TrisKem International

New Developments in TrisKem
2022 RRMC – Atlanta, 31/10-04/11/2022

Aude Bombard

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Expertise in Separation Chemistry

Overview

- New Resins
  - TK-TcScint
  - TK201
  - TK202
  - CL Resin
  - TK200
  - TK221
- Updates on TK400 Resin
- Under development
  - Extractive membranes
  - TK102
  - Radium Resin
  - TK222
  - TK225
  - « Industrial » resins
- Other projects

Tc-99 separation

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

Interest in decommissioning and radioactive waste management and in Nuclear medecine

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

➢ 1+2 resins developped for load with both acidic or alkaline media and specific elution in slightly alkaline or water

- TK-TcScint resin
- TK201 resin
- TK202 resin

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
  - Other radionulides of interest: Sr, Pb, β-emiters and gross alpha

TK-TcScint

UNIVERSITAT DE BARCELONA

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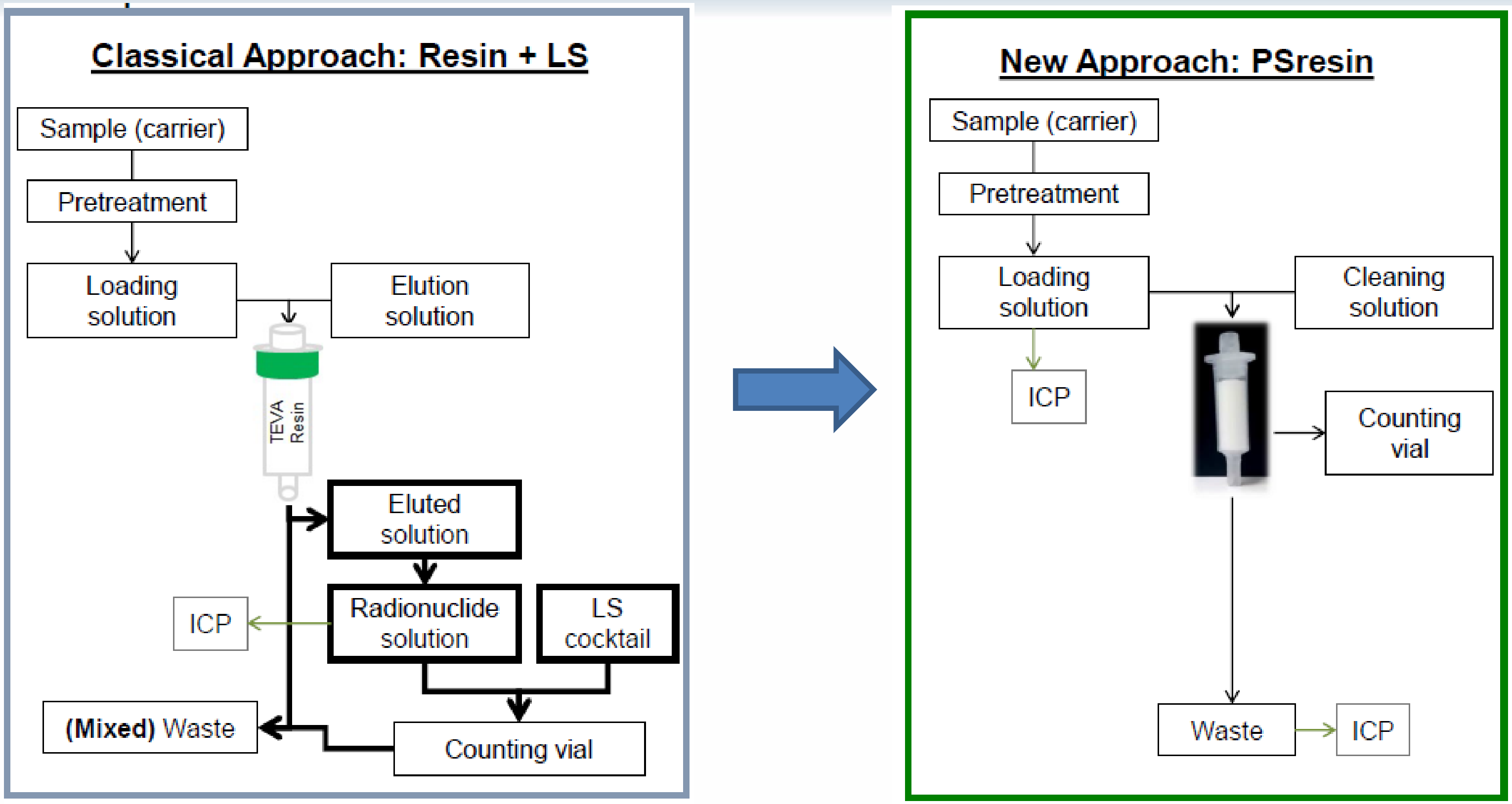


- Direct mesurement of the cartrige by LSC after loading and rinsing
  - NO elution/evaporation/aliquoting => easy automatisation
- Chemical yield via Re/ICP-MS in eluates.

TK-TcScint – Uses and results

- 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

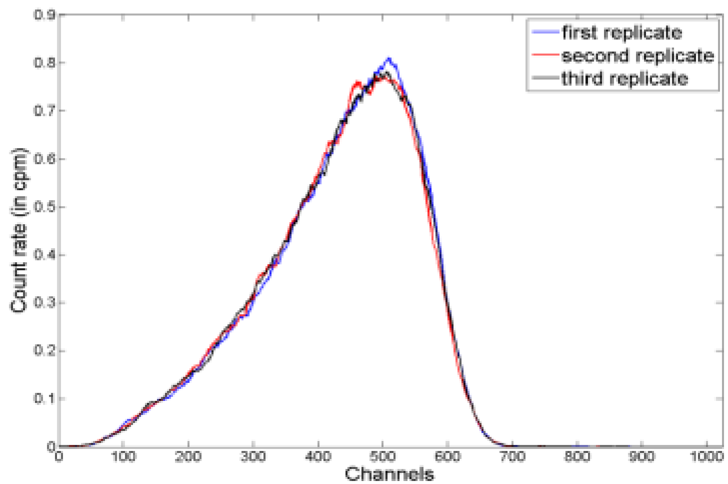
Precondition with 2ml 0.1M HCl

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-TcScint for the Determination of Tc-99 in WATER samples (Garcia et al., TKI UGM Cambridge 2018)

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MOP:

Spike sample to achieve 0.1M HCl
Rinse with DI H_2O

Results:

Sample	Activity (dpm mL^{-1})	Activity Calc (dpm mL^{-1})	Error (%)
Sea Water	24,3	23,0	**-5,3**
Sea Water	24,3	25,1	**3,3**
Sea Water	24,2	22,8	**-6,2**

TK-TcScint for the Determination of Tc-99 in URINE samples (Garcia et al., TKI UGM Cambridge 2018)

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MOP:

100ml sample

Add 10 mL of 65% HNO_3 and evaporate to dryness
Dissolved in 5 mL of 65% HNO_3
Evaporated to dryness
Heat @ 550 °C in a muffle oven for 30 min.
Dissolved in 3mL of HNO_3
Treated with 100 mL of D.D. water
Add 5 mL of H_2O_2 and heated to 90 °C for 1 h
Rinse with DI H_2O

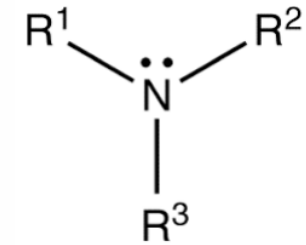
Results:

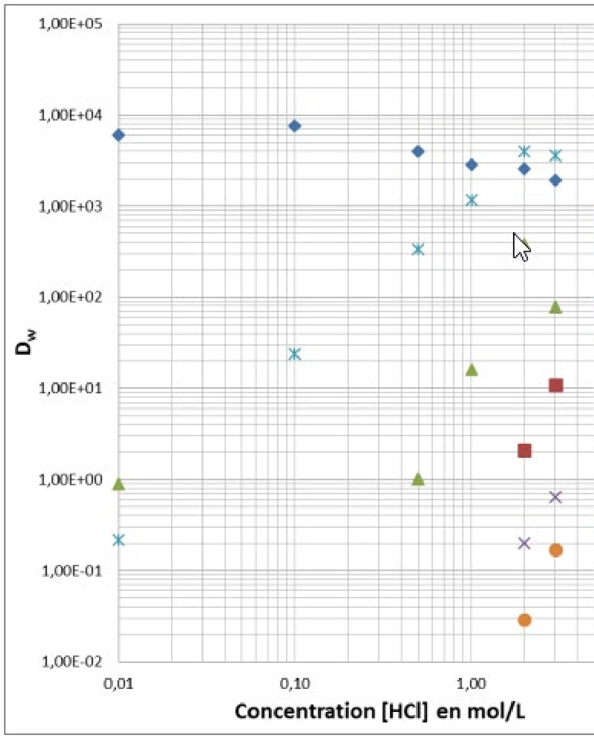
Sample	Activity (dpm mL^{-1})	Activity Calc (dpm mL^{-1})	Error (%)
Urine	0,43	0.44	**2,4**
Urine	0,46	0,42	**-6.5**

MDA (100 mL, 24h): 0.036 Bq L^{-1}

TK201 Resin

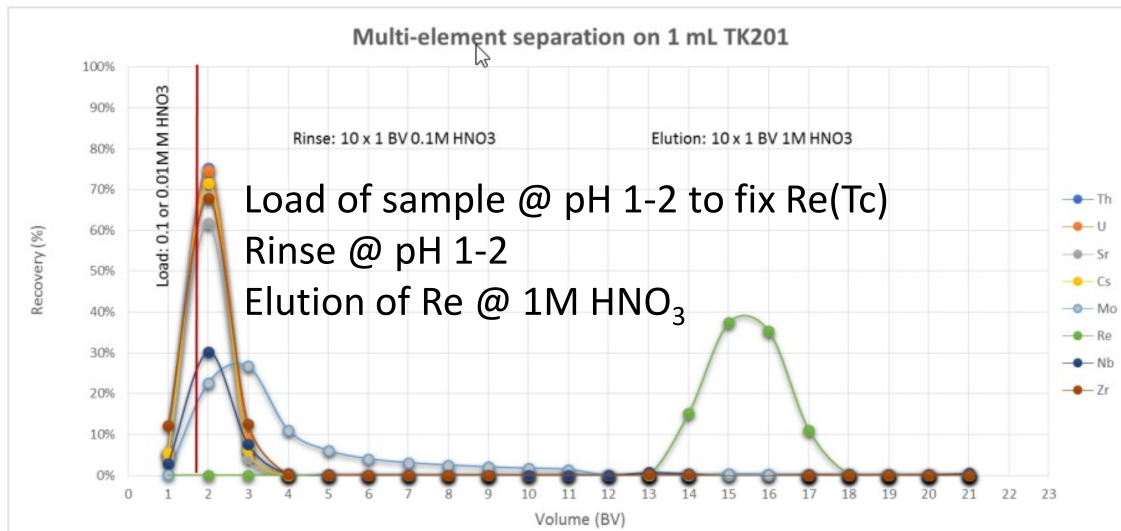
- Based on tertiary amine (weak Anion Exchanger) impregnated on inert support
- In acidic medium, exchange of the counter anion



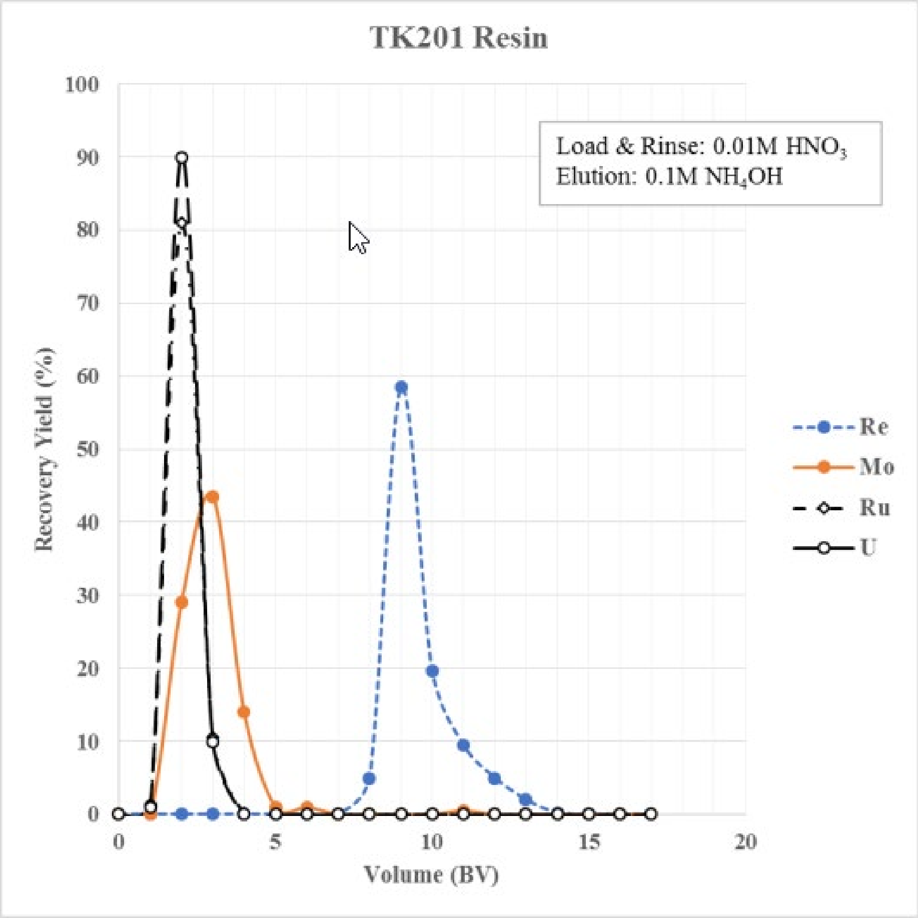


Re uptake between pH 2 – 5M HCl

In HNO_3 medium, Re fixed @ pH 1-2



TK201 Resin – Elution curve for Re(Tc)/Mo separation



MOP:

Load + Rinses in 0.01M HNO_3

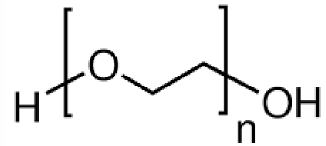
Elution in 0.1M NH_4OH

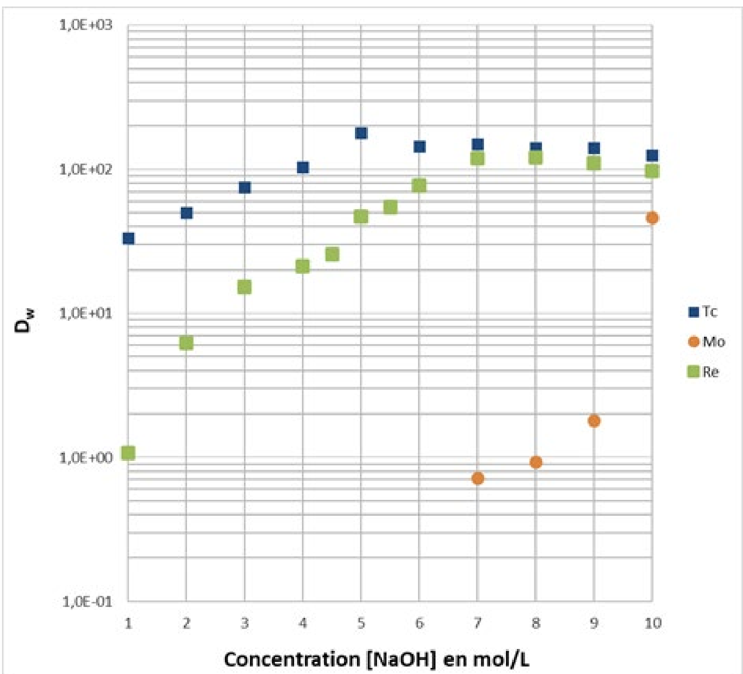
Results:

- Clean separation of Re in 6BV 0,1M NH_4OH
- Elution of Re also possible with 1M HNO_3
- No retention of other elements studied

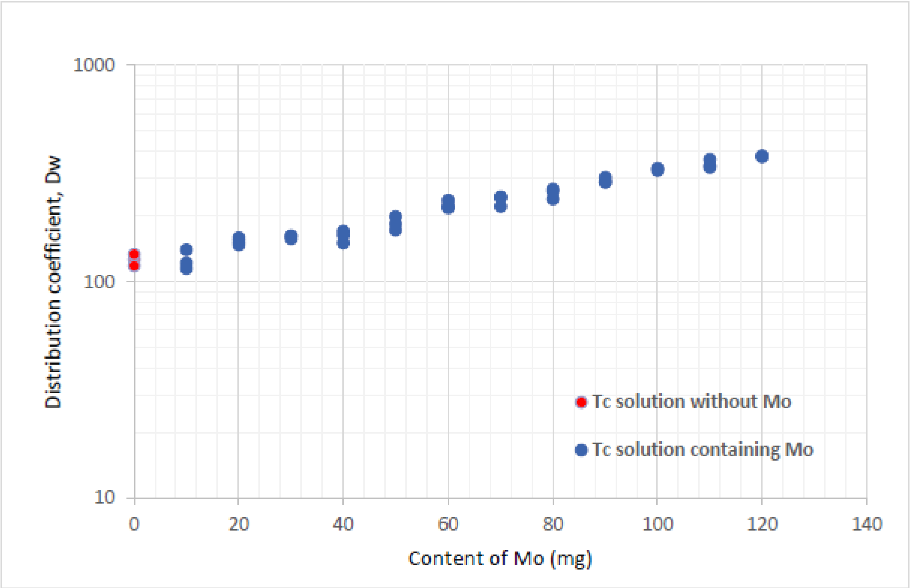
TK202 Resin

- Polyethylene Glycol (PEG) grafted on inert support
- Aqueous biphasic system (ABS)
- Retention of chaotropic anions e.g; TcO_4^- in the presence of kosmotropic anions (SO_4^{2-}, CO_3^{2-}, OH^-, MoO_4^{2-},…)
- For samples rich in Mo: Tc yield > 90% for 6 – 8g Mo per g TK202





Dw values for Tc, Re and Mo on TK202 Resin, at varying NaOH concentrations. Tc data taken from Cieszykowska et al.

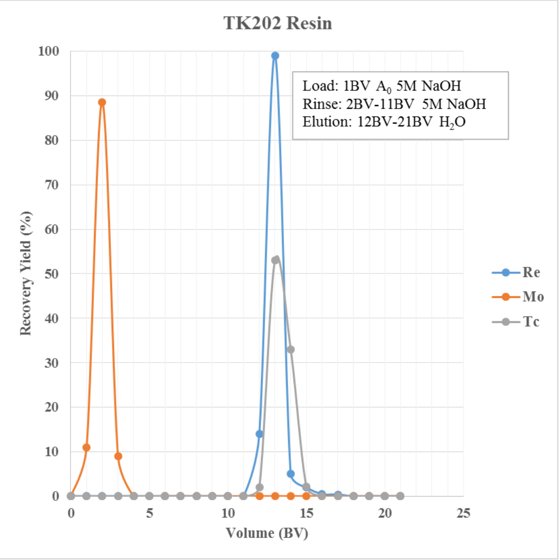


Dw values for Tc in 5M NaOH using 40 mg TK202 Resin, increasing amounts of Mo. Data taken from Cieszykowska et al.

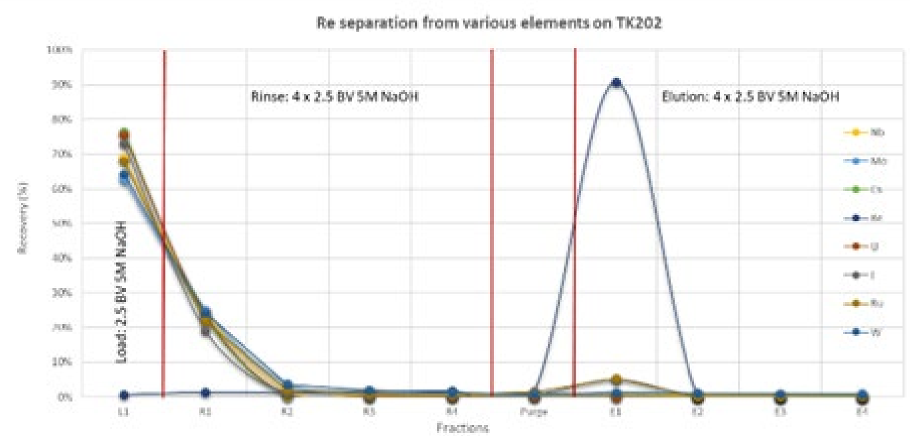
TK202 Resin

- Retention of Tc from concentrated NaOH medium (5 - 7M)
  - Alkaline Fusion e.g. decommissioning samples
  - Dissolution of Mo target
  - Clean separation from other tested elements

  => CAREFUL regarding other chaotropric anions (e.g. I^-)
- Re can be used as internal standard
- Elution in a small volume of water
  - Eluat remains alkaline
  - Load on CEX to neutralise medium + get rid of Na^+ THEN
  - Load on aluminum oxide to get rid of Mo traces + elution in 0.9% NaCl mediums



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.

CL Resin - Determination of Cl-36 and I-129 in decommisionning samples

- Cl-36 and I-129 (volatile and long-lived period radio-nuclides)
  - Cl-36(301243y, beta emitter, Emax beta-=709.682keV (98.1%) , decays to Ar-36 + Emax beta+=120keV (1.9%) decays to S-36. Ar-36 decays to S-36)
  - I-129(1.5x107y, pure beta emitter, Emax=194 keV, decays to stable Xe-29)
- Monitoring of NPP, decommissioning, radwastes, monitoring in environment with I-129
- CL resin « activated » with Ag^+
- Retention as chloride and iodide complexes
  - Reduction might be needed (e.g. with Sn(II))
- Simple and fast method
- Chemical yield by e.g. ion chromatography
- LSC measurement (and/or ICP-MS)

CL Resin – Separation scheme

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•Load Ag+ from acidic, neutral or slightly alkaline conditions (optimized condition is 1M H_2SO_4) to activate resin

•Load sample preferably in same conditions (carriers are I^-/IO_3^- and Cl^-)

•Rinse with 10ml of D.I. Water

- ➢ Eliminates matrix elements

• Elute chloride with 5ml of 0.1M SCN^-

- ➢ Directly mixed with LSC cocktail and counted

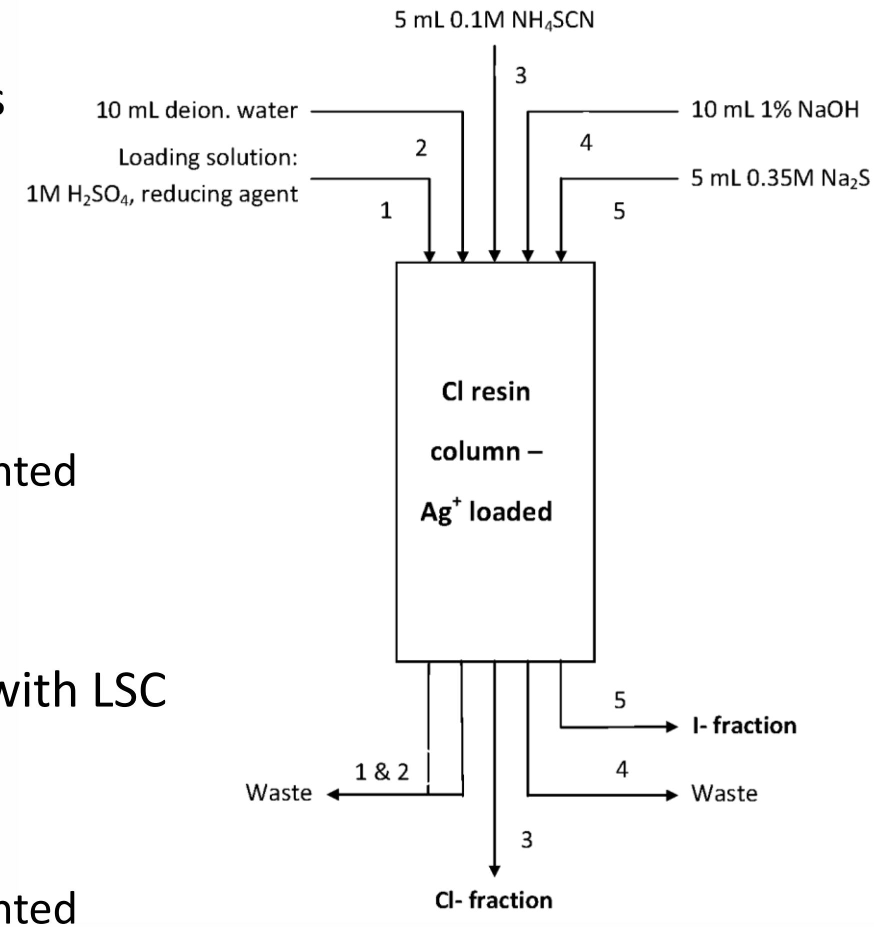
• Rinse with 10ml of 1% NaOH

- ➢ Increases iodide yield

• Elute iodide with 5ml of 0.35M Na_2S, mix with LSC cocktail (resin changes color)

- ➢ Fume hood…
- ➢ Directly mixed with LSC cocktail and counted

• Yields in general > 90 - 100%



Details about the exchanges on CL Resin

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- Sample load after resin activation with Ag^+:

$R\text{-}Ag^+ + Cl^- \Rightarrow R\text{-}AgCl$ $Ks_{AgCl} = [Ag^+]x[Cl^-] = 10^{-9,5}$

$R\text{-}Ag^+ + I^- \Rightarrow R\text{-}AgI$ $Ks_{AgI} = [Ag^+]x[I^-] = 10^{-16,07}$

- Cl^- Elution :

$Ks_{AgCl} = [Ag^+]x[Cl^-] = 10^{-9,5}$; $Ks_{AgSCN} = [Ag^+]x[SCN^-] = 10^{-11,7}$;$Ks_{AgI} = [Ag^+]x[I^-] = 10^{-16,07}$

$R\text{-}AgCl + SCN^- \rightarrow R\text{-}AgSCN + Cl^-$

$R\text{-}AgI + SCN^- \leftarrow R\text{-}AgSCN + I^-$

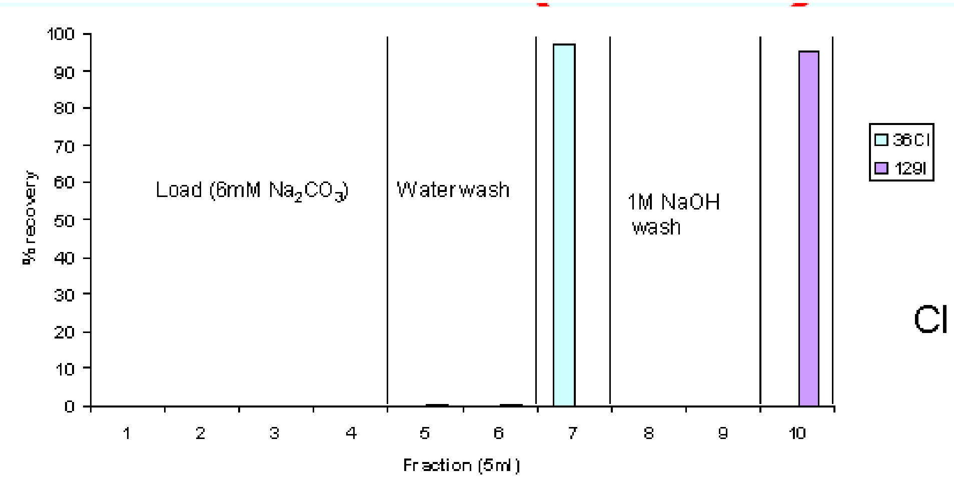
- I^- Elution:

$Ks_{Ag2S} = [Ag^+]^2x[S^{2-}] = 10^{-24,1}$; $Ks_{AgI} = [Ag^+]x[I^-] = 10^{-16,07}$

$2\ R\text{-}AgI + S^{2-} \rightarrow (R\text{-}Ag)_2S + 2I^-$

CL Resin – Cl-36 Applications

- Cl-36 in spent resin via Pyrolyser (several g samples, Warwick et al.)
  - Thermal decomposition of the samples at 900°C (ca. 2h)
  - System flushed with humidified air
  - Decomposition products trapped in bubbler containing alkaline solution
  - 6 mM Na_2CO_3 used (yield > 80%), Alternative: 1M NaOH
  - Direct load onto CL resin, additional rinse with 0.1M H_2SO_4 to remove C-14



All Data from P. Warwick, GAU Radioanalytical, Southampton (UK)

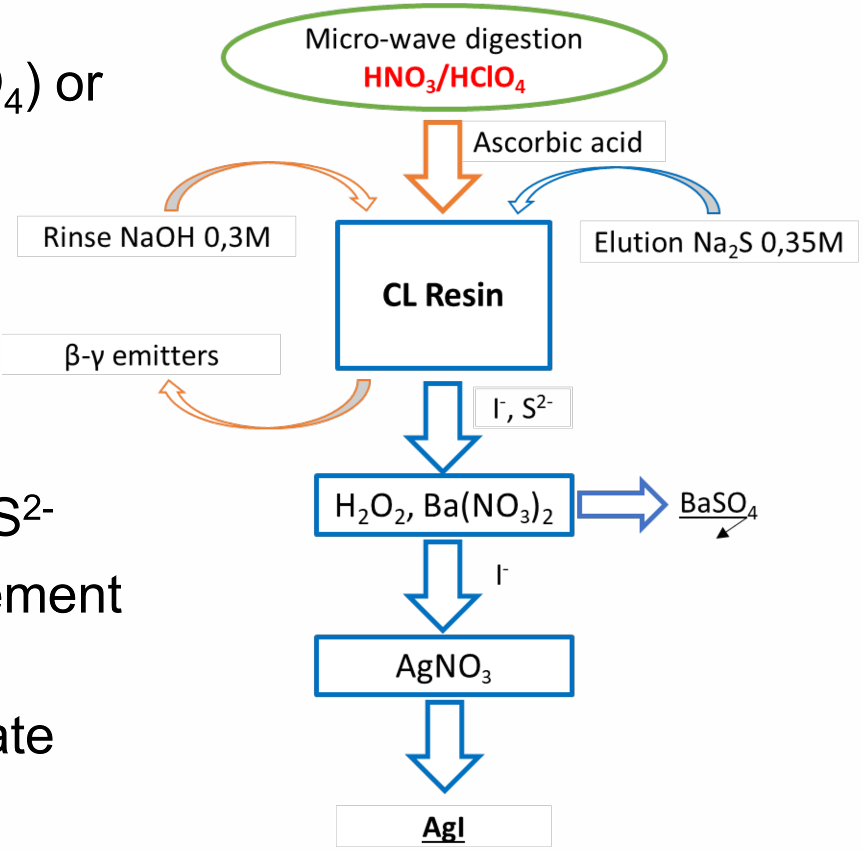
Cl recovery 98%

- Column separation yield >95%, high decontamination factors

CL Resin - I-129 in spent resin via AMS

(Nottoli E., Bienvenu P., Labet A., Bourlès D., Arnold M., Bertaux M., Accurate determination of 129I concentrations and 129I/137Cs ratios in spent nuclear resins by Accelerator Mass Spectrometry, Applied Radiation and Isotopes, http://dx.doi.org/10.1016/j.apradiso.2014.01.010)

- Resin mineralized by
  - microwave digestion ($HNO_3/HClO_4$) or
  - oxygen bomb combustion (iodine trapped in NaOH)
- Iodine purified on CL Resin using a modified purification method
  - Load and Rinse 1M NaOH
  - Cl^- elution via SCN^-, I^- elution via S^{2-}
- Samples prepared for AMS measurement by:
  - oxidation of the sulphide to sulphate with H_2O_2
  - removal of the sulphate by precipitation with Ba / centrifugation
  - AgI precipitation.



