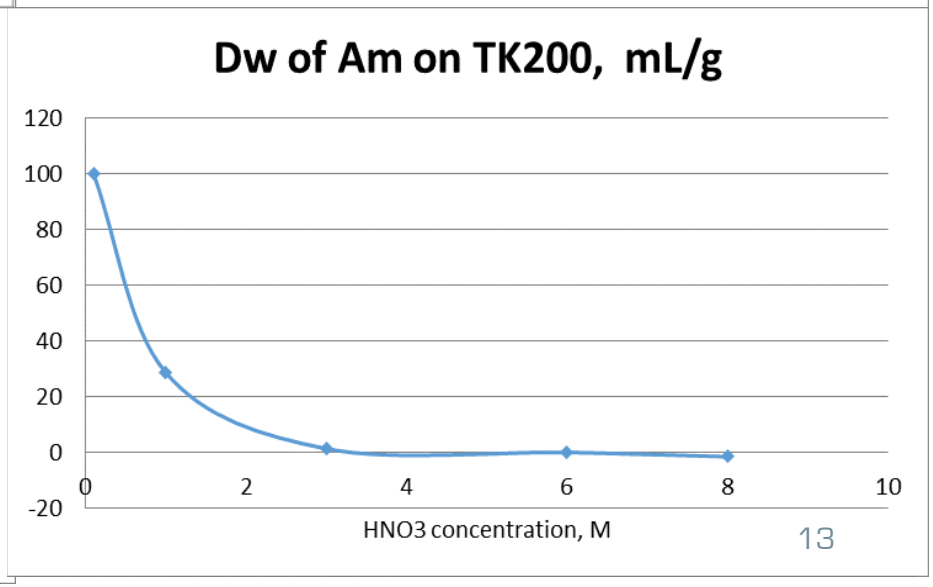
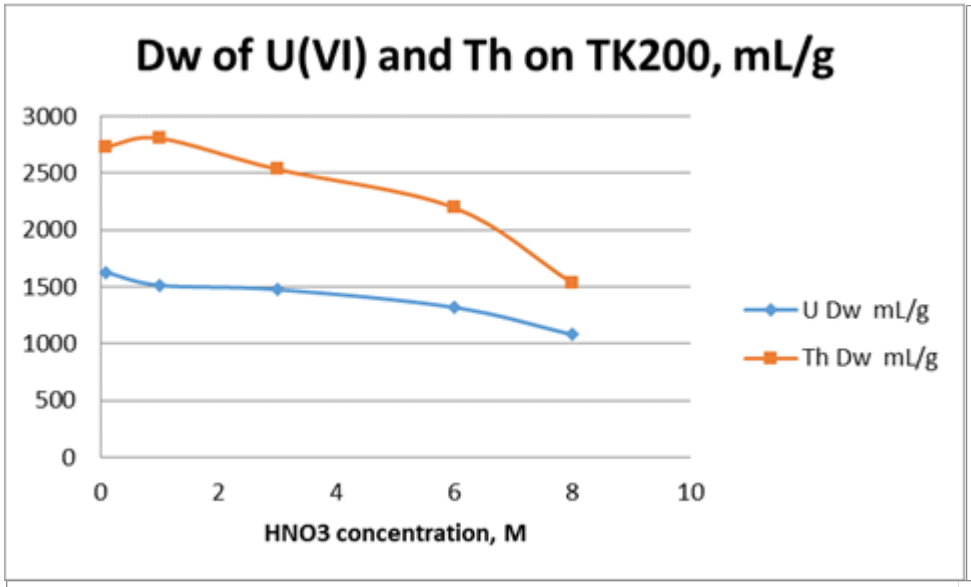
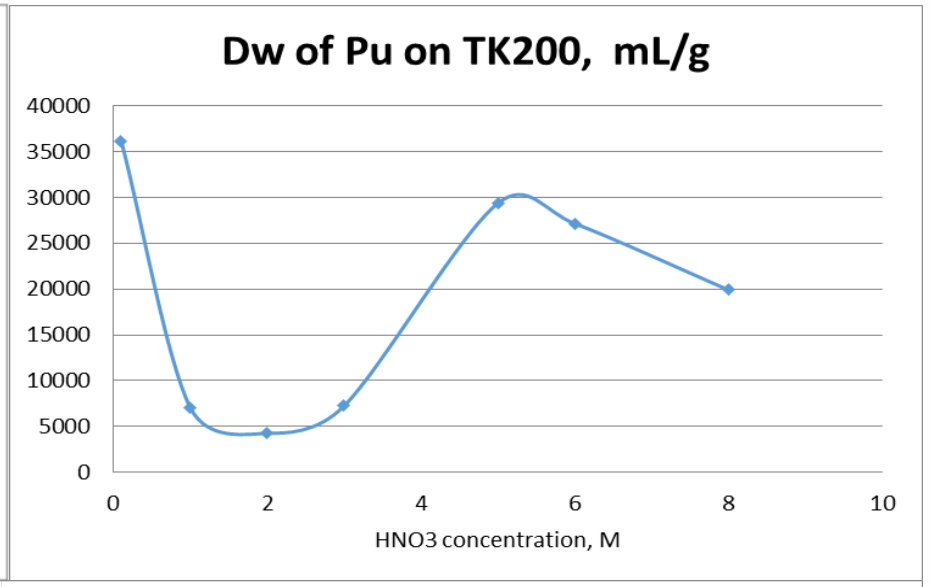


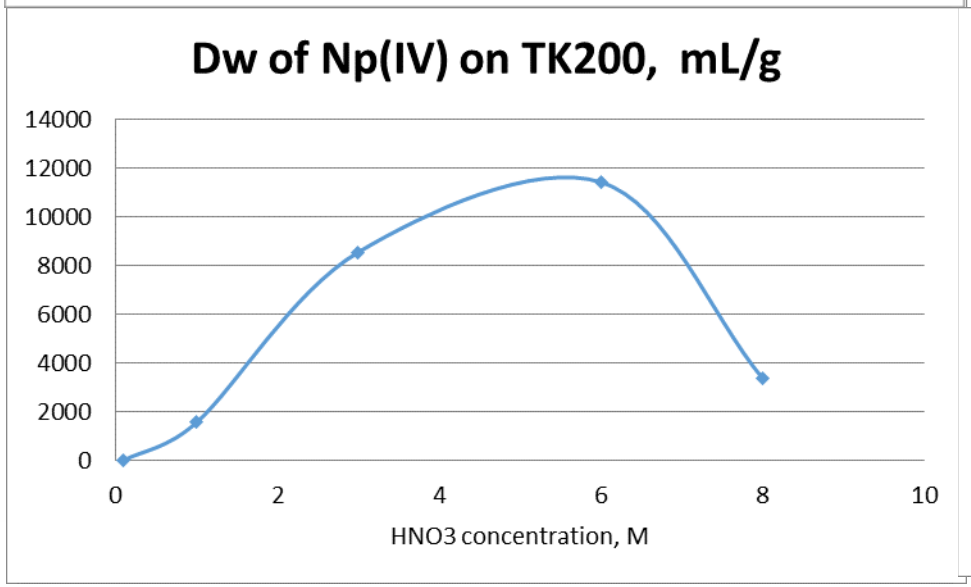


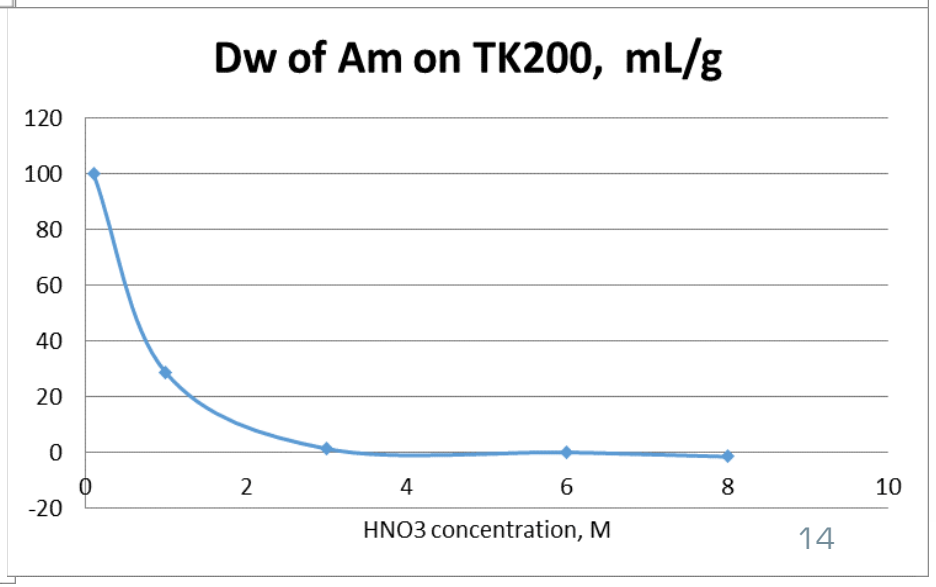


Actinides on TK200 – HNO_3
(all data N. Vajda et al)









