Extraction Chromatographic Resins, News Triskem International

Irtech Technical Workshop, 21-22nd May 2024 - Krakow

TRISKEM
Expertise in Separation Chemistry

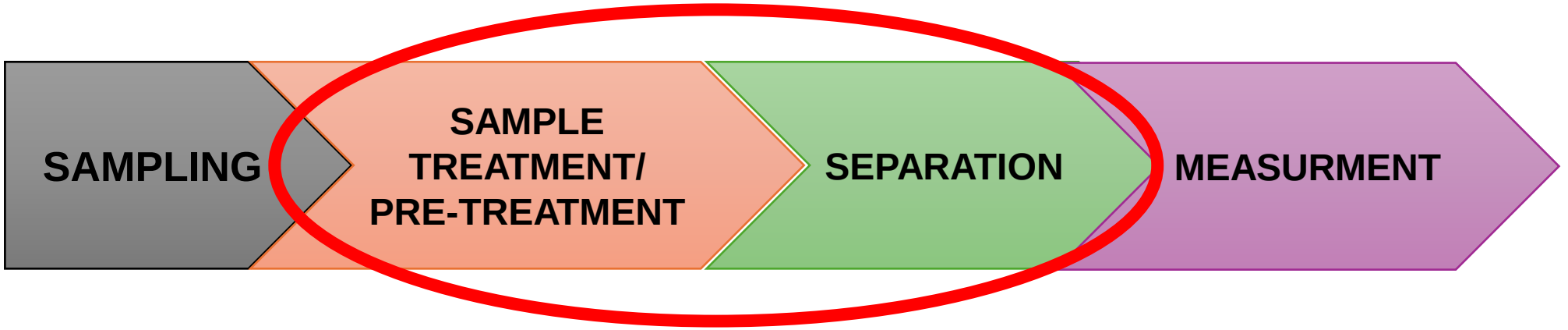
Overview

- Extraction chromatograpic resins: principles
- Sample preparation
- Sr separations
- New Resins
  - TK-ELScint: TK-SrScint and TK-TcScint
  - TK102
  - TK221
  - TK225
- Methods under development
  - Ra separation
- Conclusions

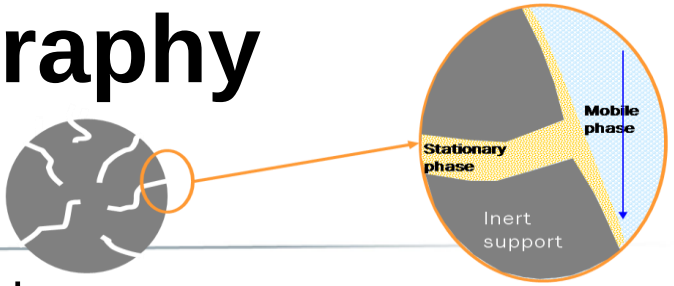
TrisKem International

- Based in Rennes (France)
- Independent company since 02/07
  - Formerly part of Eichrom Europe
  - ISO 9001 since 2007
- Main products: extraction chromatographic resins
- Staff : 22
- R&D, QC and TechSupport group:
  - 5 RadChem PhD, 3 Technicians
- R&D: Development of new resins, techniques and applications
- Products used in several domains

Radionuclides/metals separation



Extraction chromatography Principles

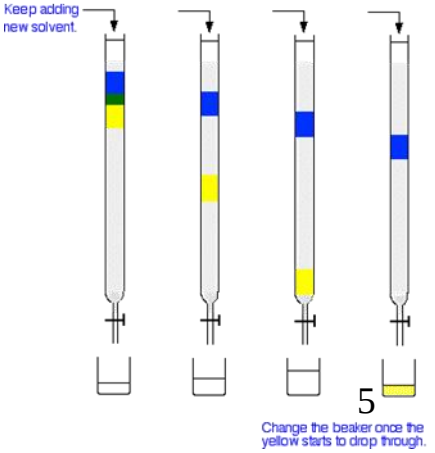


Organic phase impregnated onto an inert support referred as:

« Supported Solvent Extraction » / « Solvent Impregnated Resins »

Combination of liquid/liquid extraction and chromatographic techniques:

- 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:
  - Depending on extractant pure or in mixture used
  - **Aim: selectivity for analyte(s), no selectivity for matrix/ impurities**
- Combining several cartridges can improve/facilitate separation



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'

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

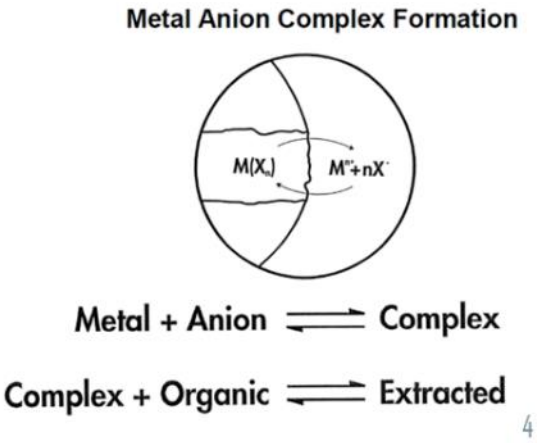
Basic e.g. Aliquat 336 (TEVA Resin)

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

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

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

Horwitz et al.

