Extraction chromatographie Theorie und Anwendungen

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TRISKEM
Expertise in Separation Chemistry

TrisKem International

- Based in Rennes (France)
- Independent company since 2007 (before part of Eichrom)
- 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
- Products used in several domains

Applications/domains - I

- Analytical
  - Radiochemistry
    - Environmental monitoring, bioassay, waste monitoring, **decommissioning**
    - **Actinides**, fission and activation products, **NORM (Po-210, Ra-226,…)**, methods/resins for **DTMs, rapid methods,** sample preparation, **bioavailability (DGT)**,…
  - Mass spectrometry
    - Isotope ratio determination (universities, petrol industry,…)
    - Sr, Pb, U, **actinides**, Cu, Sn…
      - Dating of geological samples
      - **Food provenancing**
      - Nuclear forensics
      - **Biomedical and metallomics**

Applications/domains - II

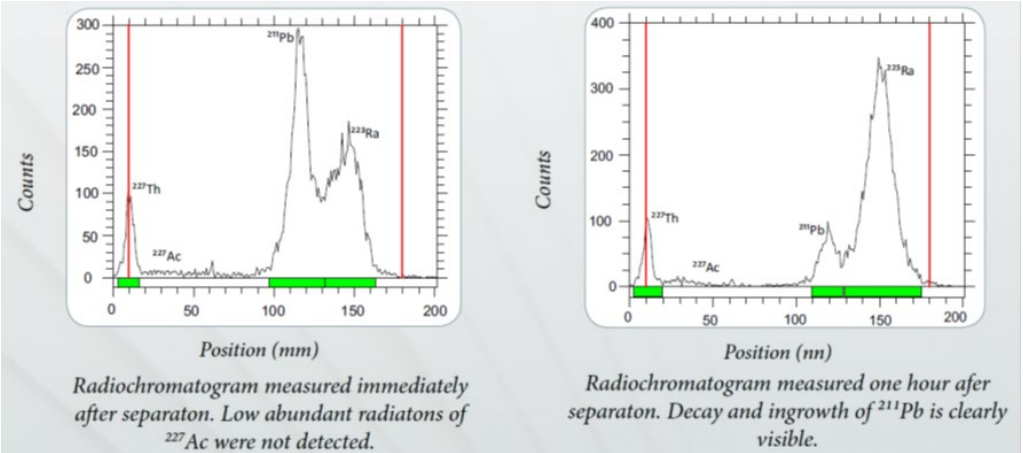
- Decommissioning/decontamination
  - Treatment of effluents / liquid wastes / environmental waters
    - Removal of radioactive contaminants & heavy metals (Cs, Sr, Ra, I…)
    - Nuclear medicine (Ge, radiolanthanides, radioiodine…
  - Inorganic compounds embedded into PAN matrix
  - 'Industrial' extractionchromatographic resins (larger beads,…)
- Hydrometallurgy
  - Recycling/production of critical metals
  - Valorisation of 'waste'
  - 'Industrial' extractionchromatographic resins (larger beads,…)

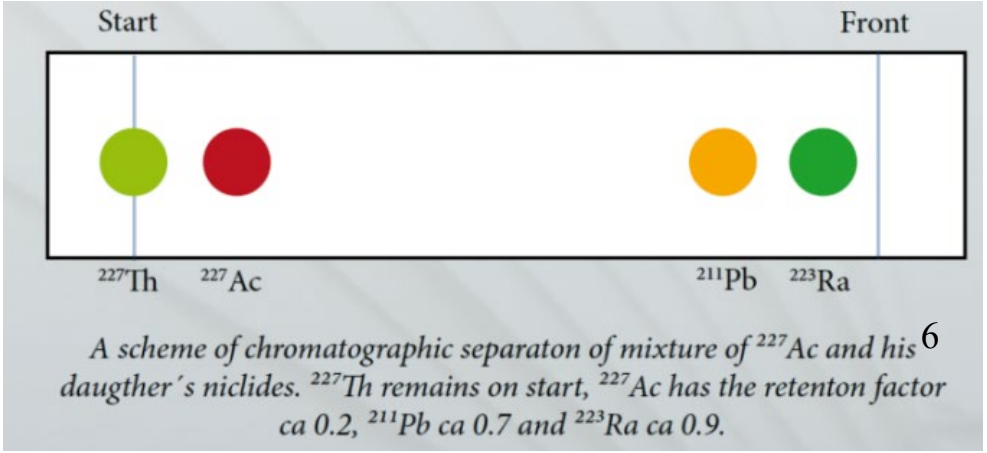
Applications/domains - III

- Radiopharmacy/Nuclear Medicine
  - Radionuclide production
    - Resin and method development ‘cold’
      - Cooperation with cyclotrons & reactors (NL, RN producers,...)
      - Equipment provider (targetry, synthesizer,...)
    - Separation of radionuclides from irradiated targets
      - Diagnostics: Zr-89, Cu-64, Ga-68, Ge-68, Ti-44/5, Tc-99m, Sc-43/4...
      - Therapy: **alpha emitters**, Lu-177, Tb-161, Cu-67, Sn-117m, Sc-47...
    - Challenges:
      - Large excess of matrix / target material (several mg to hundreds of g)
      - Generally rapid separation required
      - Very high purity (incl. radionuclidic purity)
      - Elution under ‘soft‘ conditions in small volume => labelling/injection

Applications/domains - III

- Radiopharmacy/nuclear medicine
  - Quality control
    - Cartridge based methods => e.g. **actinides** in fission derived radionuclides, Po-210, Ra-226 in Ac-225…
    - Upcoming challenge: Ac-227 in Ac-225
    - **DGA sheets** (functionalized TLC, Ra-223, Ga-68, Pb-212,…. => CVUT Prague)
  - Behavior/determination of long-lived radionuclides in environmental samples (e.g Ac-225, Lu-177,…)
  - Decontamination of contaminated effluents

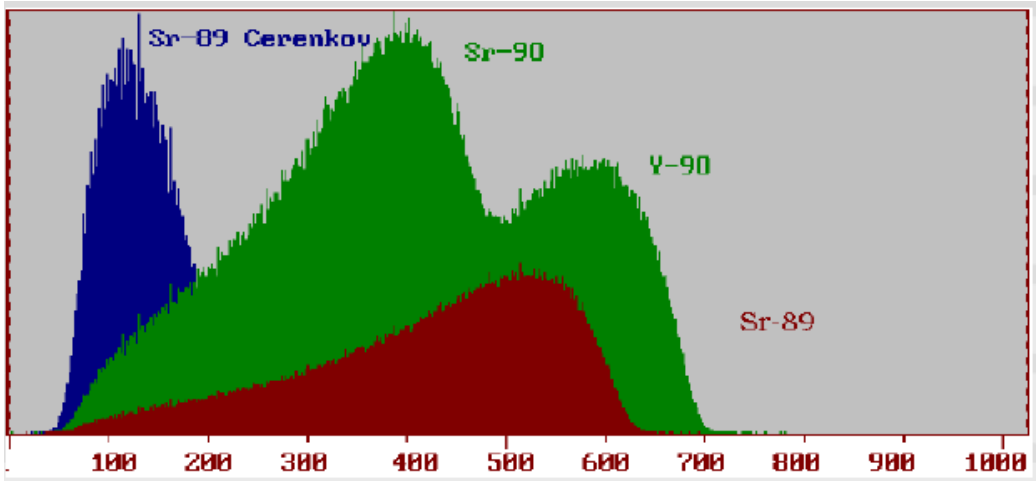




Why separation chemistry?

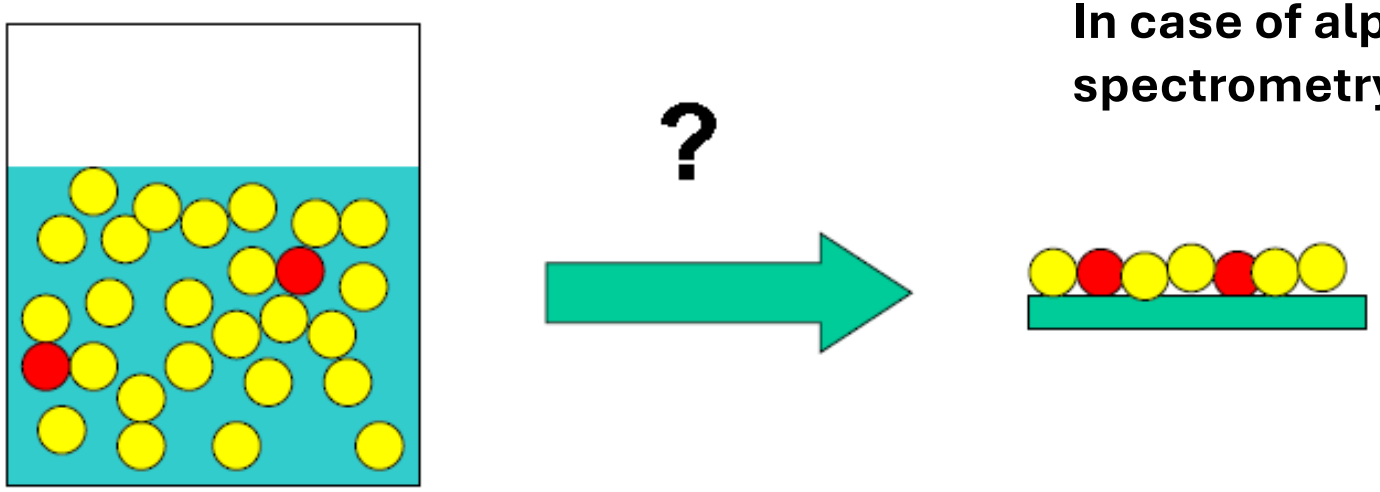
- In case of beta emitters/LSC
  - Sample compatible with LSC measurement
    - Liquid (volume usually ≤ 10 mL)
    - Can be solid (e.g. use of gellifying cocktails)
    - Stable mix with cocktail (no phase separation)
  - Elimination of quench effects
  - β^- particles show non-discrete energy
    - Energy is distributed between β^- particle and anti-neutrino $\bar{\nu}_e$
    - $E_{\beta,max}$ / $\bar{E}_\beta$

- Removal of interferences
  - Natural radionuclides (K-40, C-14,…)
  - Artificial radionuclides
  - Isotopes of same element can't be separated (beside very light elements)



Hou et al. Wallac LSC

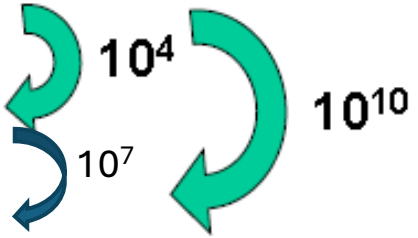
Why separation chemistry?



100 mg Ca : N = 1.5×10^{21}

1 Bq ^{238}U : N = 2.1×10^{17}

1 Bq ^{226}Ra : N = 7.2×10^{10}



Surbeck 2010

- **For alpha spec thin and 'clean' sources needed**
- Large sample volume or mass
- Great excess of matrix
- Other alpha emitters

Source thickness

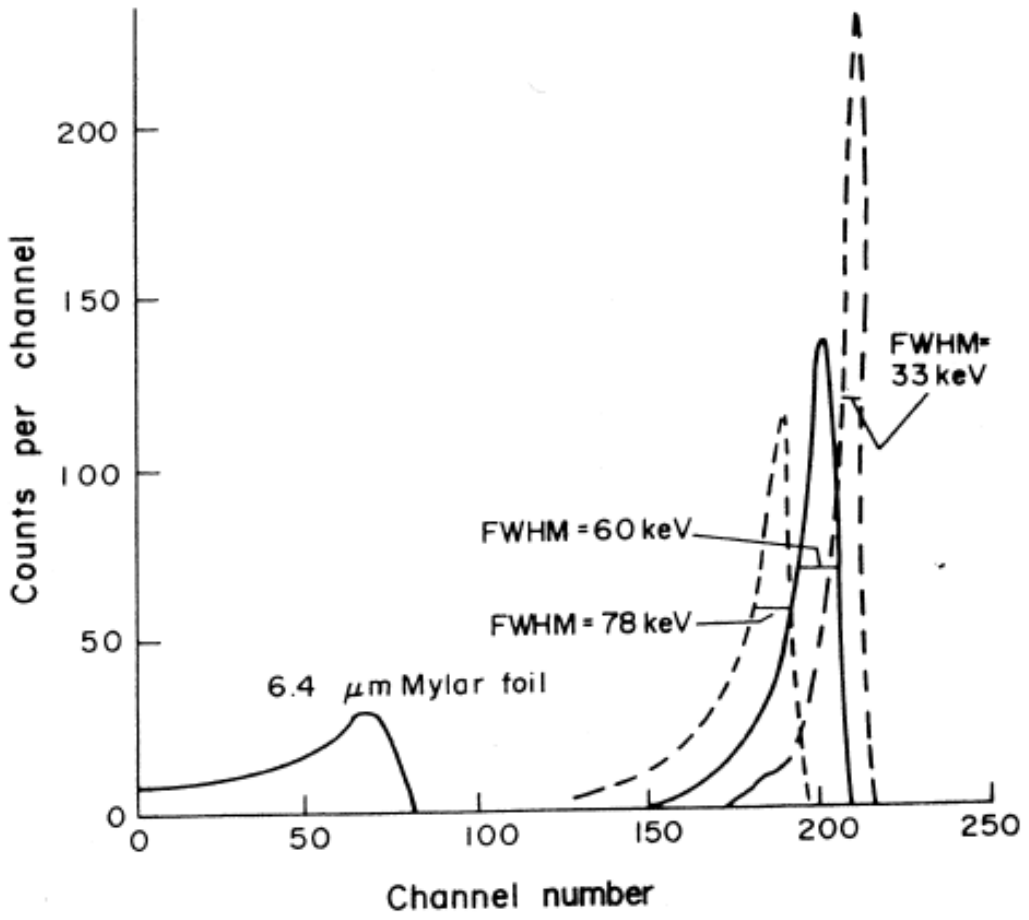


Fig. 1. Degradation of α-particle spectrum from a $^{239+240}$Pu source with varying absorber thickness (From Holm, 1984).

Strong interaction of alpha particles with matter
Increased thickness of layer leads to lower resolution

Interferences

Messanleitungen, 2006

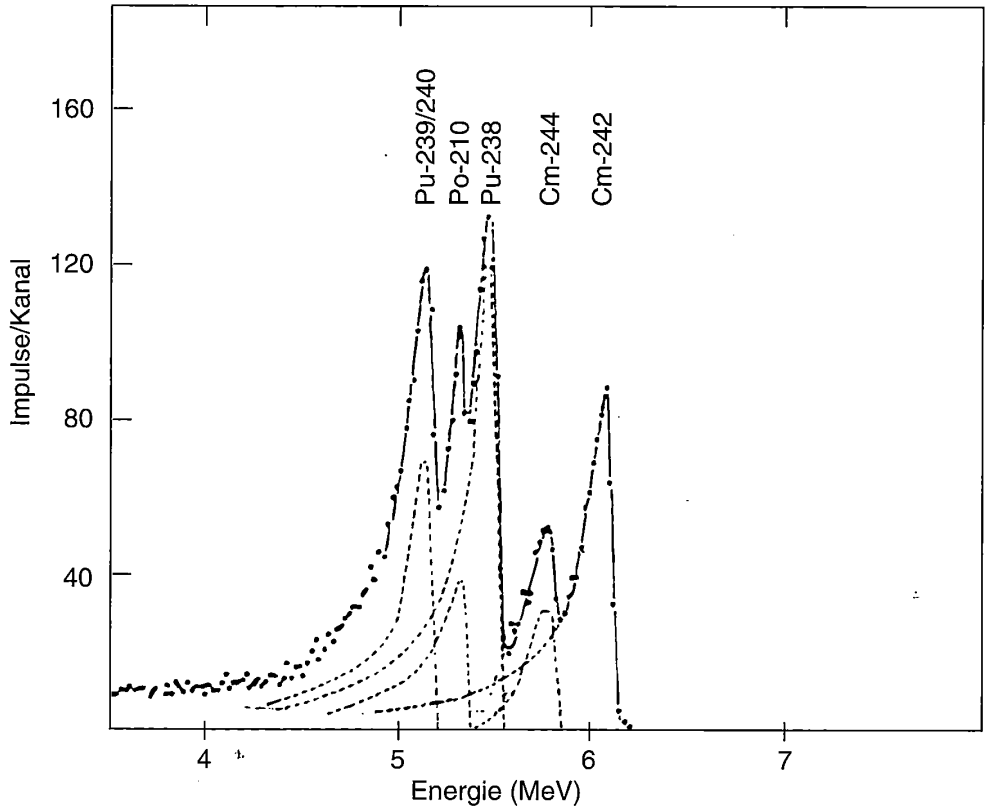
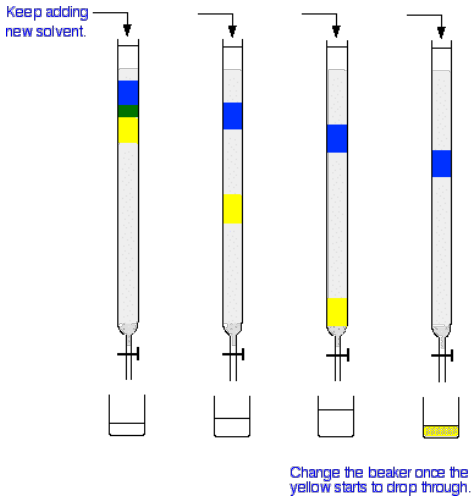


Abb. 14: Spektrum einer Probe, bei der sich die Linien der einzelnen Nuklide überlappen (52)

- Spectra with low resolution difficult to analyse
  - Matrix removal and suitable source preparation
- Certain radionuclides have so close energy that even in high resolution spectra analysis / deconvolution is not possible (e.g. Am-241 and Pu-238)
  - Chemical separation of the elements

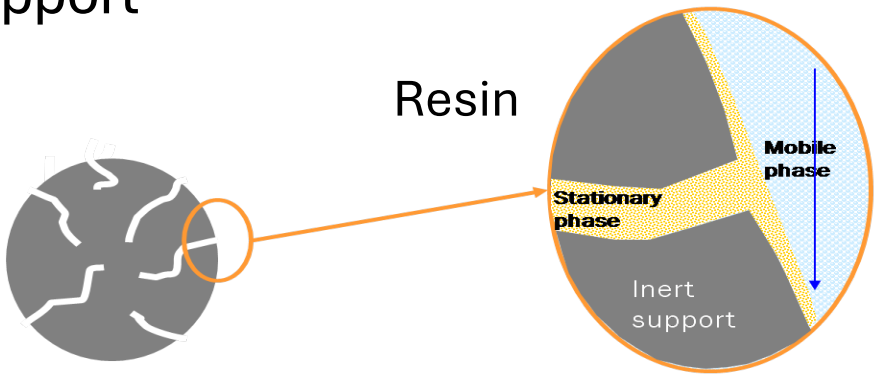
Extraction chromatography

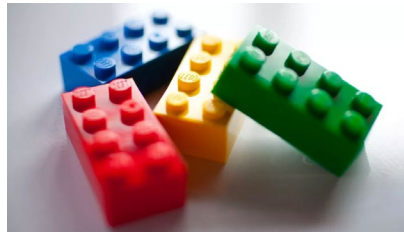
- Combination of liquid-liquid extraction (LLX) and chromatography
- Liquid-liquid extraction: distribution of an element between 2 non-miscible phases
  - Most general case: organic and aqueous phase
- Chromatography: distribution of an element between a solid and a liquid phase



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
  - Not only resin beads
- High variety of selectivities:
  - Large variety of different compounds
  - Aim: selectivity for product/analyte, no selectivity for matrix/ impurities
- Combining several cartridges can improve/facilitate separation
  - Several Analytes from one sampe
  - Conversion from high to low acid
  - Facilitation of a separation by upfront impurity removal





Inert Support

- Choice of inert support depending on application
  - Mainly polymers, silica possible – usually end-capped
  - Easy packing, radiolysis stability, plastic scintillators,…
- Inert regarding chemical reactions with
  - Organic phase/extractant
  - Elements to be isolated
  - Mobile phase
- Stable regarding mechanical actions
- High specific surface
- High loading capacity for the extractant
- Defined pore and particle size distribution
- Spherical particles
- Not only resins!

Stationary Phase

- Generally organic compounds – often amphipathic
- Non-miscible with water
- Non-volatile
- Soluble in volatile solvents
- Ideally fast kinetics
- High selectivity
  - Aim: selectivity for analyte/product, no selectivity for matrix/interferences
  - Pure extractants, synergetic mixtures, solid extractants dissolved in diluents, solids (e.g. DMG)
  - Influence of Diluents (Octanol, ionic liquids, TBP,…) => SR, PB, TK100/1/2
- Chemically, physically and mechanically stable
- High capacity for analyte/product

Extraction chromatography

Types of Extractants

Acidic — **e.g. HDEHP (LN 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)**

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

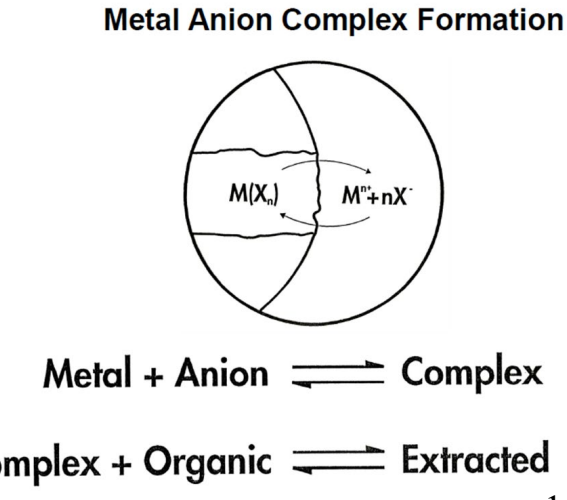
Basic — **e.g. TK201, TEVA Resins**

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

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

Horwitz et al.