Actinides on TK200 – HCl
(all data N. Vajda et al)

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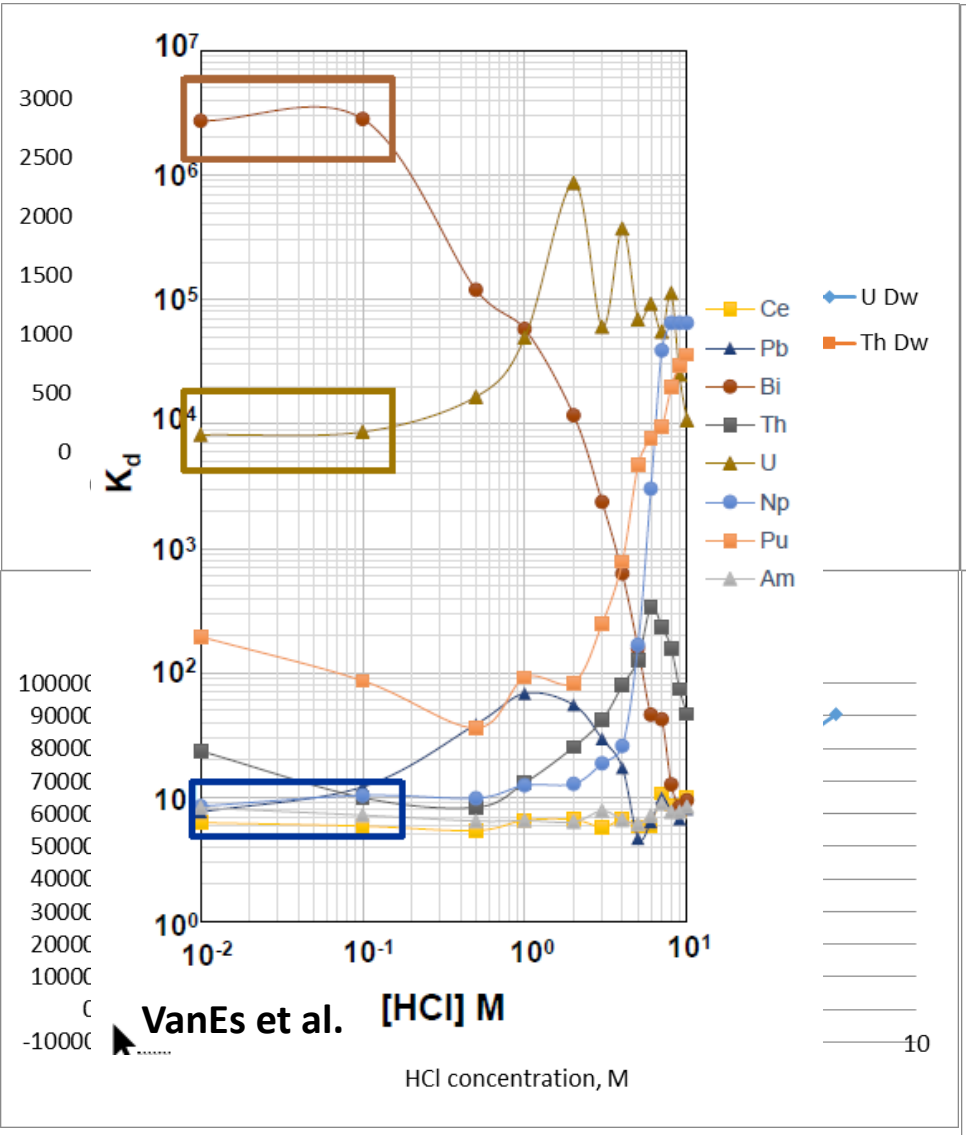

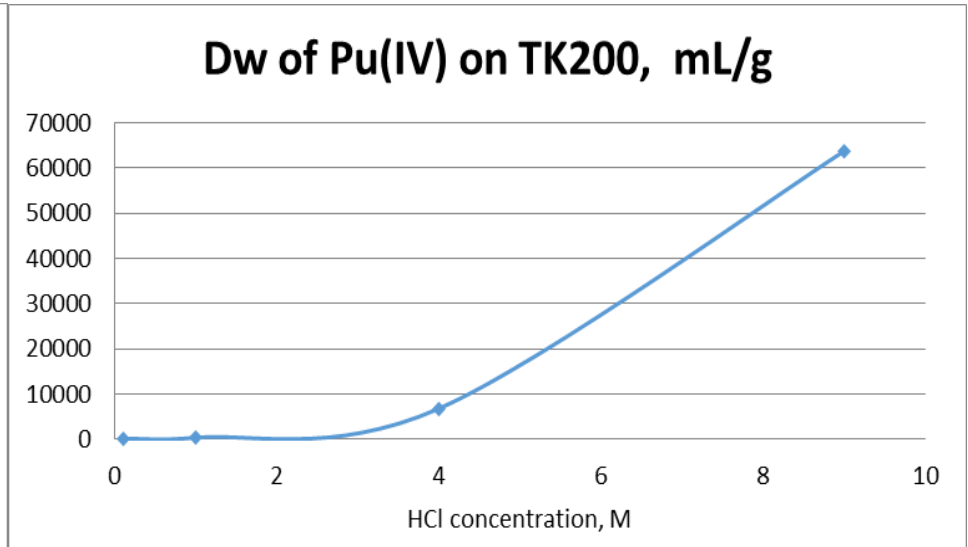

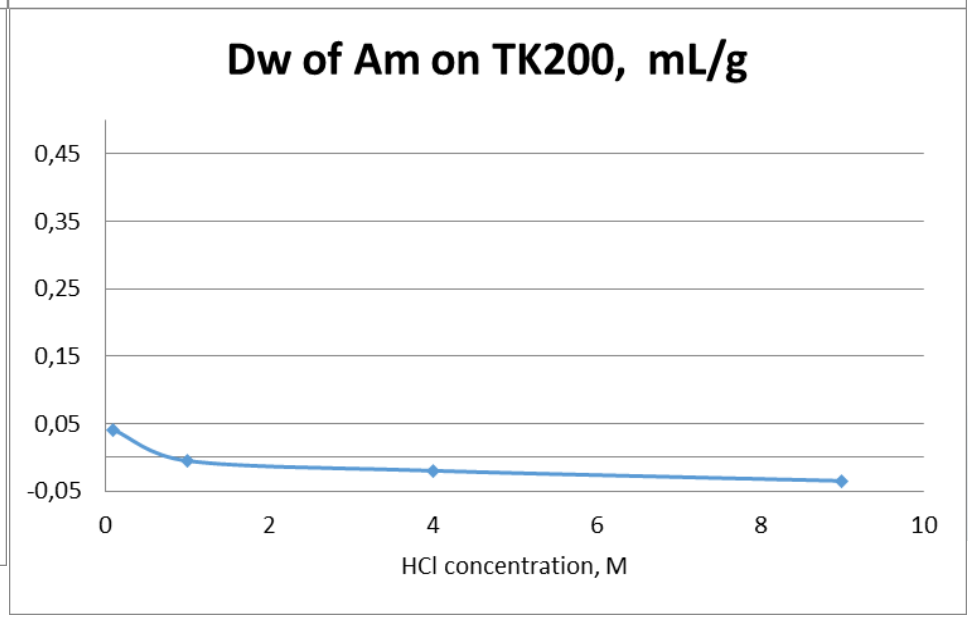

Actinides on TK200 – HCl
(all data N. Vajda et al)