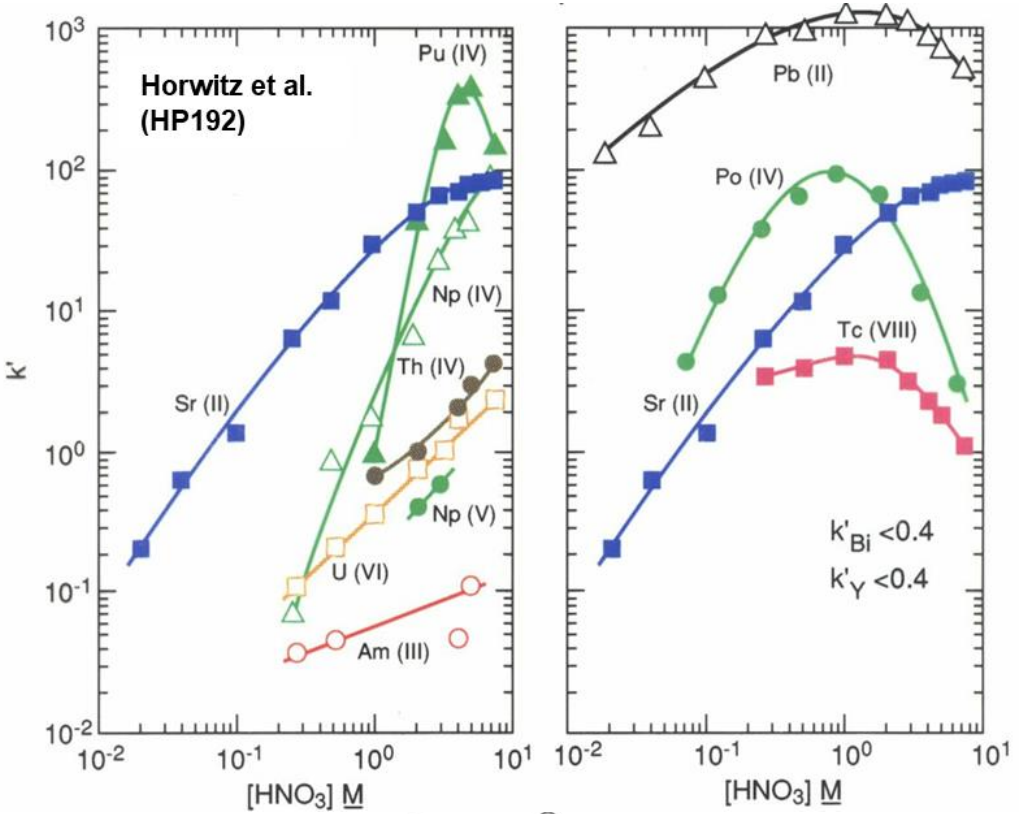


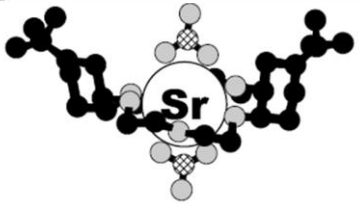
Choice of resin depends on

- Radionuclide/Metal to separate
- Matrix
- Type of measurement

=> Sample preparation = very important step for a good separation

Classic Resins: SR Resin



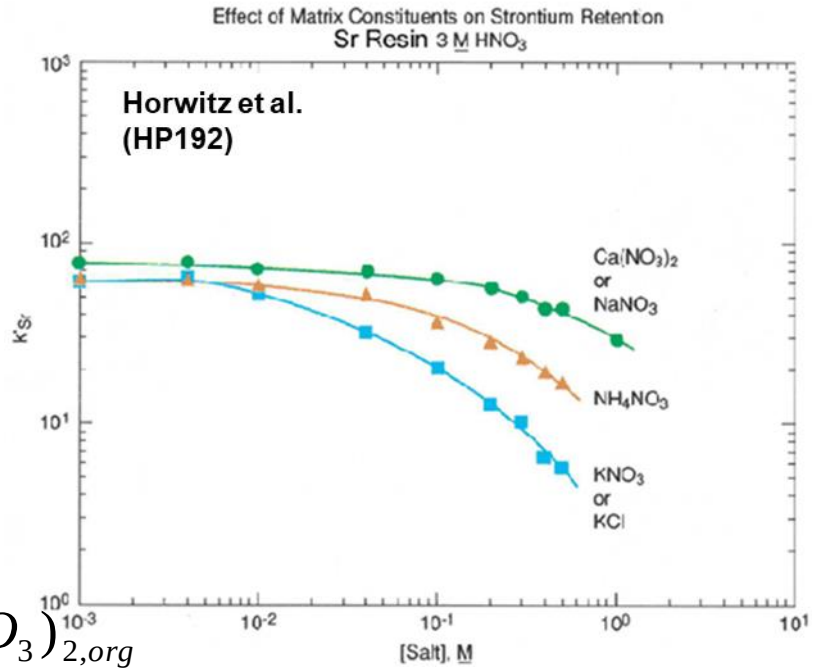


Dietz et al. 2004

Sr uptake 3-8M HNO_3

Elution with low acidic HNO_3 conc or water

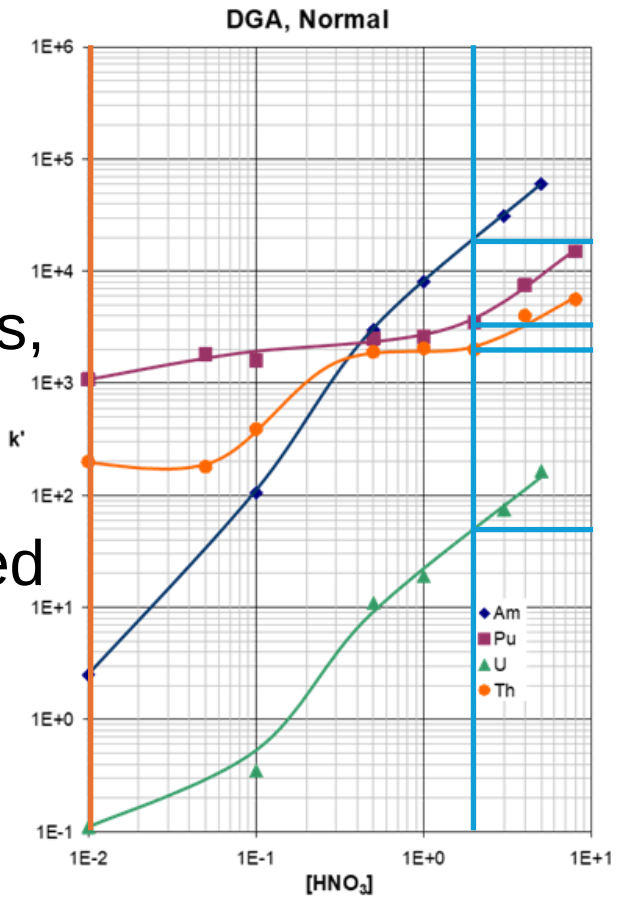
Ca, Na, K, stable Sr can interfere

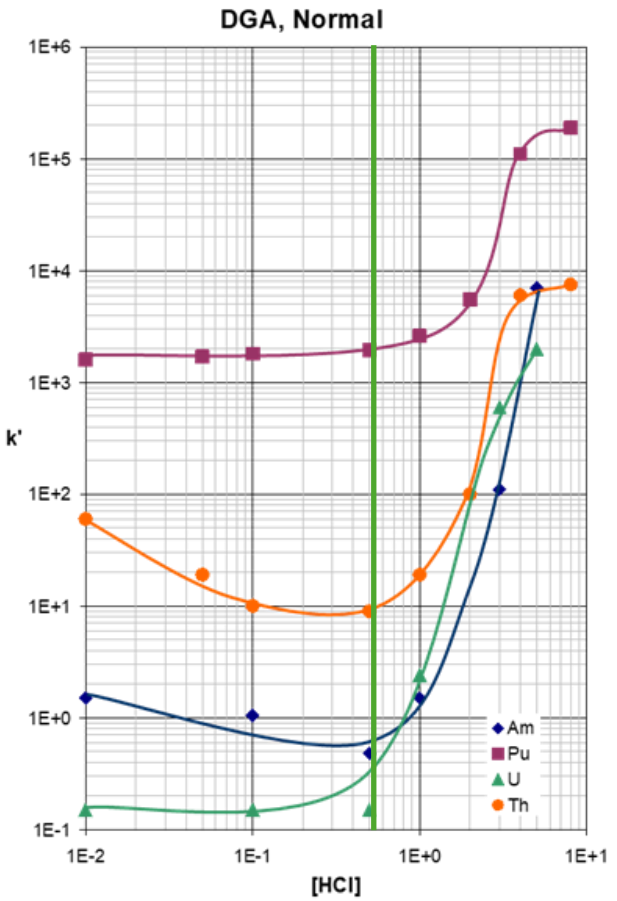


$$Sr_{aq}^{2+} + DCH_{18}C_{6,org} + 2NO_{3,aq}^{-} \Leftrightarrow Sr(DCH_{18}C_{6})(NO_{3})_{2,org}$$

Classic Resins: DGA,N Resin

- Extractant: **DGA, Normal** (N,N,N',N'-tetra-n-octyldiglycolamide)
- Separation of Actinides, especially Am
- Robust against Fe interference, often used for soil samples





Sample preparation

Eliminate the matrix / preconcentrate the elements of interest

Non exhaustive list:

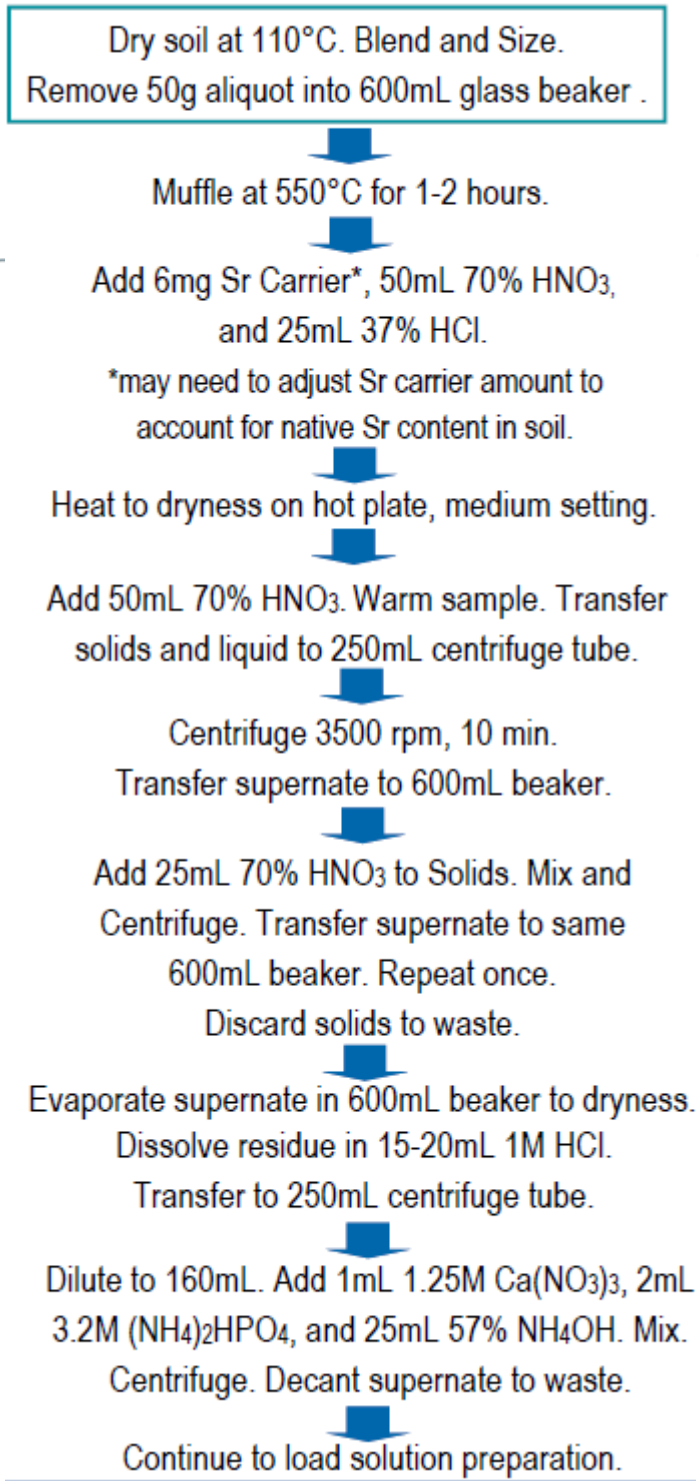
- Alkaline Fusion
- Mineralisation
- Lixiviation
- Coprecipitation
- …