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

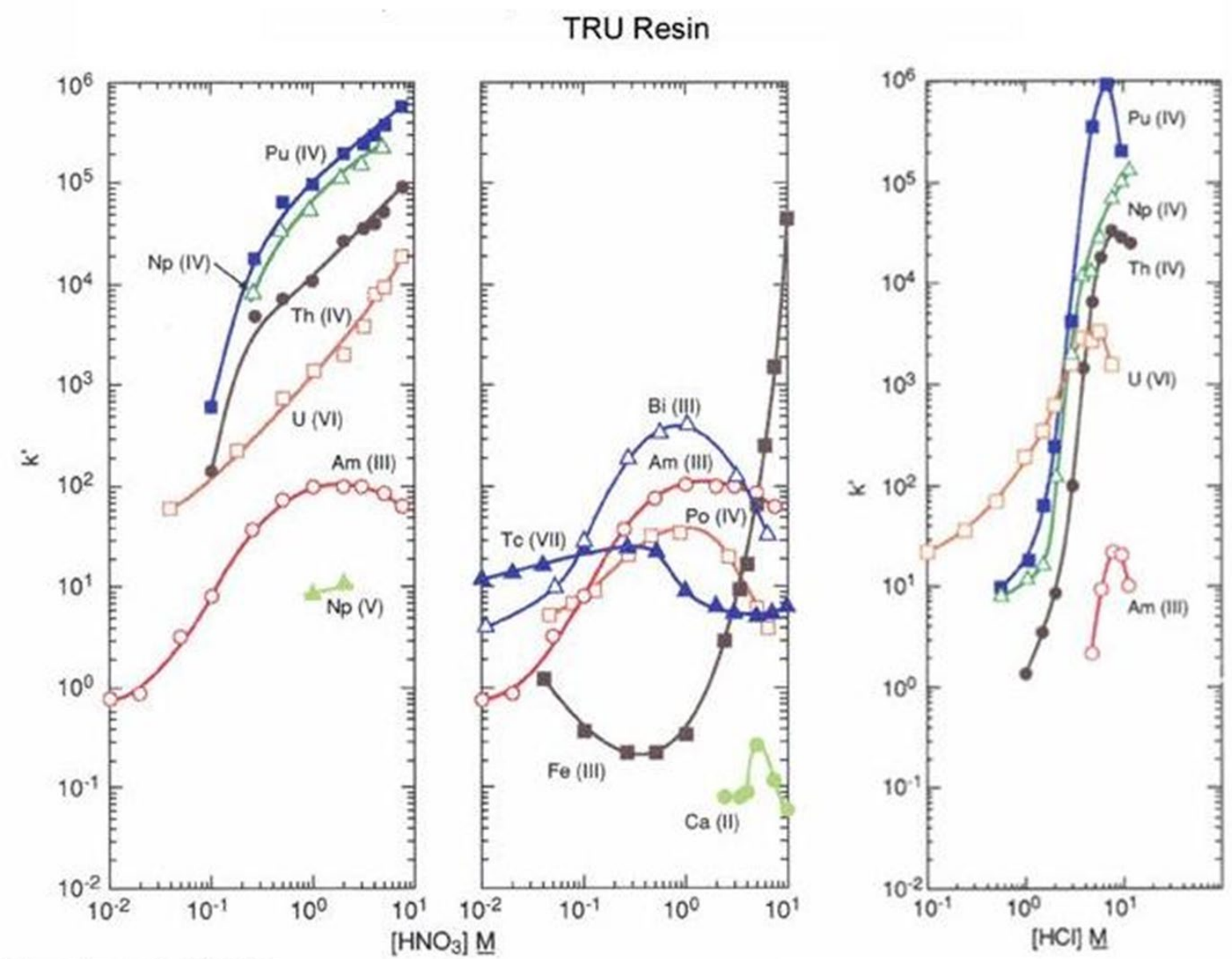


Other mechanisms:

NI Resin: DMG => on resin precipitation of $Ni(DMG)_2$

CL Resin: Phosphine sulfide based resin, loading with Ag+ => on-resin précipitation of Cl^-, I^-

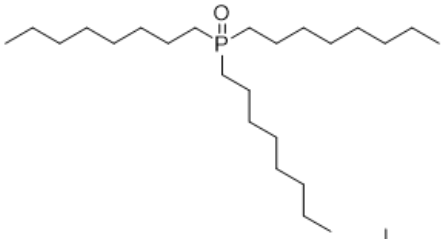
HNO_3 vs HCl



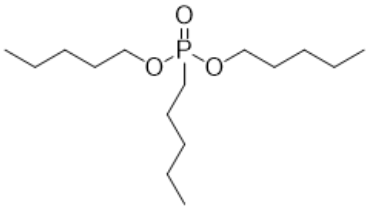
Horwitz, et al. (HP193)

Typically employed extractants

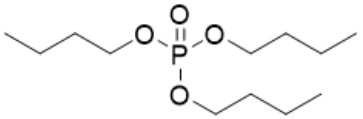
Trioctylphosphine oxide
(TOPO)

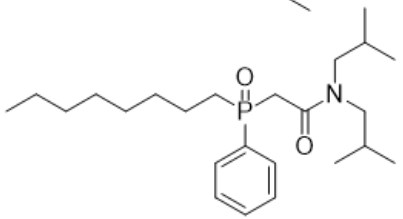


Dipentyl pentyl phosphonate
(DPPP)

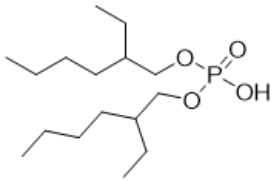


Tributylphosphate
(TBP)

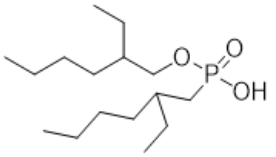




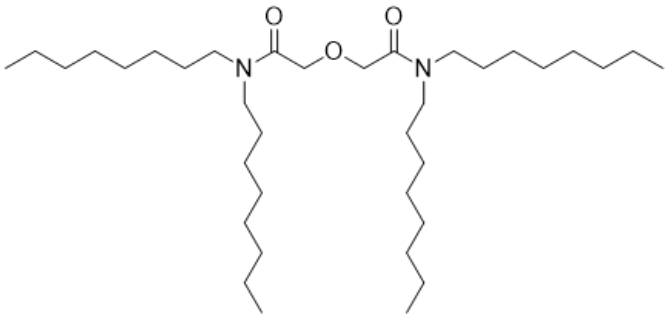
Octyl (phenyl)-N-N-diisobutyl-carbamoylmethylphosphine oxide
(CMPO)



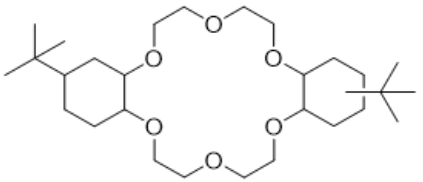
Bis(2-ethylhexyl) hydrogen phosphate
(HDEHP)



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

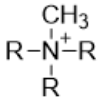


N,N,N',N'-tetra-n-octyl-diglycolamide
(TODGA)

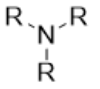


4,4'(5')-di-t-butylcyclohexano-18-crown-6

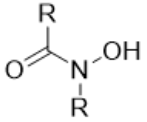
Aliquat 336 (R = 8, 10)



Tertiary amine

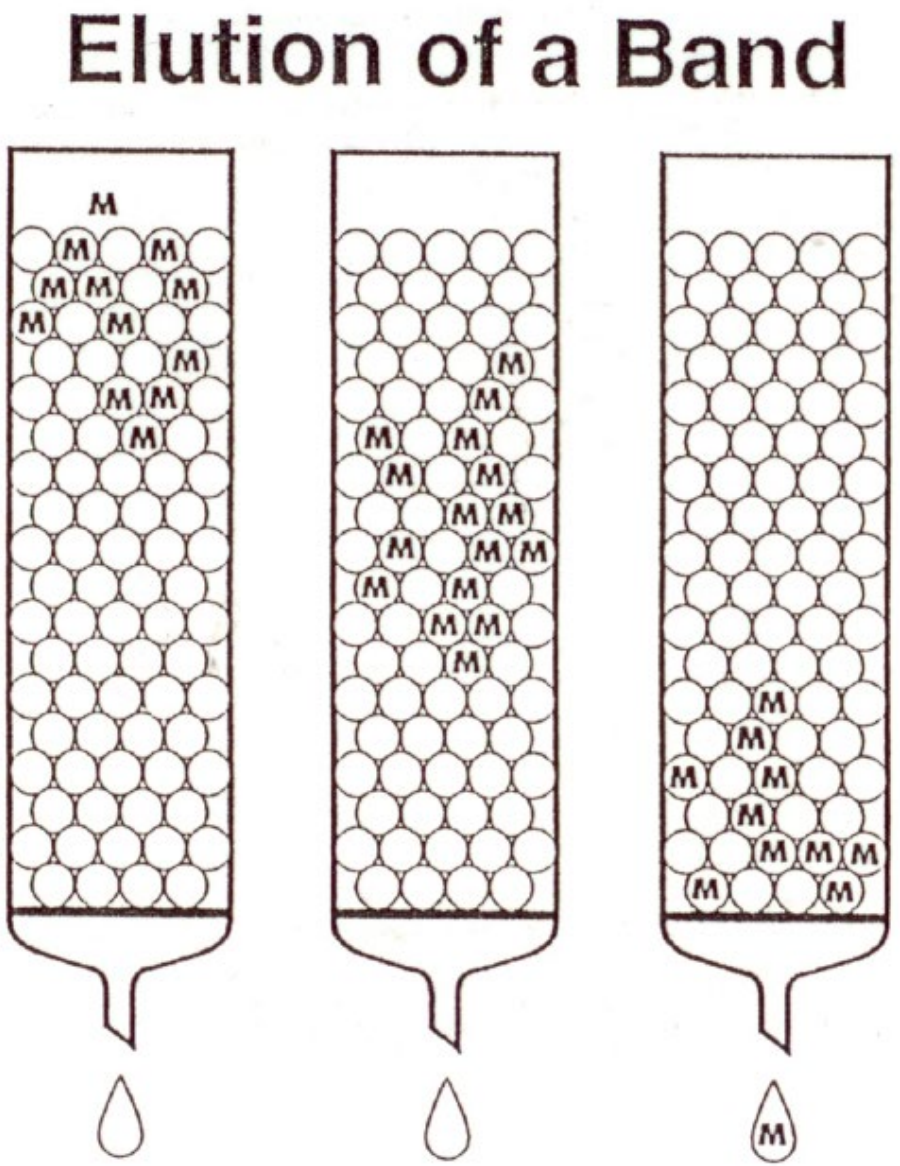


Phosphine sulfide



Hydroxamate

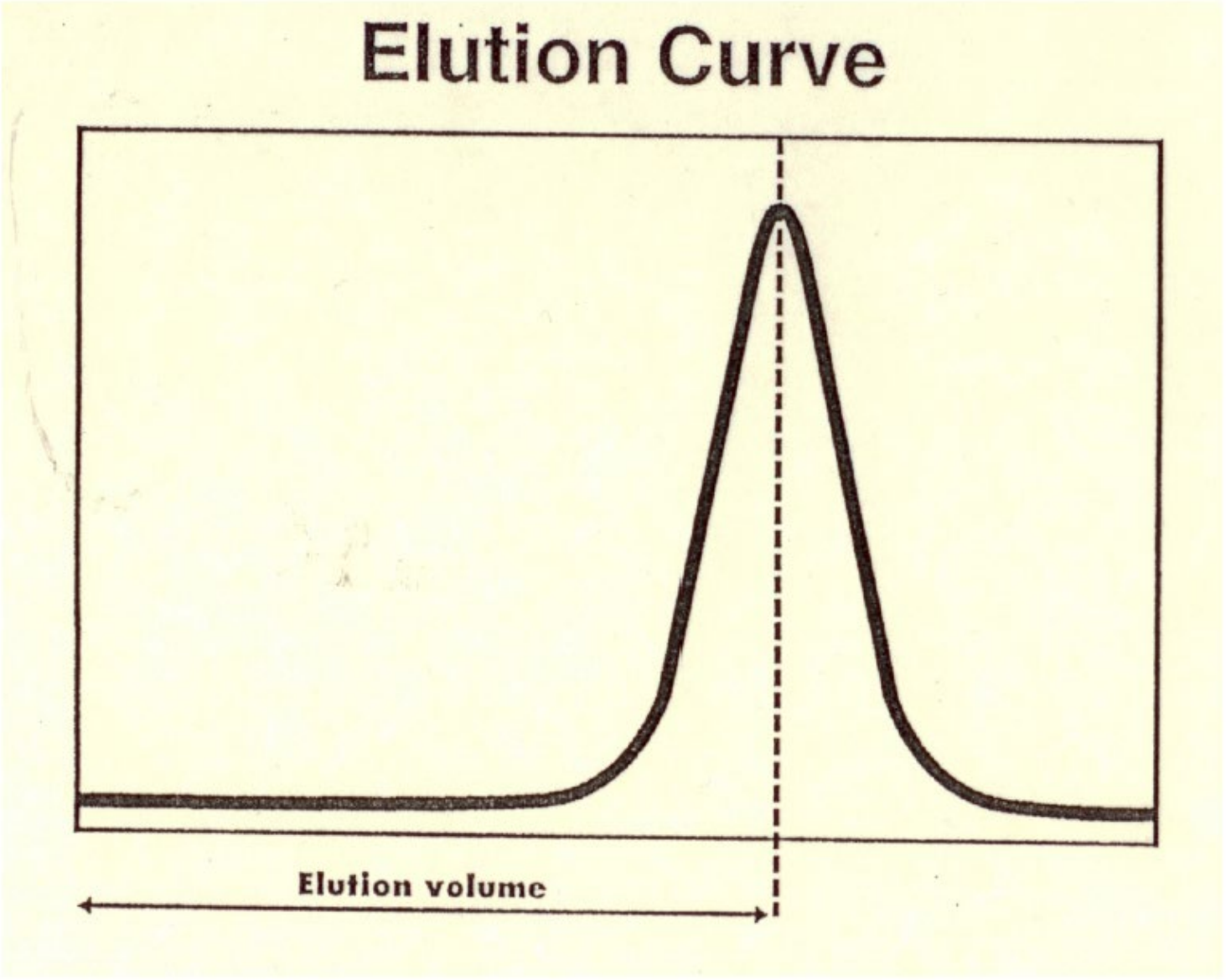
Elution experiment



Stolen from
Bill Burnett!

Detector

Elution experiment

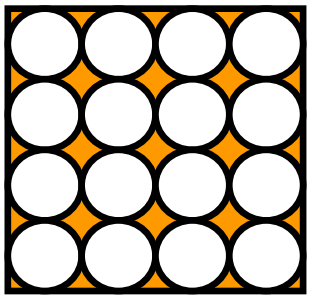


Stolen from
Bill Burnett!

Free Column Volume/selectivity

Free Column Volume

Volume of mobile phase in the resin bed:



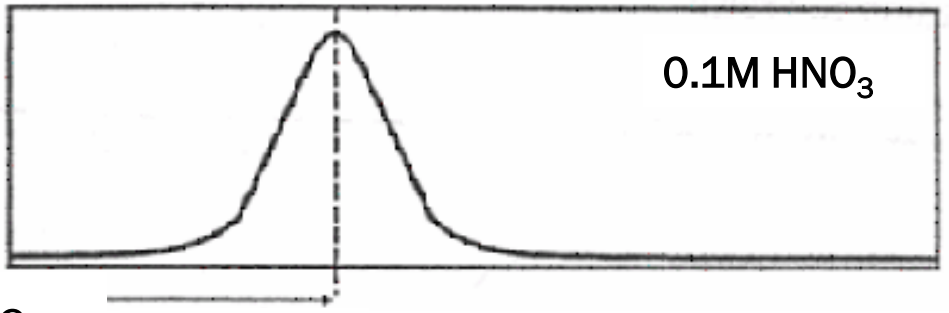
For extraction chromatography typically 0.65 mL per mL column bed

Capacity factor k' expressed in FCV for comparison of methods using different column geometry – normalisation

Selectivity α

$$\alpha = k'_1/k'_2$$

Elution curves => k'



Elution volume

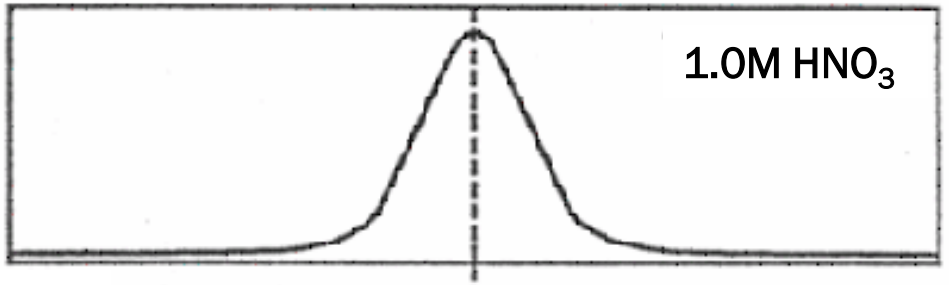
$V_1 \propto k_1$

$k_1 = V_1/FCV$

FCV = free column volume

k' = 5 => V_1 ~ 6,5 mL

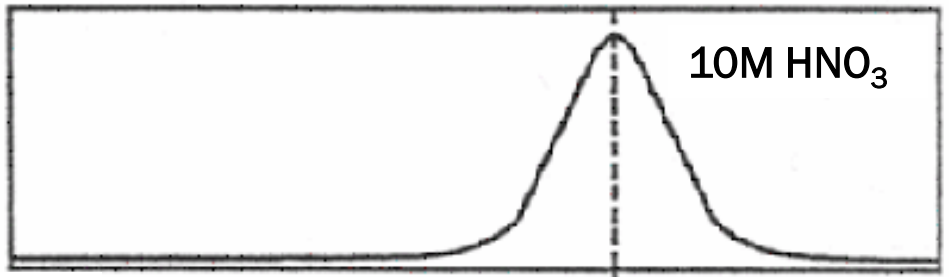
- **Need min. 15 mL for elution**



Elution volume

$V_2 \propto k_2$

$k_2 = V_2/FCV$



Elution volume

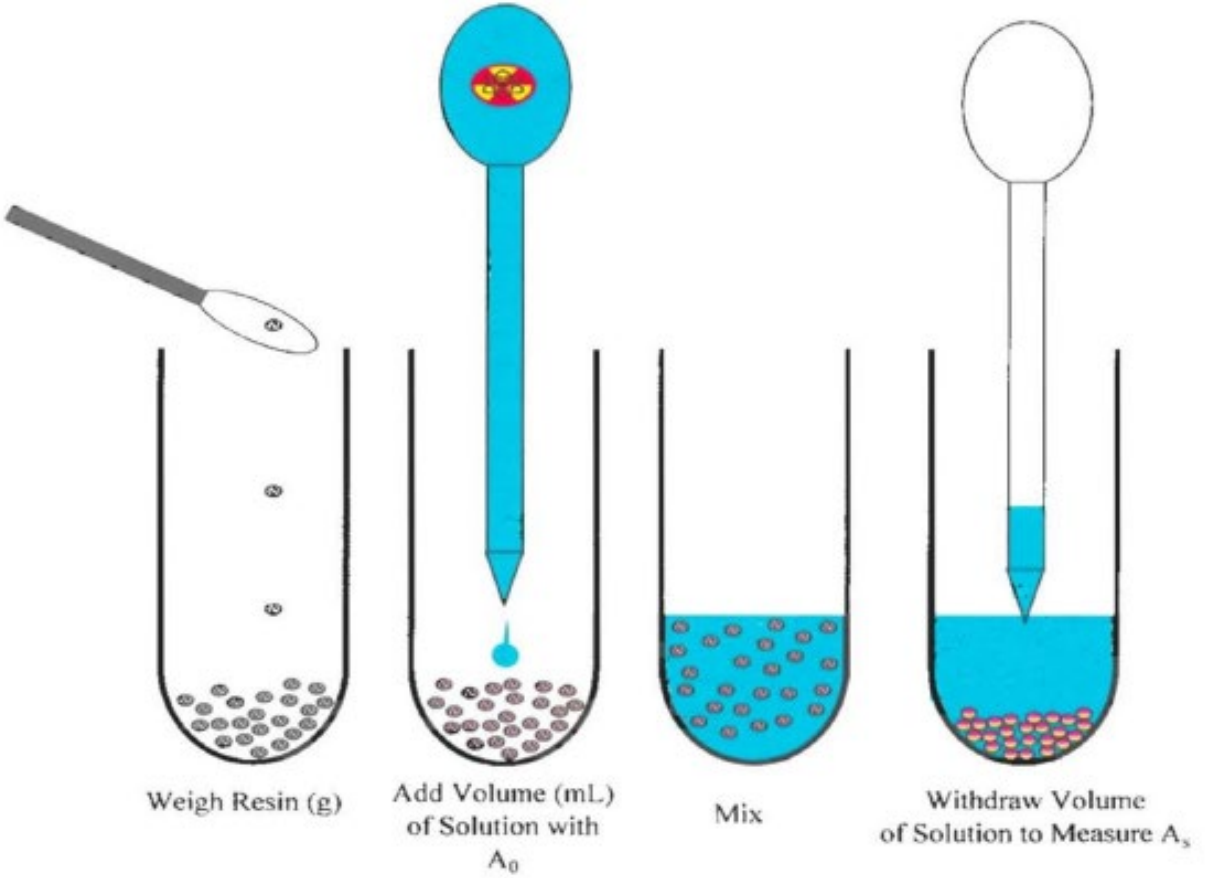
$V_3 \propto k_3$

$k_3 = V_3/FCV$

For k' = 1000

- **V_3 ~ 1,3L!**

Dry Weigh Distribution Ratio



Horwitz

$$D_w = \frac{A_0 - As}{w(g)} \Big/ \frac{A_s}{v(mL)}$$

$k' \sim D_W * 0.5$

Relationship Between SX and EXC

$$k' = D_v \bullet \frac{v_s}{v_m}$$

Measure for retention

k' = retention volume (FCV to peak maximum)

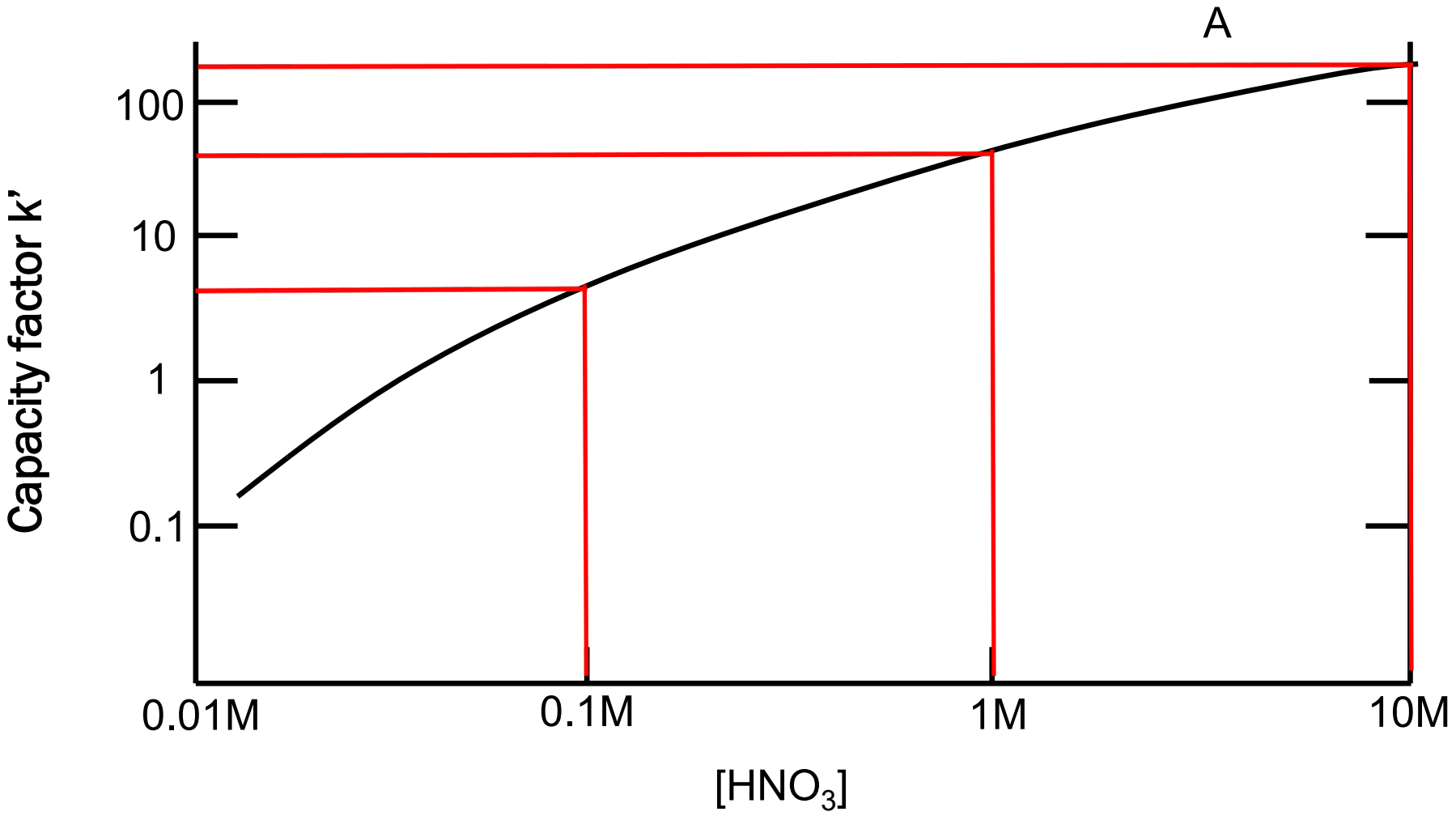
D_v = volume distribution ratio

v_s = volume of stationary phase

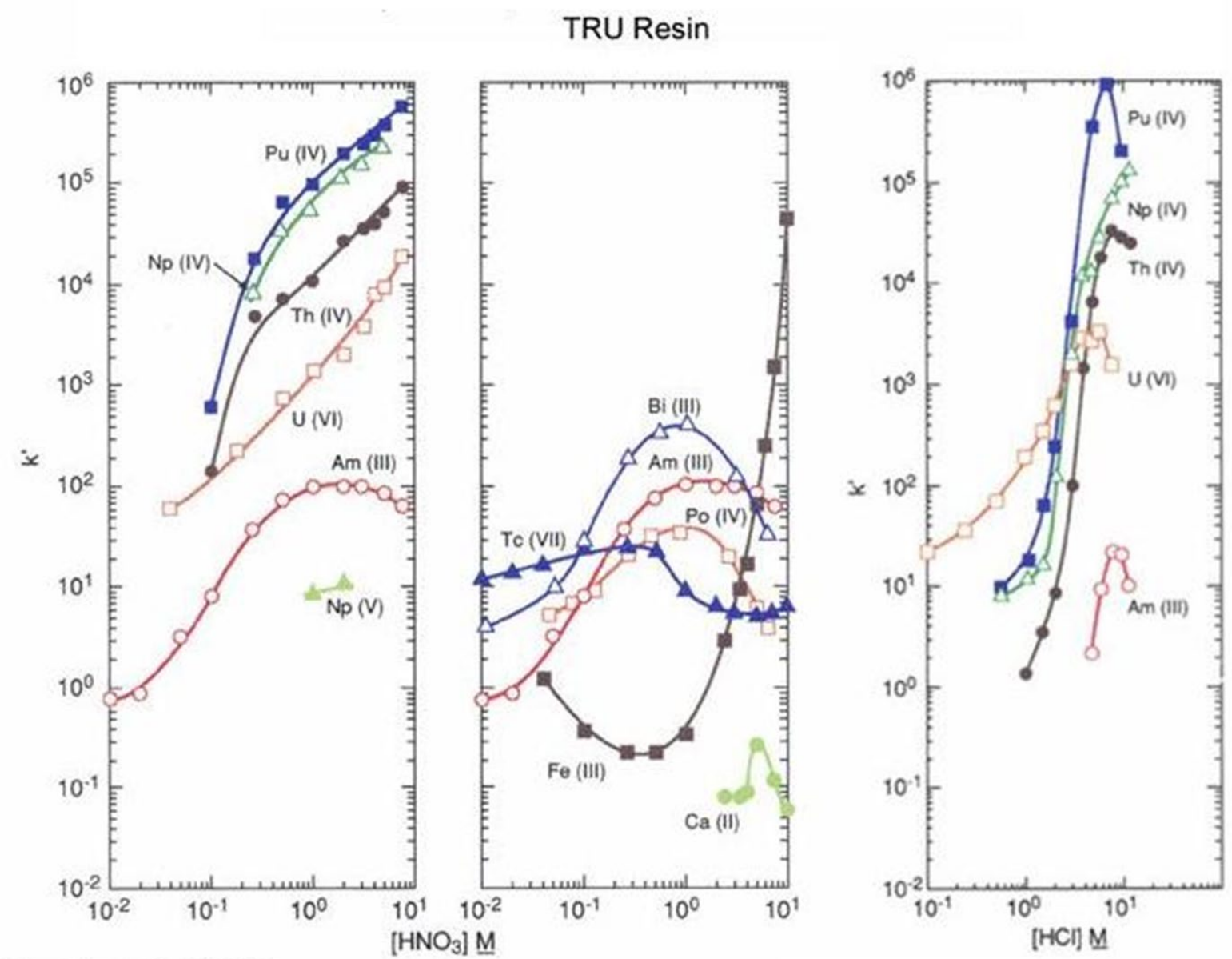
v_m = volume of mobile phases

Taken from Horwitz, 2011

k’ = f ([acid])