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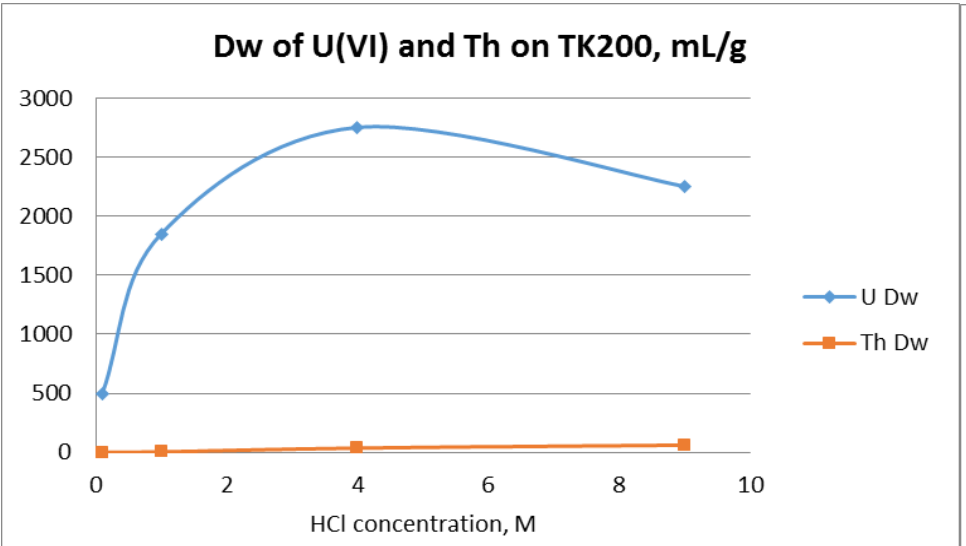
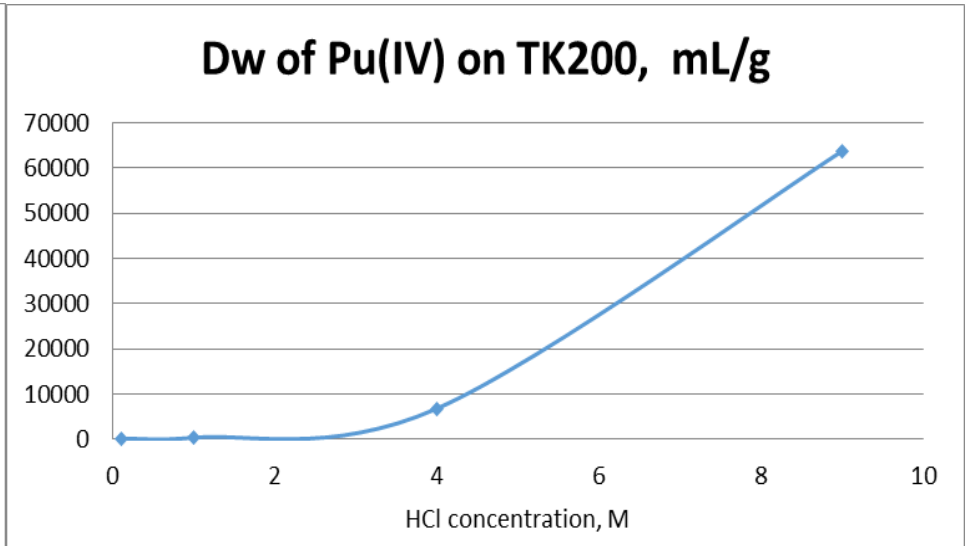
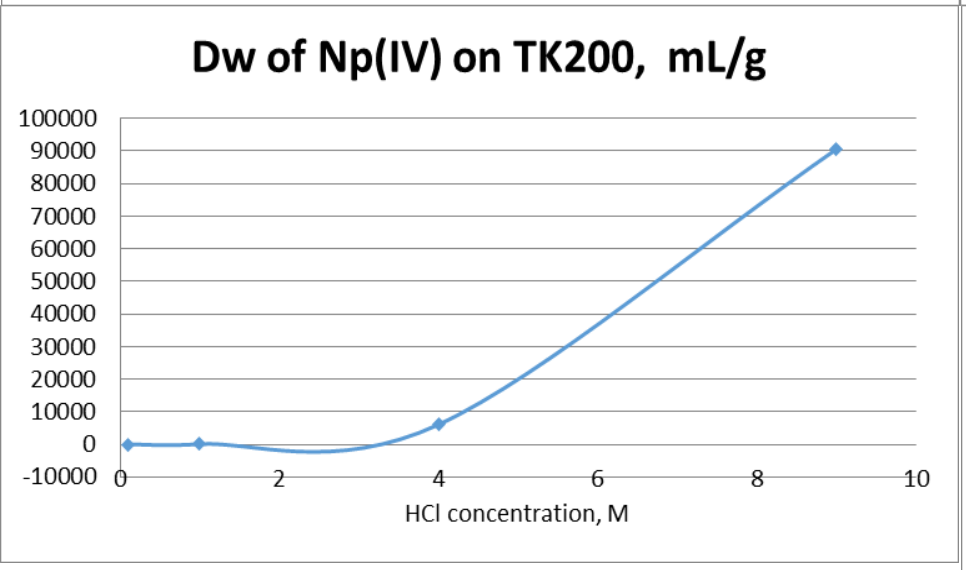
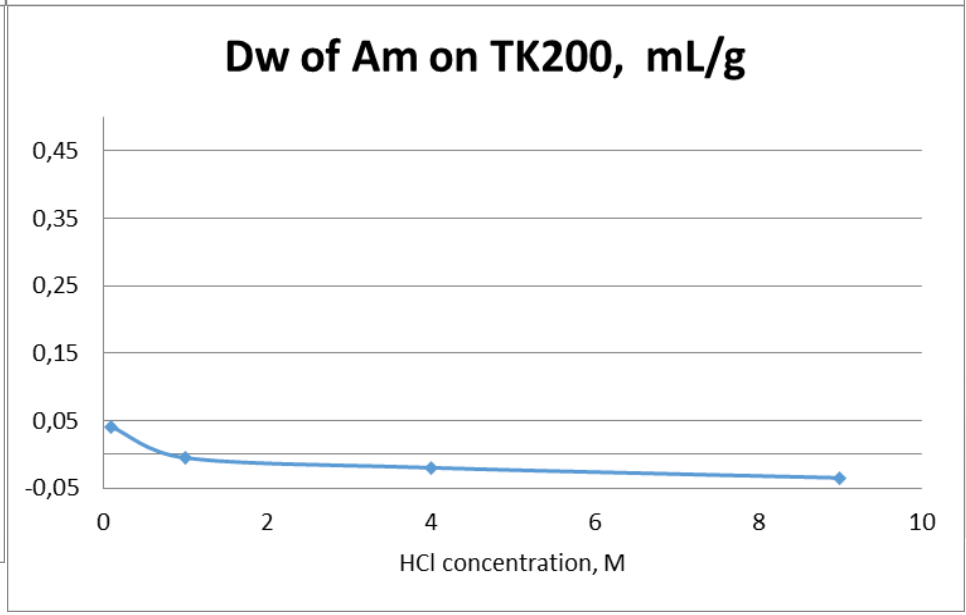
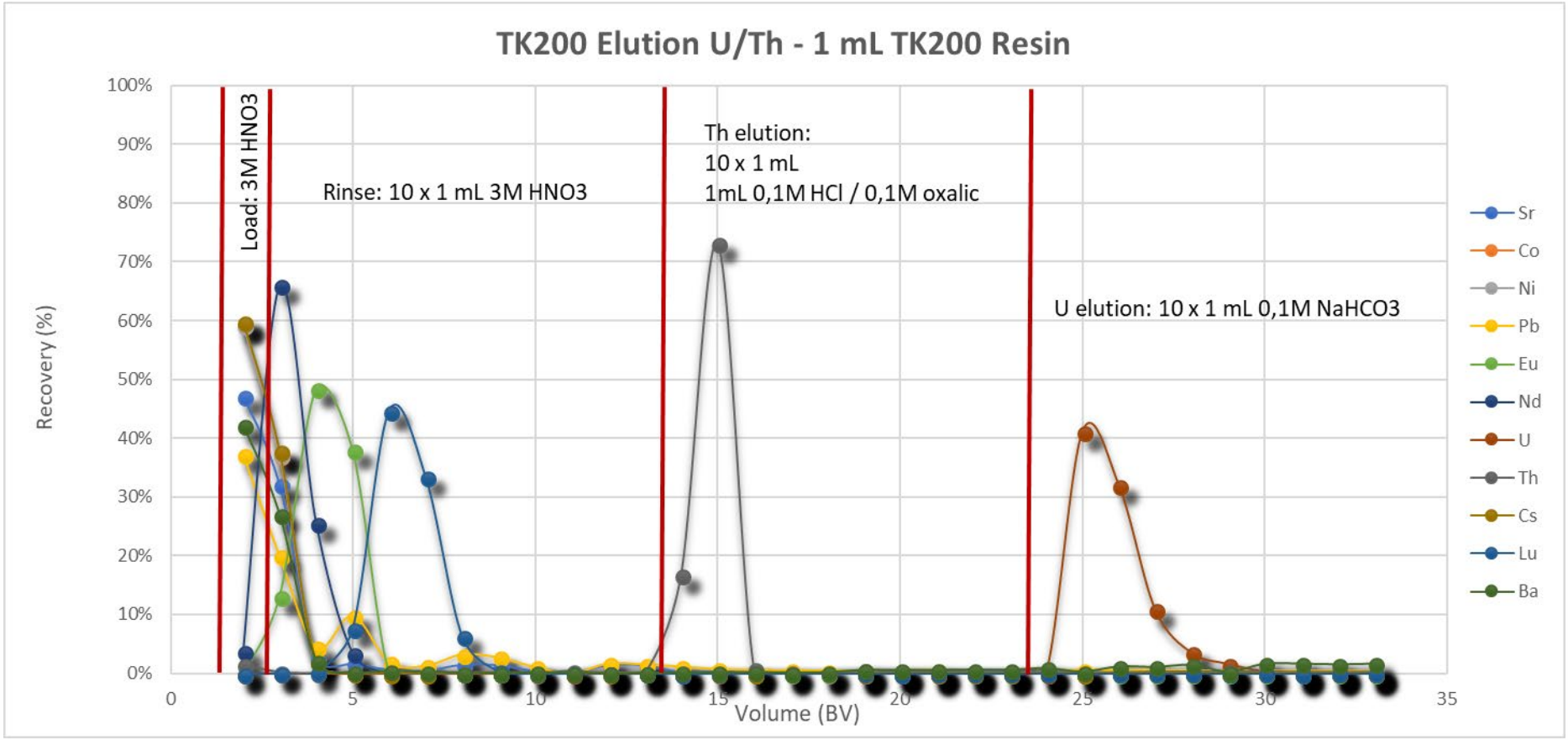