Mineralisation + Coprecipitation

Rapid Determination of Sr in 50g Soil Samples (AN-1403-10):

- Drying @ 110°C, blend/size to easily mineralise (1-2 hours)
- Add carrier* + aqua regia to mineralize the sample
- Heat to dryness + mineralise with 70% HNO_3
- Centrifuge + collect supernate (X2)
- Evaporate supernate + dissolve in 1M HCl
- Coprecipitate Sr with $Ca_3(PO_4)_2$
- Centrifuge + dissolve precipitate

Figure 1. Sample Preparation

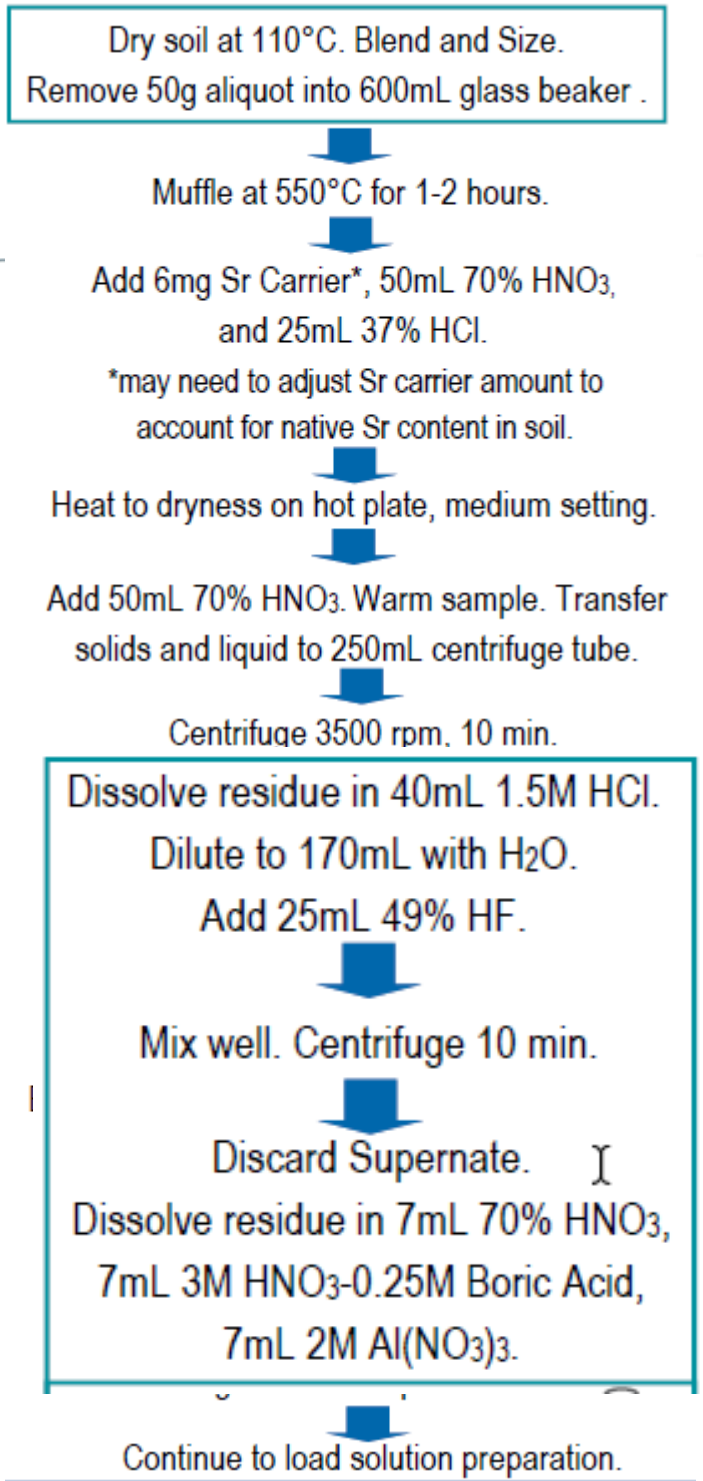


Mineralisation + Coprecipitation

Rapid Determination of Sr in 50g Soil Samples (AN-1403-10):

- Drying @ 110°C, blend/size to easily mineralise (1-2 hours)
- Add carrier* + aqua regia to wet mineralize the sample
- Heat to dryness + mineralise with 70% HNO_3
- Centrifuge + collect supernate (x 2)
- Evaporate supernate + dissolve in 1M HCl
- Coprecipitate Sr with $Ca_3(PO_4)_2$
- Centrifuge + dissolve precipitate
- Coprecipitate Sr with CaF_2
- Centrifuge + dissolve precipitate
- ➢ **Load solution**

Figure 1. Sample Preparation

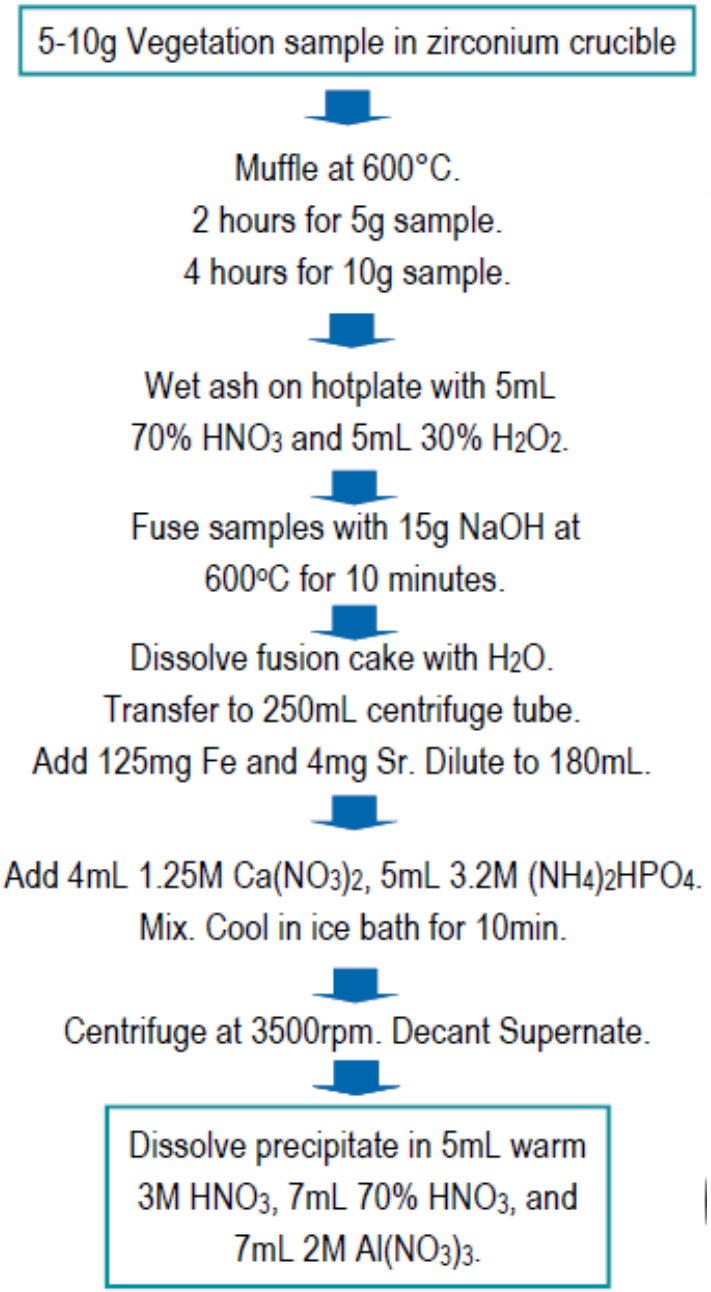


Alkaline fusion + Coprecipitation

Rapid determination of SR in vegetation samples (AN-1405-10):

- Sample drying (2-4 hours)
- Wet mineralization with 70% HNO_3 + H_2O_2
- Fusion (15g NaOH for 5-10g sample) – (10 minutes)
- Dissolution + add carrier + Fe
- Coprecipitation with $Ca_3(PO_4)_2$ and $Fe(OH)_3$
- Centrifuge + dissolve precipitate
- ➢ **Load solution**