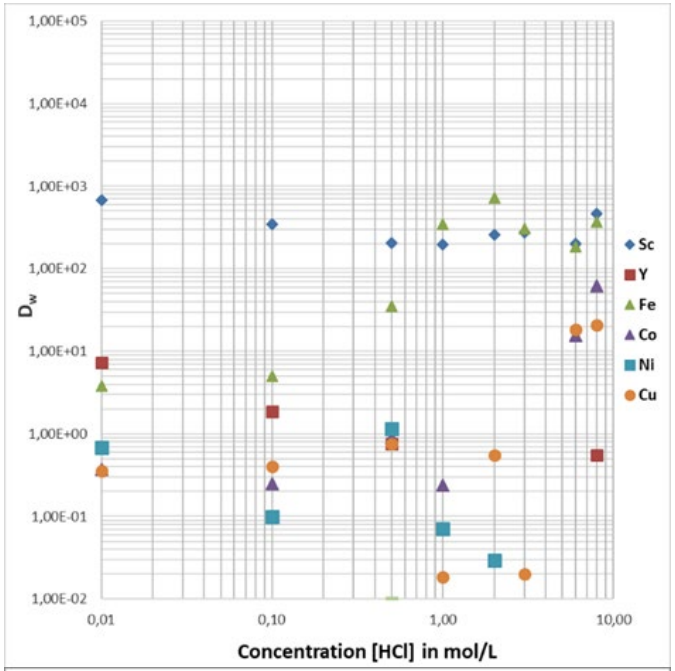


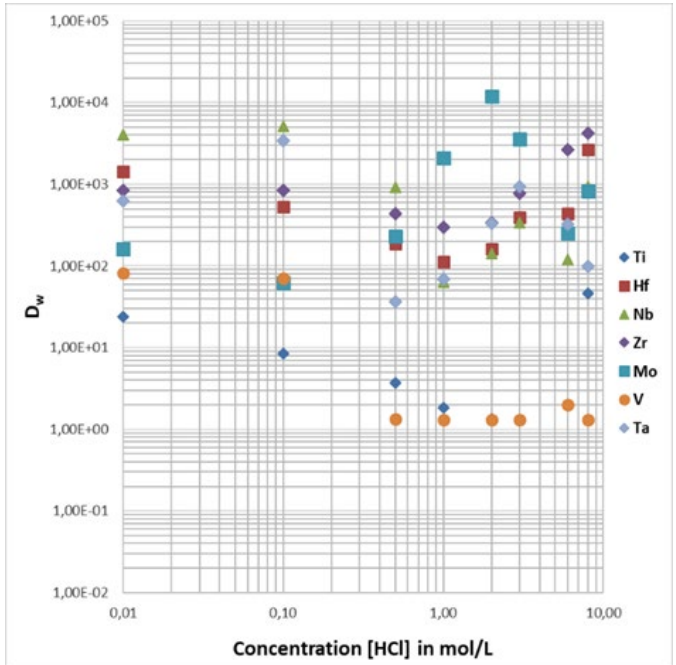
HNO_3 vs HCl

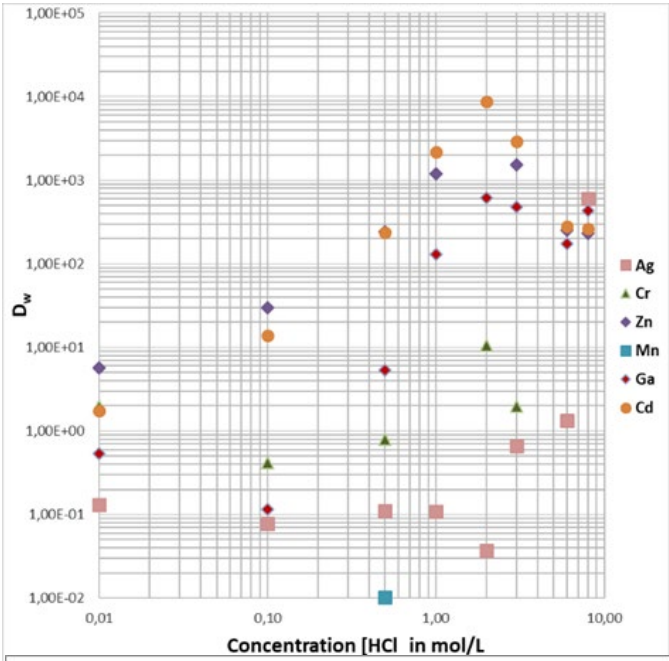


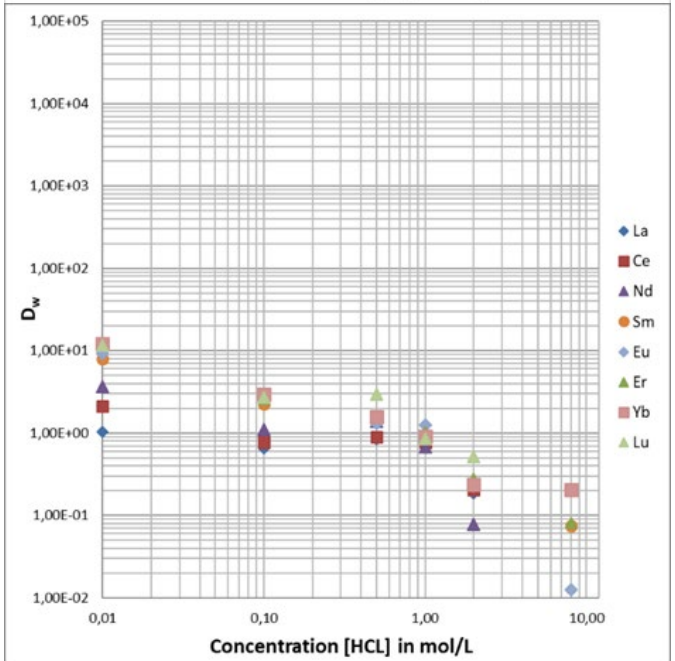
Horwitz, et al. (HP193)

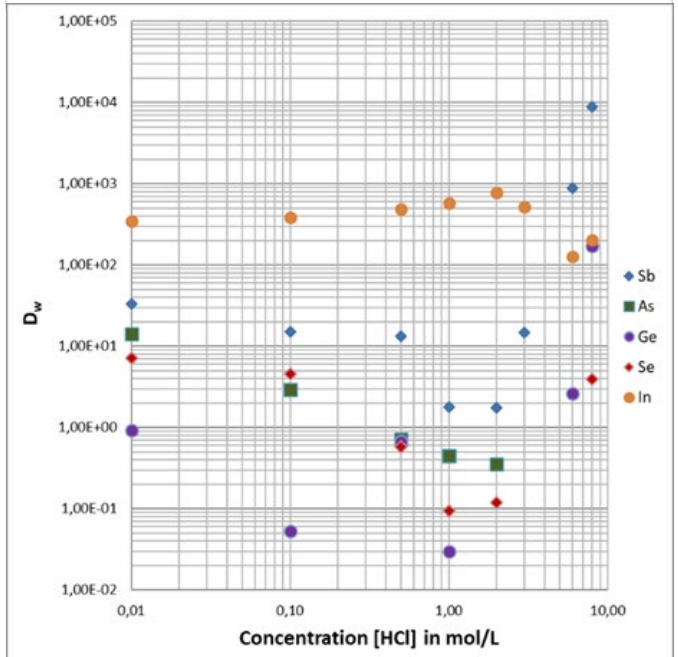
Very important: Resin characterisation
Example: TK200 - HCl

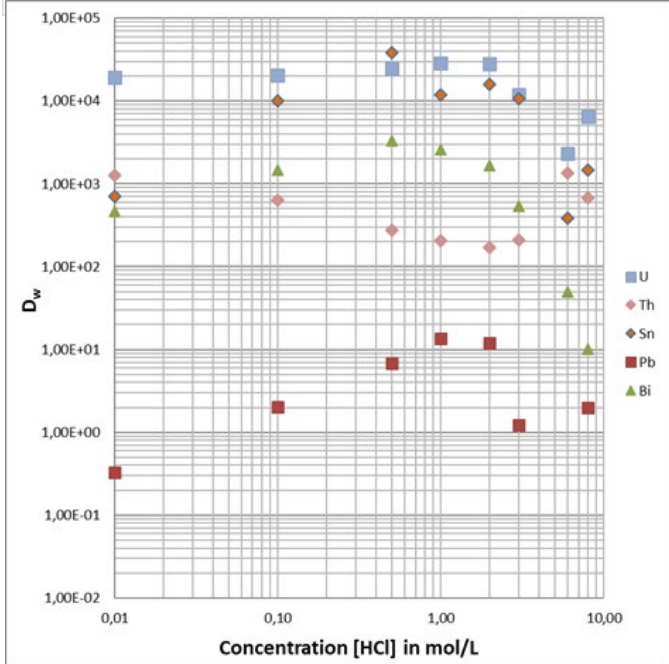












Chromatographic separations - Lanthanides

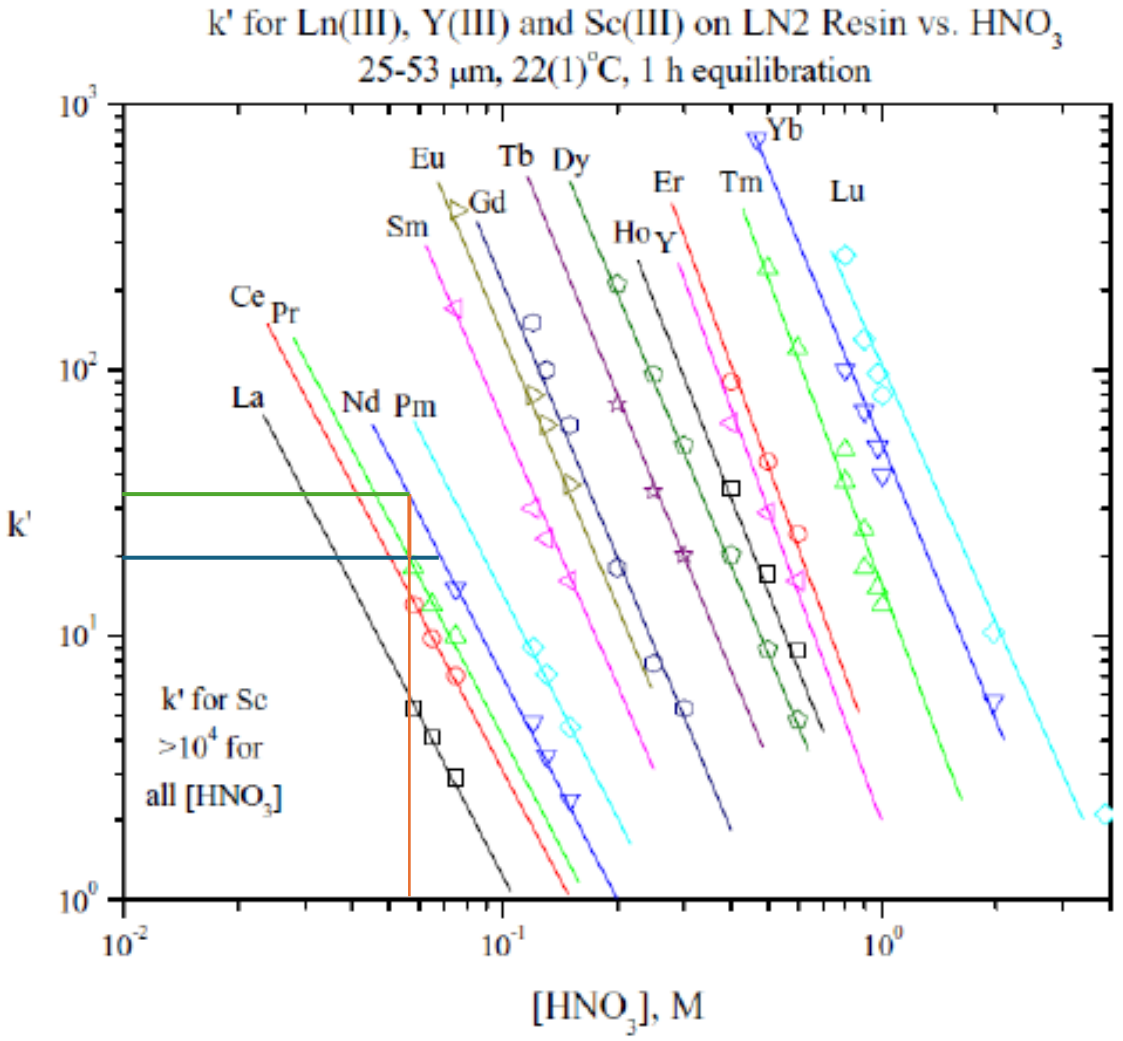
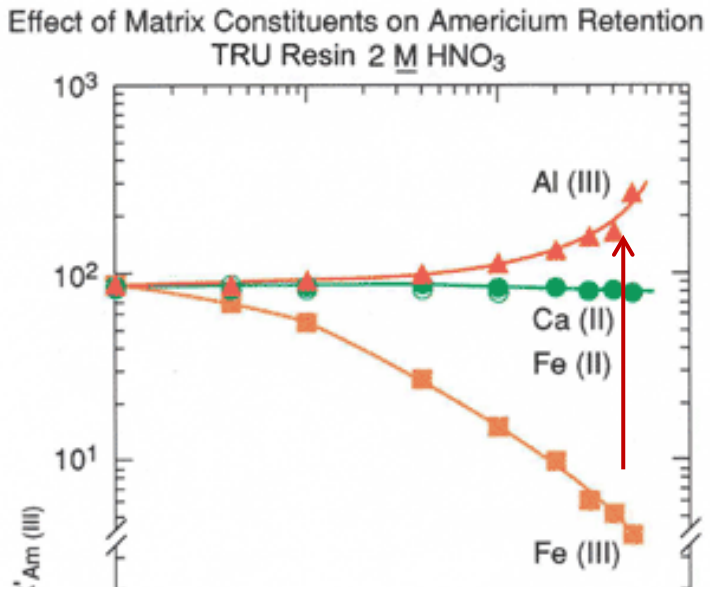


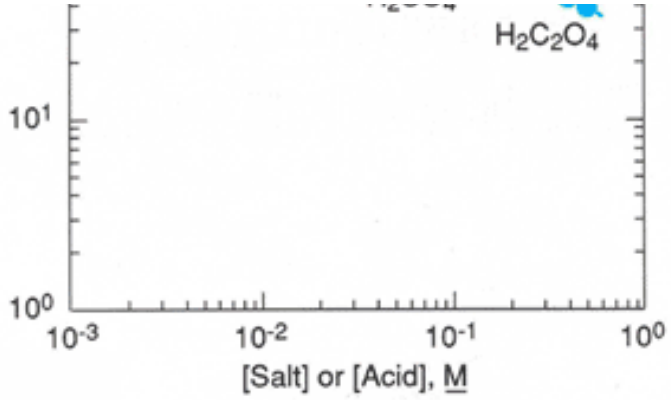
Figure 15: Capacity factor k‘ of various lanthanides in HNO_3 on LN2 resin.

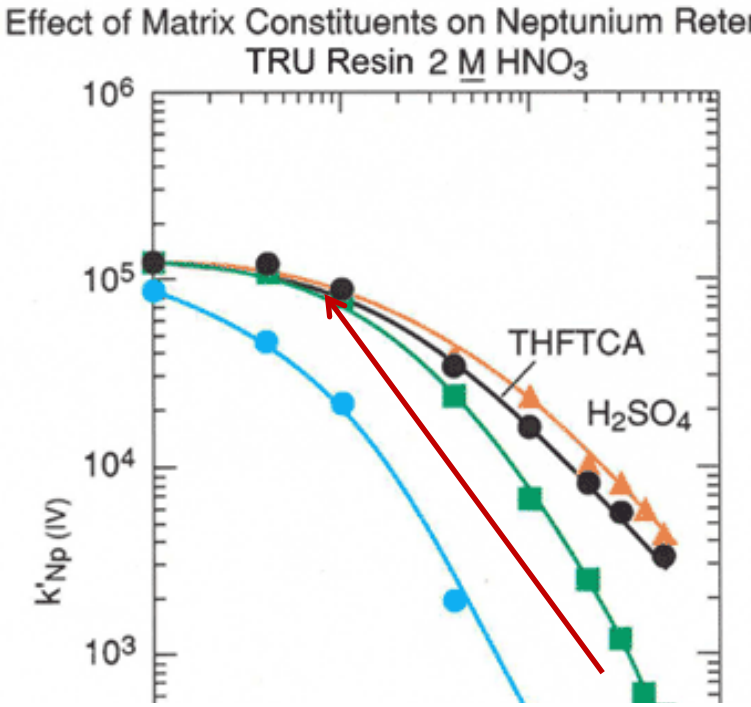
- LN/LN2/LN3
- TK211/2/3
- Chromatographic separations typically run at k’ of 20 – 30
- k’ starting point, main work on columns
- Mainly depending on H^+ concentration, less influenced by anions
- Steric component

Interferences

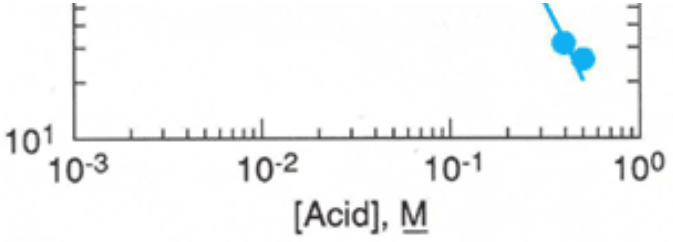


Addition of Reducing agent: Fe(III) -> Fe(II)





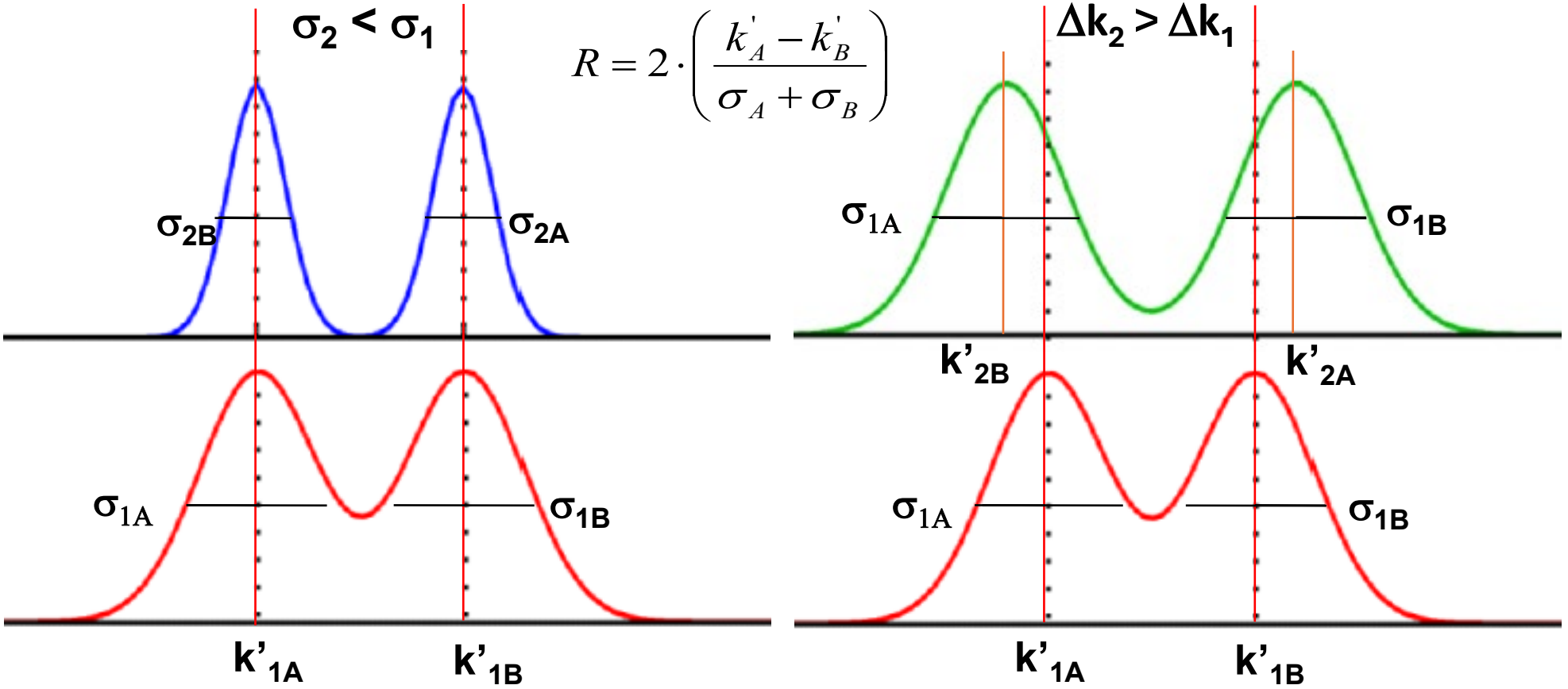
Addition of Al –> Al complexation by phosphates -> lower conc. of free phosphate -> less interference



From Horwitz (1)

(HP193)