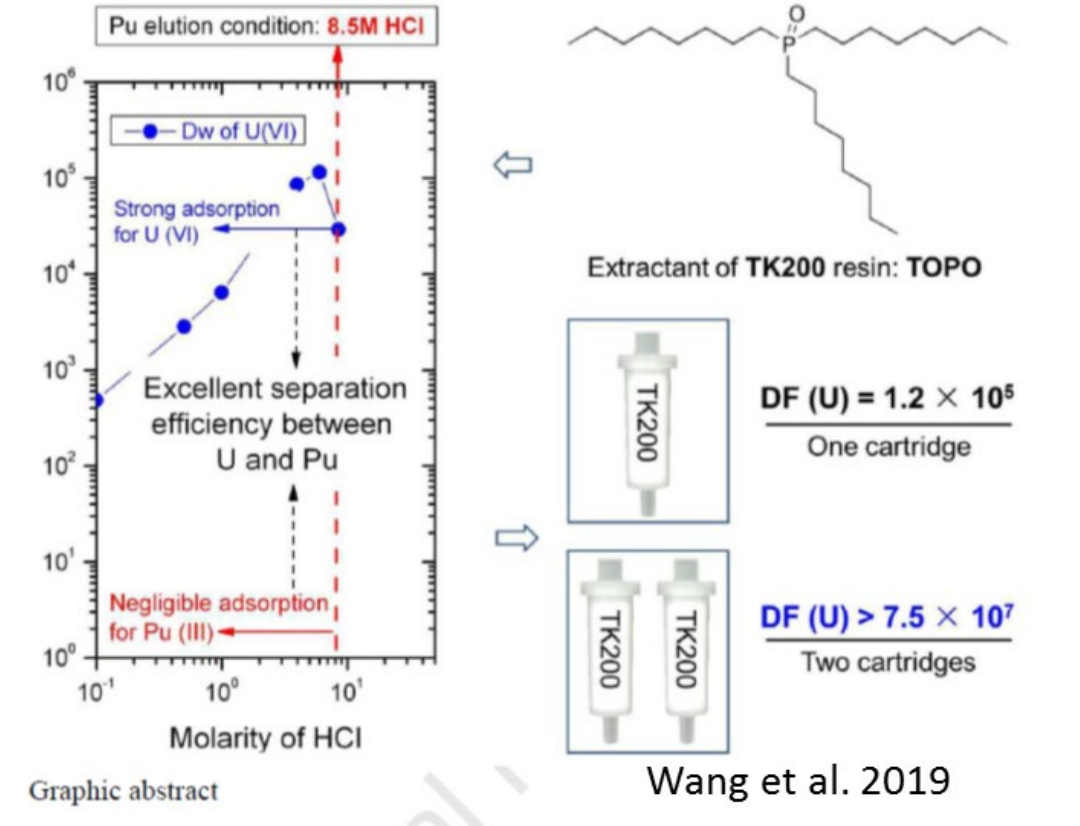


U/Th separation on TK200



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

TK200 Resin - U/Pu separation - I



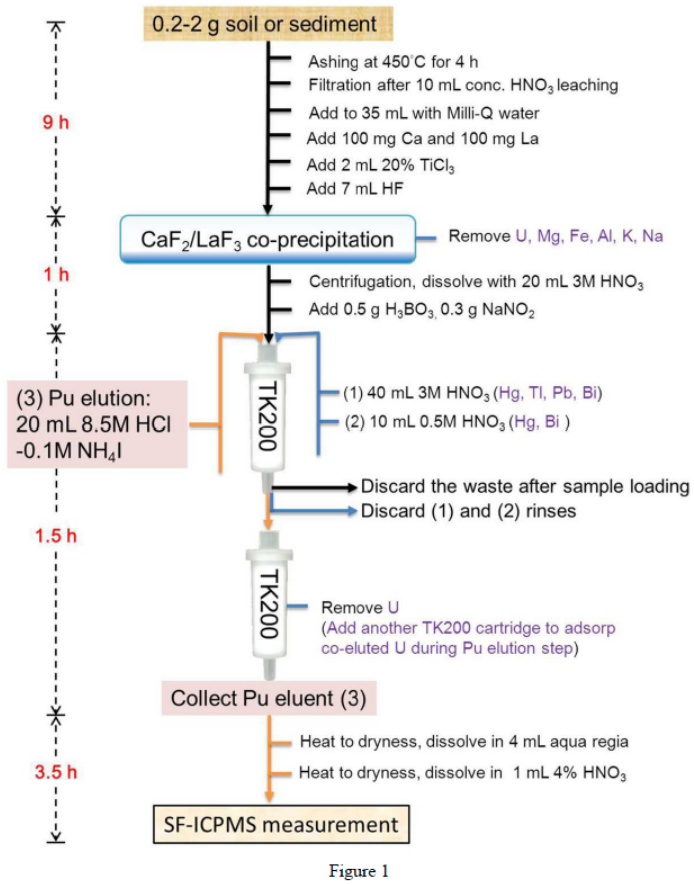


Figure 1

- Confirms very high U retention
- Pu isotope ratios by ICP-MS
- U removal via 2 x TK200 => Df >10^7
- Pu elution as Pu(III) in 8,5M HCl/0,1M NH_4I
  => U remains fixed on resin in these conditions

Zhongtang Wang, Zhaoya Huang, Yun Xie, et aL. Method for determination of Pu isotopes in soil and sediment samples by inductively coupled plasma mass spectrometry after simple chemical separation using TK200 resin, Analytica Chimica Acta, 1090, 2019, 151-158, www.sciencedirect.com/science/article/pii/S000326701931030X

TK200 Resin - U/Pu separation - II

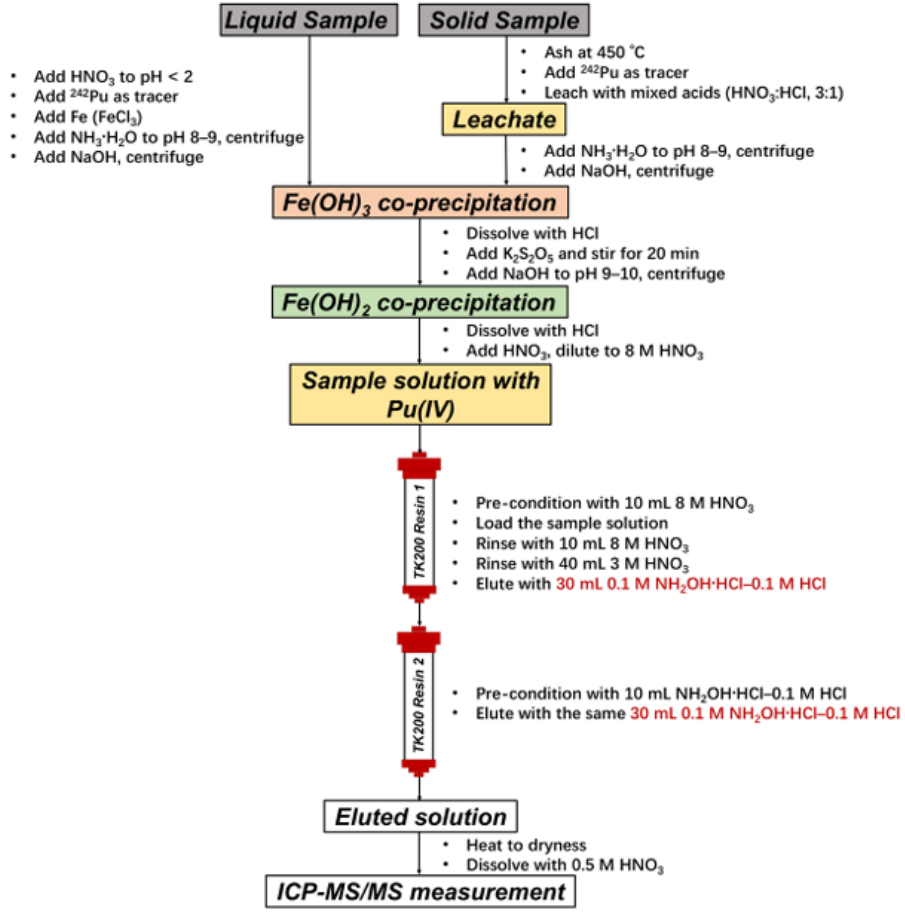
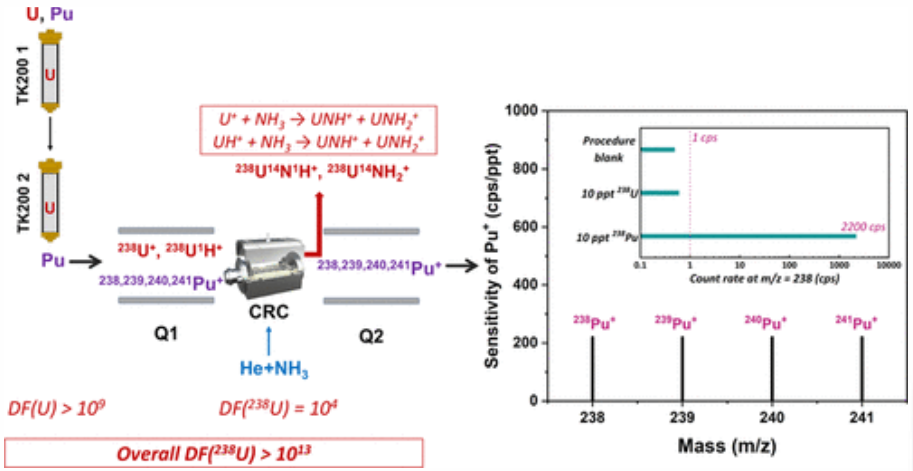