Figure 1. Sample Preparation

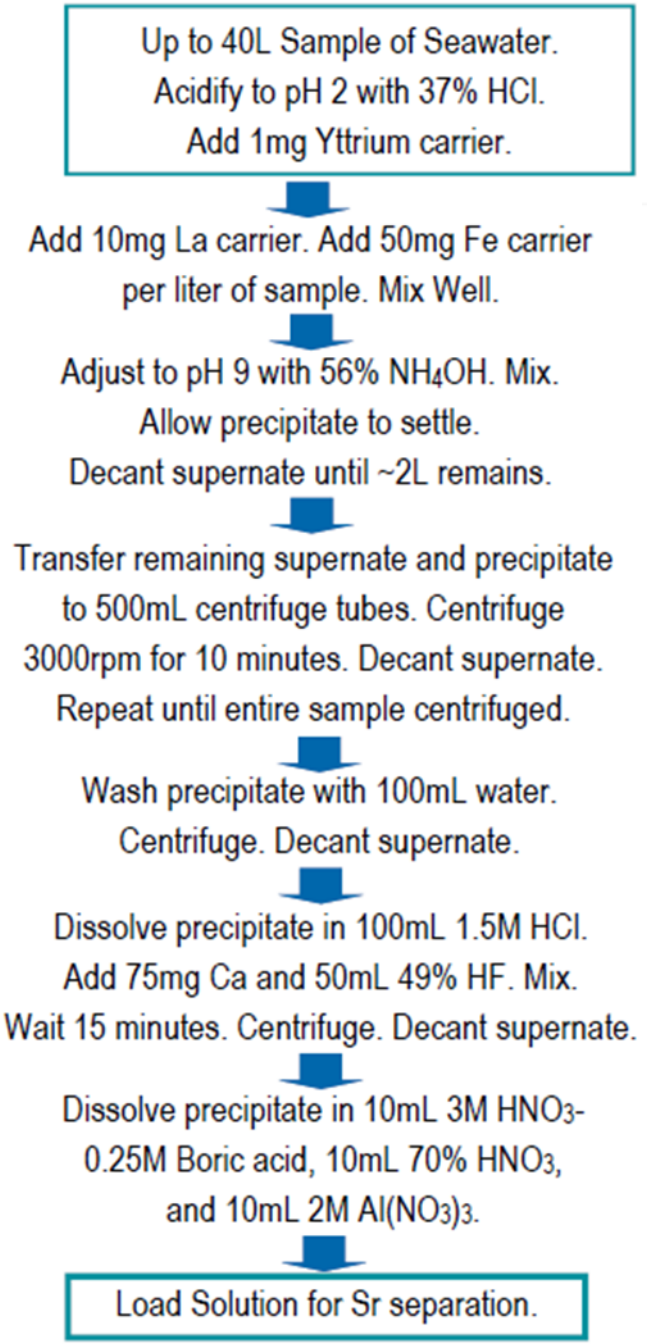


Coprecipitations

Rapid Determination of 90Sr in up to 40 Liter Seawater Samples (AN-1414-10):

- Acidification to pH2 + Y+La+Fe carriers
- $Fe(OH)_3$ coprecipitation
- Centrifuge
- Dissolve precipitate in 1.5M HCl + Ca carrier + HF
- CaF_2 coprecipitation
- Centrifuge + Dissolve precipitate
- ➢ **Load solution**

Figure 1. Sample Preparation

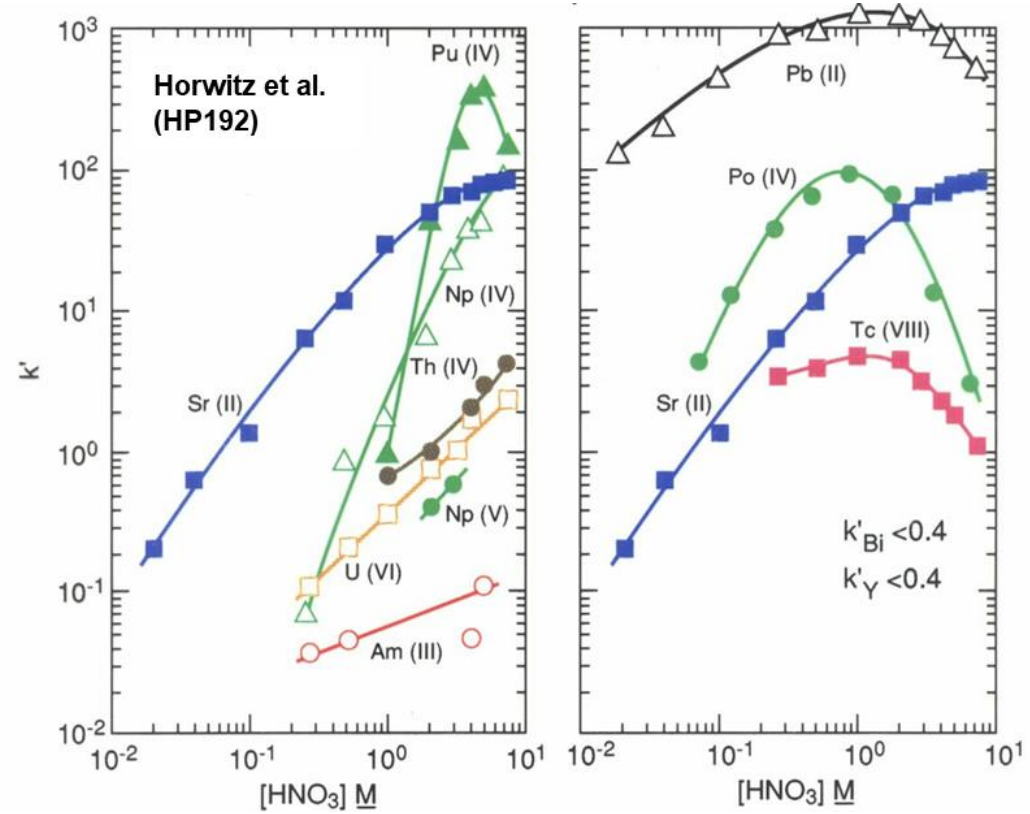


SR separations

SR separation in vegetation and soils (SR Resin)

AN-1403-10/AN-1407-10

1. Precondition SR Resin with 10ml 8M HNO_3
2. Load sample solution
3. Rinse beaker with 5ml 8M HNO_3, add rinse to SR resin
4. Rinse SR Resin with:
   - 15ml 8M HNO_3
   - 10ml 3M HNO_3-0.05M $H_2C_2O_4$
   - 10ml 8M HNO_3
5. Elute Sr with 20ml 0,05M HNO_3



SR separations

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   - 10ml 8M HNO_3
5. Elute Sr with 20ml 0,05M HNO_3

SR separation in 40L seawater (DGA Resin)

AN-1414-10

1. Precondition DGA,N Resin with 5ml 8M HNO_3
2. Load sample solution
3. Rinse beaker with 5ml 8M HNO_3, add rinse to DGA,N Resin
4. Rinse DGA,N Resin with:
   - 15ml 8M HNO_3 (Ca, Sr, Pb)
   - 20ml 0,05M HNO_3 (La, Ce, Sr, U)
   - 10ml 3M HNO_3-0.25M HF (U,Th)
   - 10ml 3M HCl (Ca, La, Pb)
5. Elute Y with 20ml 0,25M HCl

New Resins

TK-ElScint Resins – scintillating resins

UNIVERSITAT DE BARCELONA

=> presentation by Ines Llopart right after this presentation

TK102 Resin

- Modified version of SR Resin
  - Same crown-ether
  - Solvent, inert support and ratios => different
  - Solvent is a fluorinated alcohol
- Distribution coefficient Kd ~50% higher (Pb, Sr, Ba)
- Higher capacity (Pb and Sr)
- SR resin separation procedures can be transposed on TK102
- Specific separating methods under development