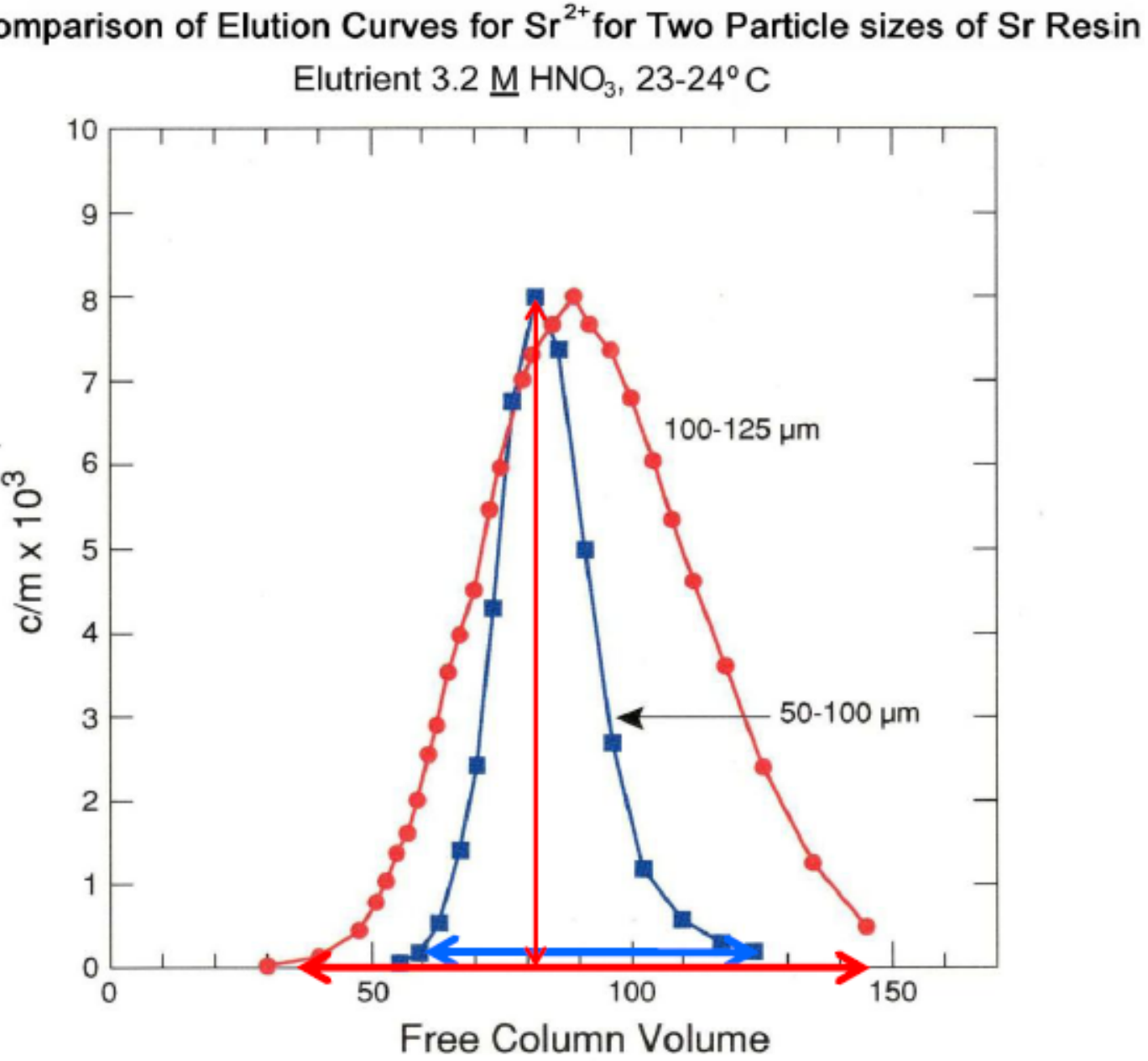
Resolution R



Improvement of resolution R

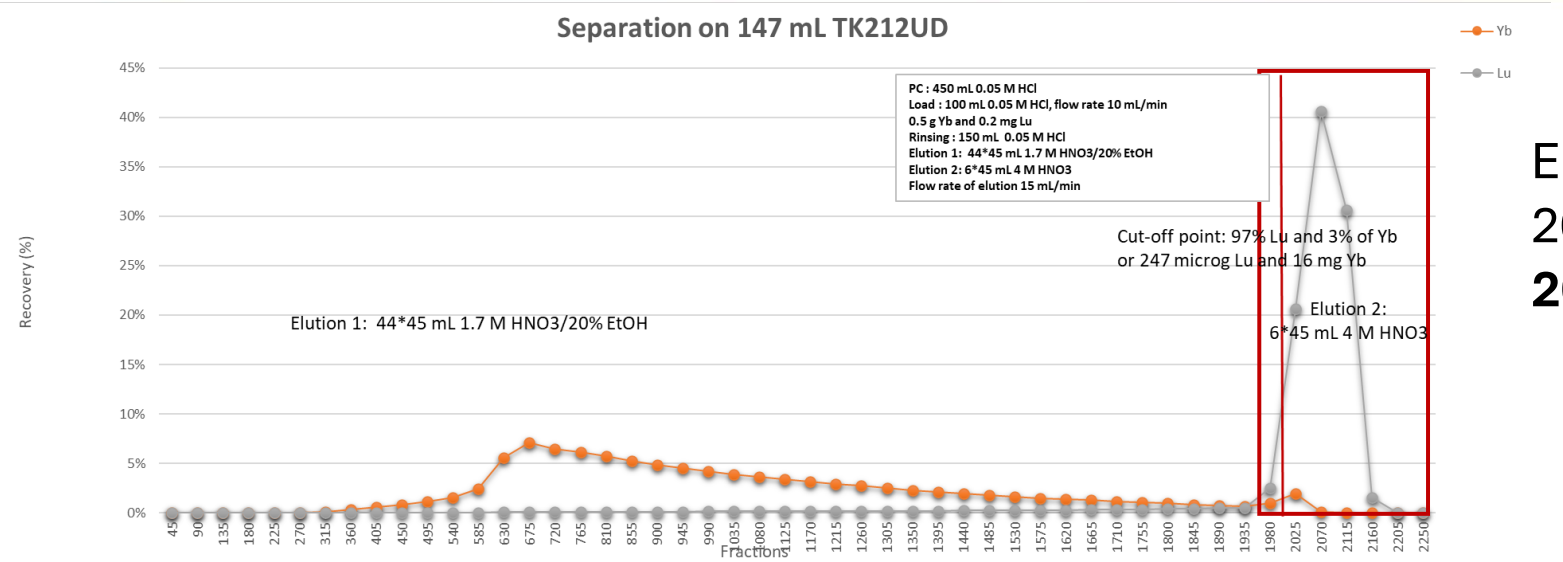
- Decrease peak width: e.g. particle diameter, flow rate
- Increase difference of k' values : modification of stationary or mobile phase, valence, auxiliary compexants

- Smaller particles, sharper elution bands
- Peak maximum corresponds to k'

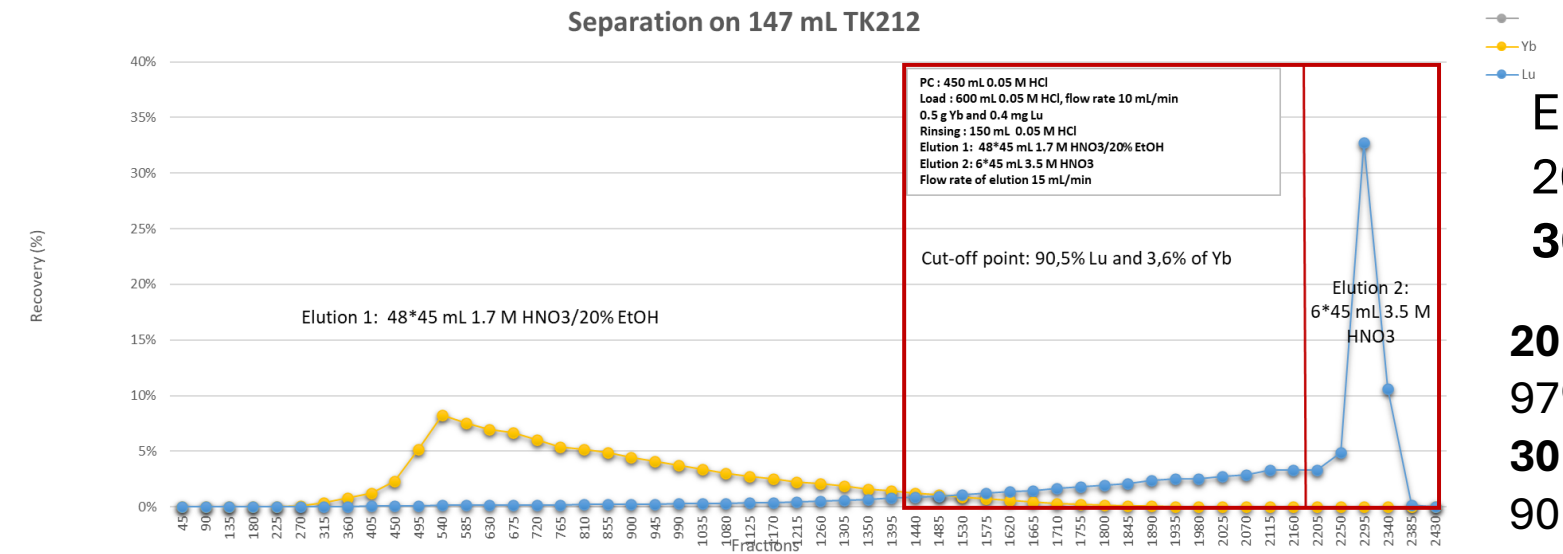


Taken from Horwitz, 2011

Lu/Yb separation 20µm vs 30µm



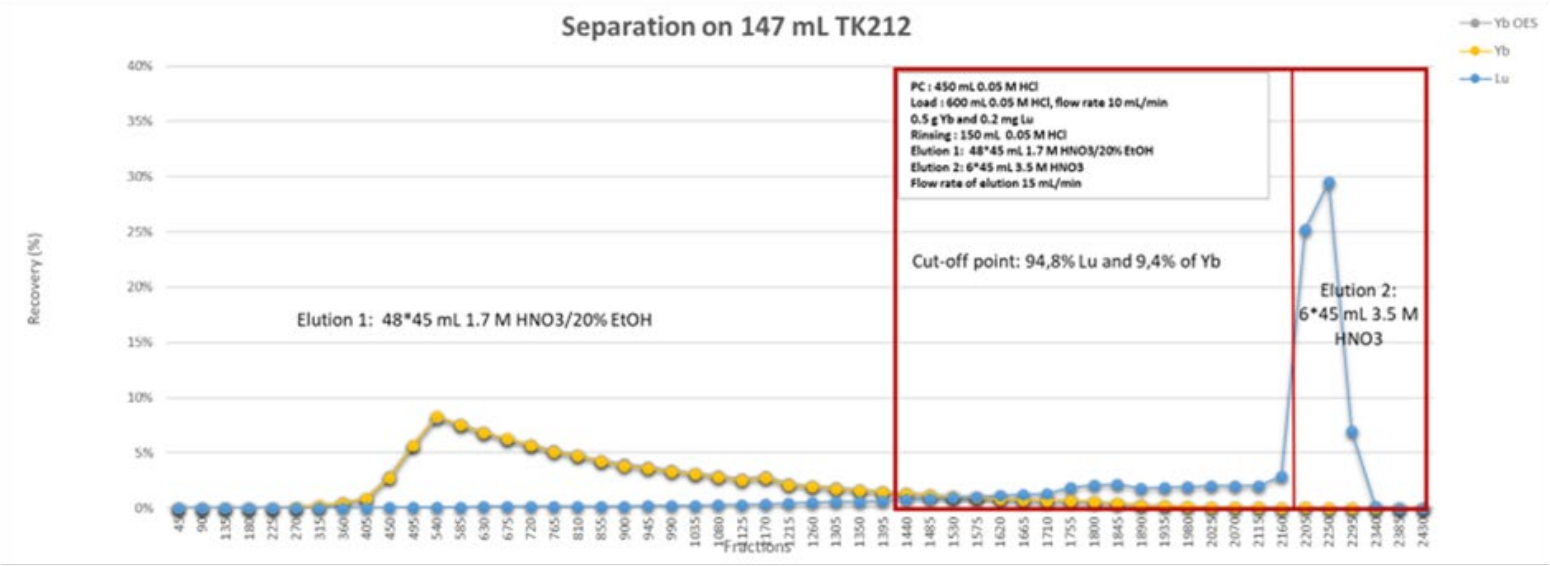
Elution with 1.7M HNO_3 / 20% EtOH – **20µm** particles



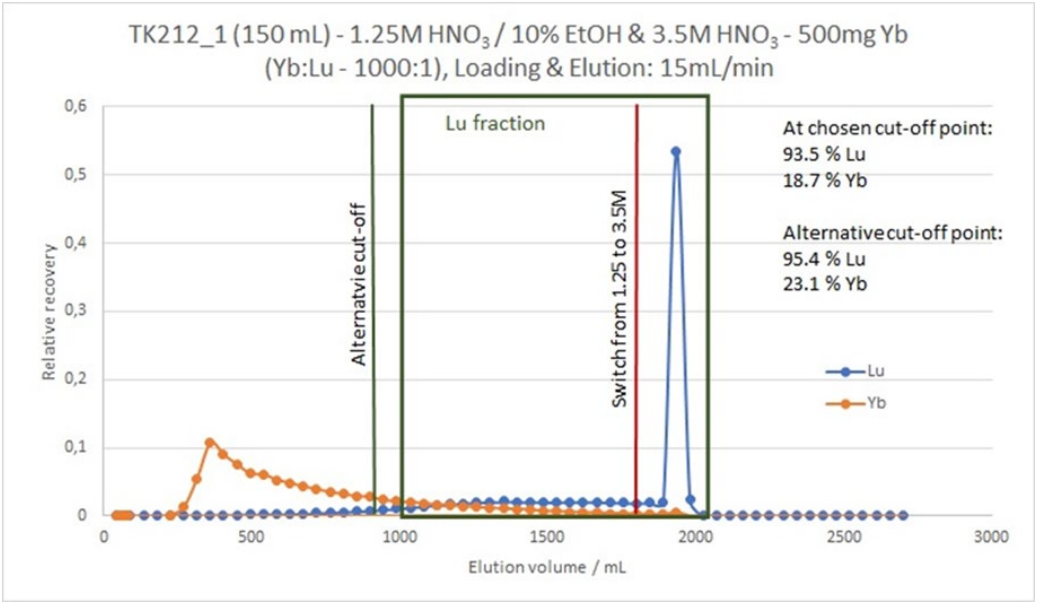
Elution with 1.7M HNO_3 / 20% EtOH – **30µm** particles

20µm at chosen cut-off:
97% Lu and 3% Yb
30µm at chosen cut-off:
90.5% Lu and 3.6% Yb
BUT higher pressure needed

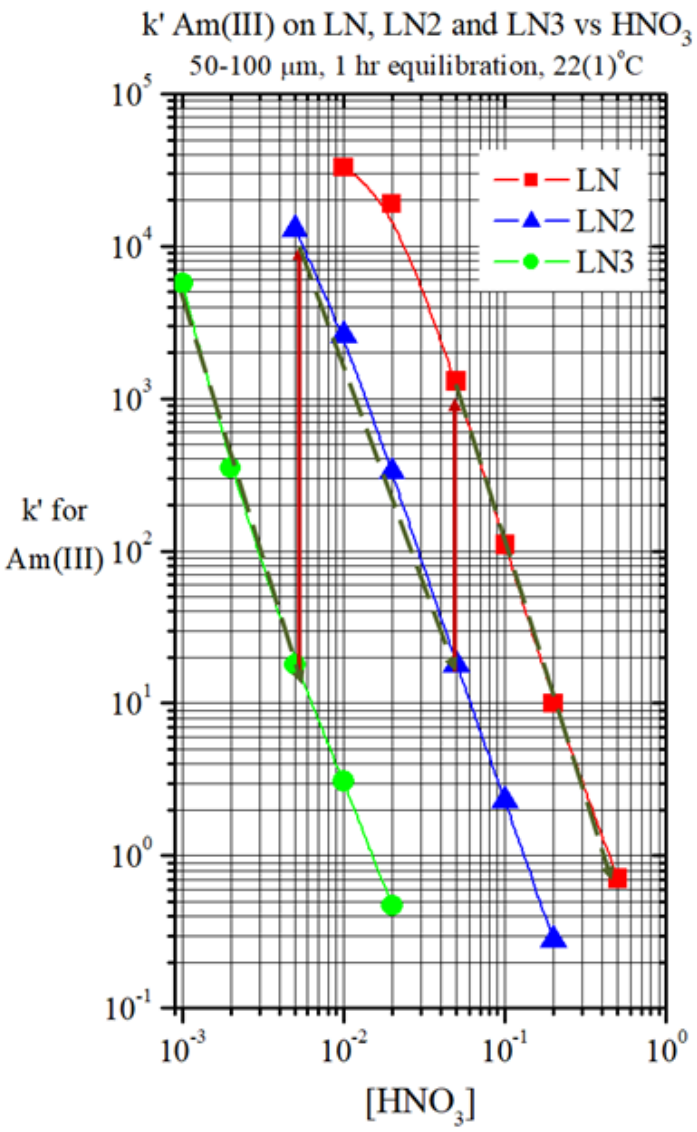
On-going improvement – amount of EtOH



- Use of 1.7M HNO_3 / 20% EtOH
- Better Yb removal compared to 1.25HNO_3/10%EtOH
- Better Yb removal also improves separation on later columns
- Higher %-age of EtOH shifts peaks to higher elution volumes
- Higher acid to lower elution volumes / gain time



Sequential separations



Lanthanide separations now main focus on TK212 and TK211.

- Better separation performance on-column than LN/LN2
- Especially for Yb/Lu and other complex systems with 10 – 20% EtOH

TK221 or DGA very useful for conversion of lanthanides from high HNO_3 (e.g. 3.5M HNO_3) to low acid (e.g. 0.05M) but small losses of Lu/Tb

Alternative: Direct load from TK212 to TK211

Methodenentwicklung

Probenvorbereitung: Leaching vs. Vollaufschluss

Aufkonzentrierung und Matrixentfernung (e.g. LNF_3)

- Entfernung von Interferenten kann sehr wichtig für die Trennung sein (K^+/SR Resin, Fe(III)/TRU,...)

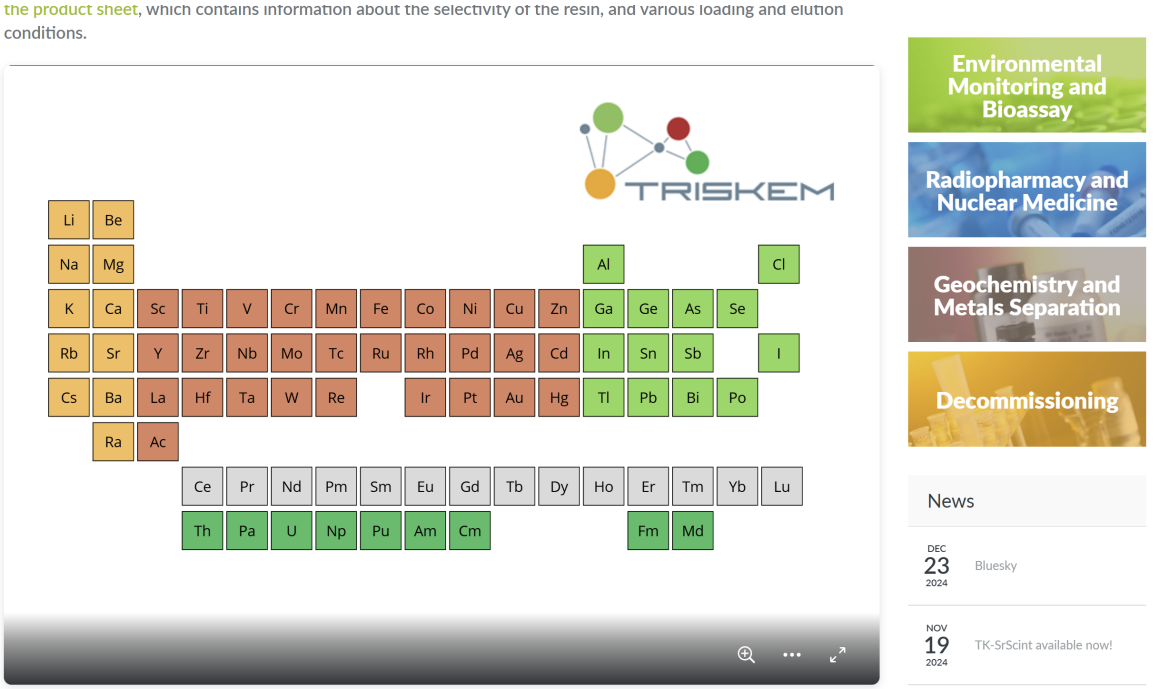
Trennchemie => Prozess

- Definition des Problems
  - A problem well stated is a problem half solved
- Ausgangslage:
  - Matrix (Säure/Säurekonzentration, Matrixelemente,...), Analyt(en), Verunreinigungen/Interferenten, Messprobenherstellung
- Ziel:
  - Messprobe, Elimination der Interferenzen (D_f), Messung,...
- Methodenentwicklung => Identifikation des/der richtigen Harze (Literatur, TechSupp)
  - Keine Selektivität für die Matrix, hohe Selektivität für den Analyten
  - Trennschritte erlauben eine Entfernung aller Interferenzen
  - Oxidationsgrad, Auxiliarien,...
  - Falls nicht möglich zweites Harz mit unterschiedlicher Selektivität
- Test der Methode und Methodenoptimierung

Methodenentwicklung

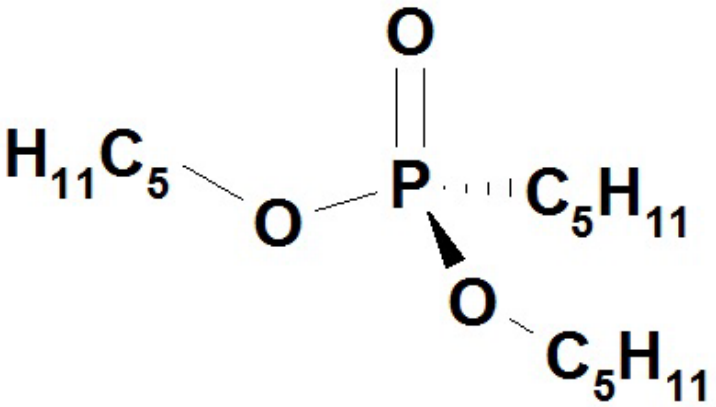
Informationsquellen:

- Publikationen
- Produktblätter/TechDoc
  - Element search tool auf unserer Webseite https://www.triskem-international.com/elements-search.php:



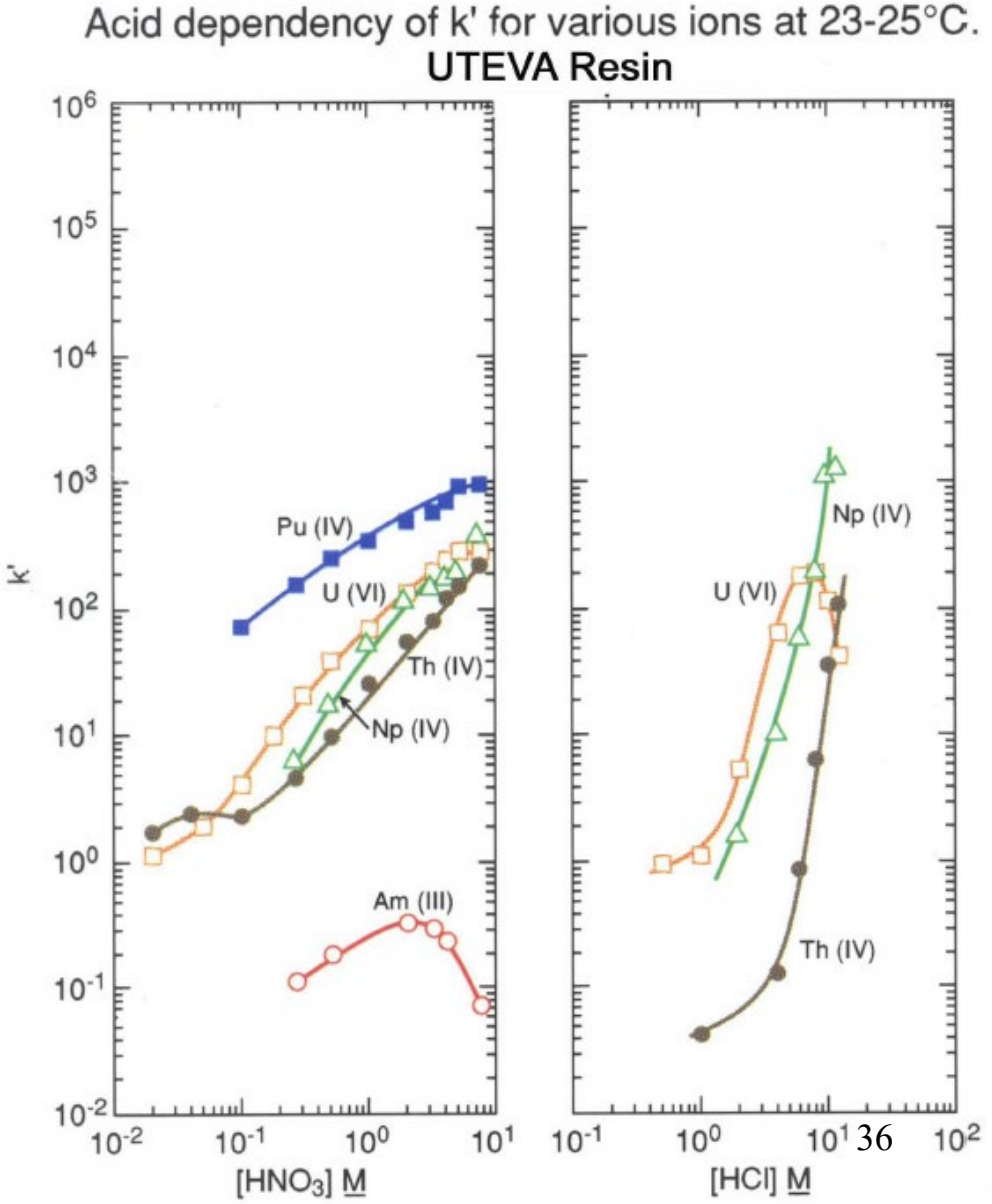
- E-Mail…
- Alte Literatur inkl. LLX Daten e.g. Ghersini/Braun, NAS Series