CL Resin - I-131 in biological samples and hospital effluents

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Talanta 206 (2020) 120224

Contents lists available at ScienceDirect

Talanta

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ELSEVIER

Fast-response flow-based method for evaluating ^{131}I from biological and hospital waste samples exploiting liquid scintillation detection

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[d] Department of Chemistry, University of the Balearic Islands, Cra. Valldemossa Km 7.5, 07122, Palma, Spain

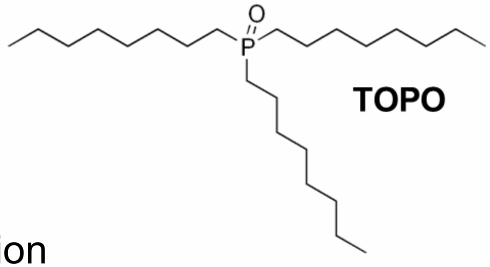
- Lab-on-valve analysis with 135mg CL resin/extraction
- >80% recovery of iodine
- MDA 0,05Bq I-131

TK200 Resin

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

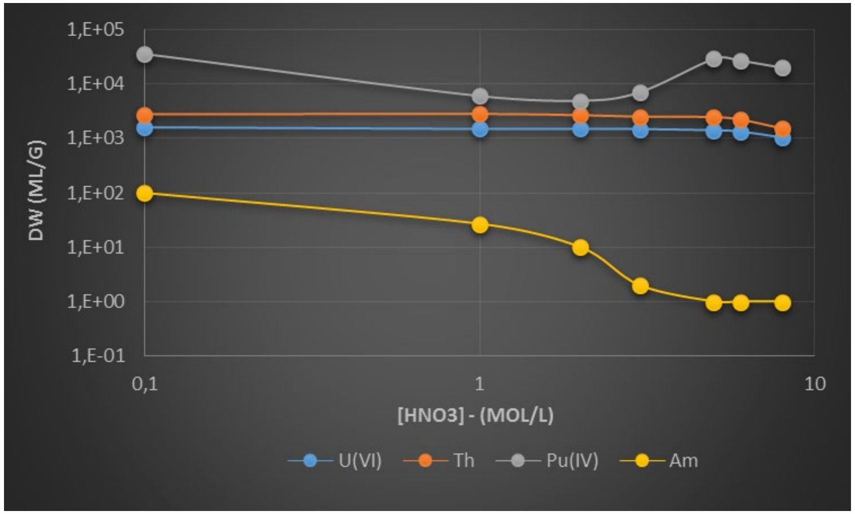
  => automized separations/ICP-MS
- U/Th separation from water samples
- Efficient U/Pu separation from soil/sediment samples (up to 2g)

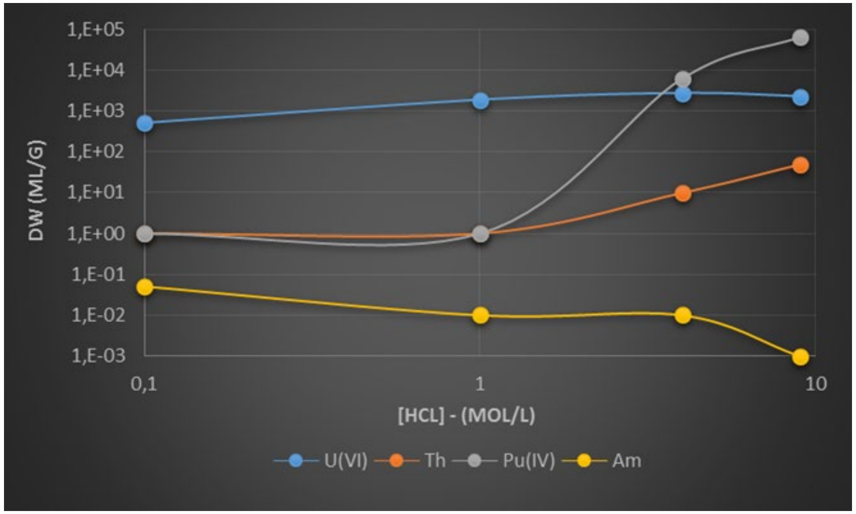
- Other applications:
  - Nuclear medecine
    - Ga-68 production (in combination with ZR Resin)
    - on-going: Pt/Ir, Zn/Cu (Zn production, Zn removal), Sc production



TOPO

TK200 Resin – Dw Studies



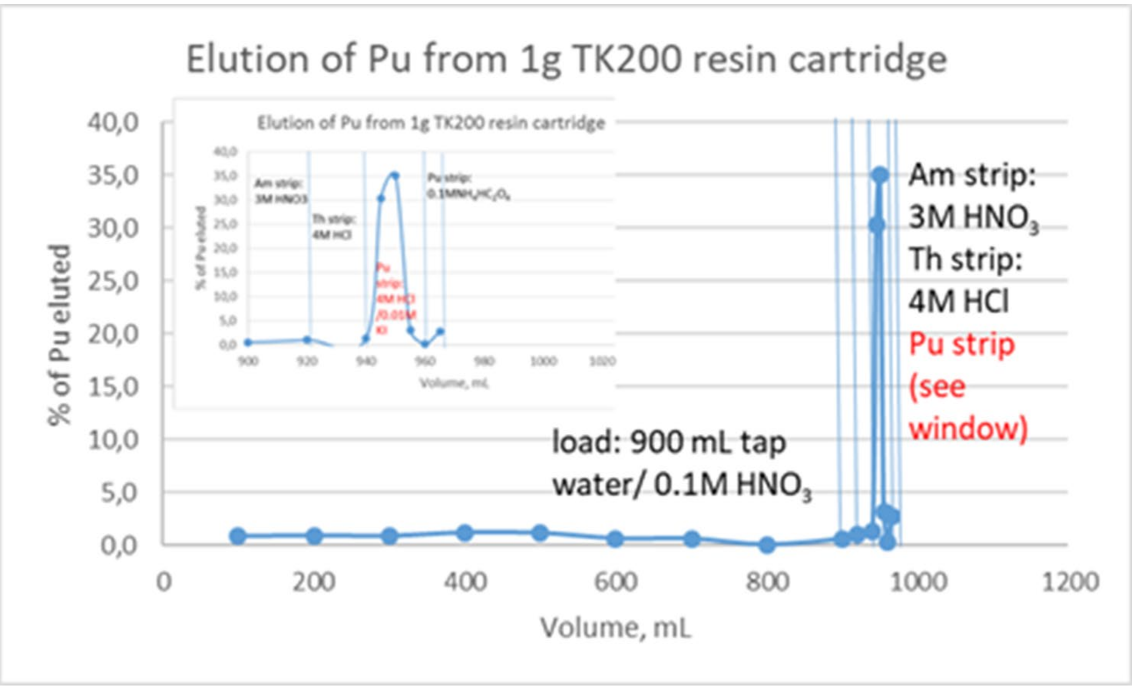


- Retention of Am < 0,1M HNO_3;
- U/Th/Pu uptake over the whole acidity range studied;
- High uptake of Bi from 0,01 – 2M HNO_3 => possibility to separate from Pb in case of MS measurement;
- Uptake of Sn from 0,1 – 10M HNO_3 (alternative to TBP Resin).

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

TK200 Resin – Elution studies

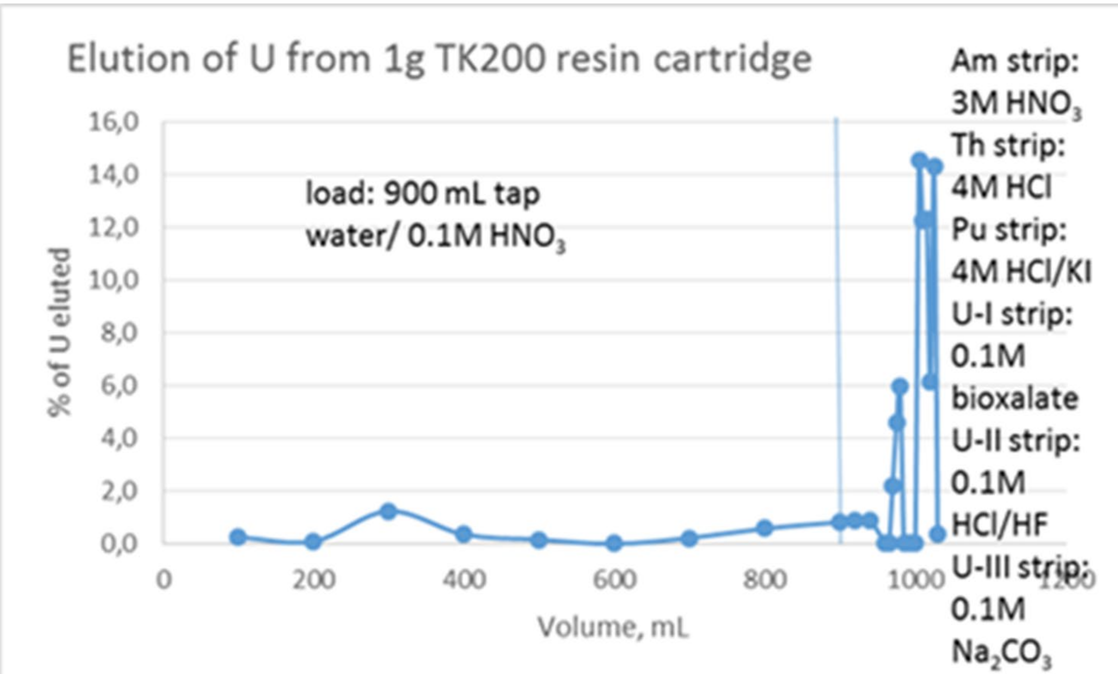
- Possibility to preconcentrate Am, U, Th and Pu(IV) in 0,1M HNO_3 (or pH2) and to subsequently elute in separate fractions
- Tests made at Radanal (N. Vajda)
- Test 1 in 900mL tap water @ pH 1 spiked with Am/Pu/Th



Load with 0,1M HNO_3;
Am eluted with 20mL 3M HNO_3;
Th eluted with 20mL 4M HCl;
Pu eluted with 20mL 4M HCl/0,01M KI

TK200 Resin – Elution studies

- Test 2 in 900mL tap water @ pH 1 spiked with Am/Pu/Th/U



Load with 0,1M HNO_3;
Am eluted with 20mL 3M HNO_3;
Th eluted with 20mL 4M HCl;
Pu eluted with 20mL 4M HCl/0,01M KI
U eluted with either

- 0,1M bioxalate
- 0,1M HCl/HF
- 0,1M Na_2CO_3

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

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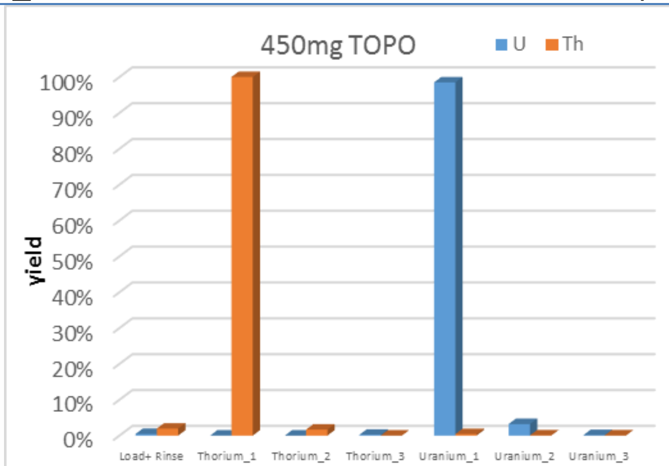
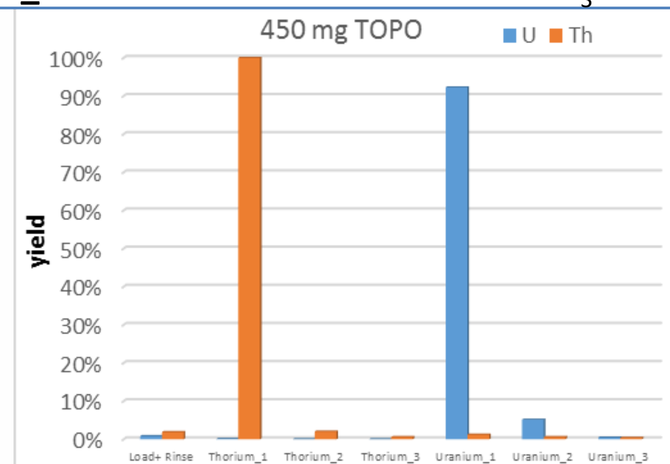
Load+ Rinse	5mL Load 3 M HNO3 + 5mL 3 M HNO_3
Th_1	10 mL 0.1 M HCl-0.1 M oxalic acid
Th_2	5 mL 0.1 M HCl-0.1 M oxalic acid
Th_3	5 mL 0.1 M HCl-0.1 M oxalic acid
U_1	10 mL 0.1 M Ammoniumoxalate pH 9
U_2	5 mL 0.1 M Ammoniumoxalate pH 9
U_3	5 mL 0.1 M Ammoniumoxalate pH 9