TK102 Resin – Kd values

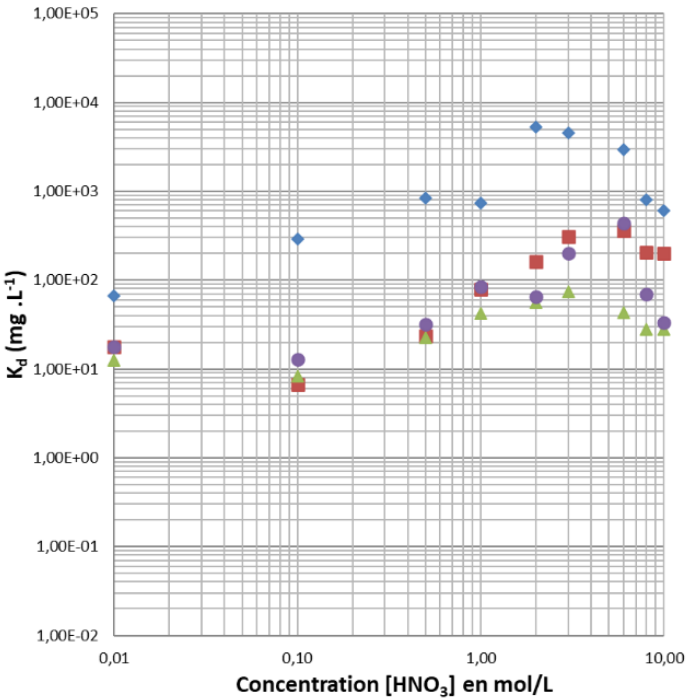


Fig. 1: Distribution coefficients of selected elements on TK102 Resin in HNO_3

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

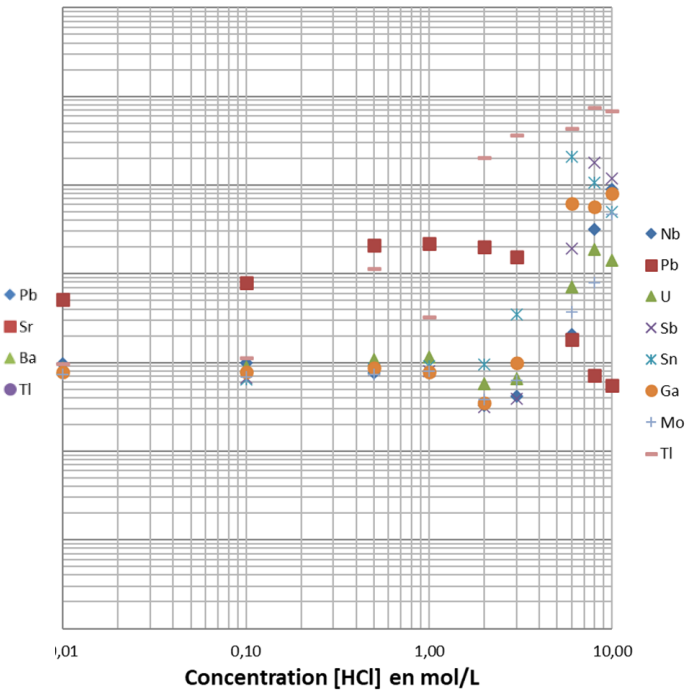


Fig. 2: Distribution coefficients of selected elements on TK102 Resin in HCl

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

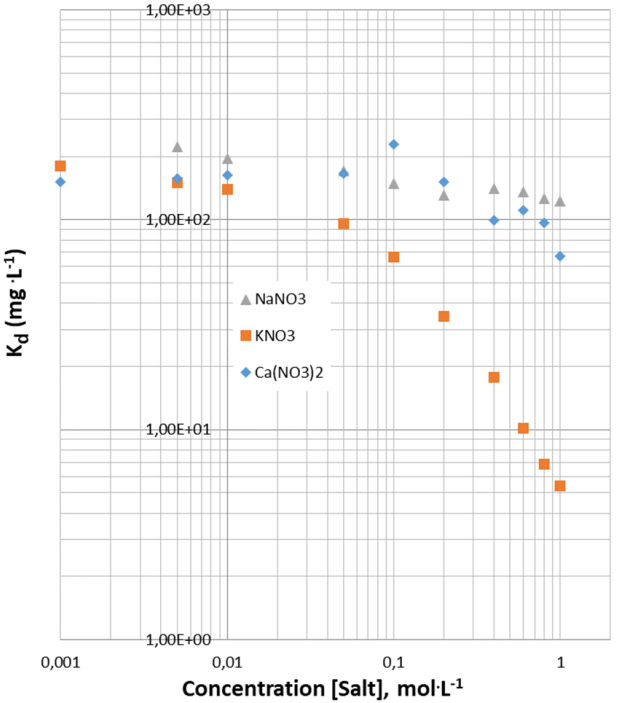
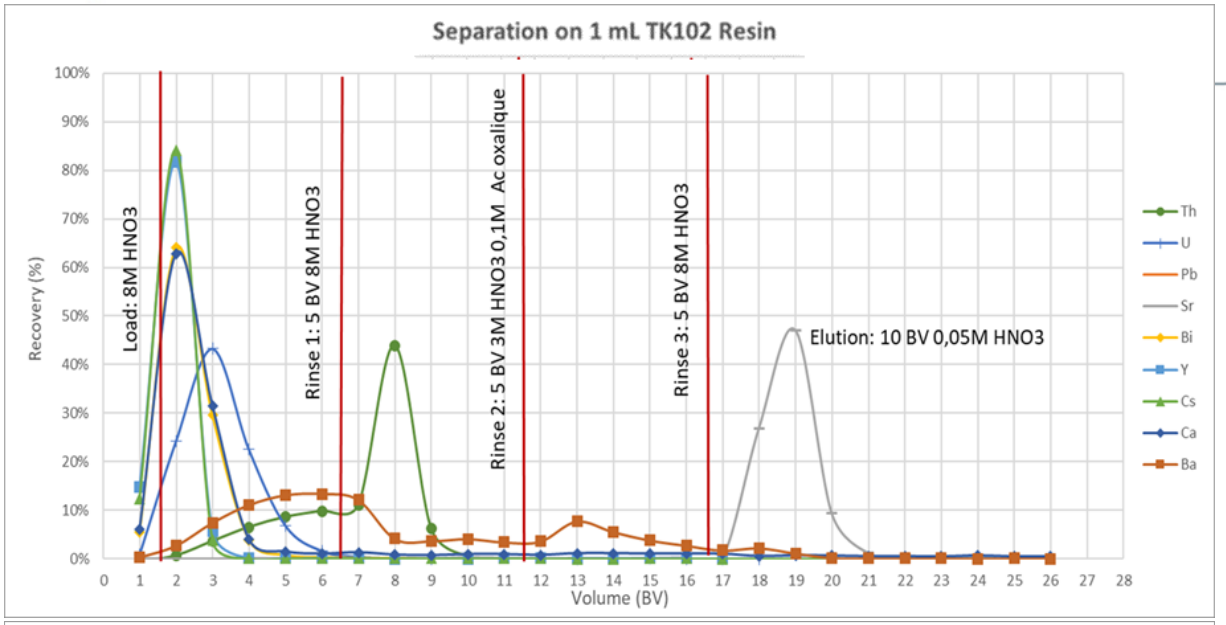


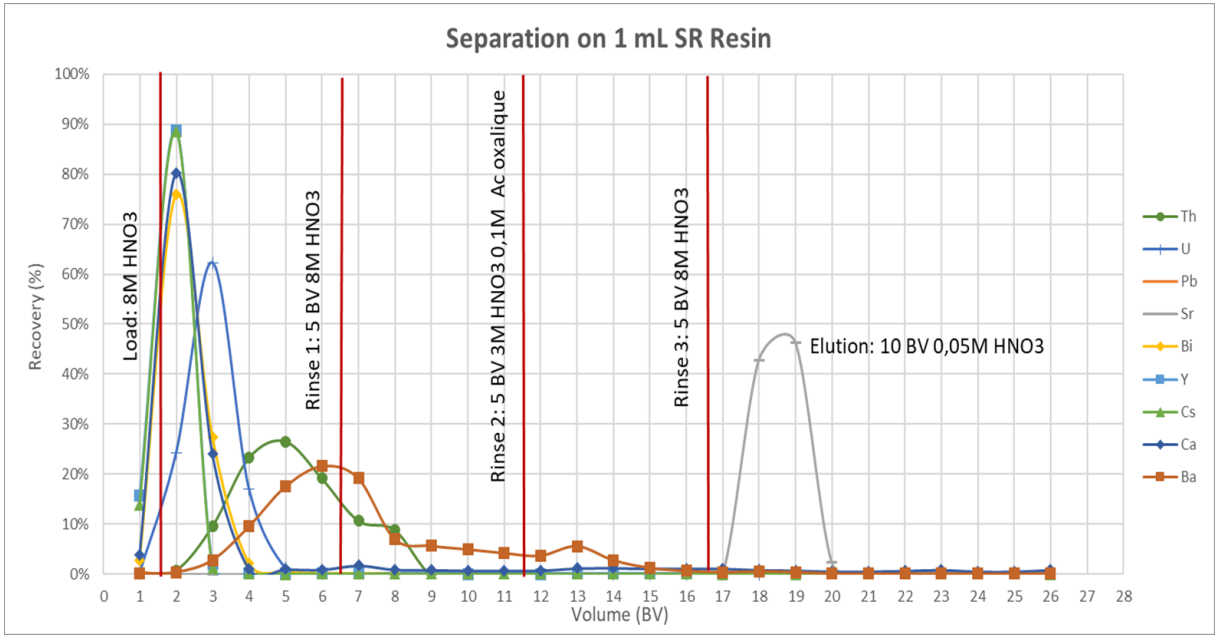
Fig. 3: Distribution coefficients of Sr on TK102 Resin in 3 M HNO_3 in the presence of different salts

►D_w Sr decreases with KNO_3 starting at 0,05 M,

► no effect of $NaNO_3$ and $Ca(NO_3)_2$ up to 1 M.