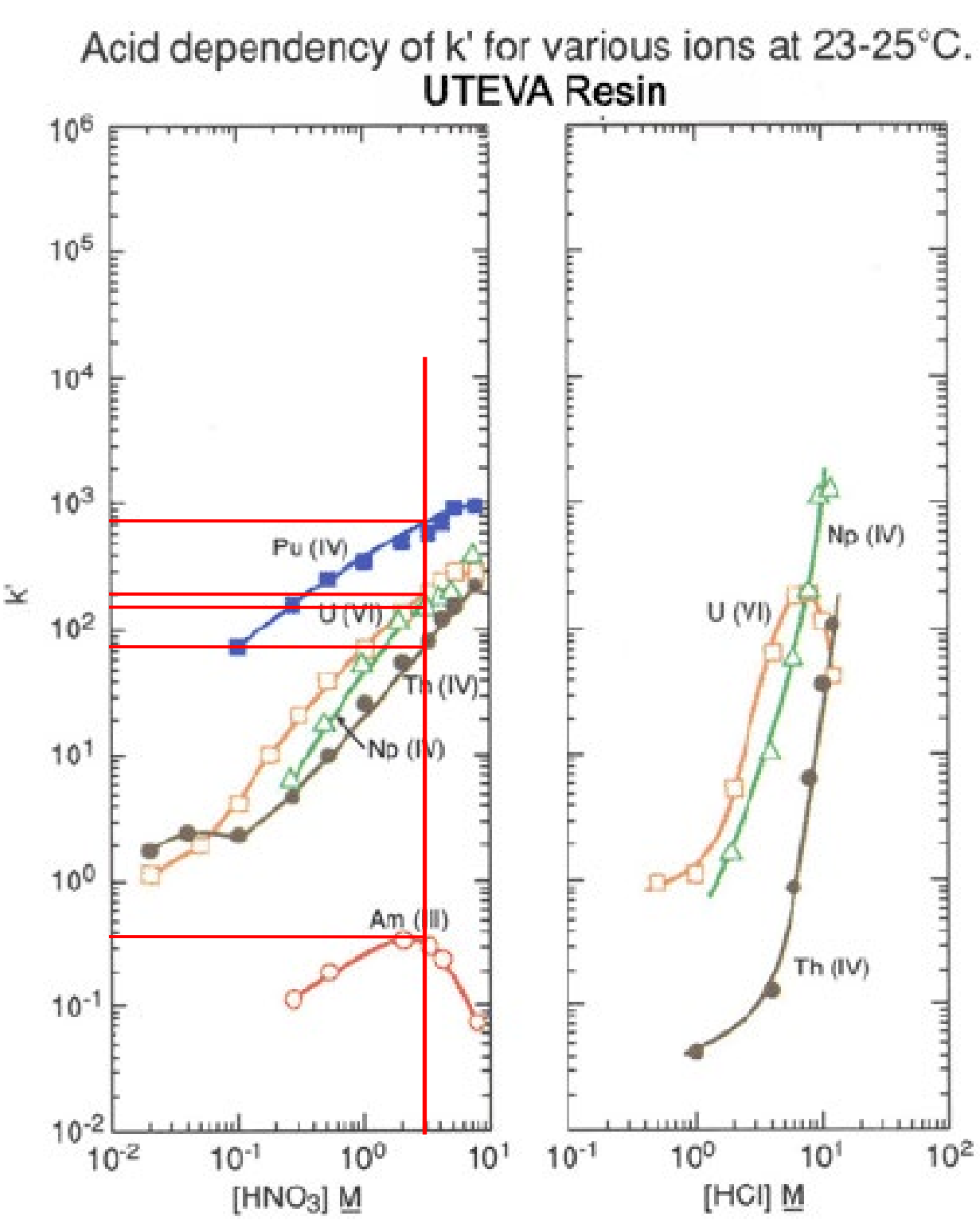
UTEVA Resin



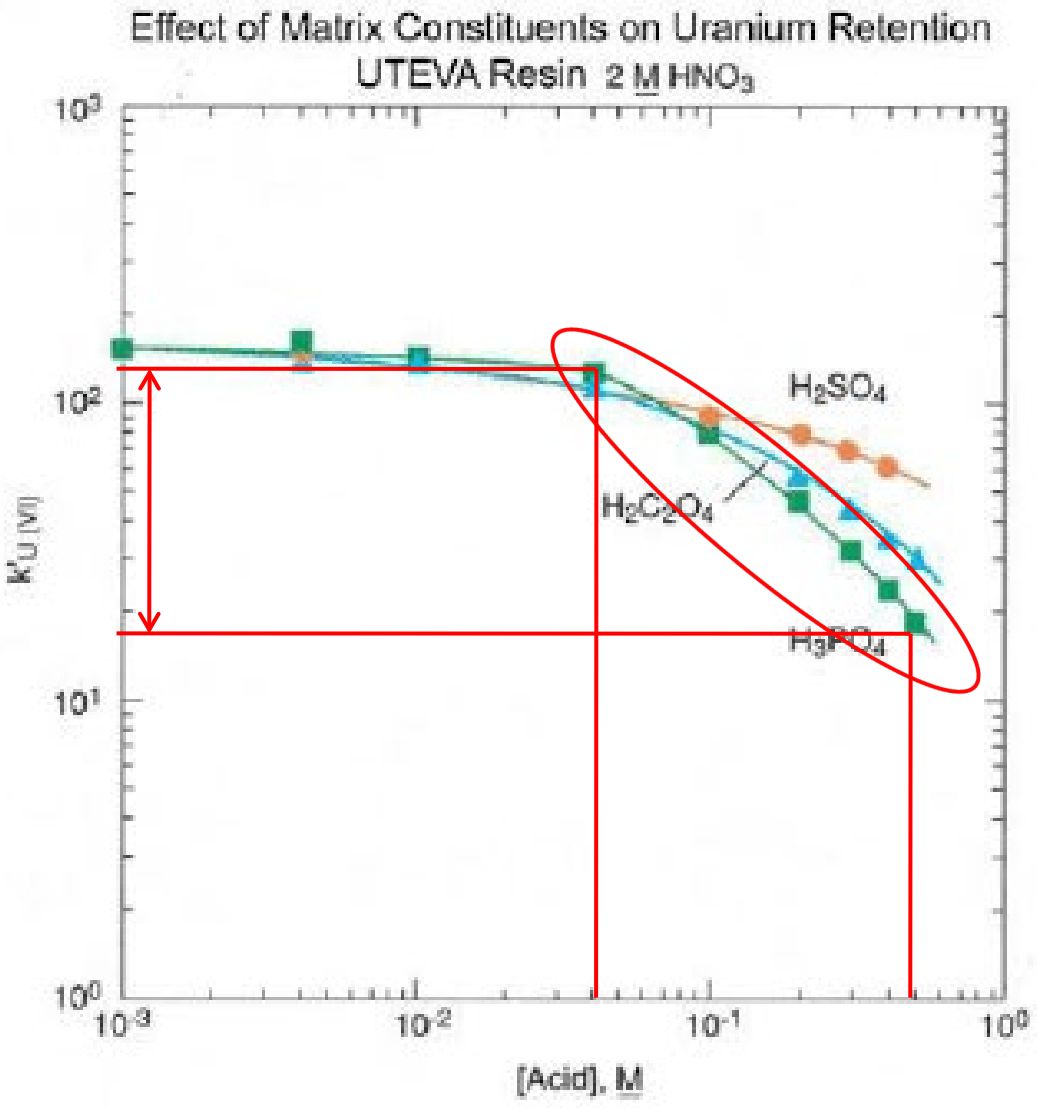
Di-Pentyl-Pentyl-Phosphonate (DPPP)

- **Extractant**: DPPP (in literature also called DAAP)
- For **U**ranium and **TE**tra**V**alent **A**ctinides
- U, Th, Zr,...

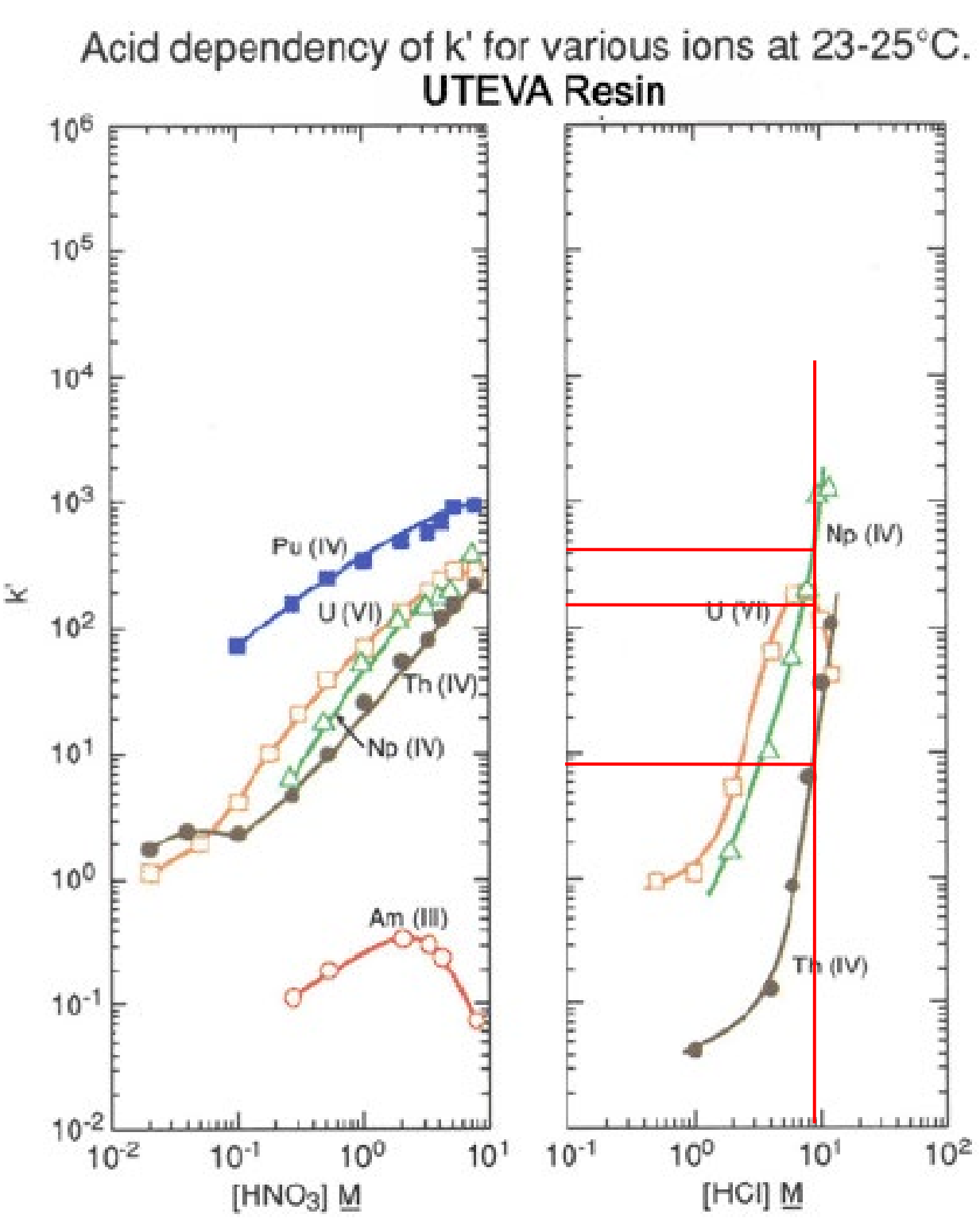




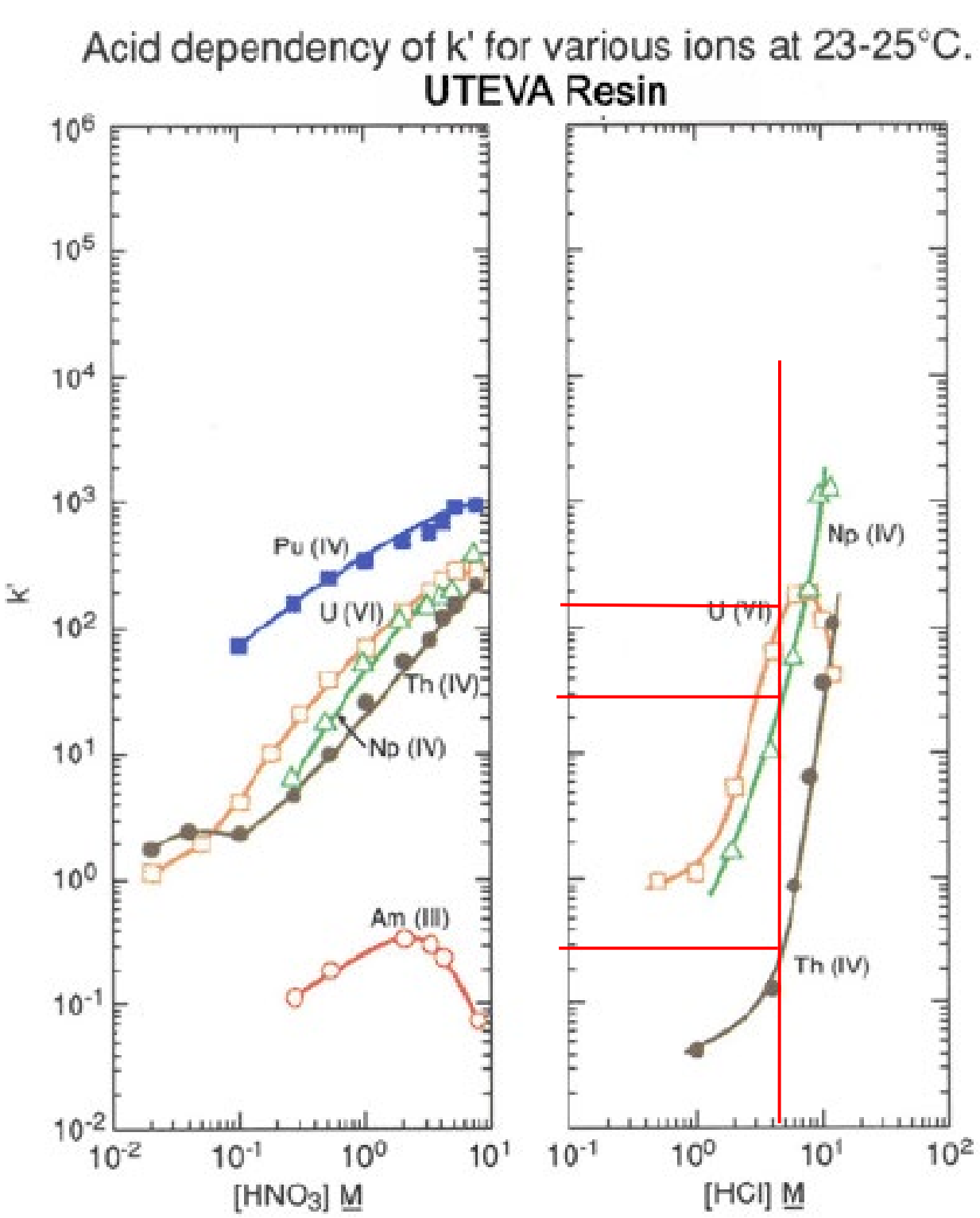
- Loading from 3M HNO_3
  - U, Th and Np(IV) retained
  - Pu(IV) also retained
  - Pu(III) and Am/Cm pass e.g. onto TRU



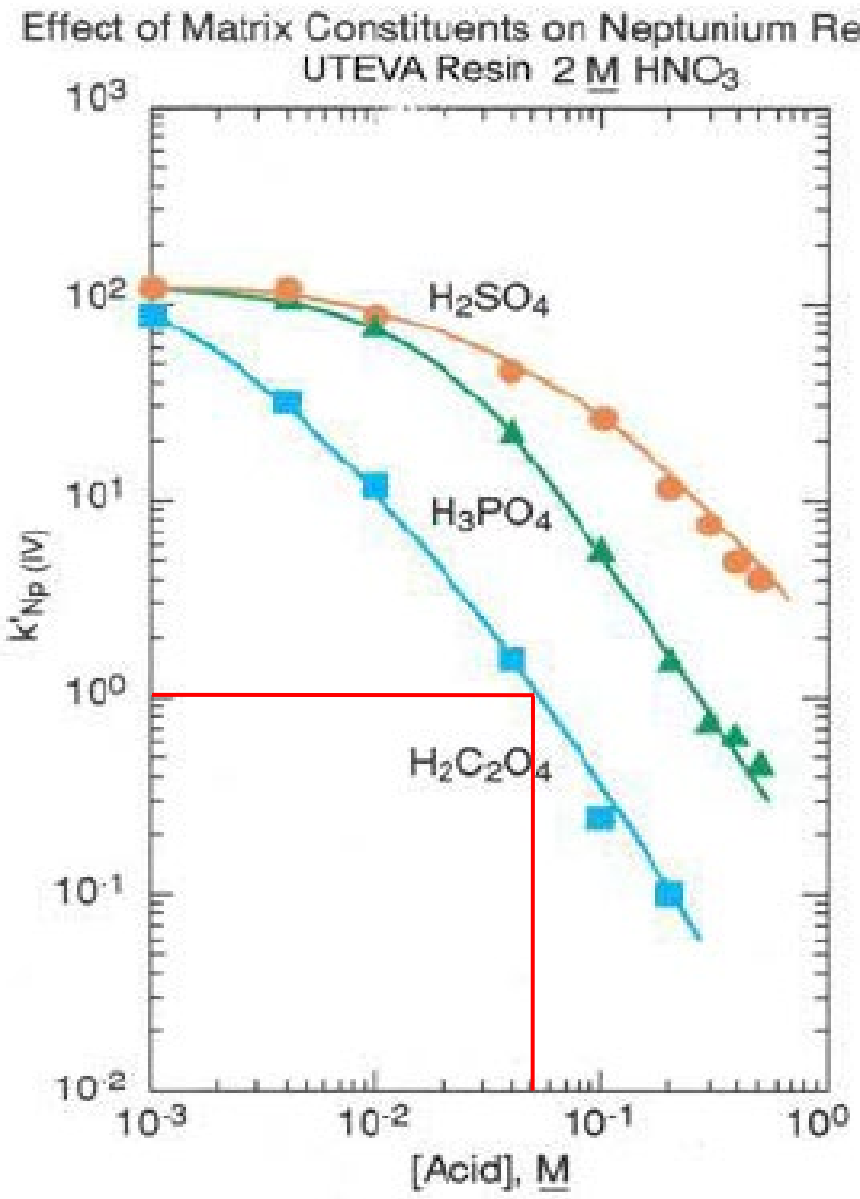
- High levels of phosphate interfere with U retention
- Addition of Al(III): Al complexes phosphate thus lowering concentration of free phosphate
- Improvement of U retention



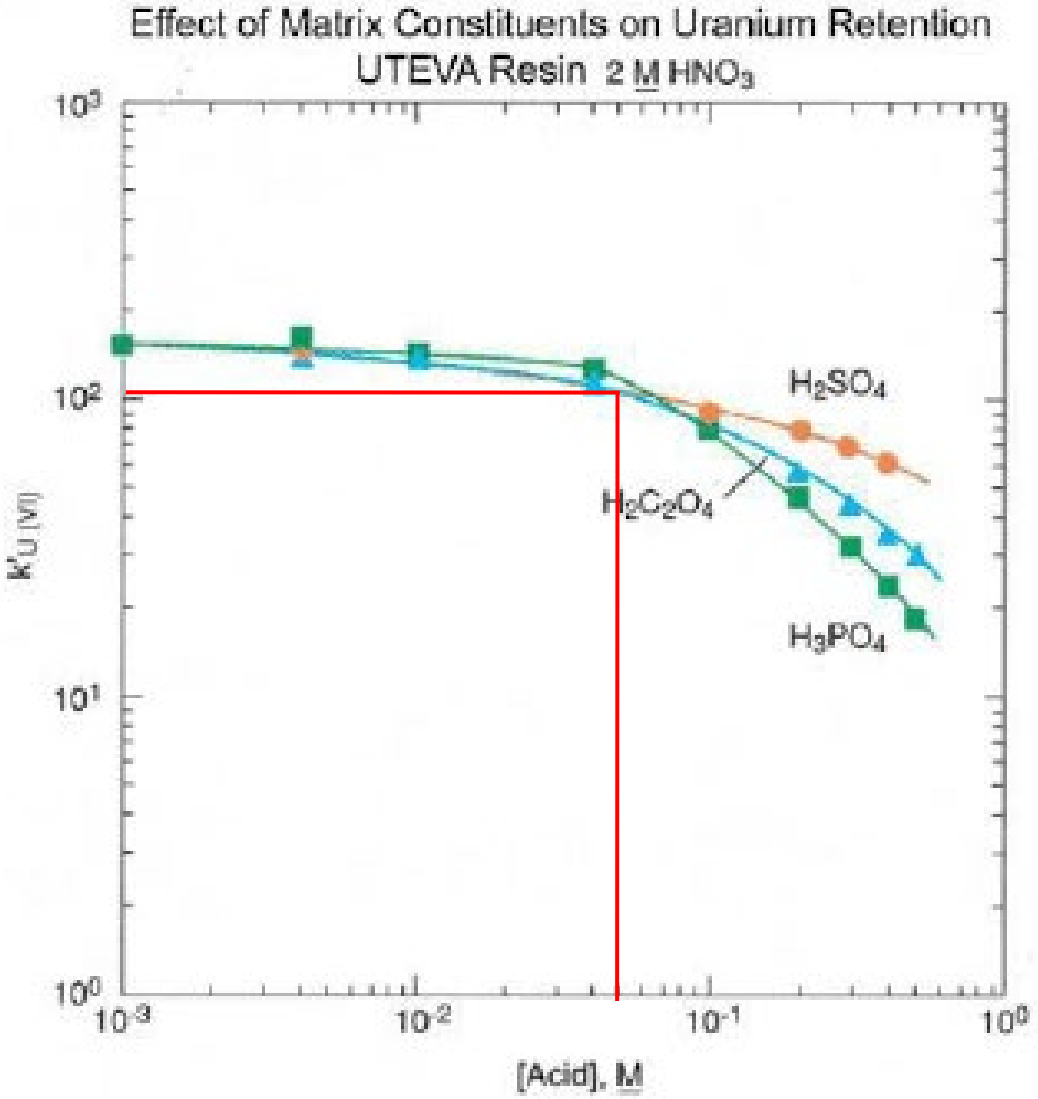
- Conversion to HCl system with 9M HCl
- U and Np(IV) (and Pu(IV) retained
- Th partially eluted



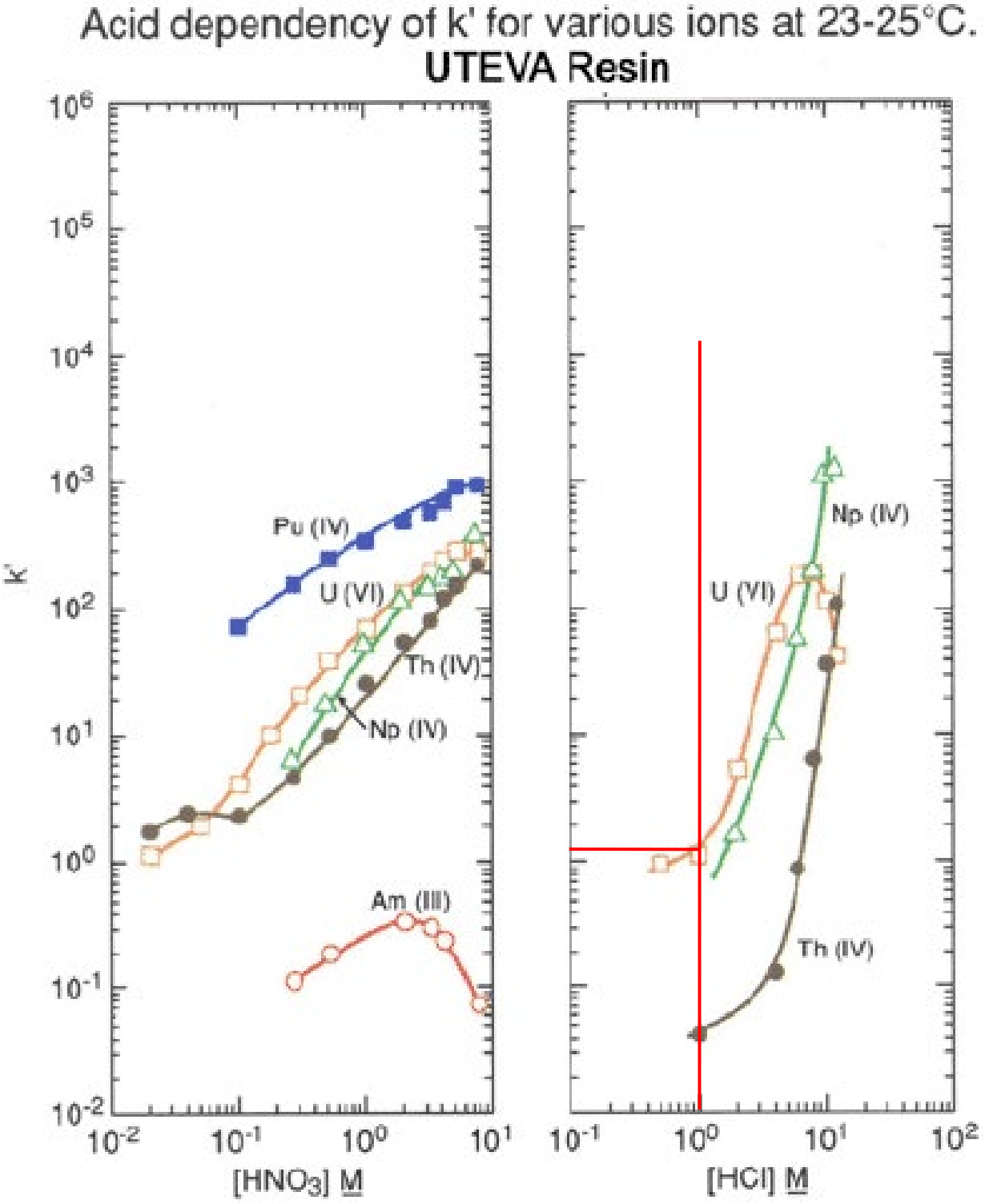
- Th elution with 5M HCl
- U retained
- Np(IV) (and Pu(IV)) weakly retained