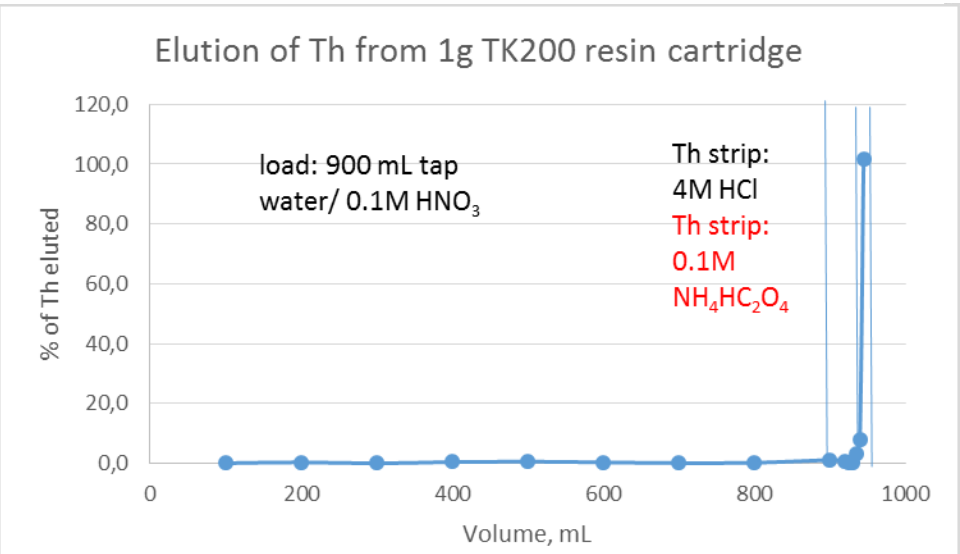
Figure S1. Analytical procedure for determination of plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu)

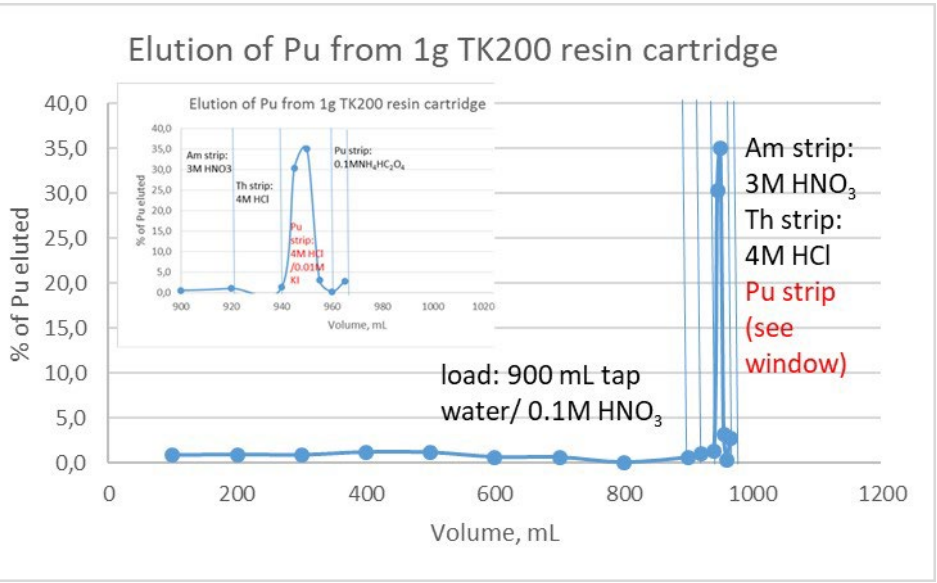
- Recent publication by Huang et al.
- Better U removal: $D_f(U) > 10^9$
- Additional U removal via He+NH_3
- Overall $D_f(U) > 10^{13}$
- Pu isotopes incl. Pu-238 via ICP-MS/MS

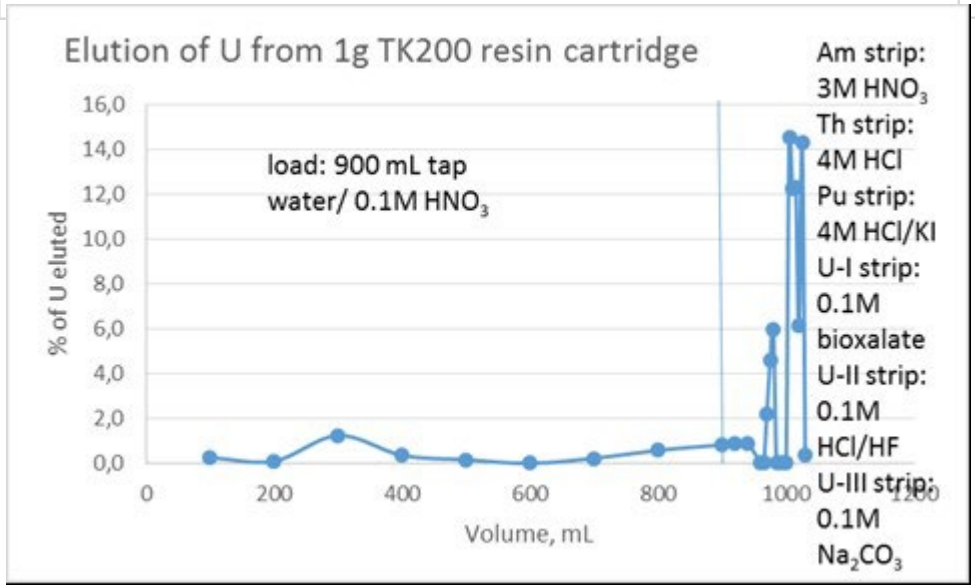


Zhao Huang, Xiaolin Hou, Xue Zhao, Rapid and Simultaneous Determination of 238Pu, 239Pu, 240Pu, and 241Pu in Samples with High-Level Uranium Using ICP-MS/MS and Extraction Chromatography, Anal. Chem. 2023, 95, 34, 12931–12939, https://doi.org/10.1021/acs.analchem.3c02526

Actinides on TK200 – Preconcentration







- Data by N. Vajda (RadAnal)
- Method development on-going
- Direct load of U, Th and Pu from acidified water samples (here 900 mL on 1g TK200)
  - ~10 mL/min)
- Sequential separation on TK200
- Automatisation & 'in the field' preconcentration'?