TK102 Resin – Sr separation

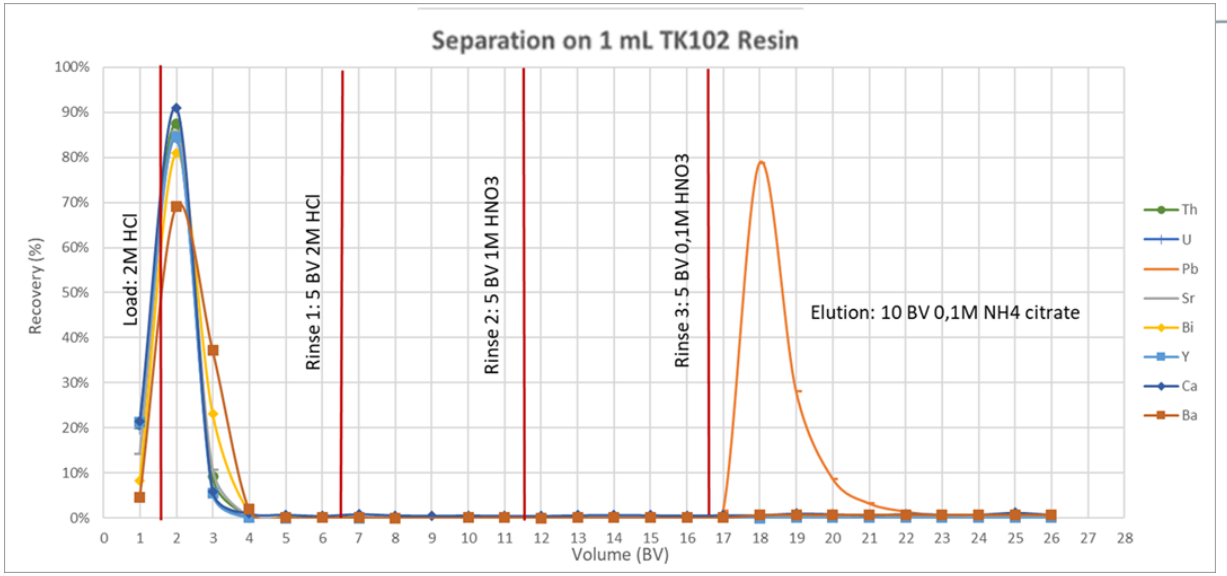


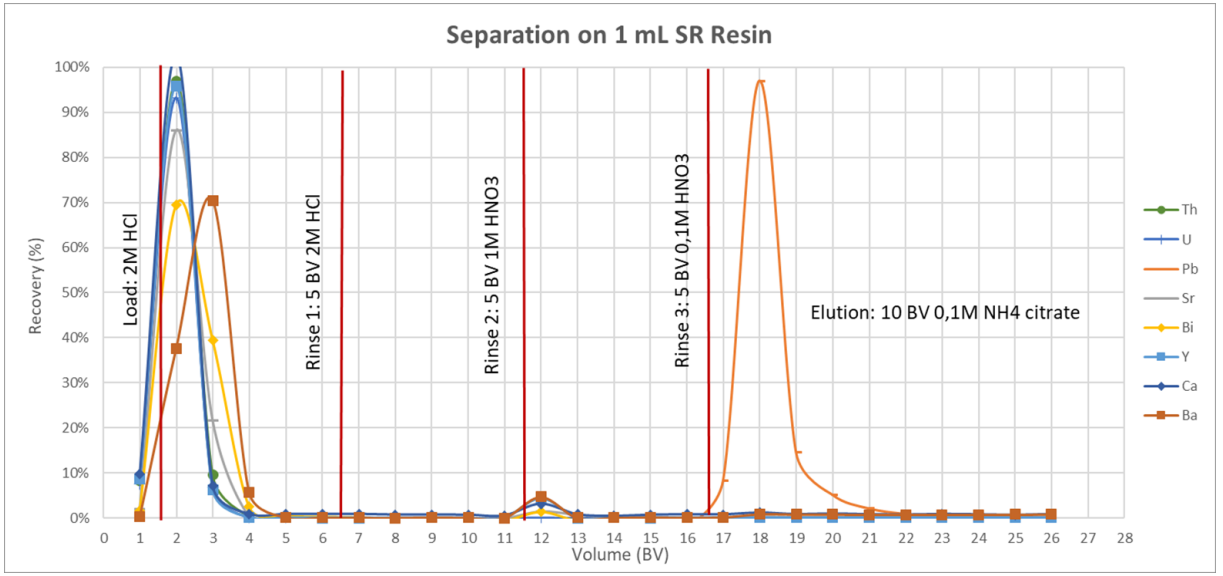


Sr elution study in 8M HNO_3 load medium

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

TK102 Resin – Lead separation





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/Ba

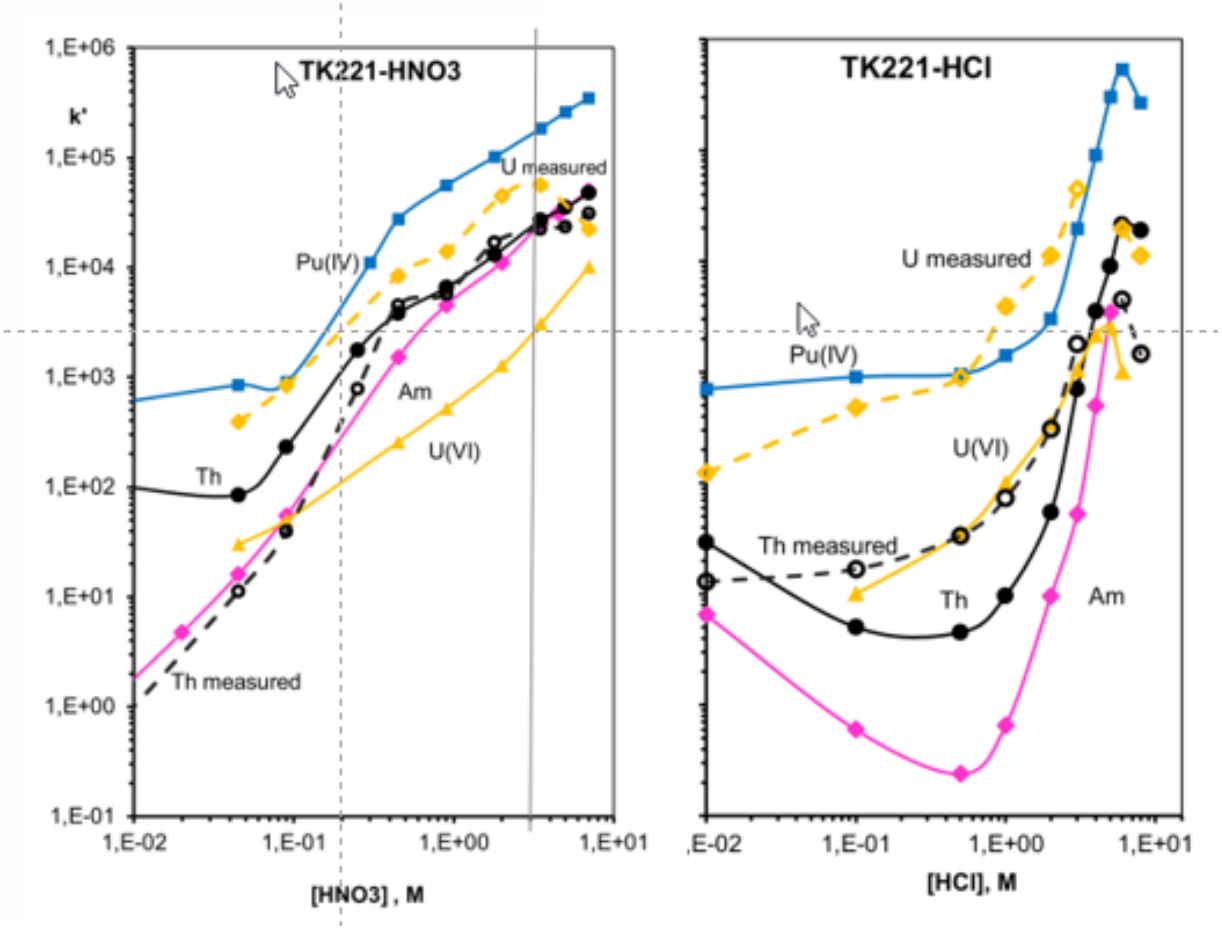
TK221 Resin

(Papp, I., Vajda, N. & Happel, S.. *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