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



Th selectively separated from U and recovered quantitatively

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

U/Th separation on TK200

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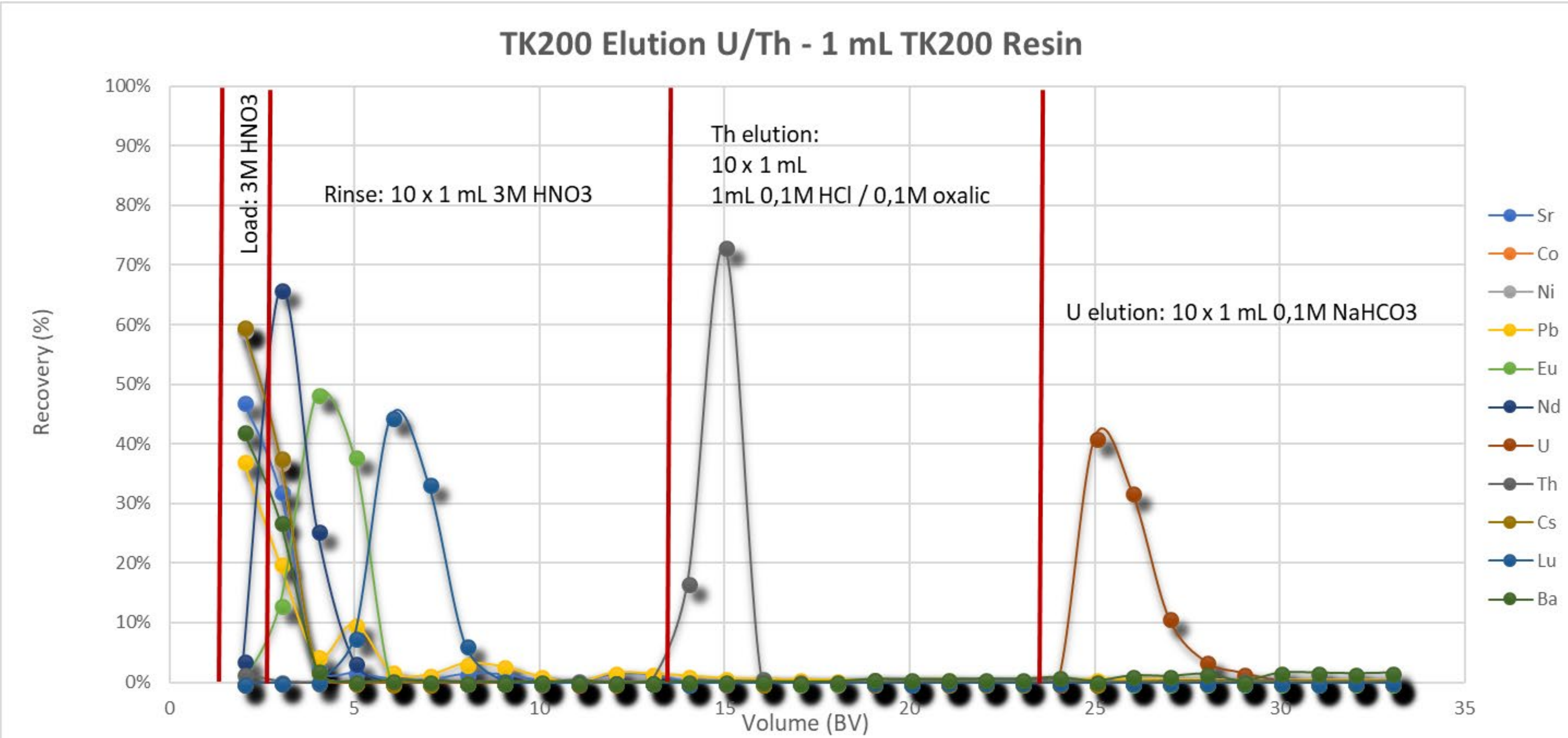

- Load: 3M HNO_3 or ≥ 1L pH2 (HNO_3)
- Very clean U/Th separation
- Alcaline oxalate instead of carbonate

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

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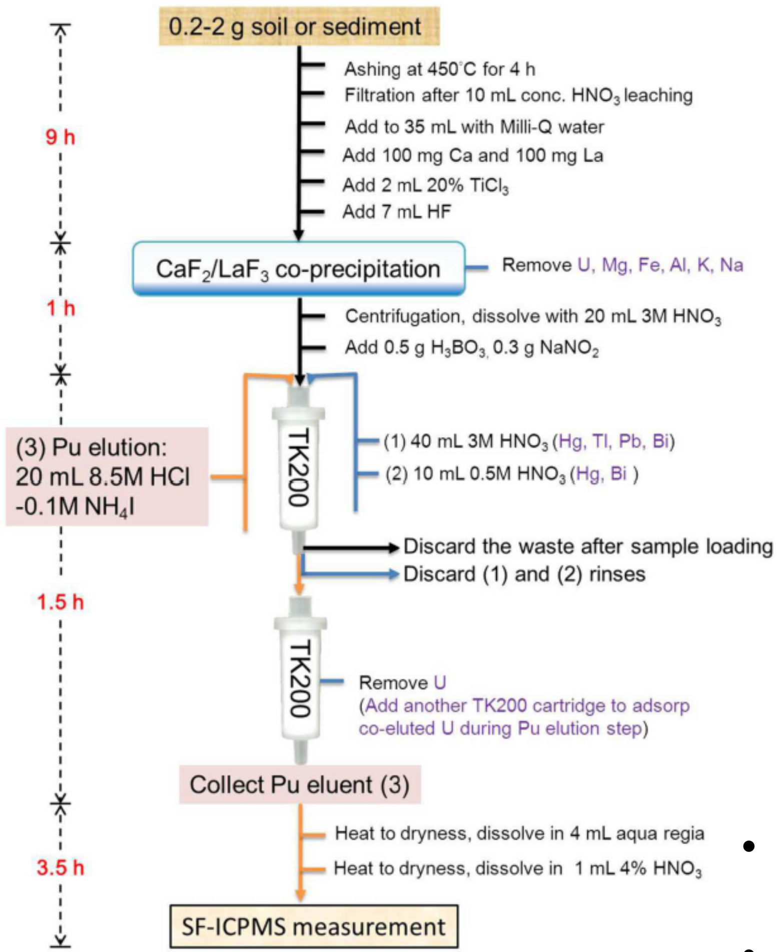
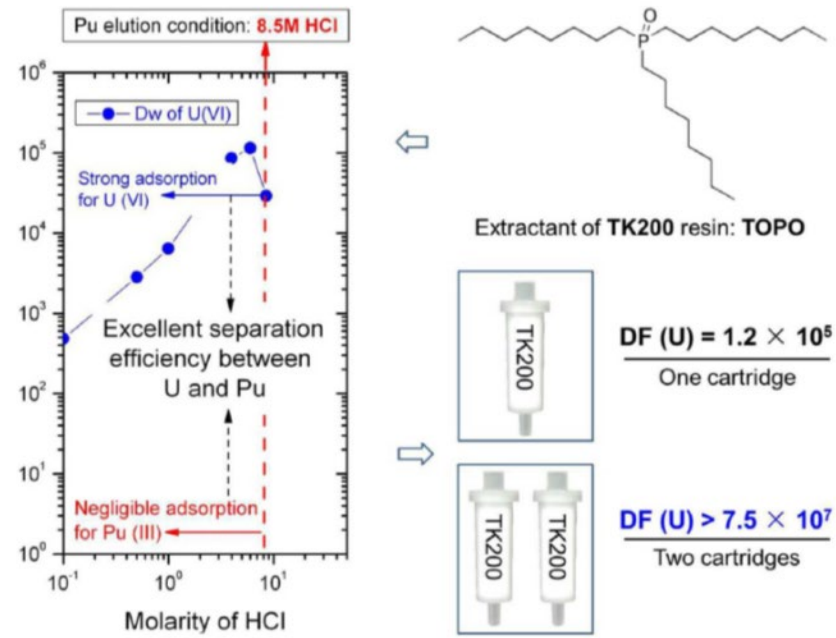


Figure 1



Graphic abstract

Wang et al. 2019

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

TK200 Resin – Conclusions

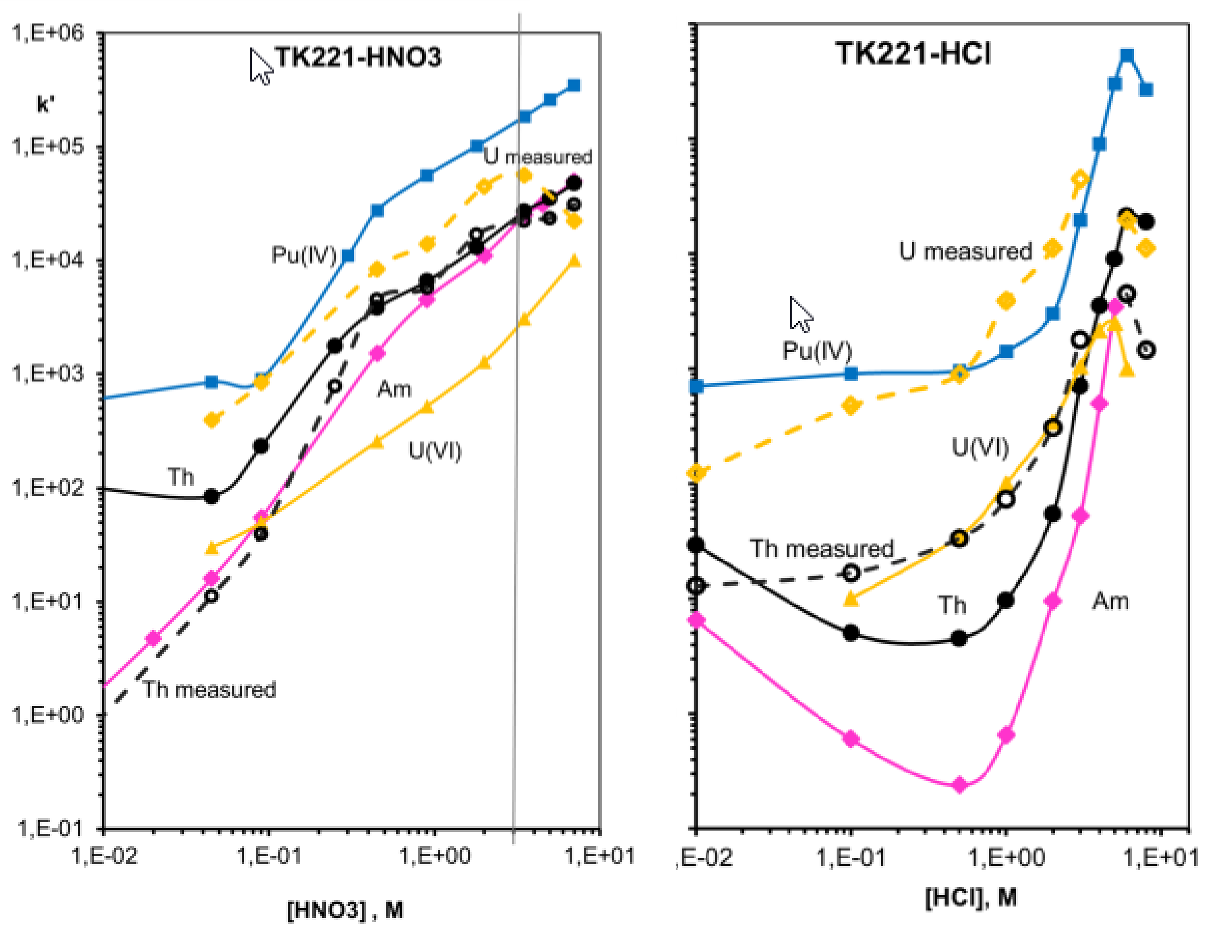
- Preconcentration of actinides from pH1-2 solutions => medium usually used to preserve samples for storage and prior to analysis
- Th/U and U/Pu Separations are efficient
- Possibility to extract/concentrate Sn and Cd in HCl and elute in low HNO_3 concentration.
- Zr/Hf are well extracted in HCl (1-10M)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

TK221 Resin

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

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

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



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

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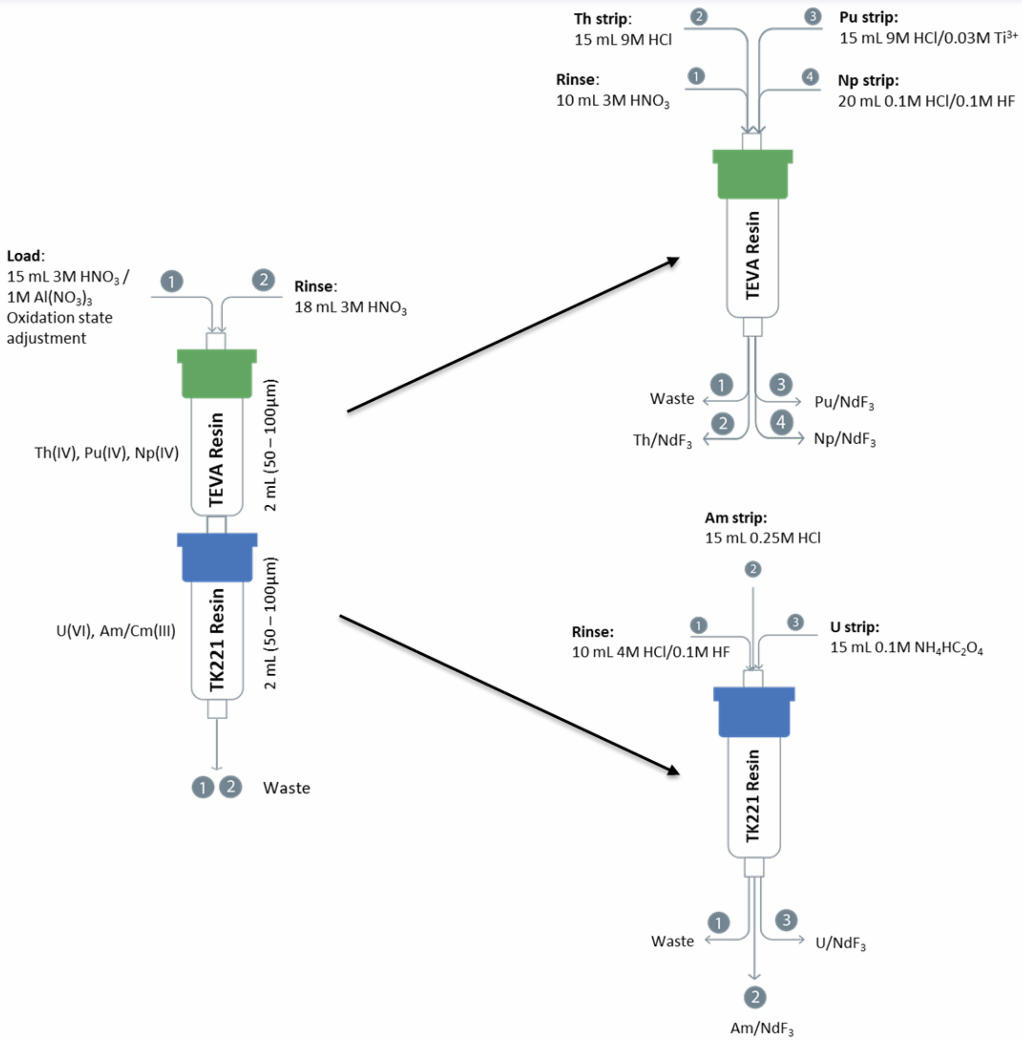
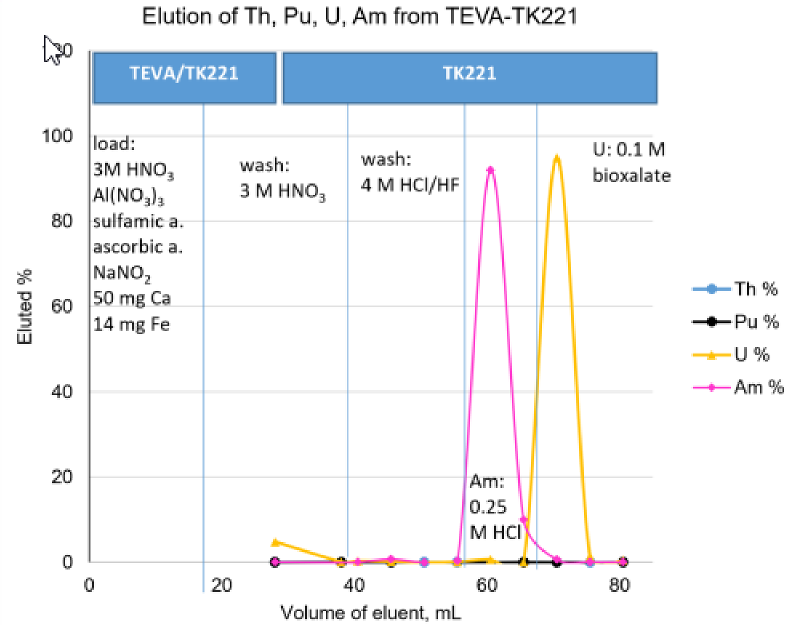
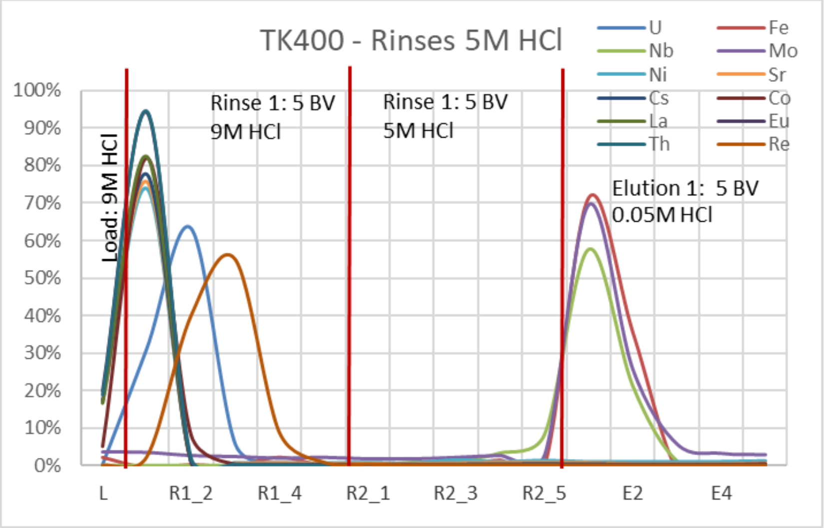