TK200 – direct Pu load/separation

- Acidified water samples (1 L)
- One TK200 cartridge
  - Preconcentration and purification
- Automized separation
- 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

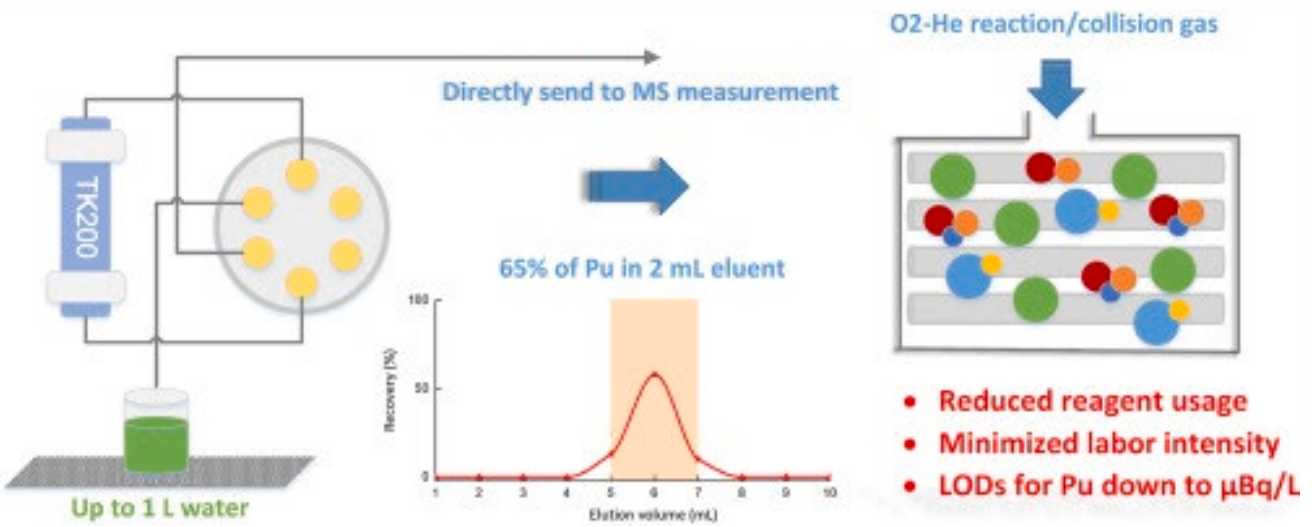
ELSEVIER

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

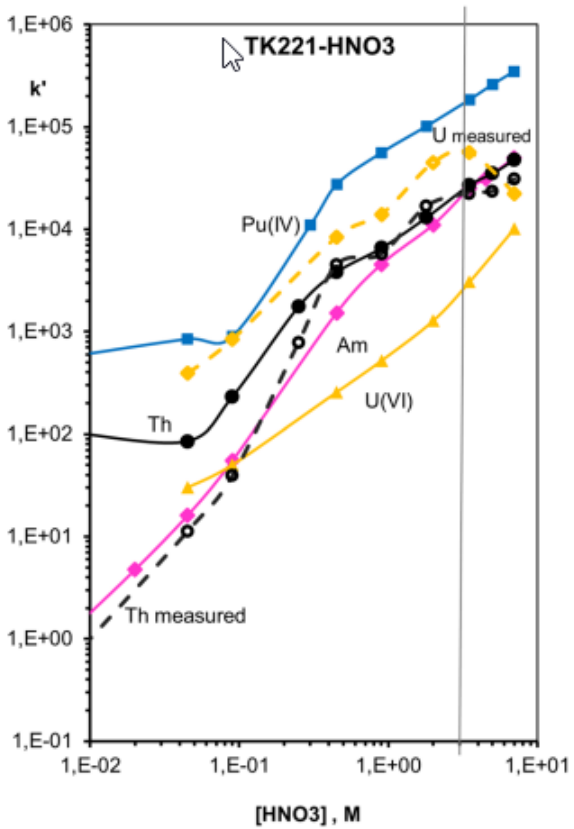
Youyi Ni [a], Wenting Bu [a], Ke Xiong [a], Sheng Hu [a], Chuting Yang [a], Liguo Cao [b]

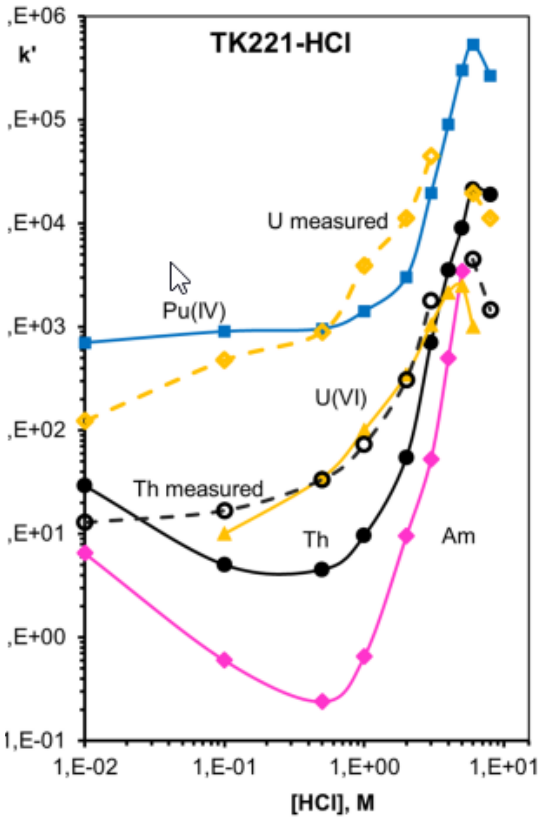


‘New’ - TK221 Resin

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

- Main applications in RadPharm:
  - Lu, Tb concentration from high acid and elution in small volume of dilute HCl
  - Ac-225 purification
- Potential interest for Actinides separation
  - Higher U retention than DGA
  - Higher Am retention than TRU

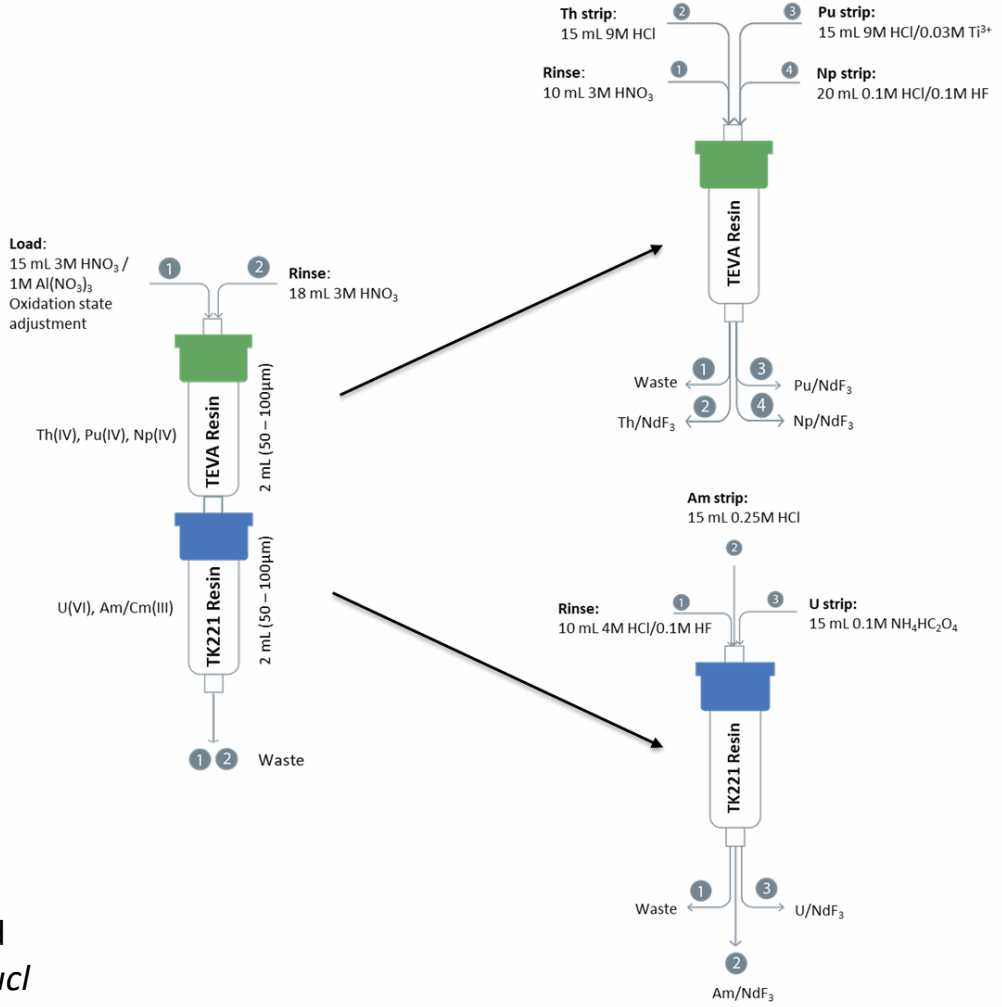




Data by Papp et al.