- Np(IV) (and Pu(IV)) retention strongly interfered even at low oxalate concentrations (0.05 M oxalate)
- Oxalate facilitates tetravalent actinide elution from UTEVA



- 0.05M oxalate not interfering with U retention on UTEVA
- U remains on column while Np(IV) is eluted



- U not retained on UTEVA at ≤ 1M HCl

Determination of Sr, Pu, Am, Th and U in water and urine samples

Stacked TEVA, TRU and Sr cartridges

Separation in < 6h (vacuumbox / cartridges)

- Flow rates: 1 $mL.min^{-1}$ (load and elution), 3 $mL.min^{-1}$ (rinse)

Typically: 1 L water (pH 2) or mineralised urine

Addition of internal standards and Sr-carrier (or Sr-85)

Ca-Phosphat co-precipitation

Dissolution in 3M HNO_3 / 1M $Al(NO_3)_3$

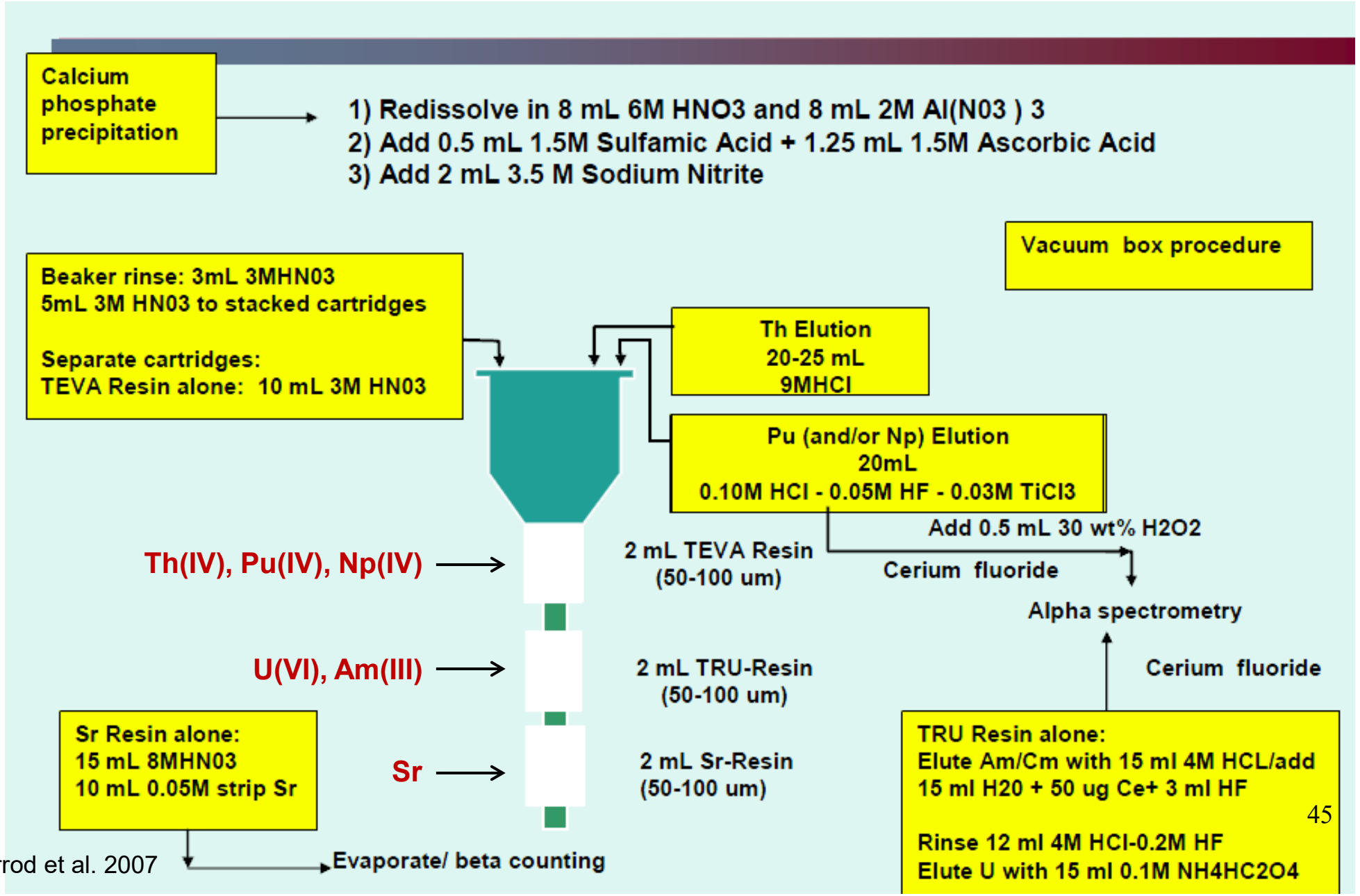
Redox (Pu(IV)): Fe(II) / $NaNO_2$

Load through all 3 cartridges

Rinse with 3M HNO_3

S.L. Maxwell: Rapid Analysis of Emergency Urine and Water Samples, Journal of Radioanalytical and Nuclear Chemistry , 275(3), 2008, 497 - 502

Determination of Sr, Pu, Am, Th and U in water and urine samples

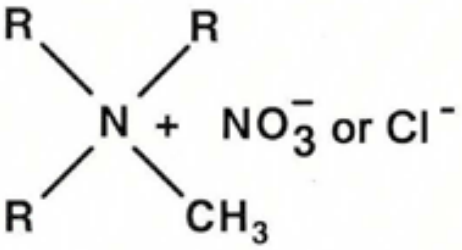


Sherrod et al. 2007

Vacuum Box

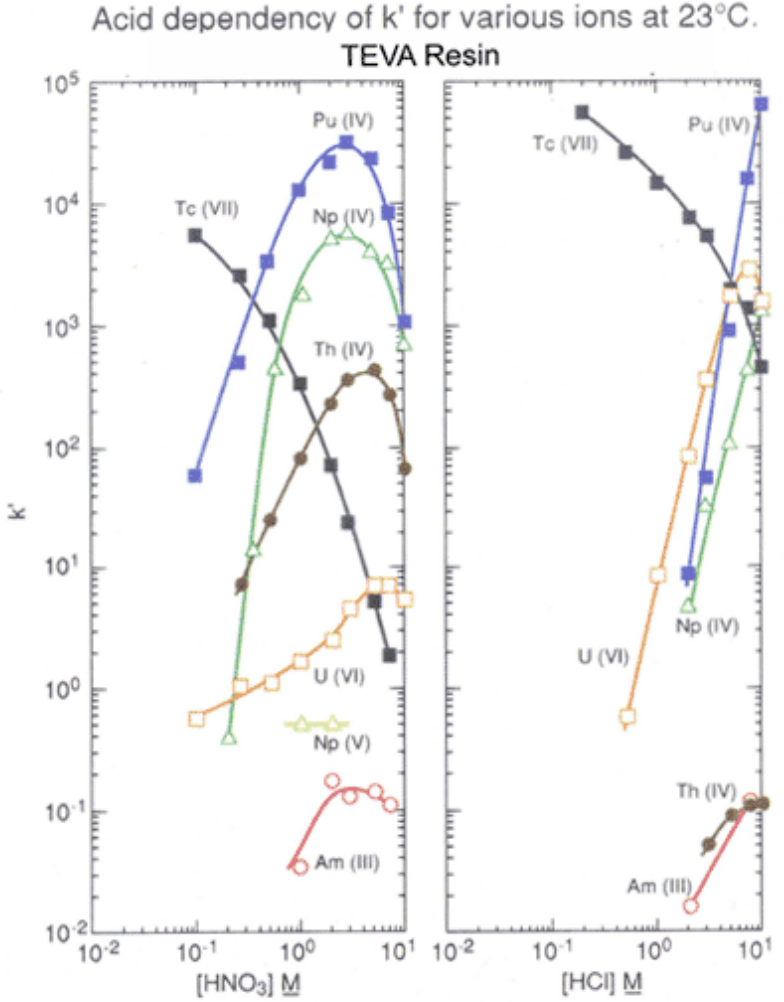
TEVA Resin

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),...



Horwitz, et al. (HP195)

Separation on TEVA

Rinse: 10 mL 3M HNO_3

1

2

Th Elution: 20 - 25 mL 9M HCl

3

Pu (and/or Np) Elution:
20 mL 0.1M HCl – 0.05M HF –
0.03M $TiCl_3$

TEVA

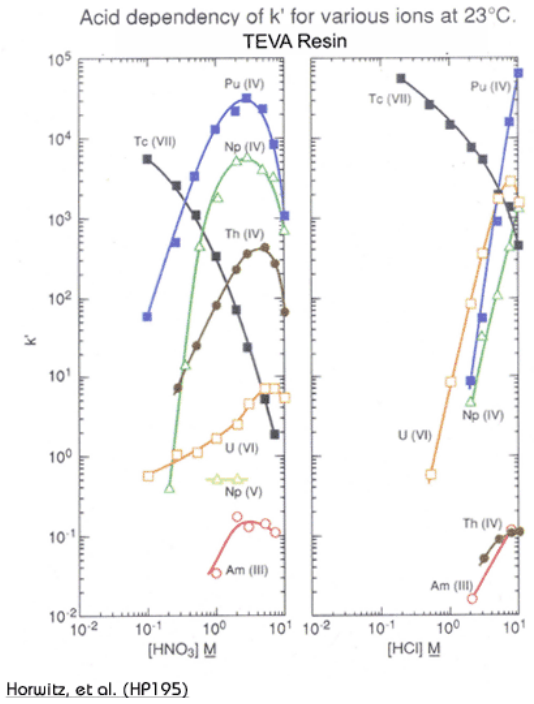
Typical Yields:

- Pu: > 95%
- Th > 80%

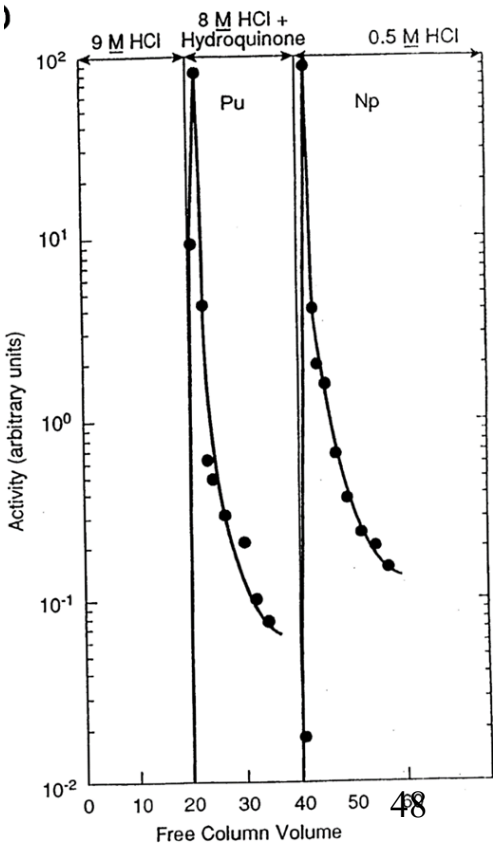
3 → Pu eluate

1 → Waste

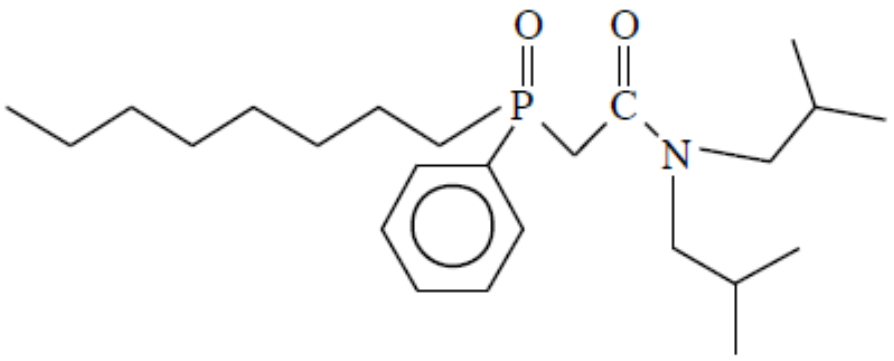
2 → Th eluate



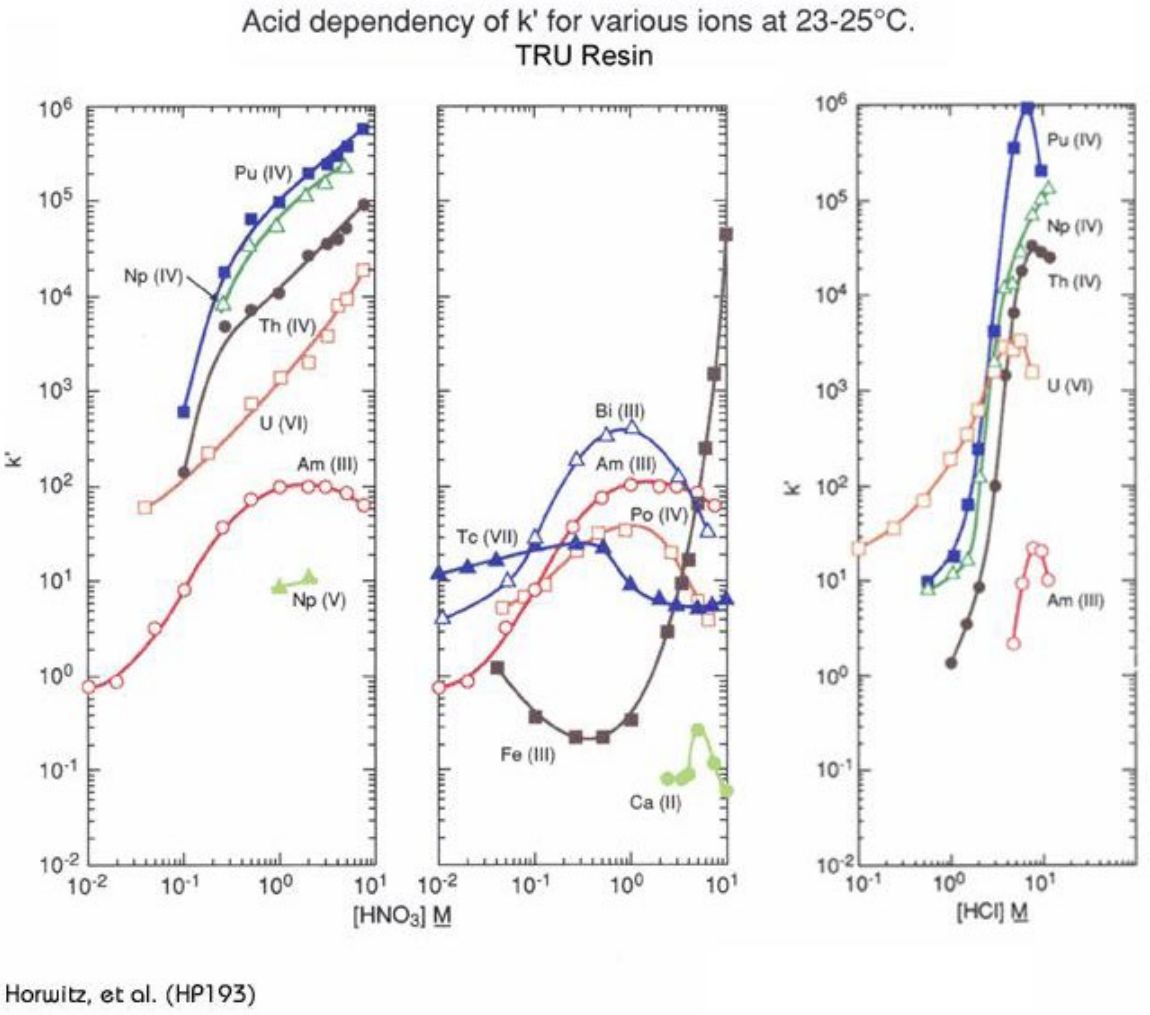
Horwitz, et al. (HP195)



TRU Resin

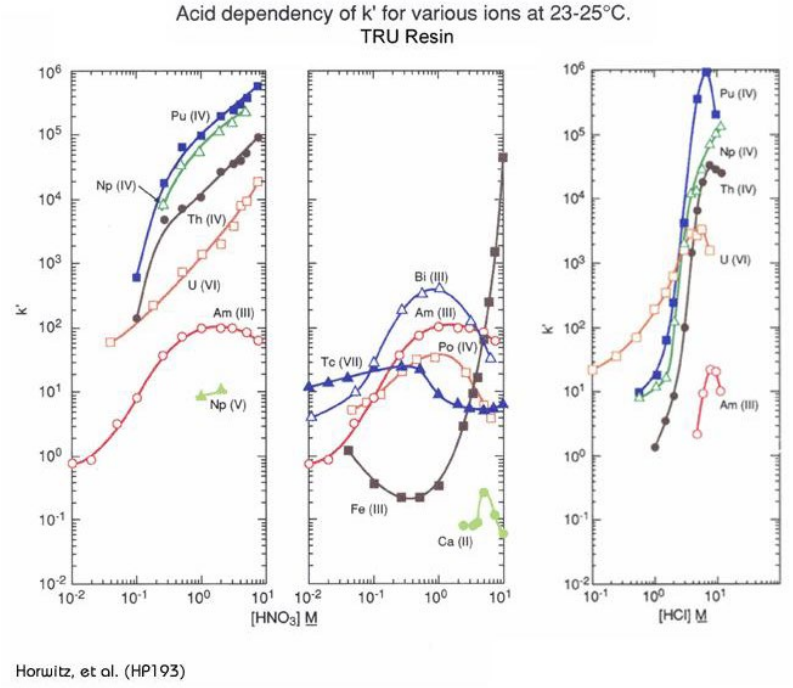


octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide



- **Extractant**: CMPO in TBP
- **TR**ans**U**ranium elements
- Am/Cm, U, Pu,...

Separation on TRU



2

Rinse: 12 mL 4M HCl – 0.2M HF

1

Am Elution: 15 mL 4M HCl

3

U Elution: 15 mL 0.1M $NH_4C_2O_4$

TRU

Typical Yields:

- U: > 90%
- Am > 95%

3

U eluate

1

Am Eluate

2

Waste

TEVA/TRU vs UTEVA TRU

TEVA/TRU:

- Pu(IV) required, accordingly presence of Fe(III) => problematic on TRU

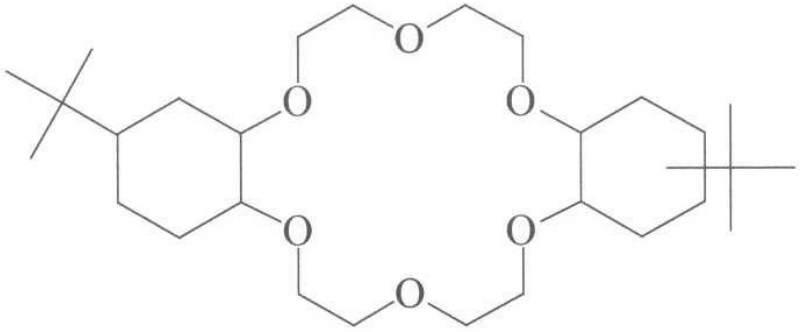
  => Replace TRU with DGA (U...)… or TK221?

- TEVA allows for Pu/Np separation or elution together (Pu-236)

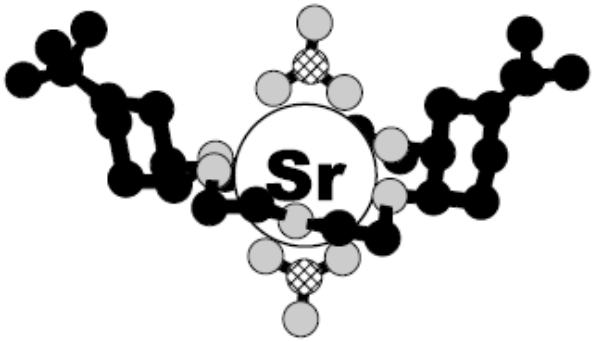
UTEVA/TRU

- Pu(III) follows Am(III) onto TRU
- Th retention on UTEVA not very strong
- Presence of Fe(II) => more compatible with TRU
- Np/Pu co-elution impossible (Np on TEVA, Pu on TRU)
- For decommissioning samples Pu reduction not always easy

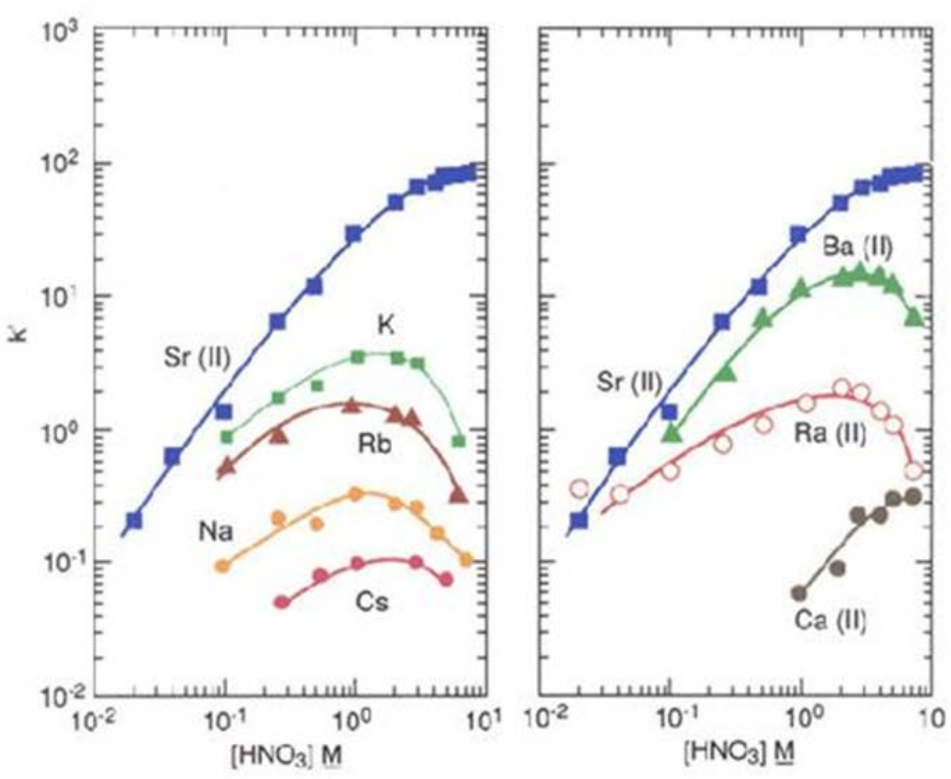
Sr Resin



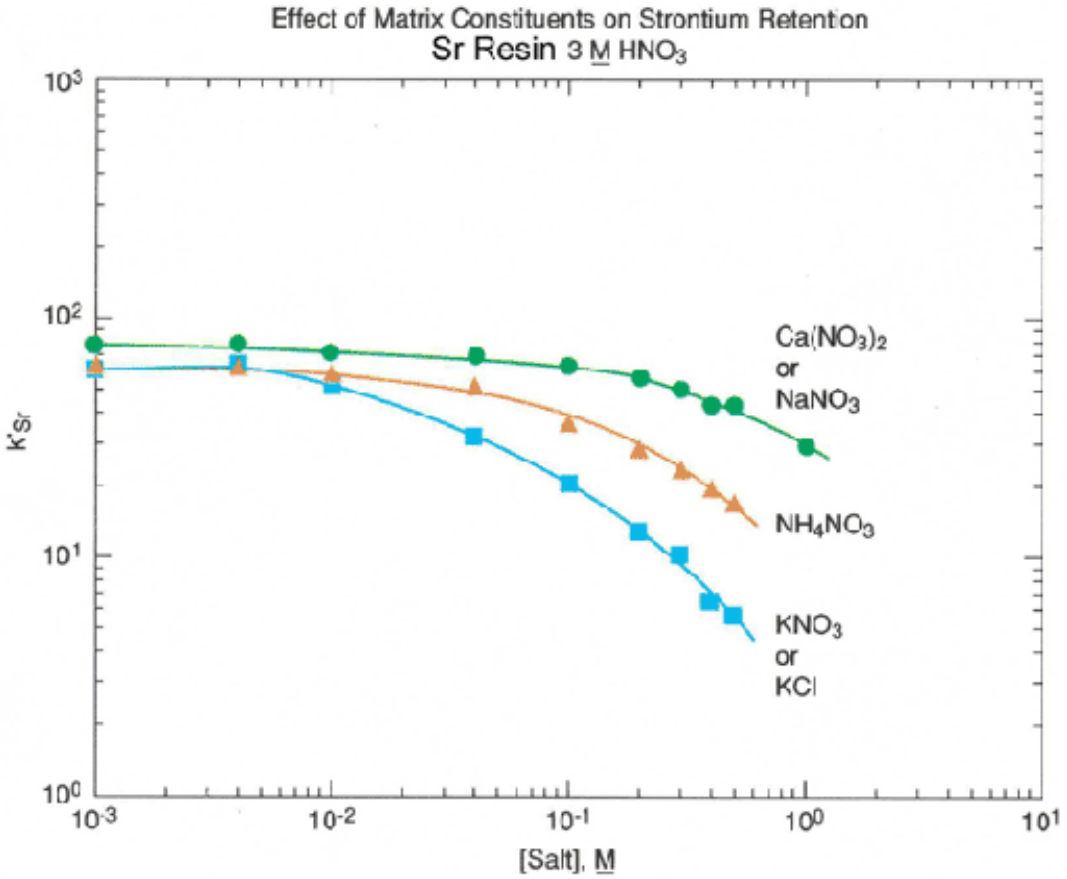
Diluent: 1-octanol



Dietz et al. 2004



Sr Resin - Interferences



- High impact of K/NH_4 ; elimination necessary when present in high concentration (ion exchange or co-precipitation: e.g. carbonate, phosphate, oxalate)
- Moderate impact of Ca, nevertheless problematic when present in high concentration - column size needs to be adapted