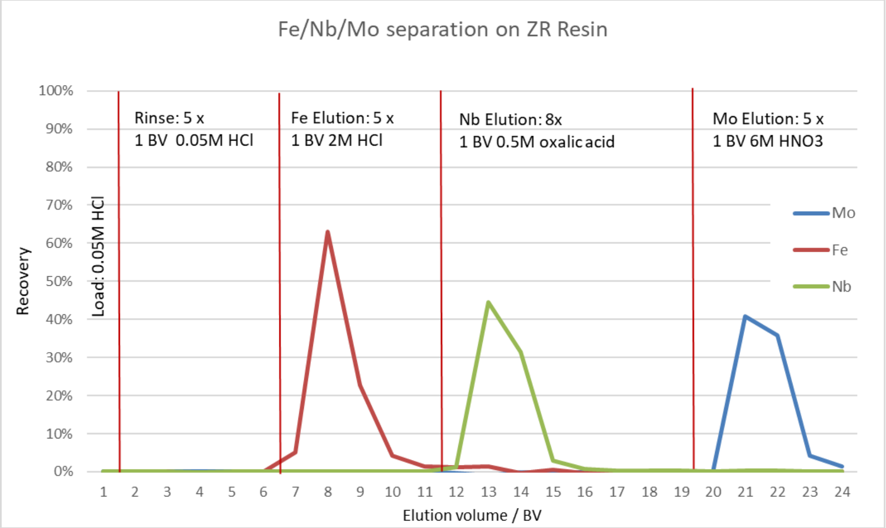


TK221 Resin	Yield (%)	Am (%)
RN	Without Np separation	With Np separation
	TAP WATER	
Am-241	103 +/- 7	97 +/- 6
U-233	103 +/- 7	70 +/- 7
	SEA WATER	
Am-241	89 +/- 7	92 +/- 6
U-233	88 +/- 7	59 +/- 6

TK400 Resin - Fe Separation

- Separation of Fe/Nb/Mo in concentrated HCl medium on TK400
  - Most of other element present in solution are eluted during load and rinses (HCl 9M et 5M)
  - Fe/Nb/Mo eluted in diluted HCl medium => separation e.g. on ZR Resin

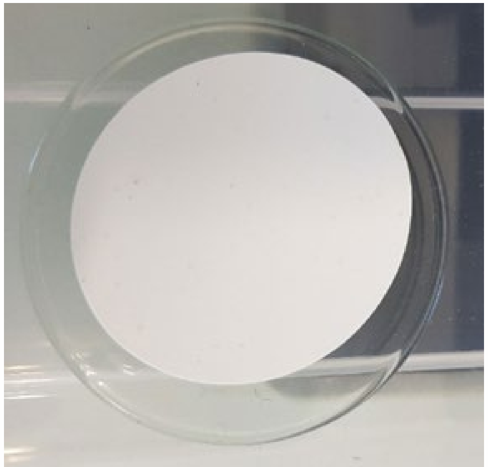




- TK400 also used to separate Nb (and Fe) from Zr or Pu(-241)
  - Zr-93 in decommissioning sample=> method under development (with UTEVA Resin)
  - Capacity determined @ ~ 20 mg Fe/ml TK400 Resin in 9M HCl and a load solution @ 10mg Fe/ml
- TK400 used in Radpharm (presentation by S. Happel)

Coming products – impregnated filtering membranes

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



TK201 membranes: Re separation

Product description: The disks can be used for the purification and concentration of Tc from aqueous samples. TK201 disk provides a large surface area for sample contact.

Re is used as carrier and chemical homolog of Tc

MOP:

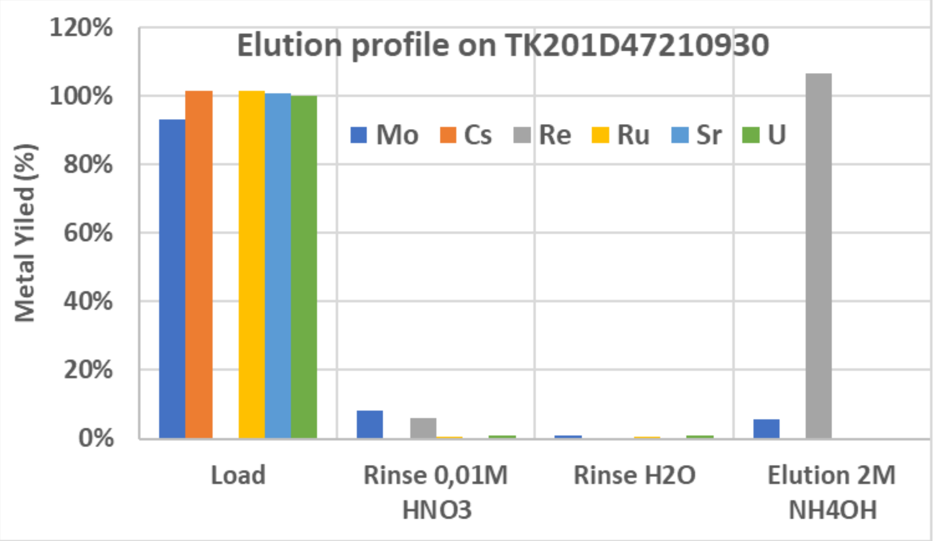
Loading solution: 1L of tap water spiked with Mo, Cs, Re, Ru, Sr and U acidified with HNO_3 to pH 2.

25mL 30% H_2O_2 added + mixed and heated to 60°C for 60min, then cooled to RT.

Steps of the experiment:

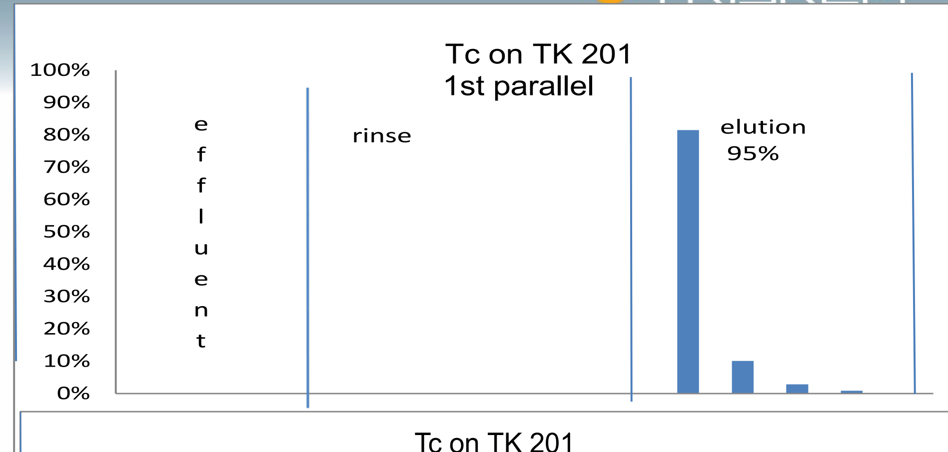
- PC: 50mL 0,01M HNO_3
- Loading 1L of A0 after activating it with 25mL of H_2O_2 (10mL/min),
- Rinse1: 10mL of 0.01M HNO_3,
- Rinse2: 20mL of DI. H_2O
- Elution: 20mL of 2M NH_4OH

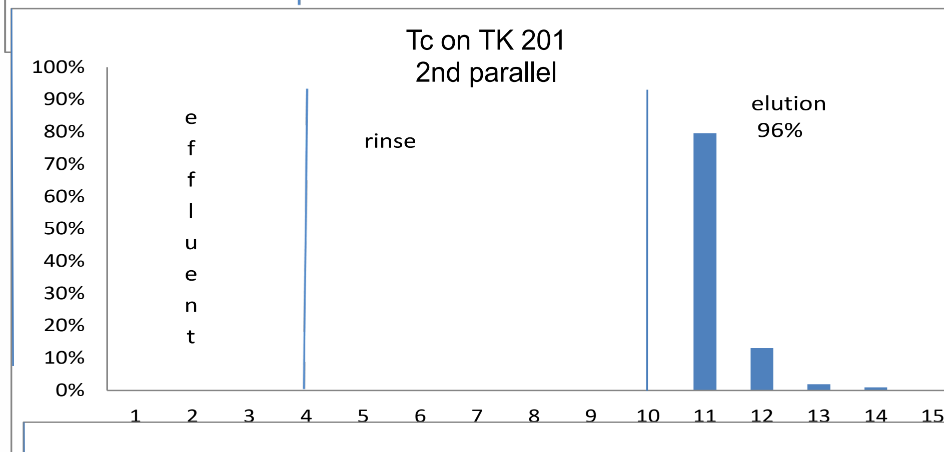
	Load	Rinse 0,01M HNO3	Rinse H2O	Elution 2M NH4OH	Load+ Rinse
Mo	93,0%	8,3%	0,8%	5,5%	**102,1%**
Cs	101,3%	0,1%	0,0%	0%	**101,3%**
Re	0,0%	6,2%	0,3%	106,6%	**6,5%**
Ru	101,3%	0,5%	0,5%	0,4%	**102,2%**
Sr	100,7%	0,3%	0,1%	0,0%	**101,0%**
U	100,0%	1,1%	0,9%	0,4%	**102,0%**

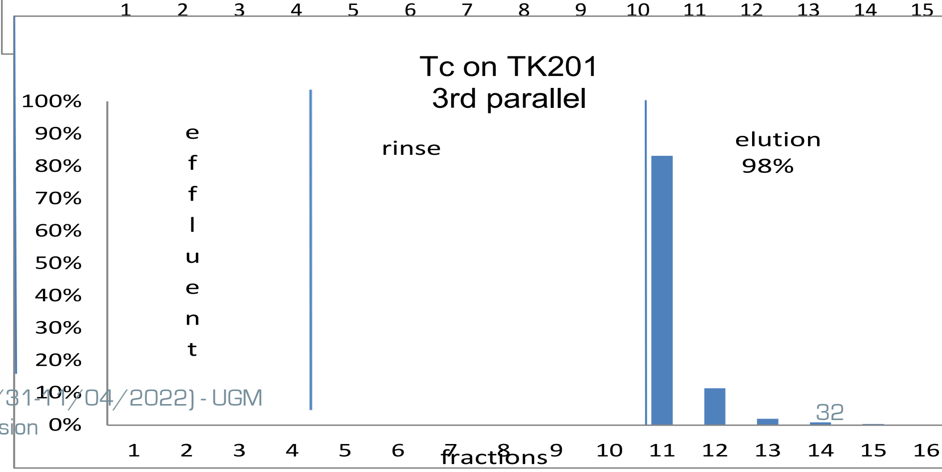


TK201 membranes: Tc separation

fraction		1st parallel		2nd parallel		3rd parallel	
		eluted %	unc %	eluted %	unc %	eluted %	unc %
1	Ef1	LD	-	LD	-	LD	-
2	Ef2	LD	-	LD	-	LD	-
3	Ef3	LD	-	LD	-	LD	-
4	Ef4	LD	-	LD	-	LD	-
5	R1	LD	-	LD	-	LD	-
6	R2	LD	-	LD	-	LD	-
7	R3	LD	-	LD	-	LD	-
8	R4	LD	-	LD	-	LD	-
9	R5	LD	-	LD	-	LD	-
10	R6	LD	-	LD	-	LD	-
11	El1	81.5%	0.5	79.6%	0.5	83.2%	0.5
12	El2	10.1%	1	13.1%	1	11.4%	1
13	El3	3%	2	1.9%	3	1.9%	3
14	El4	1%	5	1.0%	4	0.9%	5
15	El5					0.4%	9
16	El6					0.1%	20
Eluent yield %		95%		96%		98%	
Total yield %		95%		96%		98%	





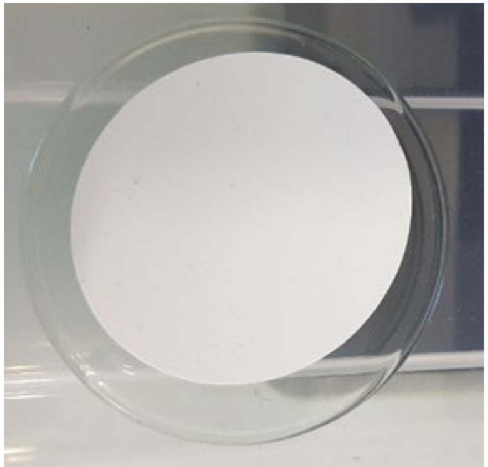


- Tc **fully retained** on TK201 disc from 1 L tap water acidified with HNO_3 @ pH 2 spiked with Tc,
- <u>**NO**</u> Tc leakage detected during loading nor rinsing steps,
- **> 95% of Tc eluted/recovered** with 20 mL 2M NH_4OH.