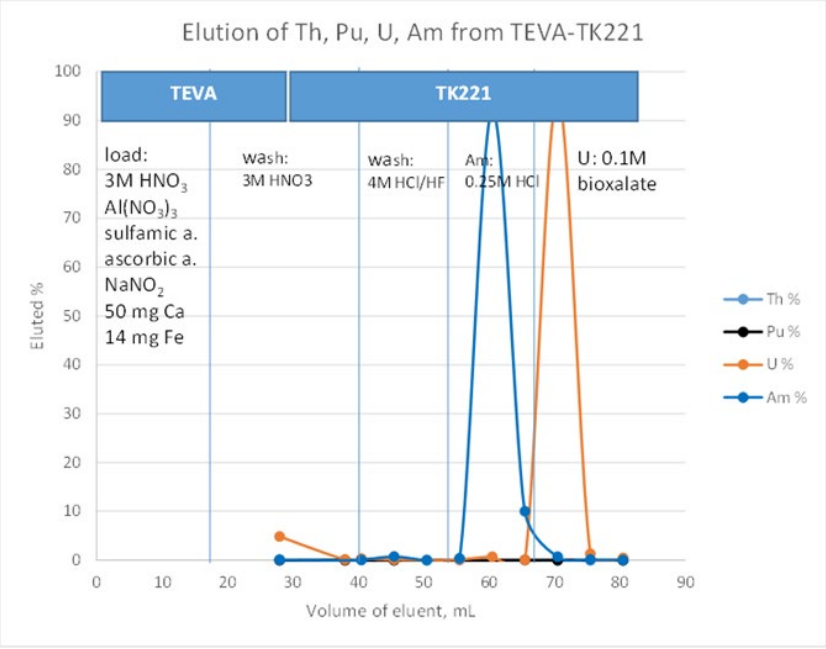
TK221 Resin – actinide separation

- Cooperation with Nora Vajda
- Method development for water samples
- Ca Phosphate co-precipitation
- TEVA/TK221 separation method
  - TEVA: Pu(IV)/Np(IV) and Th(IV) separation
  - TK221: U(VI) and Am(III) separation
- Ideally later also test on soil and decommissioning samples



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



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

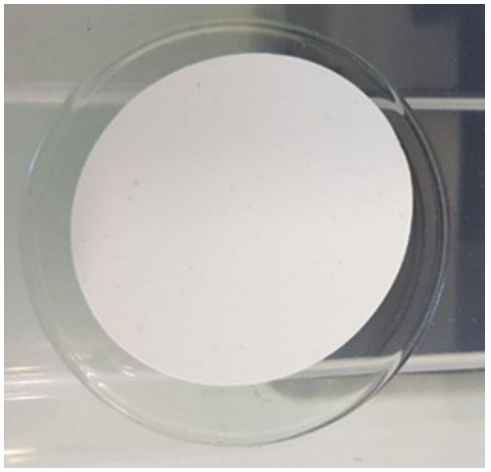
Analyte	Target values		Measured values			Relative bias	MARB[a]	Z-score[b]	Test evaluation
	Mean activity concentration	Standard deviation (sd)	Activity concentration	Standard uncertainty	Relative standard uncertainty				
	Bq/kg	Bq/kg	Bq/kg	Bq/kg	%	%	%		
^{239}Pu	5.93	2.27	5.09	0.24	4.7	14	25	0.37	Accepted
^{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

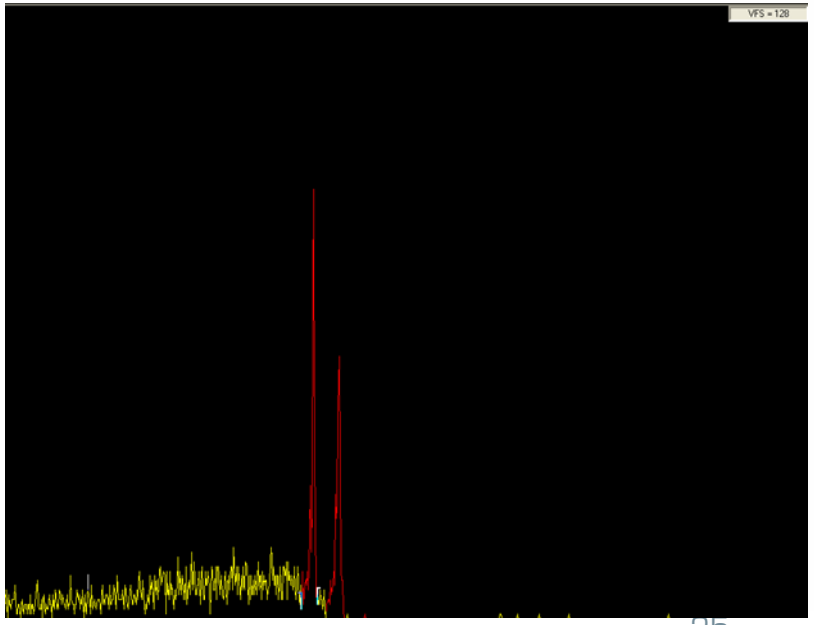
[a]Maximum Acceptable Relative Bias
[b]Z = |Xreported—Xtargetl/sdtarget

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

Under development: gross alpha discs

- On-going work: development of impregnated membrane filters
- First filters under beta testing:
  - TK100 (DGT of Sr, Pb, Zn, LN in soil samples)
  - TK201 (determination of Tc-99 in aqueous samples)
  - 25mm and 47mm
- Currently under testing, membrane filter for gross alpha measurement
- pH 2, 10mL/min, typically 100mL samples
- High retention of actinides
- Peak resolution/spectrum still to be improved





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

Thank you for your attention!

In case of questions or interest in R&D cooperation:

shappel@triskem.fr

TRISKEM
Expertise in Separation Chemistry

Some other on-going projects

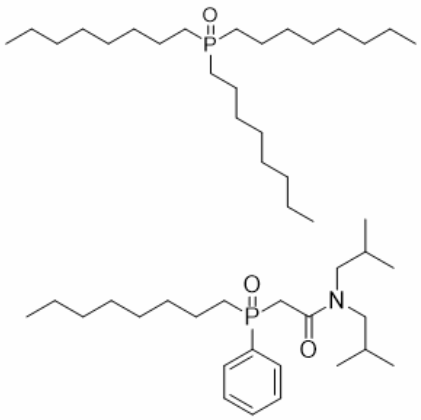
- Impregnated membrane filters
  - AC Discs for gross alpha?
  - Replacement of Nucfilm U discs
  - Passive sampling
- Impregnated PSm resins
- Range of 'Test sticks'
  - Suitable impregnated support
  - JCU => rapide isotope ratio analysis by MS (metallomics)
  - Uni Southampton/NPL
    - Ideally multiple layers of resins for multi RN screening
    - LSC measurement
    - Scintillating supports for non-LSC options
    - Decommissioning/screening

- Separation of DTM
  - SE Resin
  - Zr-93, Fe, Mo, Nb,…
- Fate' of RN in the environment
  - Separation methods
  - Mainly longer lived RN (=> therapy)
    - Ac-225/7, Lu-177(m), radioiodine,…
  - Quantification
- In-field preconcentration
  - Impregnated membranes
  - Cartridges
- Microfluidics
- Other 'geometries' &

'Non-resin' separation materials

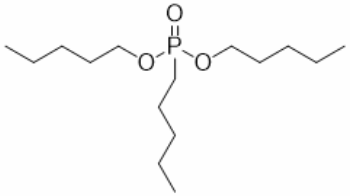
Typically employed extractants

Trioctylphosphine oxide
(TOPO)

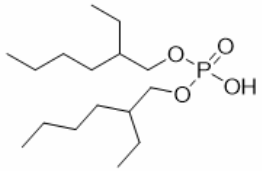


Octyl (phenyl)-N-N-diisobutyl-carbamoylmethylphosphine oxide
(CMPO)

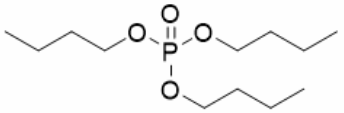
Dipentyl pentyl phosphonate
(DPPP)



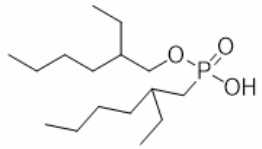
Bis(2-ethylhexyl) hydrogen phosphate
(HDEHP)

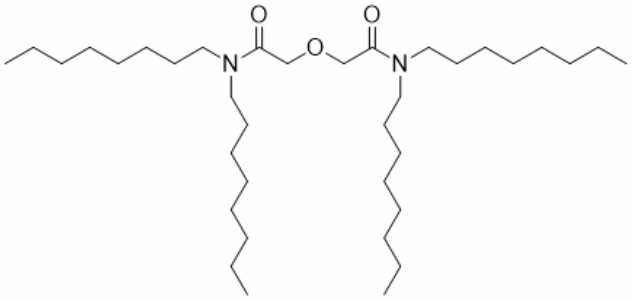


Tributylphosphate
(TBP)

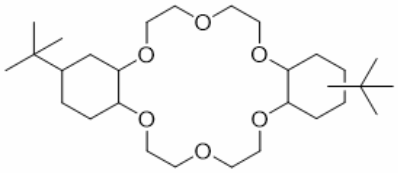


2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester
(HEH[EHP])





N,N,N',N'-tetra-n-octyl-diglycolamide
(TODGA)



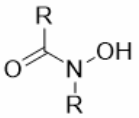
4,4'(5')-di-t-butylcyclohexano-18-crown-6

Aliquat 336 (R = 8, 10)