Separation on SR

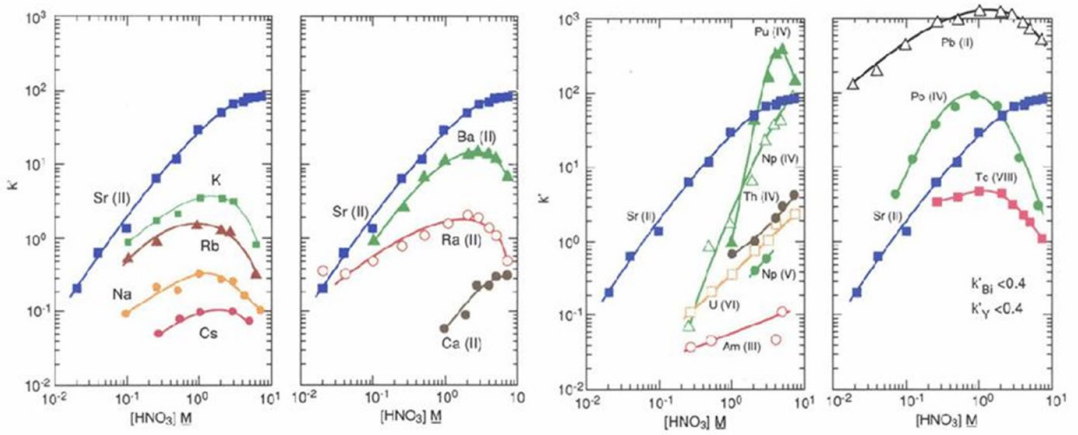
Rinse: 15 mL 8M HNO_3 — 1

2 — Sr Elution: 10 mL 0.1M HNO_3

SR

Typical Yields:

- Sr: > 90%



1 — Waste

2 — Sr eluate

- LSC or GPC

High matrix samples: TK102 instead of SR? Higher capacity and D_W

Wunschthemen

Am and Pu in large soil samples

Horwitz, E.P.; et al: Synergistic Enhancement of the Extraction of Trivalent Lanthanides and Actinides by Tetra-(n-Octyl) Diglycolamide from Chloride Media, Solvent Extraction & Ion Exchange, Vol. 26(1), in press(2008)

Tait, D., Kock B.: Further development of a fast methd for determining plutonium and americium in soild in Germany. Environmental Radiochemical Analysis IV. Ed.: Peter Warwick, RCS Publishing, 2011, 9 – 20

Maxwell, S.L.; Culligan, B.K.: Rapid Column Extraction Method for Actinides in Soil, Journal of Radioanalytical and Nuclear Chemistry, Vol. 270, No. 3, pp 699-704(2006)

Maxwell, S.L.: Rapid Method for Determination of Plutonium, Americium and Curium in Large Soil Samples, Journal of Radioanalytical and Nuclear Chemistry, Vol. 275, No. 2(2007)

Determination of Am and Pu in large soil samples

Detection limits requested in environmental monitoring make analysis of large soil samples necessary

- Depending on country 30g to >100g

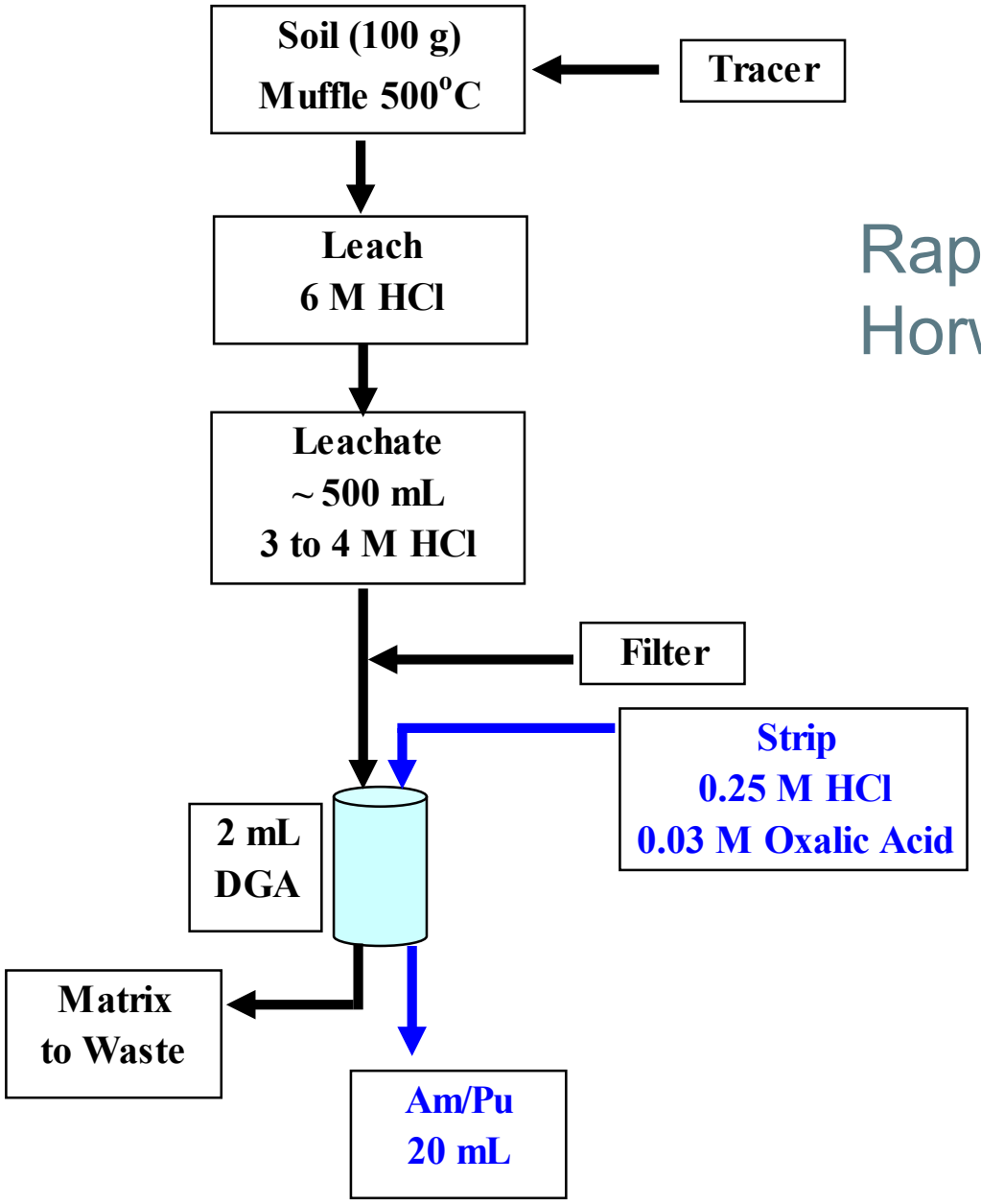
Existing methods:

- TRU sensitive to Fe(III) interference, Fe needs to be removed or reduced quantitatively
- e.g. Ca-Oxalate precipitation for matrix/Fe removal

DGA shows very high Am uptake and robustness against Fe interference

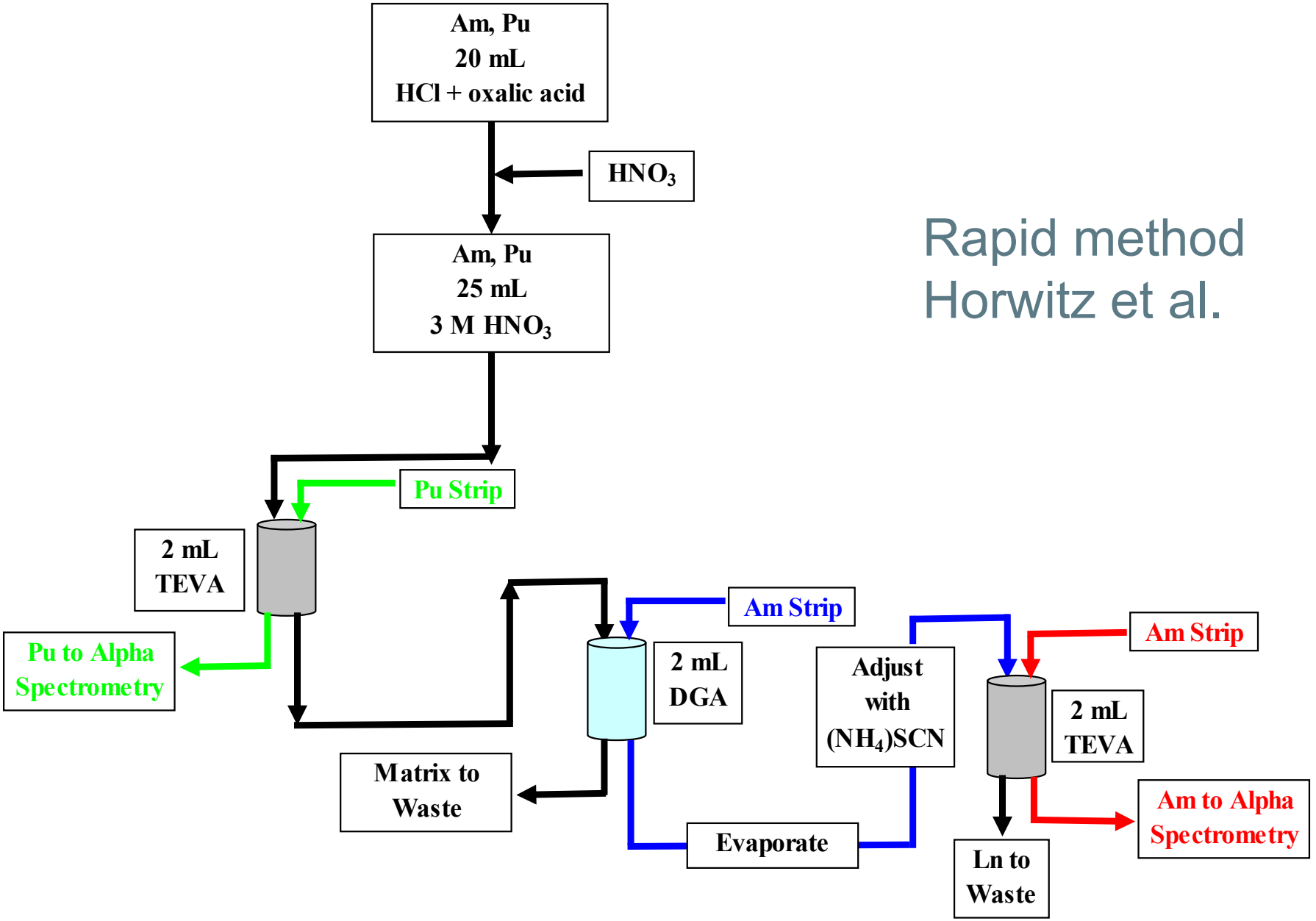
- Preconcentration and Am separation on DGA
- Method developed by Horwitz, updated by Tait et al.

Flowchart for the Preconcentration of Am and Pu from 100 g of Soil



Rapid method
Horwitz et al.

Flowchart for the Separation of Pu and Am from Preconcentrate



Rapid method
Horwitz et al.

Modified Horwitz method – Tait et al. (2010)

100g soil ash (can also be applied to hay, maize, sediments and sludge)

Ashing of sample at 700°C for 18h, Micro-wave supported acid extraction (10 bar)

Filtration through three glassfiber and one membrane filter to remove fine particles

Preconcentration / matrix removal via DGA

Modified Horwitz method – Tait et al. (2010)

2 TEVA columns before 2nd DGA column

- removal of Th from Am spectra
- Alternatively: 1 UTEVA and 1 TEVA (Jaeggi et al.) or only 1 TEVA and additional rinsing step on DGA (Maxwell et al.)

Tested method against in-house reference method

- Very good agreement of results

- Obtained chemical yields:
  - Pu: 87% ± 11%; Am: 72% ± 14%

Jaeggi et al. Showed interference of high Ca samples

- DGA Resin also used for Ca separation => careful choice of loading/rinsing conditions
- TK221 showed improved Am retention in presence of high Ca => additional option?

100g soil ash+450mL 8M HCl
Add tracers and carriers + stirring bar

Microwave and irradiate 30min @100°C
Let cool to <60°C

Centrifuge content
Transfert supernatant in beaker
Add 60mL 6M HCl to residue
and centrifuge – collect supernatant
Repeat residue rinsing

Combine all supernatants and filter

Column load solution

Sample preparation (100g of ash soil sample)
Dry ashing + leaching

Load solution
~500mL 6-7M HCl

DGA (2mL)
Resin preconditionned with 5mL 4M HCl
Load solution
Rinse with 2x5mL 4M HCl
2x2.5mL 3M HNO_3
Pu/Am elution with 20mL 0.03M oxalic acid/0.25M HCl
Add 4.7mL 65% HNO_3 and 0.5g $NaNO_2$

TEVA (1) + TEVA (2) + DGA resins (2mL)
Resin preconditionned with 15mL 3M HNO_3
Load Pu/Am fraction
Rinse with 10mL 3M HNO_3
Separate resins, discard TEVA (2)

TEVA (1)
Rinse with 10mL 3M HNO_3 and 20mL 9M HCl
Pu elution with 20mL 0.03M $TiCl_3$/0.05M HF/0.1M HCl
Evaporate fraction

DGA
Rinse with 5mL 3M HNO_3 and 20mL 0.1M HNO_3
Am elution with 20mL 0.1M HCl
Evaporate fraction and dissolve in 10mL 4M NH_4SCN/0.1M HCOOH

TEVA (unused) - further purification of Am fraction
Resin preconditionned with 5mL 2M NH_4SCN/0.1M HCOOH
Load on resin
Rinse with 10mL 1.5M NH_4SCN/0.1M HCOOH
Am elution with 25mL 0.25M HCl

Preparation for alpha spectrometry
Micro-precipitation

Total analysis in 2-3 days

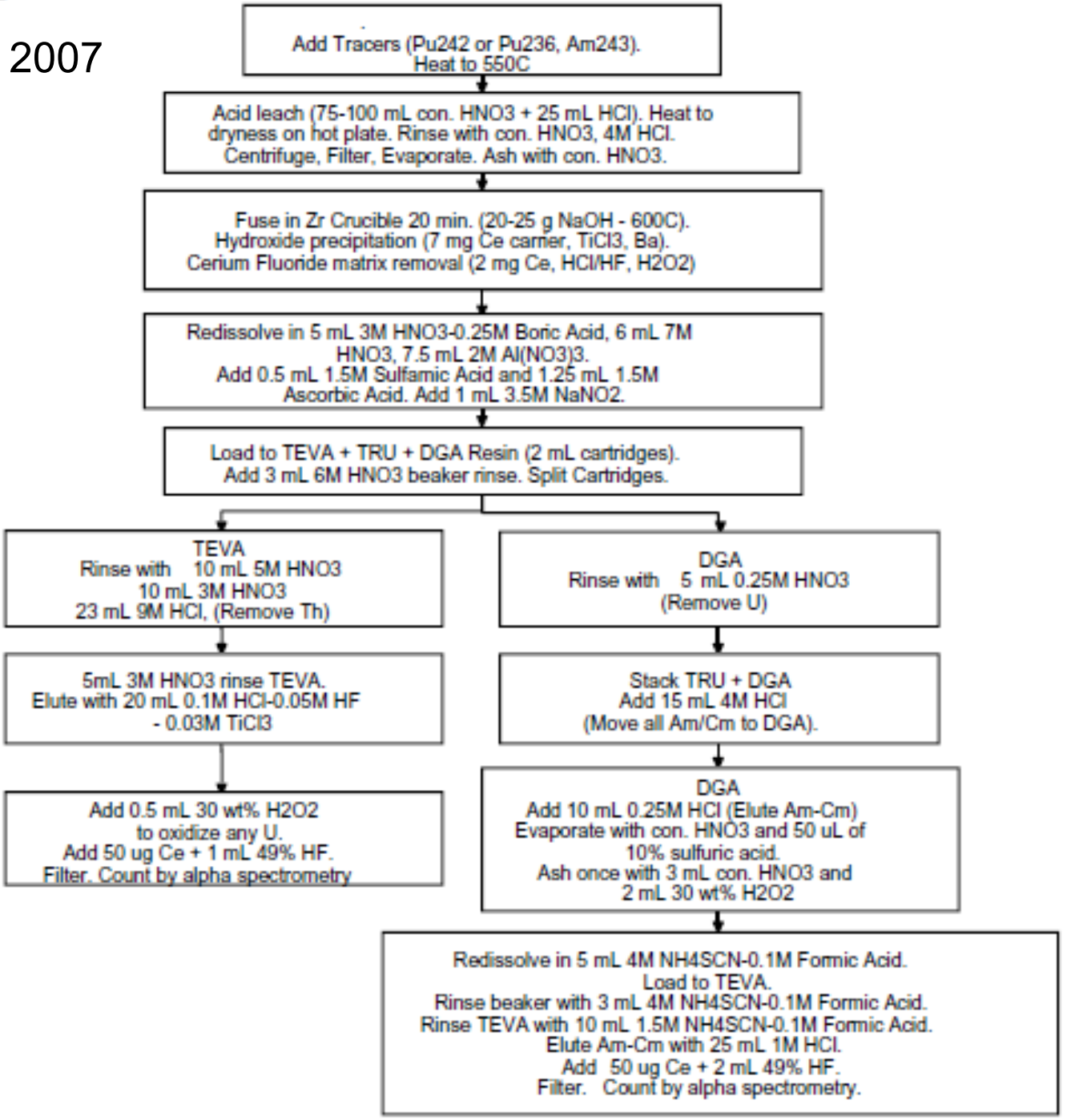
RN	PTB ref value (Bq/kg dm)	Mean of lab means (Bq/kg dm)
^{238}Pu	19.6 (s=1.3)	20 (s=1.4)
$^{239/240}$Pu	1.1 (s=0.1)	1.2 (s=0.3)
^{241}Am	154 (s=5)	133 (s=12)

Other matrix elimination steps

- Sherrod Maxwell (SRS laboratories)
  - CeF_3 or LnF_3 co-precipitation
    - Precipitation under oxidative conditions removes U
  - Stacked TEVA/TRU/DGA cartridges
  - Leached soil samples up to 200 g (Pu/Am)
    - leaching HNO_3/HCl
    - Pu and Am recoveries 80 – 90%
    - Detection limit: 1 mBq/kg (16h counting)

100-200g Soil Method

Sherrod et al. 2007



Bodenproben - Fusion

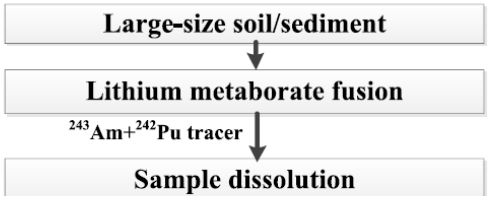


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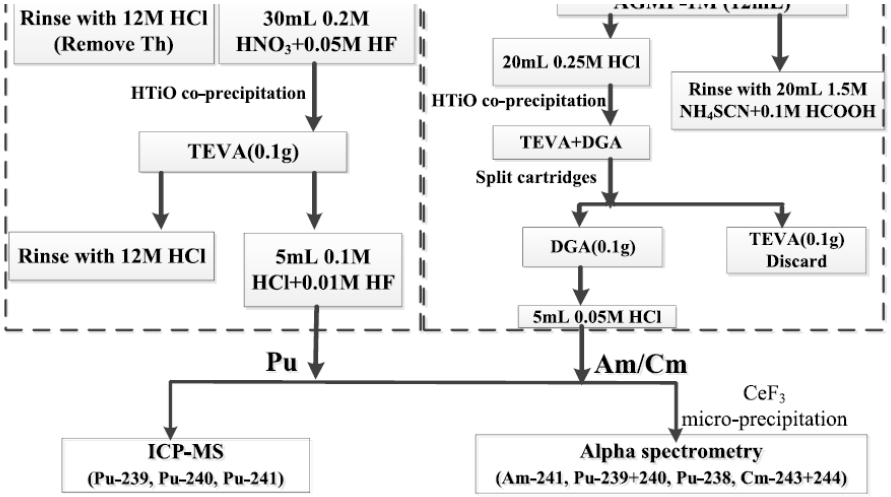
Table 4
Results of $^{239+240}Pu$, ^{238}Pu and ^{241}Am measured for the IAEA reference materials.

Reference material	Overall recovery (%)		$^{239+240}Pu$ (mBq/g)		^{238}Pu (mBq/g)		^{241}Am (mBq/g)	
	Pu	Am	Certified	Measured	Certified	Measured	Certified*	Measured
IAEA-384	101 ± 3	89 ± 3	107 (103–110)	109 ± 4	39 (38.6–39.6)	39.7 ± 1.5	8.2 (7.82–8.52)	8.11 ± 0.45
	96 ± 5	95 ± 5		108 ± 5		38.4 ± 1.7		8.23 ± 0.56
	100 ± 5	102 ± 5		105 ± 3		39.8 ± 1.2		8.38 ± 0.33
IAEA-385	101 ± 7	69 ± 3	2.96 (2.89–3.00)	2.96 ± 0.71	0.44 (0.42–0.48)	0.47 ± 0.15	4.46 (4.40–4.63)	4.45 ± 0.66
	92 ± 5	80 ± 3		2.90 ± 0.59		0.43 ± 0.13		4.60 ± 0.45

*The certified values of ^{241}Am have been corrected for the in-growth from ^{241}Pu.