TK201 membranes: Bi/Pb separation

MOP:

- Pre-conditionning : 10mL 10%EtOH + 5ml 1M HCl
- Load : 100mL solution 1M HCl spiked with 0,1µg/ml Pb, Bi – flow-rate 10ml/min (600ml/h)
- Rinses : 3x10mL 1M HCl



Results:

Metal	Load + Rinses fraction yield (%)
Pb	94 +/- 1
Bi	<1%

- Pb is not retained on TK201
- Bi fully is retained
- Possibly Po is retained => to be tested

Under development – TK102 Resin

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

TK102 Resin - Determination of Kd values

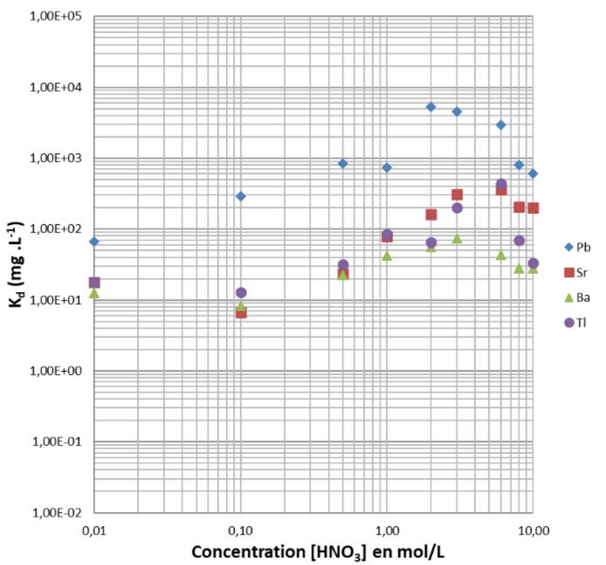


Fig. 1: Distribution coefficients of selected elements on TK102 Resin in HNO_3

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

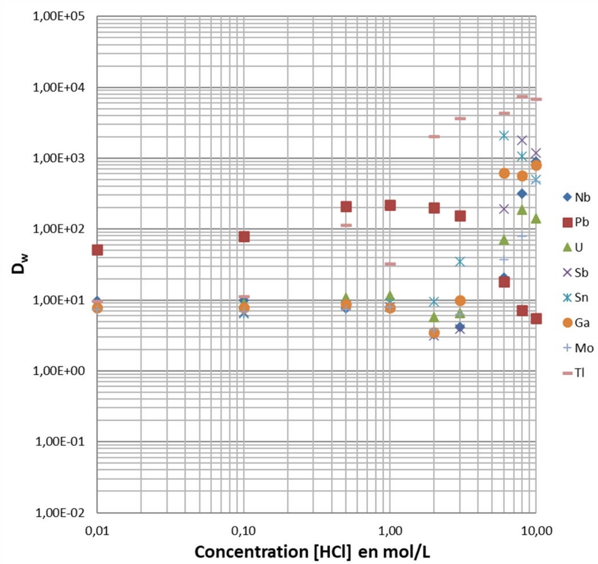


Fig. 2: Distribution coefficients of selected elements on TK102 Resin in HCl

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

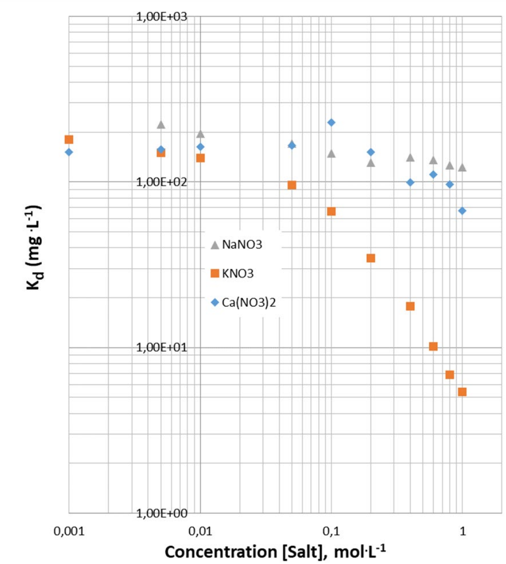


Fig. 3: Distribution coefficients of Sr on TK102 Resin in 3 M HNO_3 in the presence of different salts

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

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

TK102 Resin - Determination of capacity (column experiment)

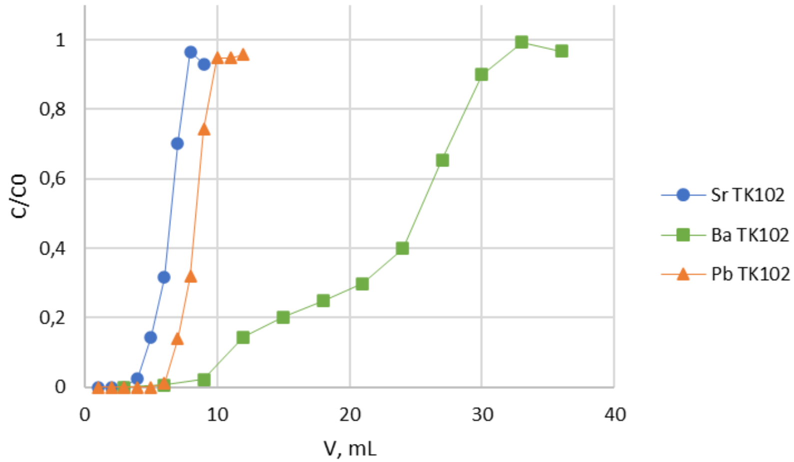


Fig. 4. Sorption curves of Sr, Ba and Pb on TK102.

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

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

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

TK102 Resin - Determination of capacity (Langmier isotherm)

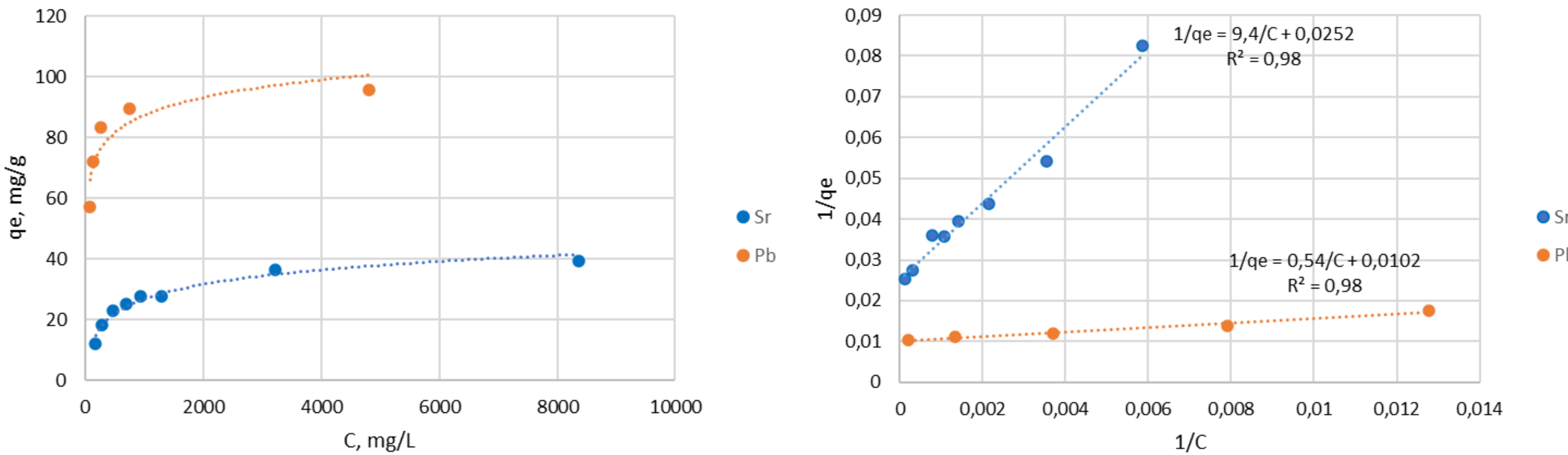


Fig. 5. Sr sorption isotherms with TK102: q_e – C plot (a), linearized in coordinates: $1/q_e$ – 1 / C plot (b),

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

TK102 Resin – Elution curves comparison Vs SR Resin regarding Sr

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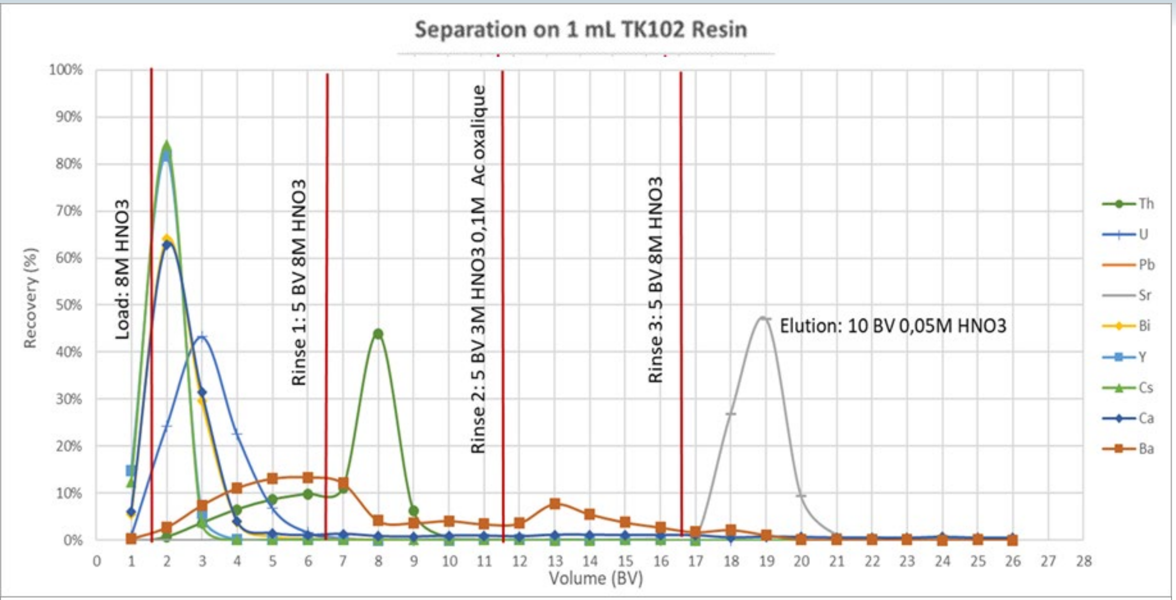
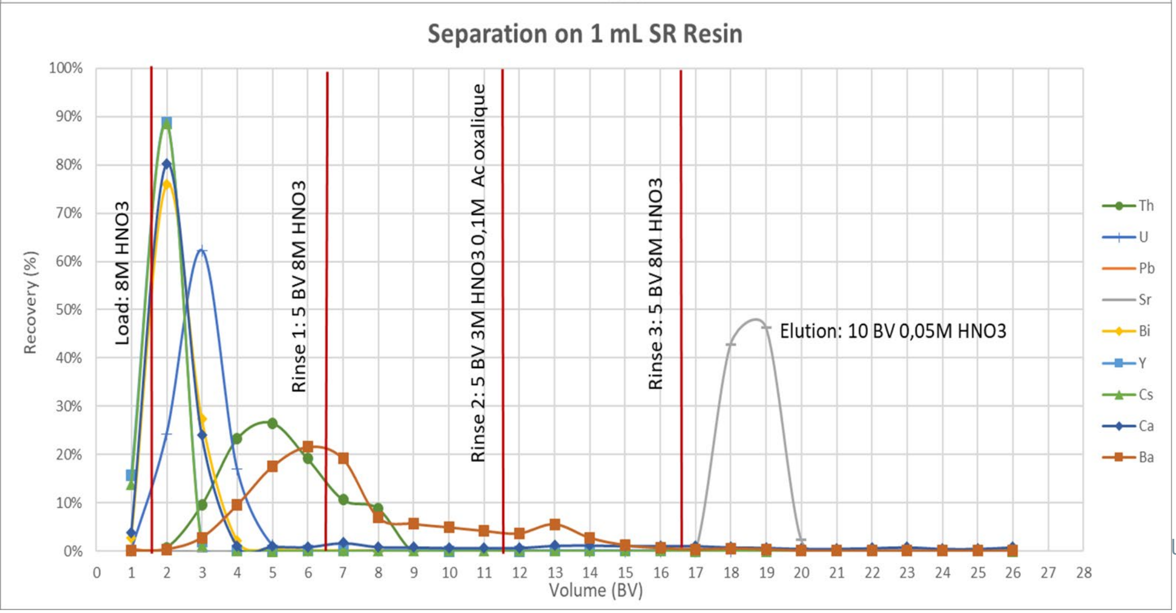
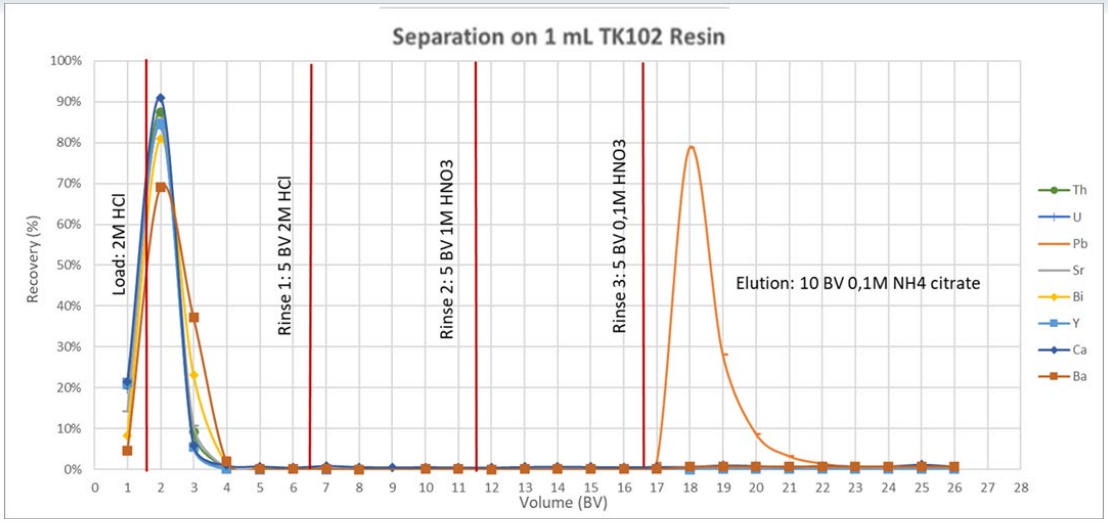