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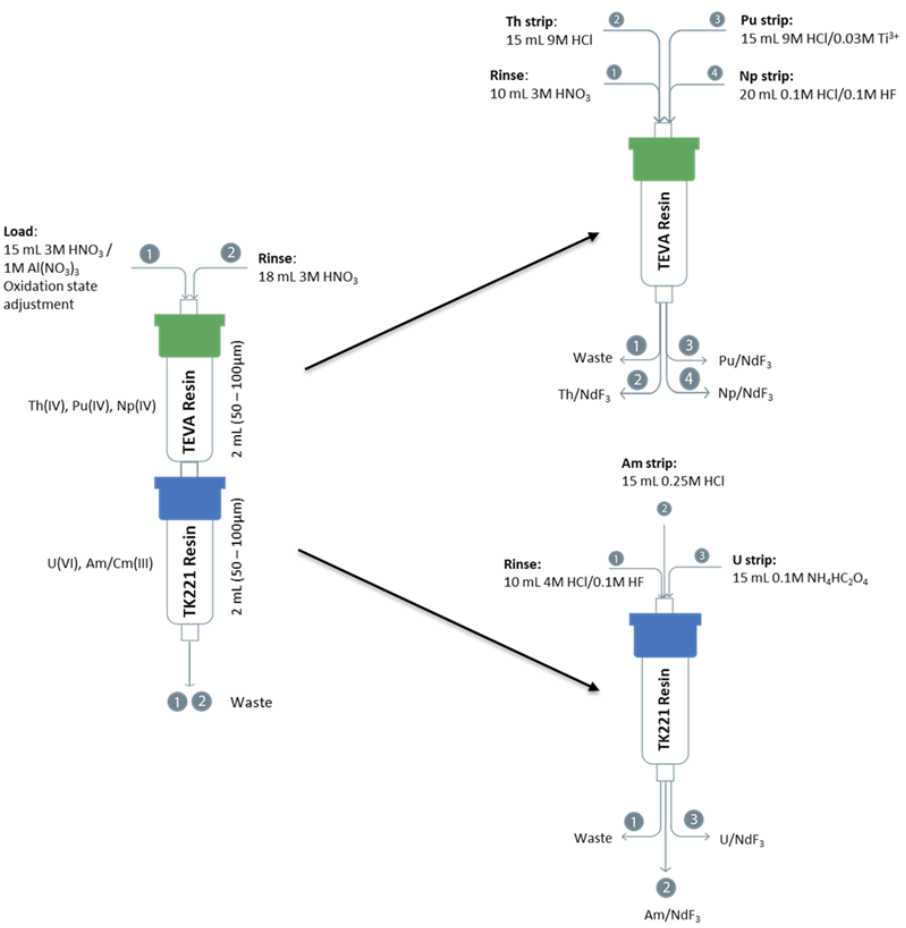


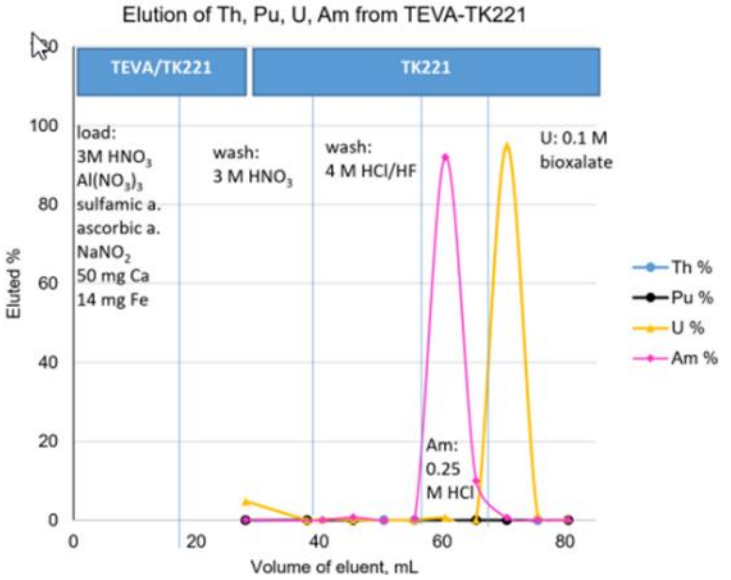
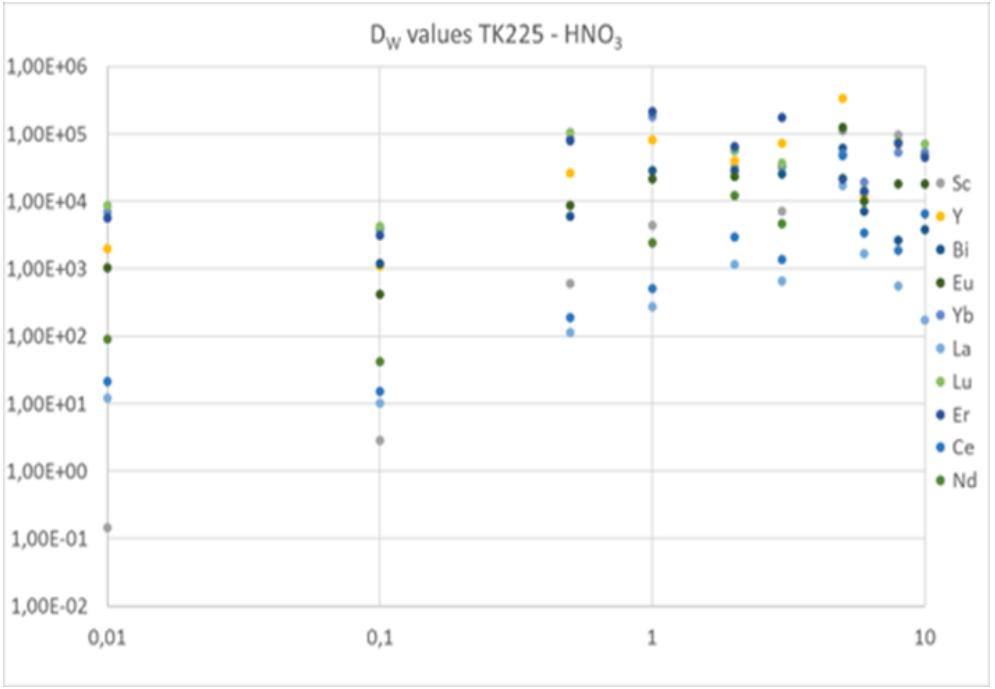


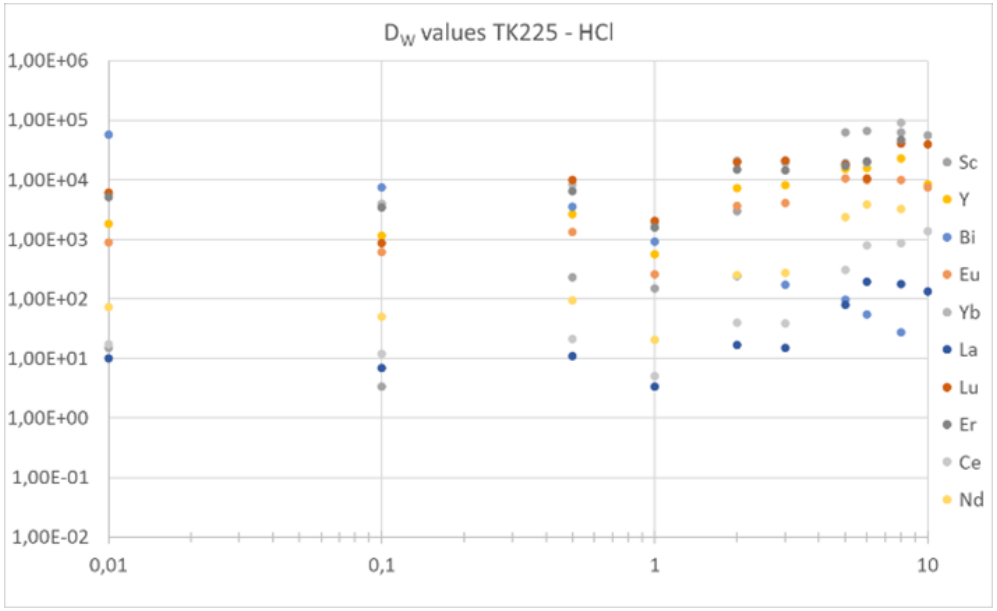
Table 3 Recovery of actinide tracers from spiked water samples

	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

TK225 Resin

- TO-DGA plus ionic liquid
- Very high retention of lanthanides at medium to high acid
- Especially heavy lanthanides also very well retained at low acid concentrations
- **Main application: Removal of radiolanthanides from effluents**