Phosphine sulfide

Tertiary amine

Hydroxamate



TK221 Resin => product sheet…

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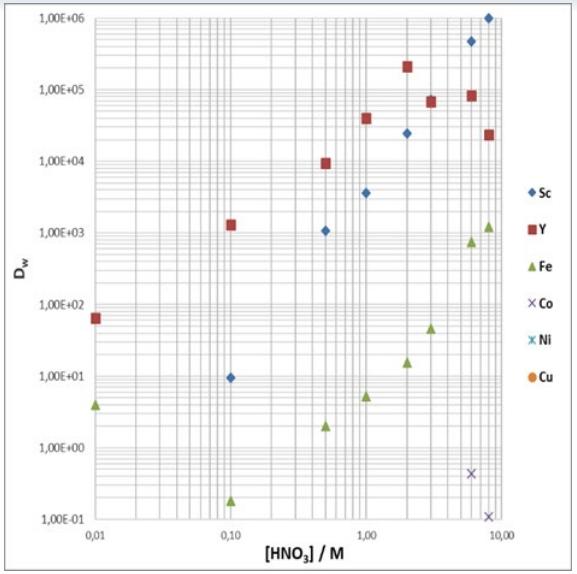

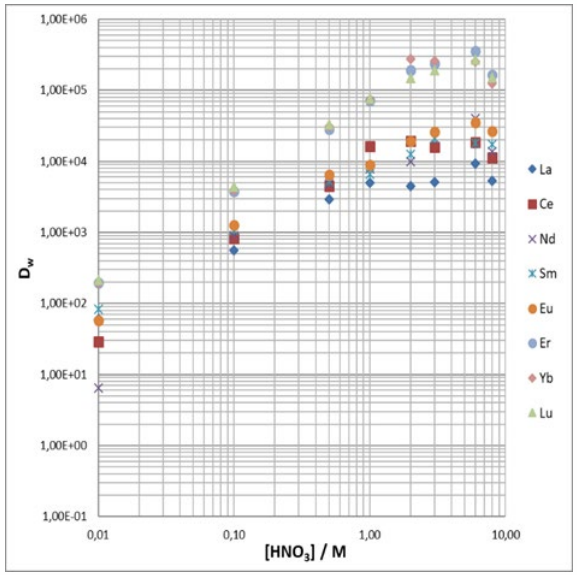

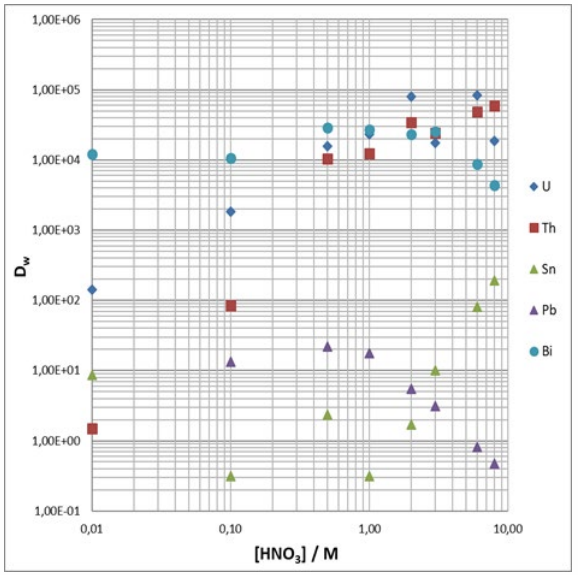

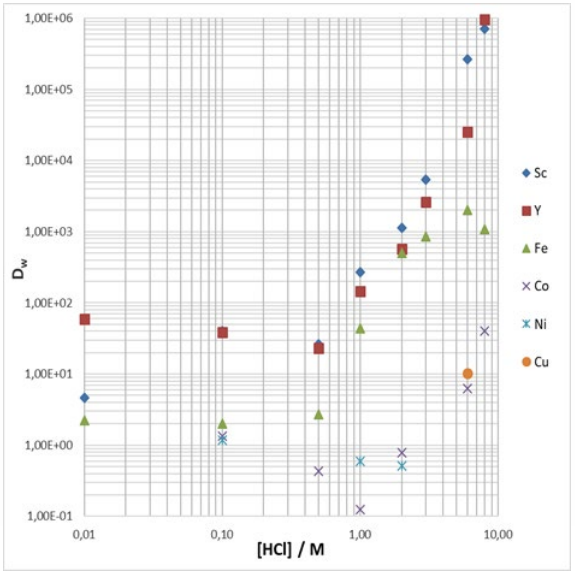

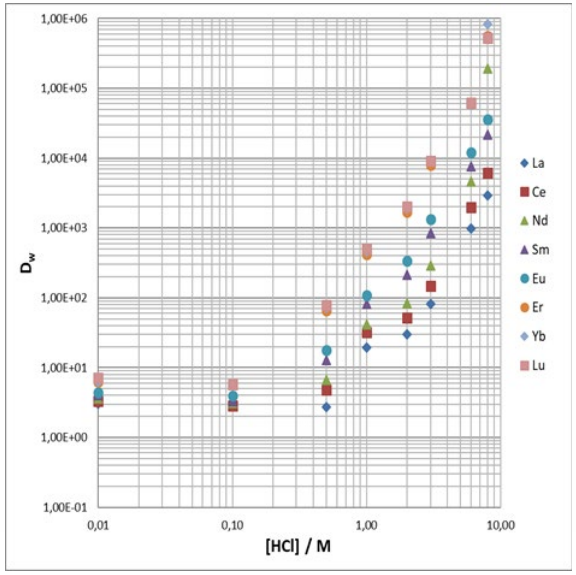

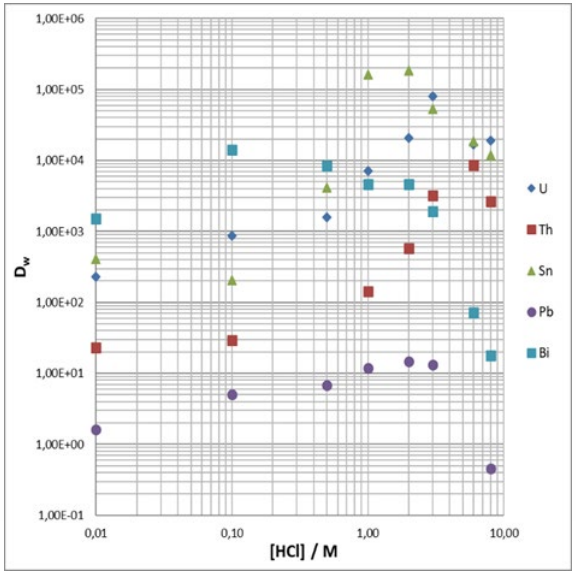

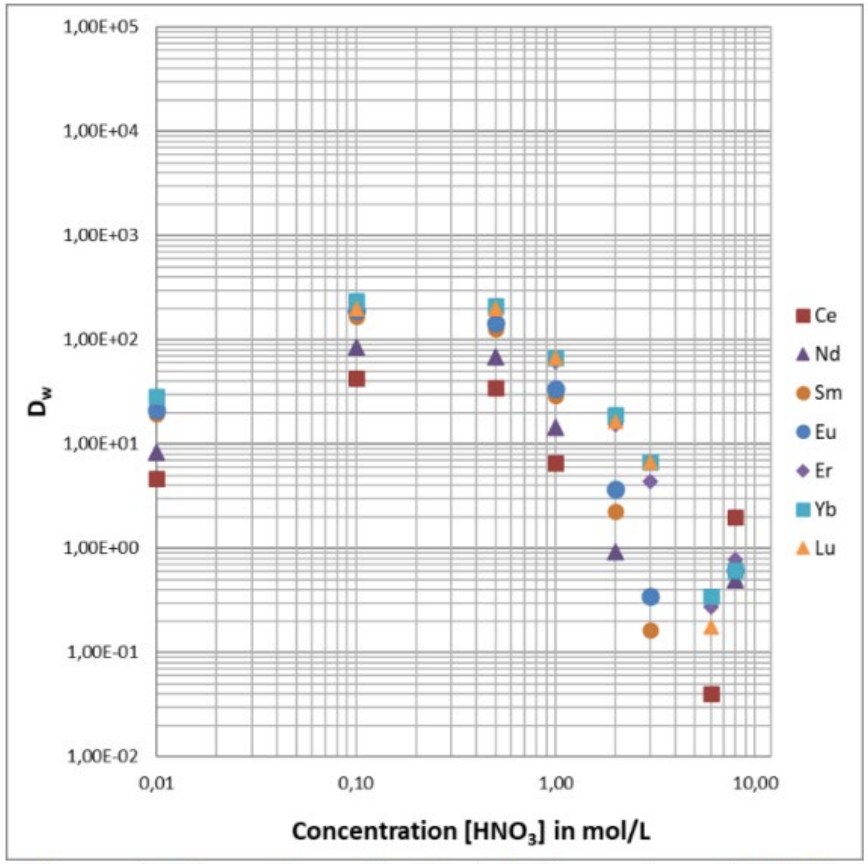

Figure 6: Dw values of selected elements on TK200 Resin in HNO_3