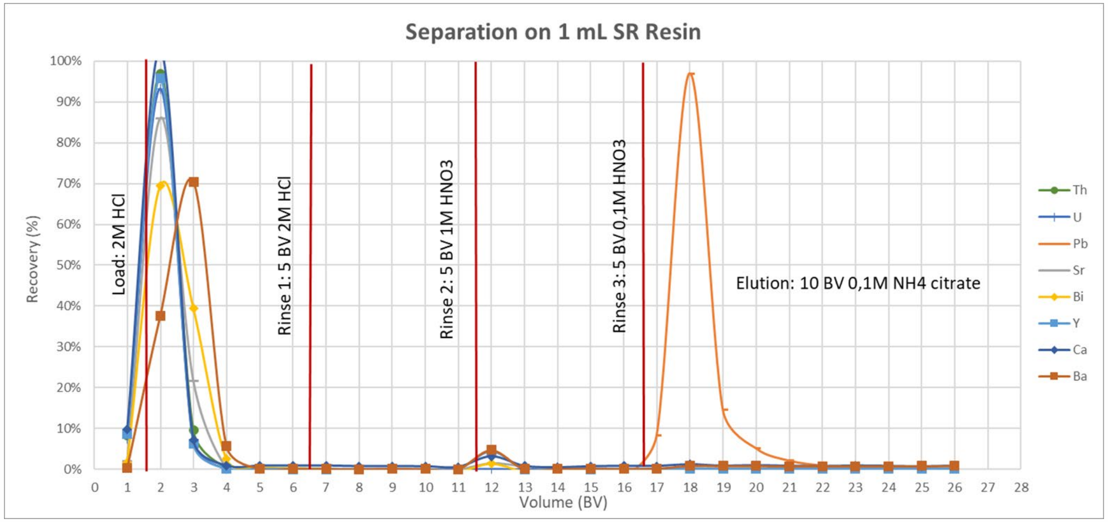


TK102 Resin vs SR resin:
Sr elution study in 8M HNO_3 load medium

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

TK102 Resin – Elution curves comparison vs SR Resin regarding Pb

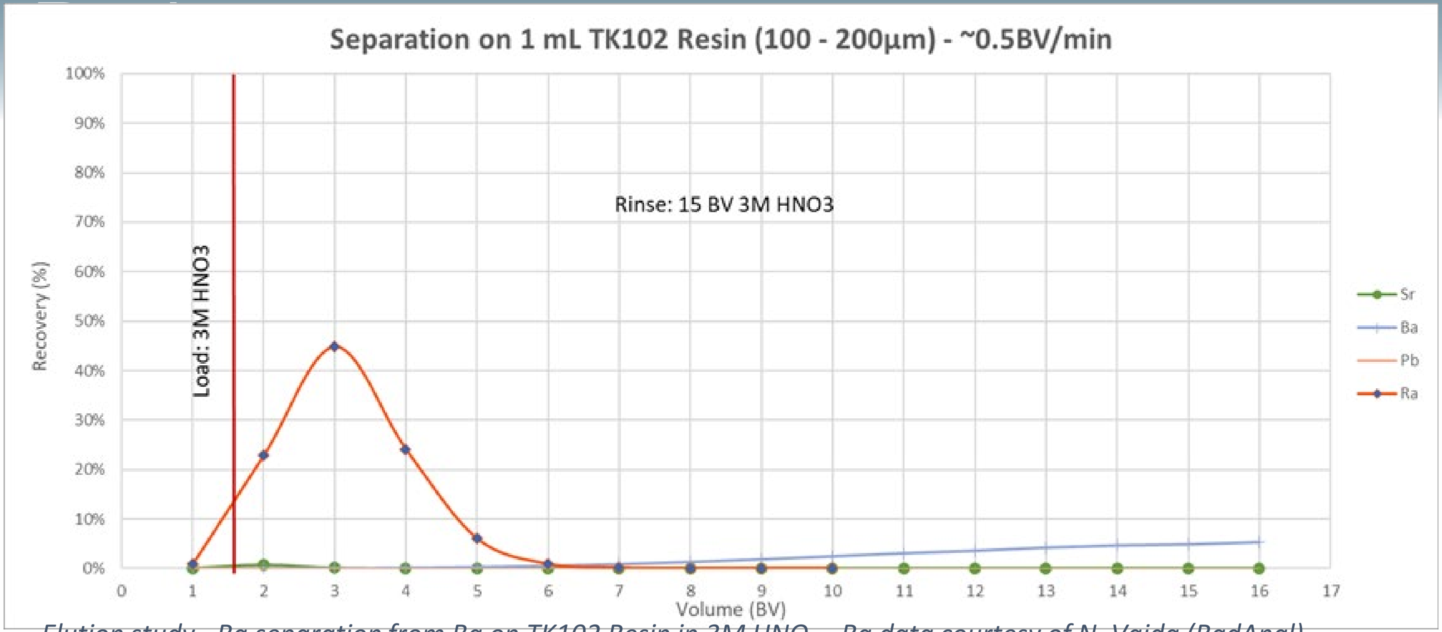




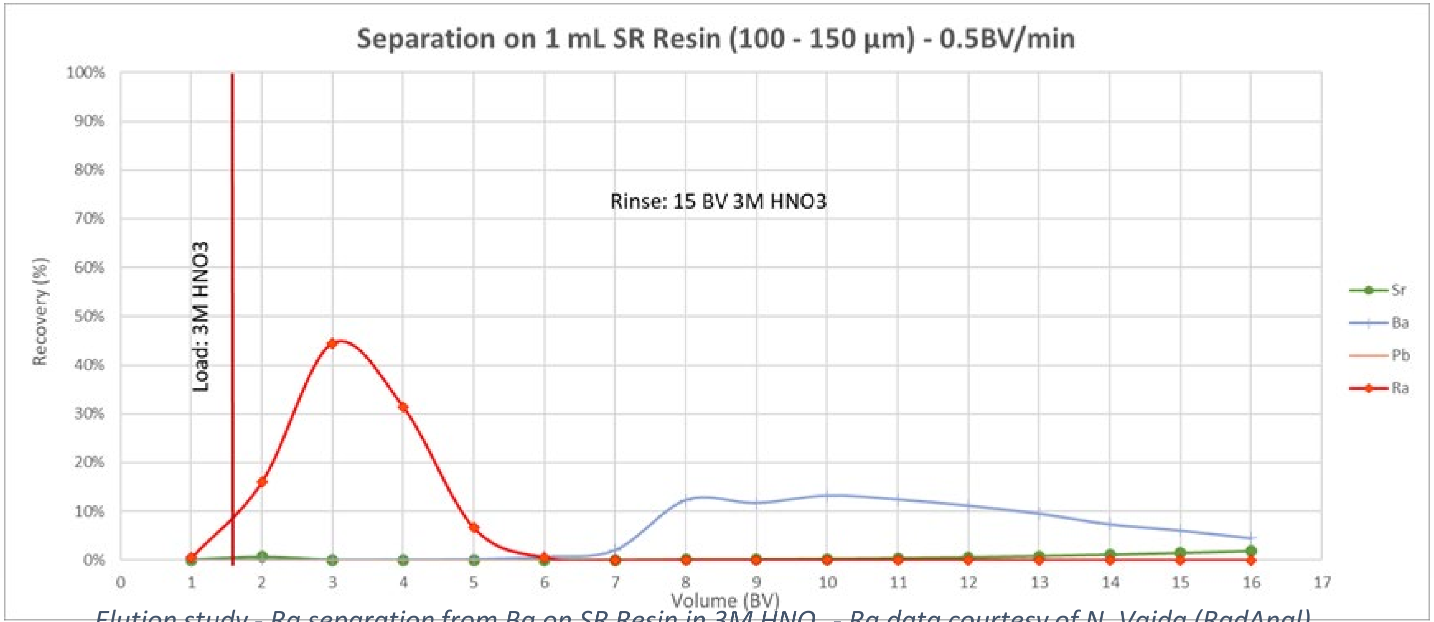
TK102 Resin vs SR resin:
Pb elution study with 2M HCl loading medium

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

TK102 Resin – Ba/Ra behaviour vs SR Resin



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



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

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

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Under development – Radium Resin for environmental purposes

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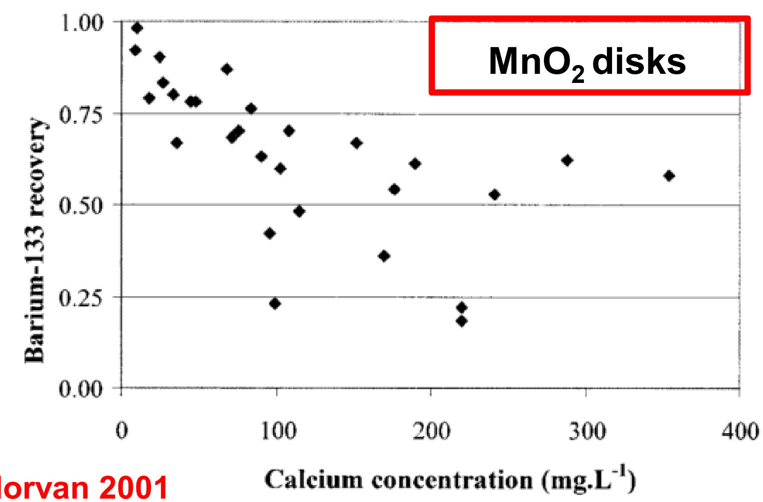
- Work done by S. Khalfallah and continued with Dr. Fenqgi XU

Background: Ra separation techniques

- **Fractional precipitation $RaCl_2$**
- **Ion exchange columns**: ammonium citrate/EDTA
- **Co-precipitation**: $BaSO_4$/$BaCO_3$
- **Synthetic clay**: Na-4-mica ($Na_4Al_4Si_4Mg_6O_{20}F_4 \cdot xH_2O$)
- **MnO_2 (resin, disks, fibers)**: Most common used procedure

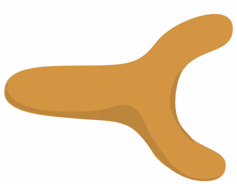


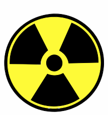
Morvan 2001

Limited applicability

Alternative approach

MRT: Molecular Recognition Technology





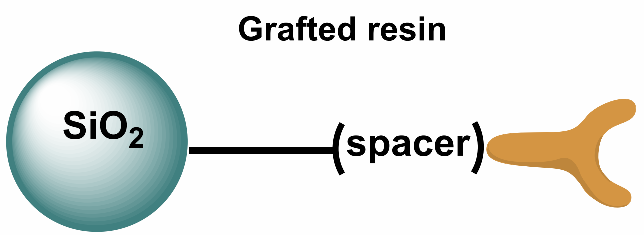
Non-ion exchange process, using specially designed organic chelating agents.

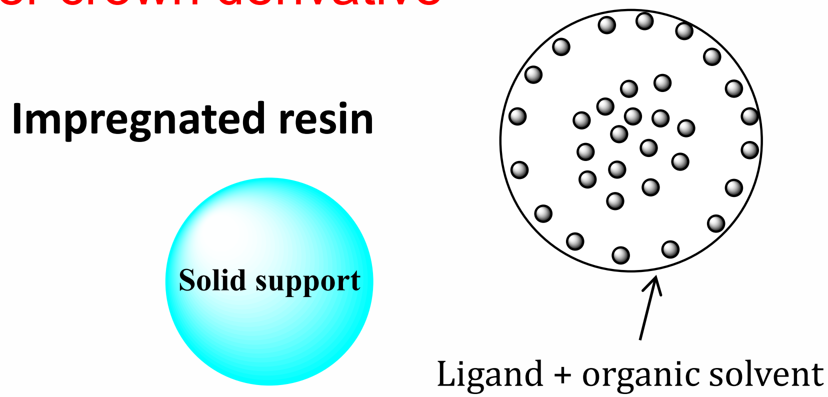
Our developed Ra resins

Chelating agent choice

- **Ra ion radius ≈ 1.7 Å**: adapted cavity
- **Ra hard Lewis acid**: Oxygen donor
- **Ra coordination sphere :** 8-12 (solid phase)

→Chelating agent: Ether crown derivative

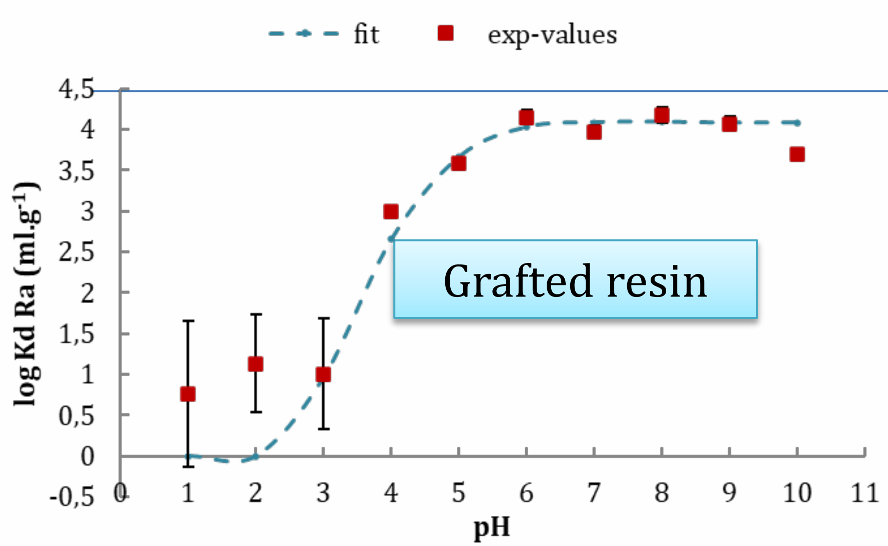


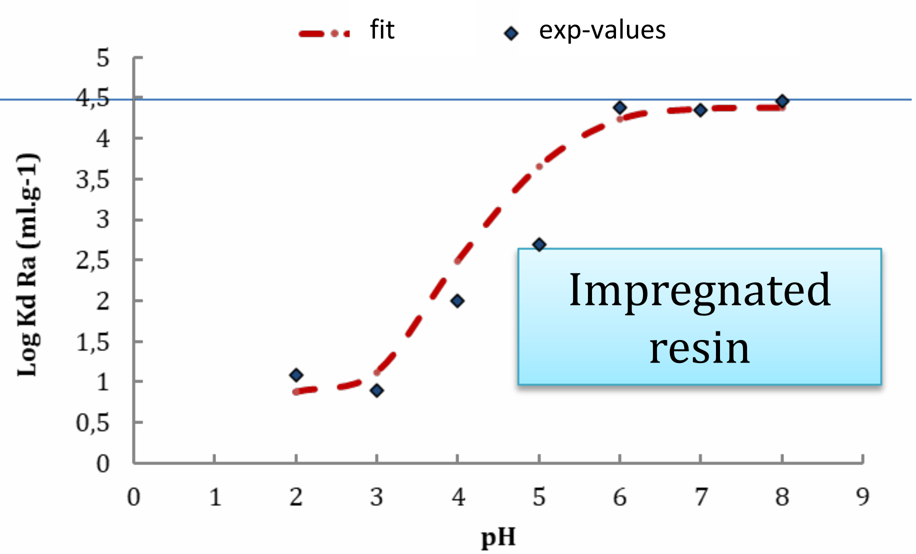


- **Solid Support:** SiO_2 100 mesh.
- **Spacer:** short alkyl chain.

- **Solid Support:** aliphatic polymer (acrylic ester)
- **Solvent:** Fluorinated alcohol

Resin applicability conditions: effective pH range





- No sorption was detected for pH ≤3 (Grafted resin), pH ≤4 (Impregnated resin),
- Maximum adsorption is reached over pH 5 (grafted resin) and over pH 6 (impregnated resin)

➢ In acidic conditions the extractive molecule is protonated and no neutral complexes can be formed in the presence of Ra^{2+}

➢ With the organic solvent, the deprotonation is delayed.