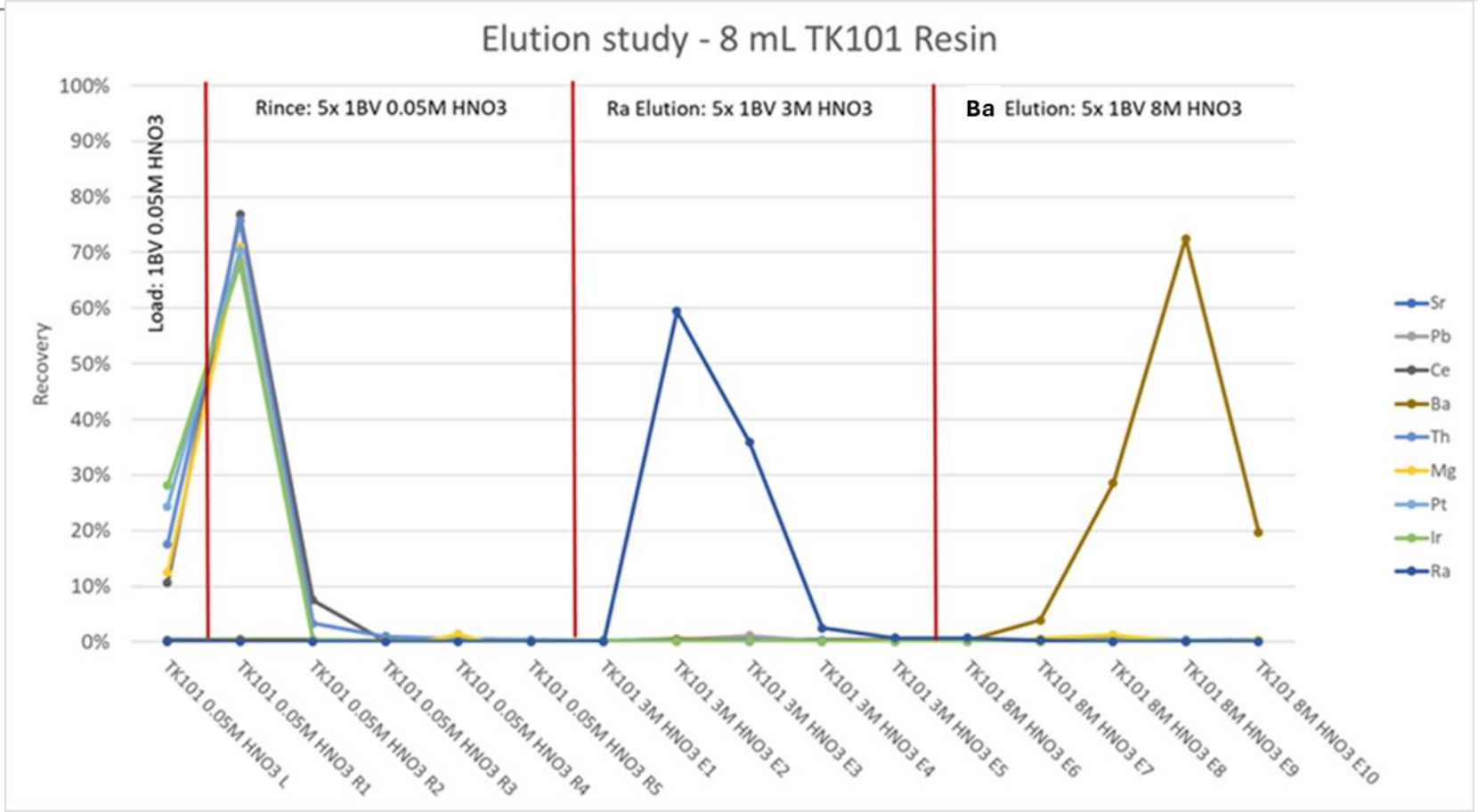


Under development
Ra purification/recycling

- In case Ra needs to be purified on-column (e.g. dissolved Ra needles) => Use of TK101 for Ra retention / purification
- TK101 => crown-ether + but ionic liquid

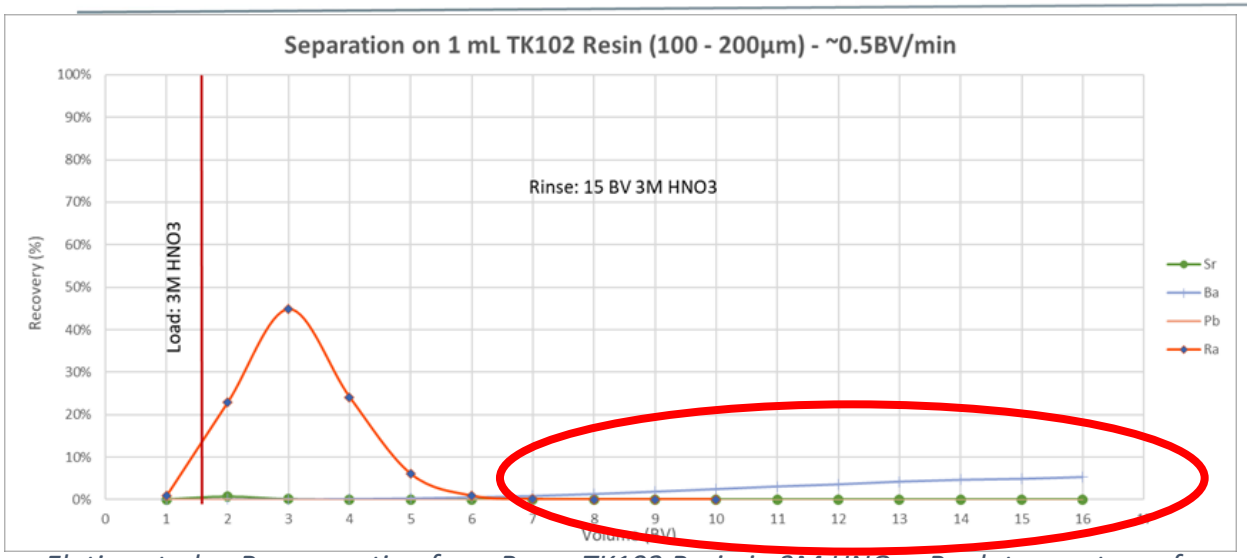
  Use of ionic liquid (=> TK101 Resin) allows for retention of Pb, Sr, Ba, Ra,… from pH ~2 – 7 without extensive extraction of other elements
- Ra separation from TK101 + further purification of Ra from Ba on TK102

Under development
Ra purification/recycling

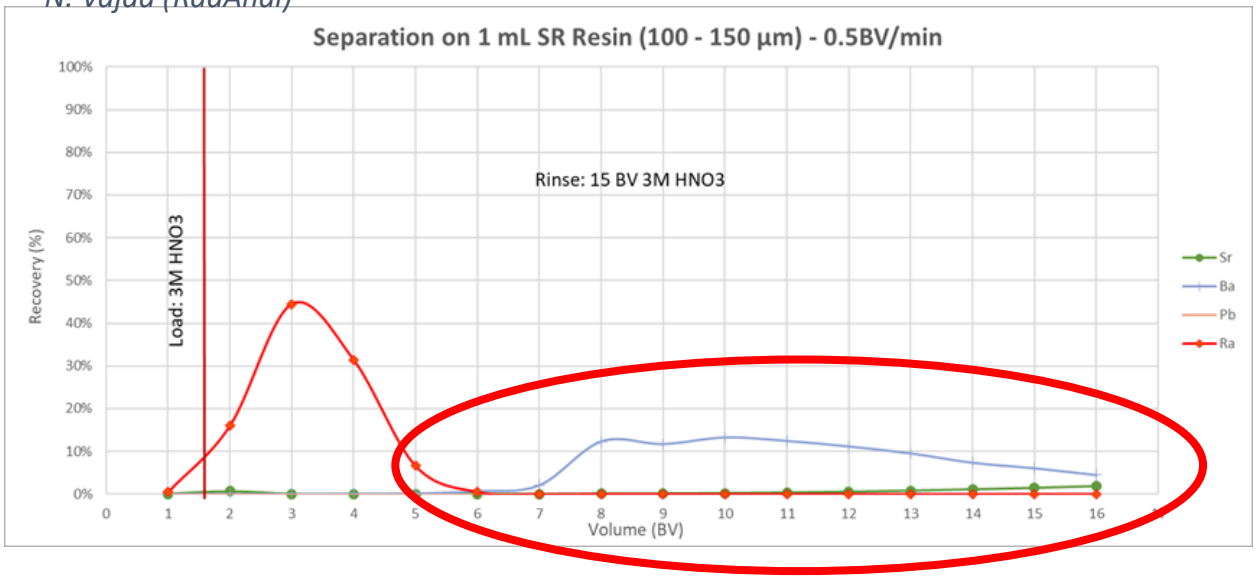


- Good Ra separation when loading from dilute HNO_3/HCl
- When eluting Ra in 3M HNO_3, Ba, Pb, Sr remain retained
- No retention of U, Th, Pt, Ir,…
- Ra eluted in 3M HNO_3
- Tl and Ba eluted in 8M HNO_3

Under development
Ra purification/recycling



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)

Further Ra fraction purification from Ba on TK102

Conclusions

To perform the measurement of a RN/Metal from a given matrix

- Choice of resins
- Pretreatment of the sample to
    - Eliminate matrix
    - Concentrate RN/metal of interest
- Perform separation to collect RN/Metal of interest in pure fraction
- Perform measurements

Thank you for your attention !

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