Grafted Ra-Resin: kinetics behavior investigations

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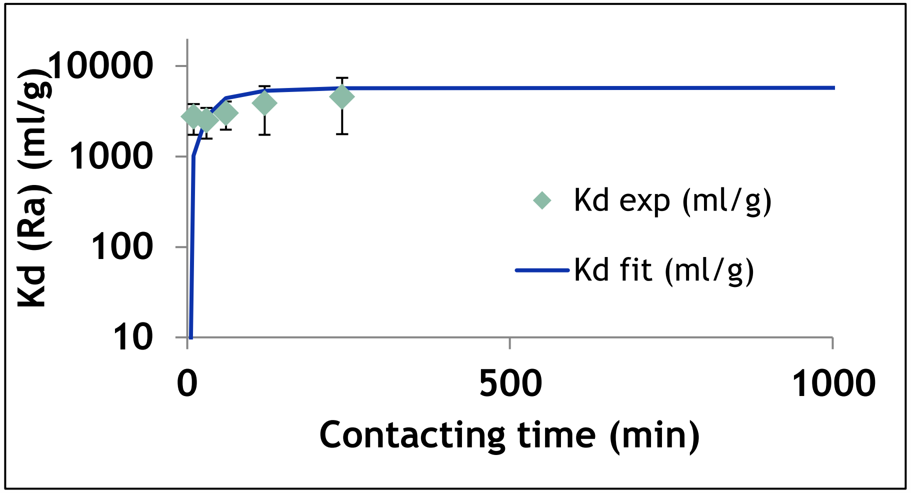
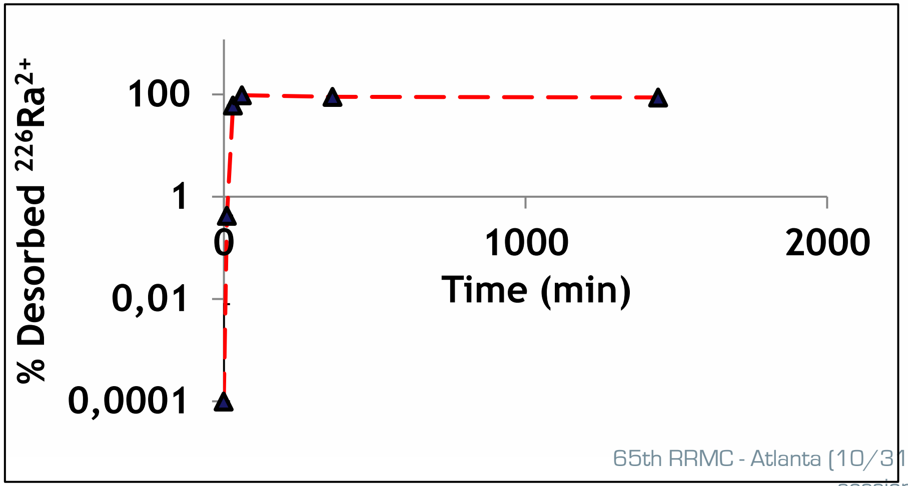
Ra uptake (pH=7)



→ > 80% of $^{226}Ra^{2+}$ adsorbed after 10 min of contact.: **Rapid kinetics**

Ra desorption (pH<0)



→ **Rapid** desorption and reversible process:

Starting material **Regeneration**

Effect of salt on Ra adsorption on Grafted Ra resin (GR)

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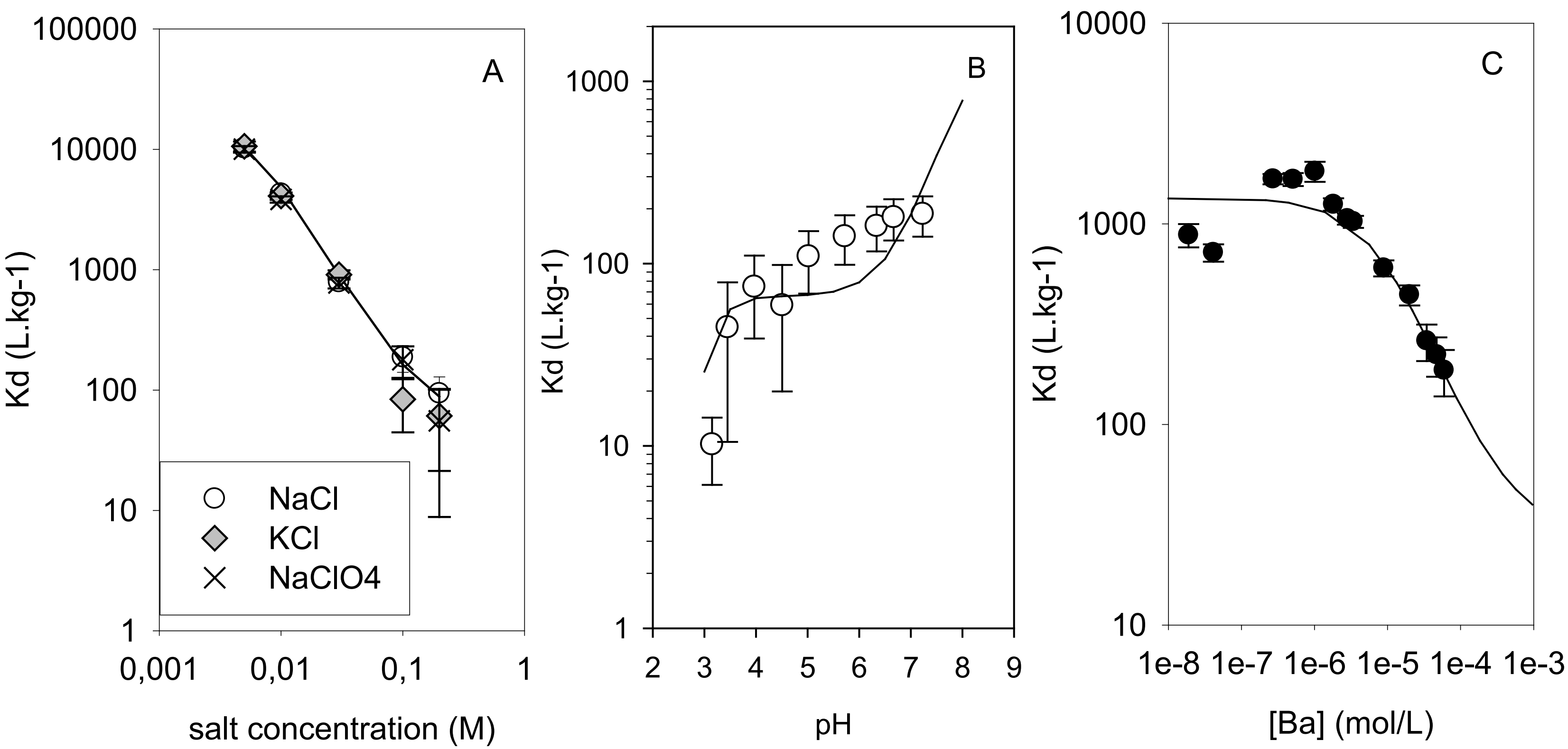
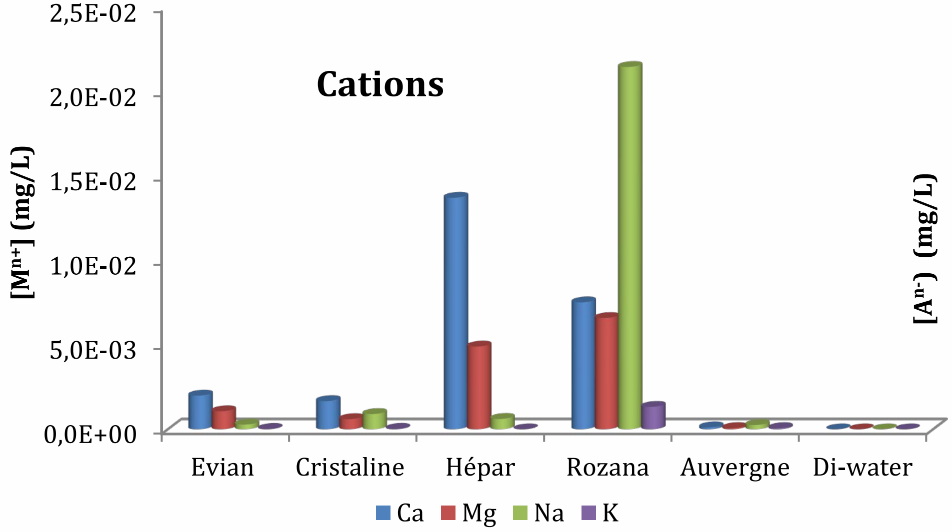
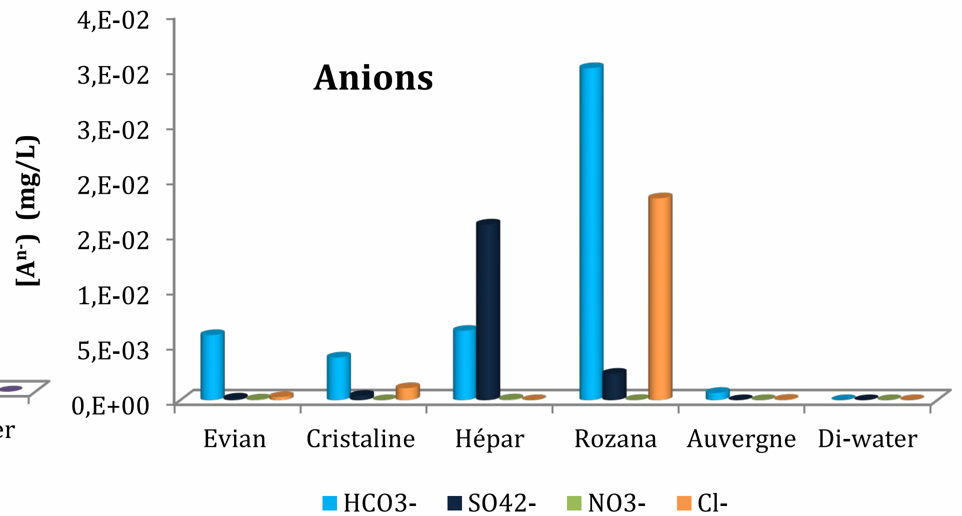


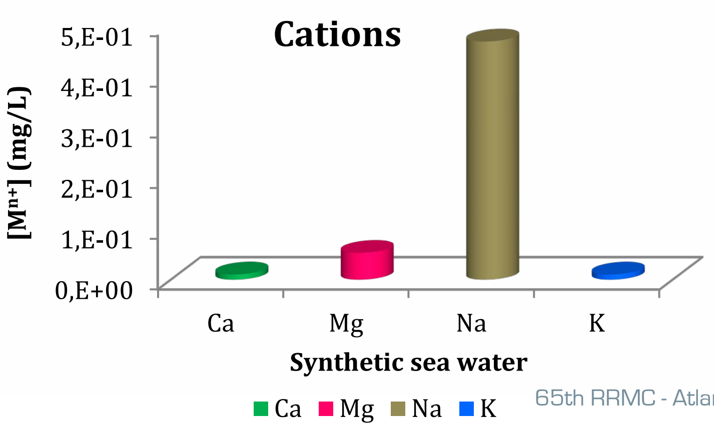
Sorption of Ra and Ba on GR in salty waters; m/V of 1 g.L^{-1}. (A) Effect of the type of salt and its concentration on Ra adsorption; pH=7.0 ± 0.1;. (B) Effect of the pH on Ra adsorption in 0.1M NaCl. (C) Sorption isotherm in concentration for Ba in the presence of 9.2 10^{-3} M of NaCl.

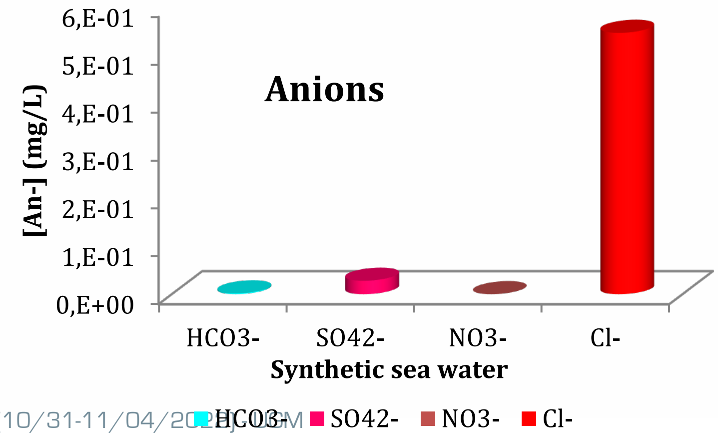
Application: results from French mineral waters

Chosen waters









Ra uptake tests using different spiked chosen waters

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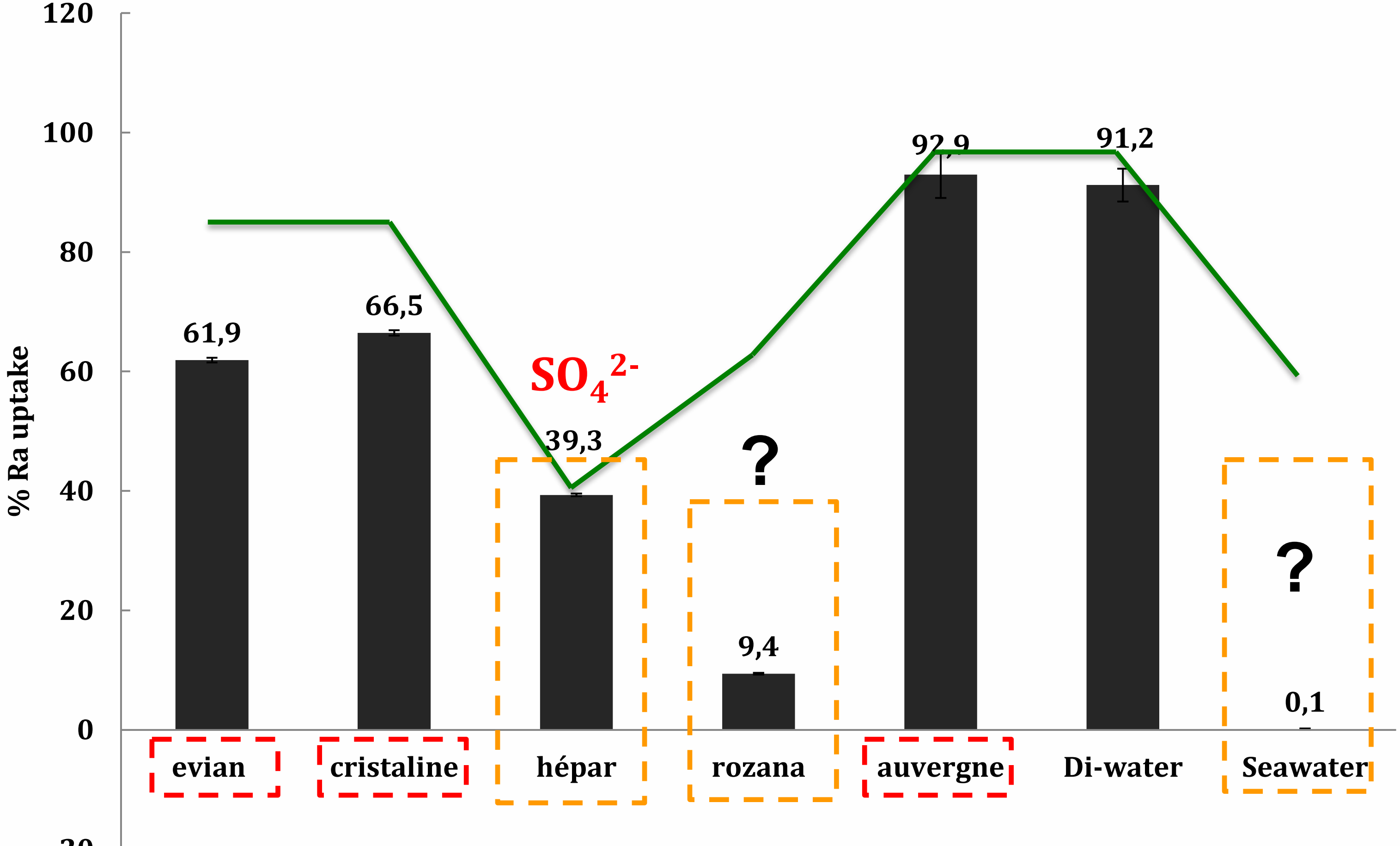

Batch experiments; solid/liquid ratio =1g/L

Radium resin

- Both graphted and impregnated resins work @pH>3-4
- No sorption below pH 3
- For waters rich in salts, Ra uptake is impacted
- Resin under further testing

Under development

- TK222
  - TEH-DGA version of TK221 resin

- TK225
  - Resin based on TO-DGA and ionic liquid
  - Selectivity similar to DGA,N Resin
  - Presence of ionic liquid => increase of the selectivity towards trivalent elements (difficult to remove from the resin)

Production of « industrial » extraction chromatographic resins

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

see S. Happel's presentation after the break

Thank you for your attention!

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