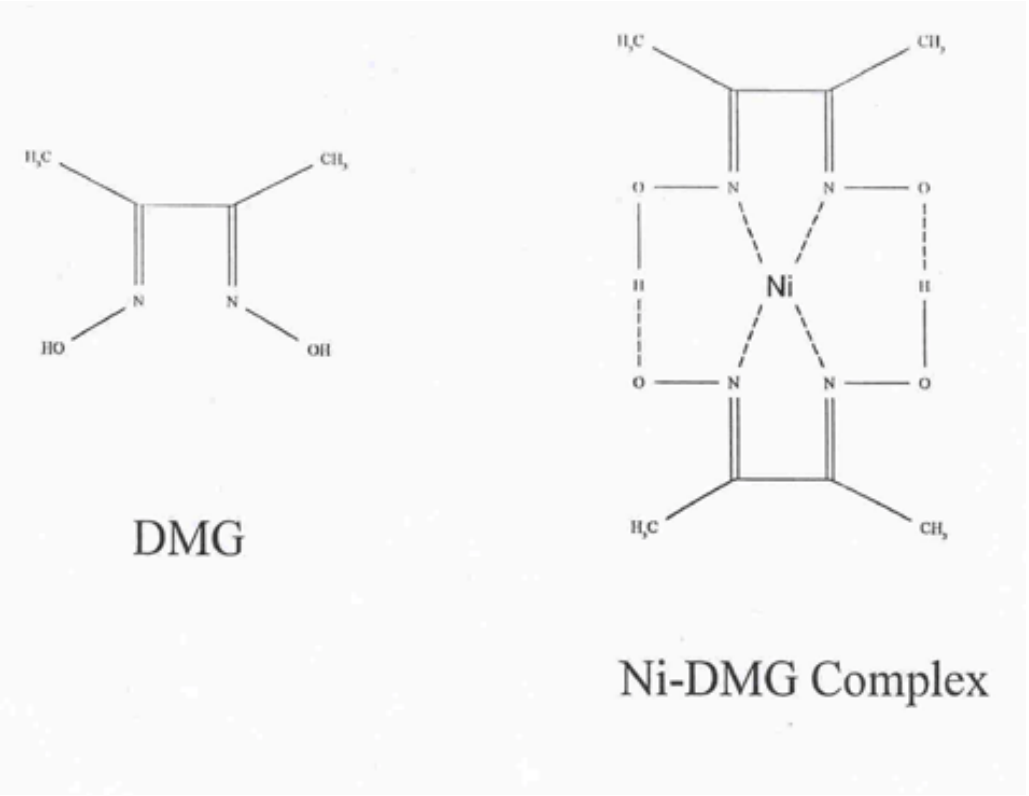
Several co-precipitations

Elaborate separation chemistry

Chemical yields > 70 - 80%

Tested on IAEA Reference materials

Determination of Ni-63 via Ni Resin



-**Extractant:** Dimethylglyoxime

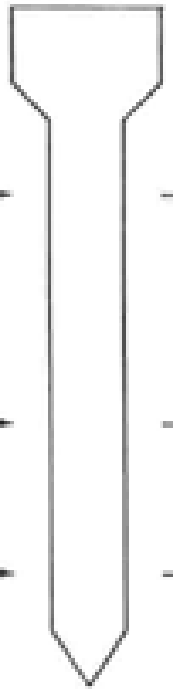
- Ni precipitation with DMG on the resin (pink-red precipitate on the resin)

Ni-59/63 in water

- Fe (and Co) removal upfront (TRU or TEVA/anion exchange)
  - ➢ Use of TRU Resin allows for determination of Fe-55
- Routine 100 mL sample, addition of 2 mg Ni
- Evaporation to dryness, redissolution in 1M HCl
- Addition of 1 mL 1M amm. citrate, adjust to pH 8 – 9
- Load sample (red/pink layer appears)
- Rinse with amm. citrate (pH 8 – 9)
- Elute with minimim amount of 3M HNO_3 (until red colour disappears) -> LSC

Typical Procedure

- Load: Sample + 2 mg Ni carrier → Discard
- Rinse: 20 ml 0.2 M ammonium citrate at pH = 8 - 9 → Discard
- Strip: 3 mL 3 M HNO_3 → Measure Ni-63 by LSC and Ni-59 by X-Ray



Eichrom Nickel separation procedure NIW01

Method performance

- Chemical yield typically > 90% for water samples

RN	Decontamination factor
Cr-51	> 37 000
Mn-54	270 000
Co-58	110 000
Co-60	113 000
Nb-95	13 700
Cs-134	> 9 000
Cs-137	58 000

Cahill (CD195)

Ni-59/63 in spent ion exchange resin and activated charcoal

Taddei et al. ARI, 77 (2013) 50 – 55

2g samples, wet or dry ashing

Addition of 2 mg Ni

$Fe(OH)_3$ precipitation at pH 9 in presence of NH_4OH

Ni remains in solution

Supernatant evaporated to dryness and dissolved in 9M HCl

Solution loaded through anion exchange resin (Ni passes, trace Fe and Co retained)

Ni-59/63 in spent ion exchange resin and activated charcoal

Effluent evaporated to dryness and dissolved in 1M HCl

Ni resin column chemistry as for water samples

Sample preparation for X-ray by DMG precipitation

- Ni-59 determination

After X-ray sample dissolved in 10 mL 3M HNO_3 and evaporated to near dryness at 80°C

Residue dissolved in water, aliquote taken for ICP-MS, rest LSC (Ni-63 determination)

Chem. Yields 70 – 90%

Xiaolin Hou:
Determination of ^{63}Ni, ^{59}Ni in decommissioning waste

Hou, et al. Anal. Chim. Acta, 2005

Conventional metods for separation of Ni

Precipitation as $Ni(OH)_2$, separation from Sr, Cs, ^{3}H, ^{14}C, Ba, Ca, Cl.

Precipition by ammonium, separate Ni from Fe, Mn, Eu, Pb, Al, Cr.

- Low recovery of Ni in this method (Ni can be also partly precipitate in ammonium solution)
- Cannot separate Cu, Co, etc.

Ion exchange to separate Ni from Co, Cu, Zn, Fe, and transuranics.

Precipitation or extraction of complex of Ni with dimethylglyoxime (DMG).

- Co and Cu can also form a complex with DMG and extracted

Evaporation of $Ni(CO)_6$

Separation of Ni by hydroxides precipitation

Element	Precipitation, %		Solution, %
	NaOH (pH9)	NH_4OH	NH_4OH
Ni^{2+}	>99.8	>20	< 80
Co^{2+}	>99.5	<20	< 80
Ba^{2+}	<30.5	<30.0	>70
Eu^{3+}	>99.8	>99.8	<0.2
Cs^{+}	<0.2	<0.2	>99.8
Sr^{2+}	<37.5	<35.0	>60

- Most of matrix in concrete and environmental samples, such as C, S, Ca, Si, Na will be separated.
- The recovery of Ni is not satisfied using ammonium to separate Ni from other matals by hydroxides precipitation
- Other metals such as Mn, Cr, V, Al, Pb, and transuranics will also be precipitated by NaOH, and cannot be separated from Ni.

Behaviors of Ni and other metals on anion exchange column

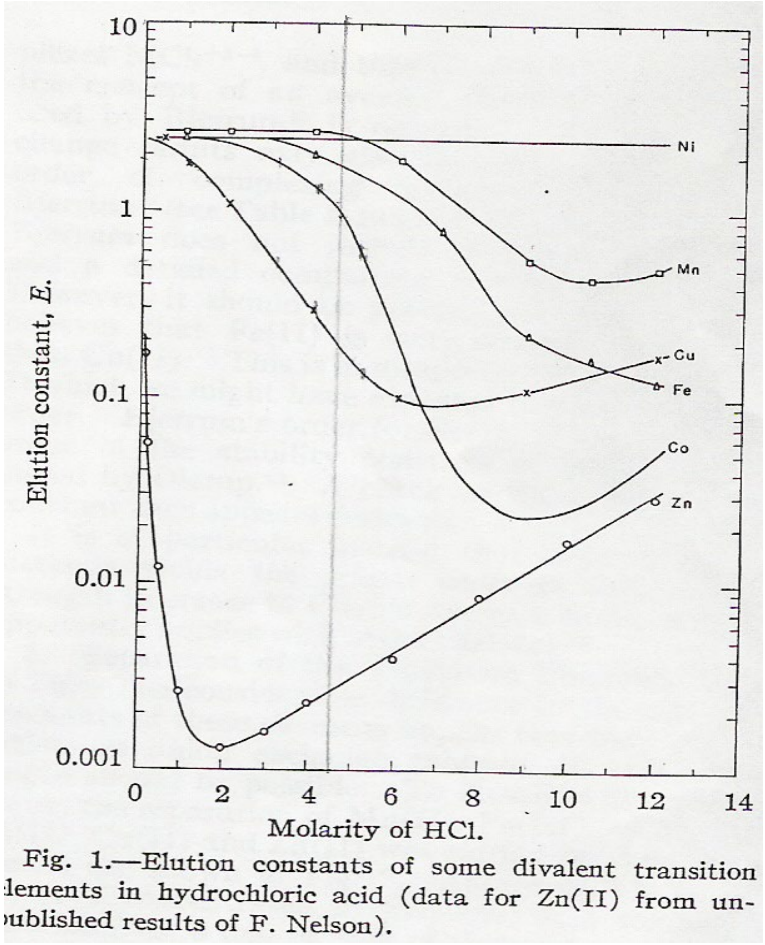


Fig. 1.—Elution constants of some divalent transition elements in hydrochloric acid (data for Zn(II) from unpublished results of F. Nelson).

Many metals can form a anion complex with Cl^- in HCl solution (MCl_x^-), so can adsorbed on anion exchange column

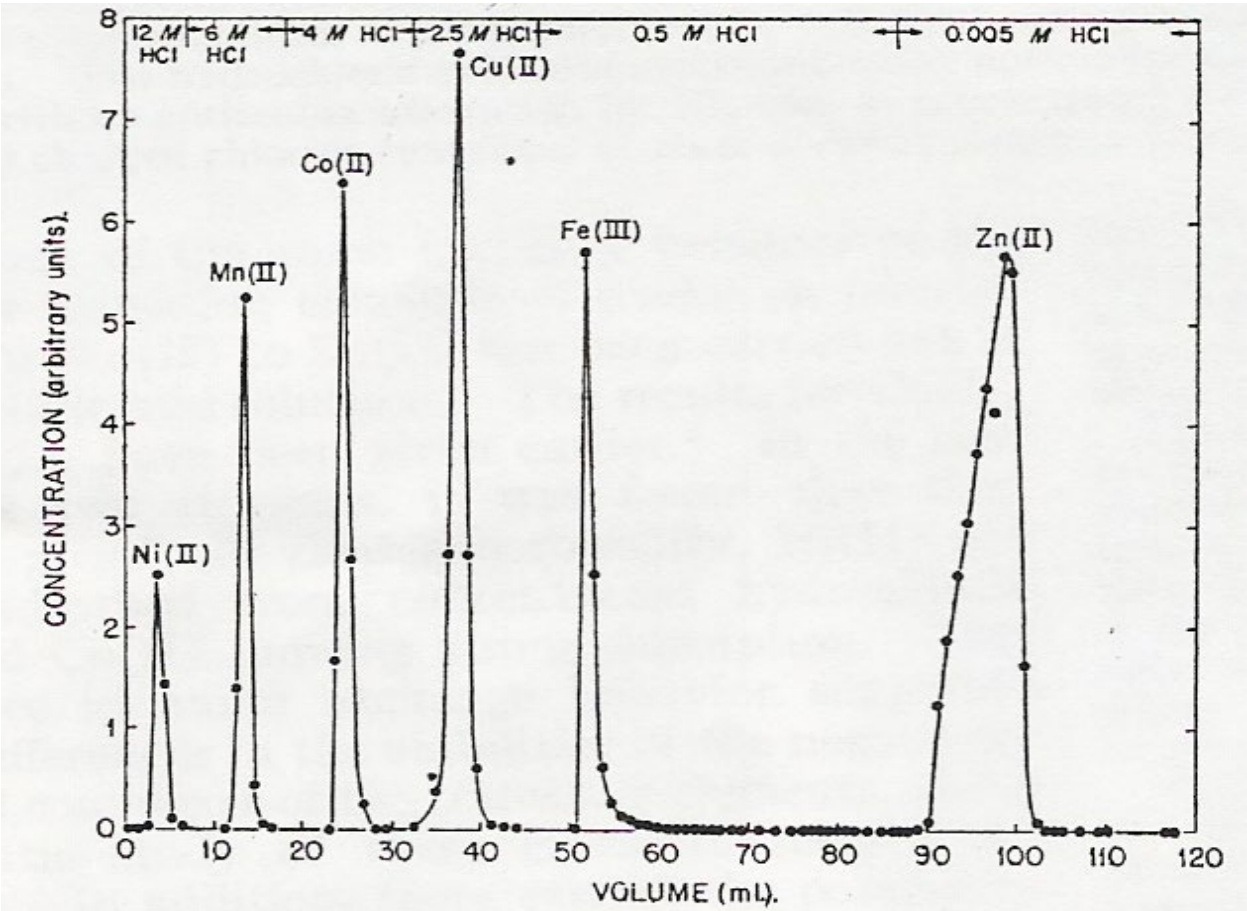


Fig. 2.—Separation of transition elements Mn to Zn (Dowex-1 column; 26 cm. × 0.29 cm.; flowrate = 0.5 cm./min.).

Separation of Ni, Co, Eu, Ba by anion exchange chromatography

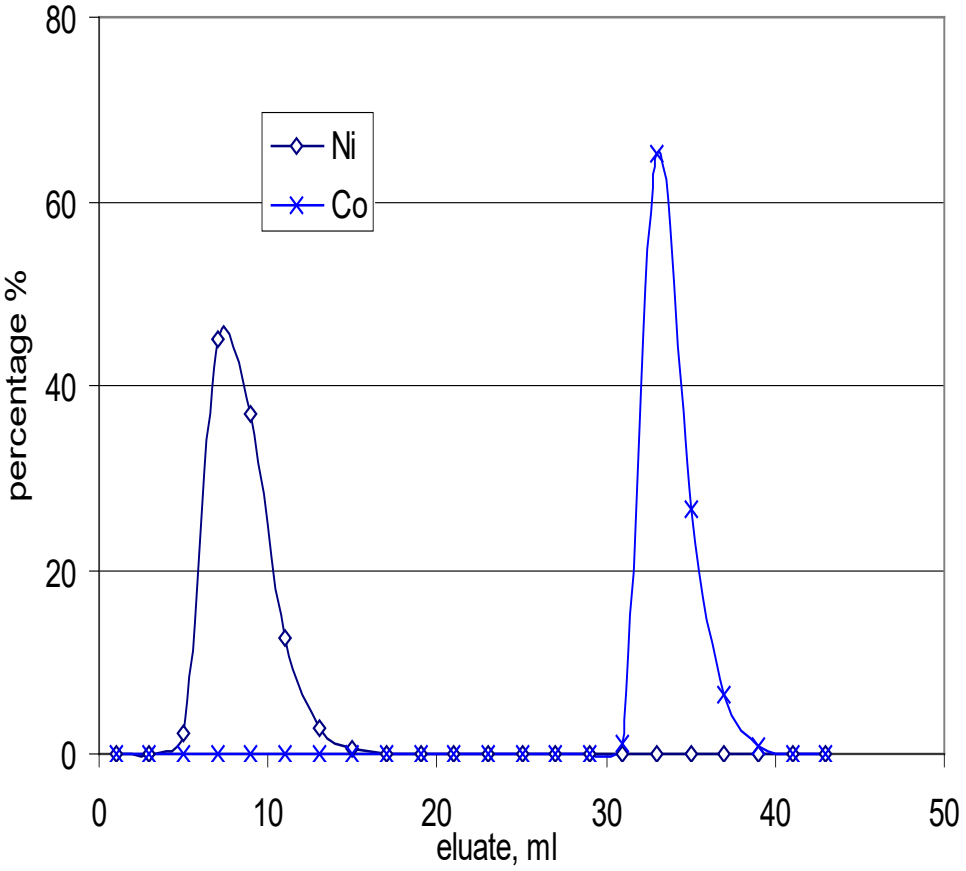
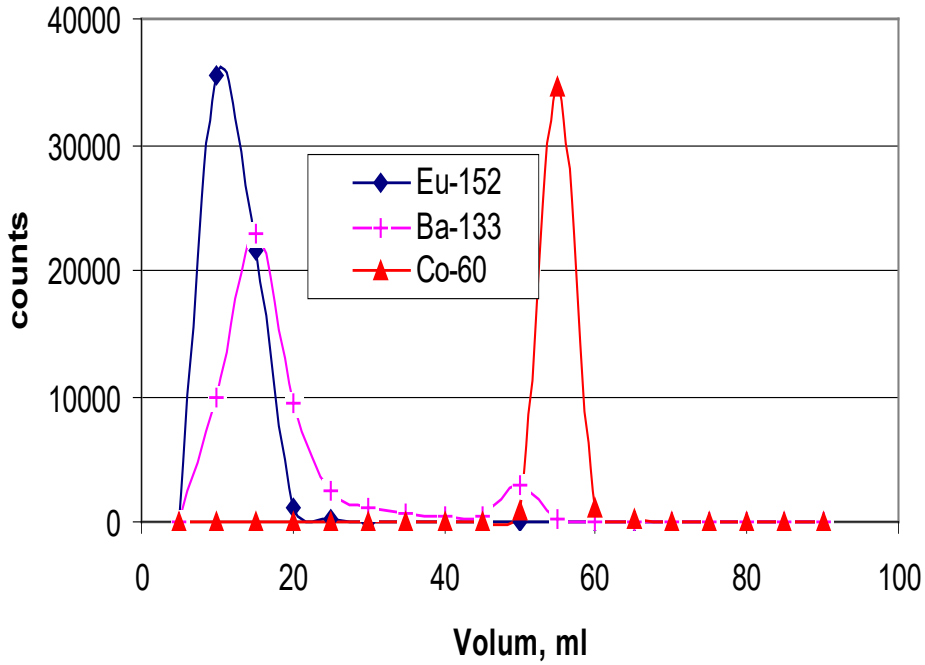


Fig. Separation of Ni from Co by ion exchange, eluted by 9 N HCl (3-20ml) for Ni and 2 N HCl (21-44 ml) for Co. Bio-Rad AG1x4. 1x15 cm column



Separation of Eu, Ba, Co by anion exchange chromatography, Bio-Rad AG1x4, 1x15 cm, 0-40ml:9M HCl, 40-70ml:4M HCl, 70-90ml, 0.05M HCl

Separation of Ni by anion exchange chromatography

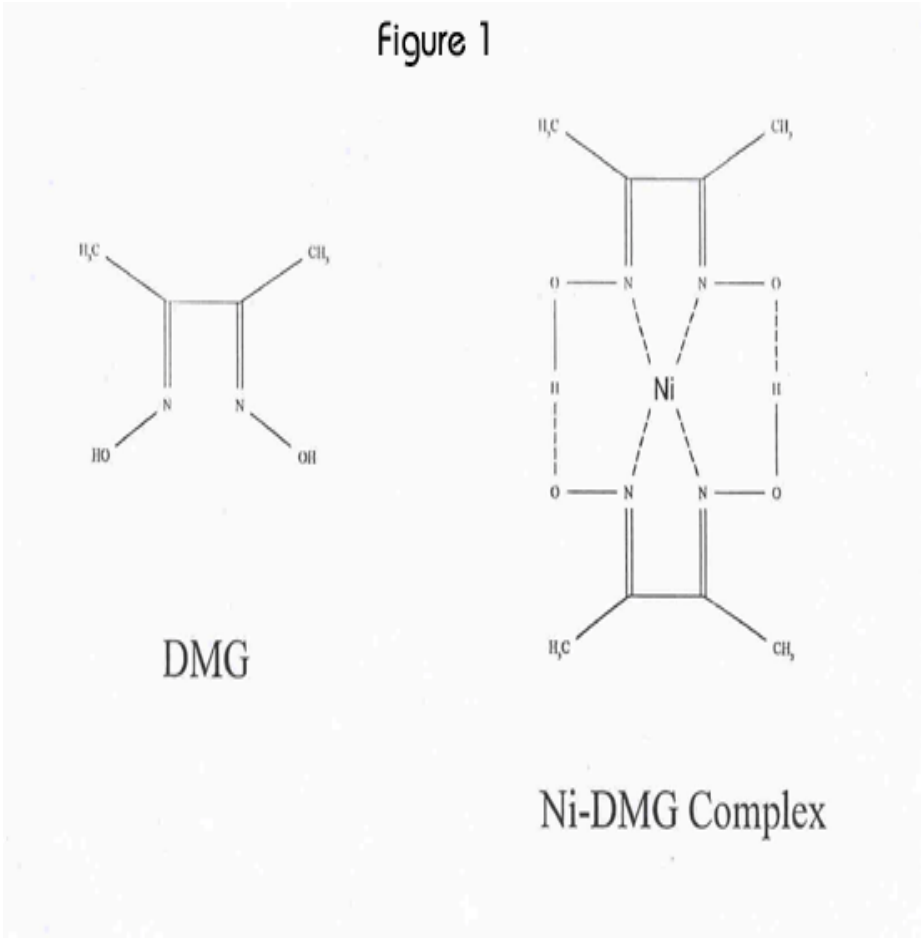
Element	Content, %
Fe^{3+}	<0.001
Ni^{2+}	>99.5
Co^{2+}	<0.01
Ba^{2+}	<7.5
Eu^{3+}	>99.8
Cs^{+}	>99.5
Sr^{2+}	>99.5

Ni can be completely separated from Fe, Co, Cu, Zn, U, Pu, etc.

- Ni cannot be efficiently separated from Cr, Eu, Sm, Mn, V, Sc, Ti, Zr, Ba, Th, Am. Of them, the radioisotopes of Eu, Sm, Ba, Zr, Mn, Cr and matrix elements of Cr, Mn V in metal and alloy seriously interfer the determination of Ni-63.

Thus: a further purification for both Ni and Fe is needed.

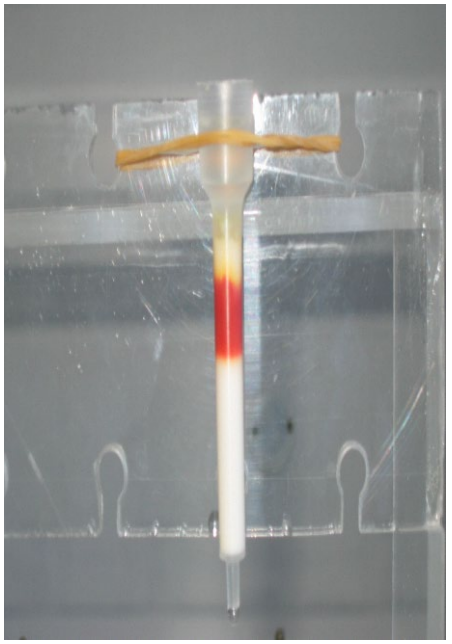
Application of Ni-DMG complex for the separation of Ni



Ni can form a stable specific complex with dimethylglyoxime. By Ni-DMG precipitation or organic solvent extraction of Ni-DMG complex at low concentration, Ni can be separated from many other elements.

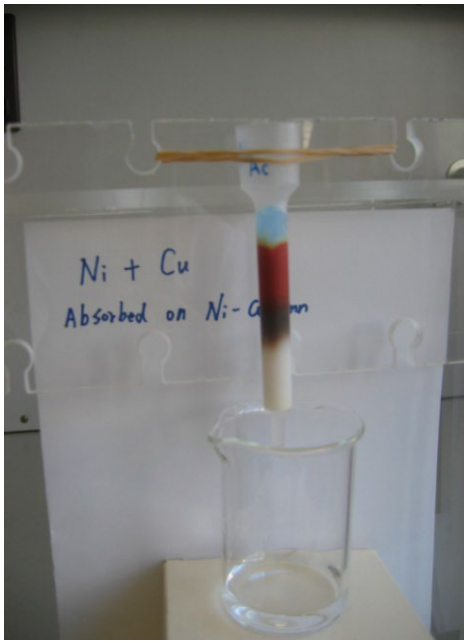
While, some other metals, such as Co, Cu can also form a complex with DMG and interferring the separation of Ni.

Behaviors of Ni、Co、Cu、Fe on Ni resin column



2mg Ni^{2+}

2mg Ni^{2+} +
2mg Co^{2+}



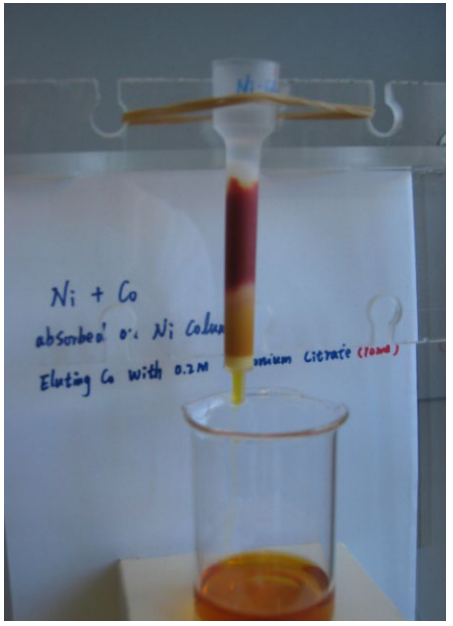
2mg Ni^{2+} +
2mg Cu^{2+}

2mg Ni^{2+} +
8mg Fe^{3+}

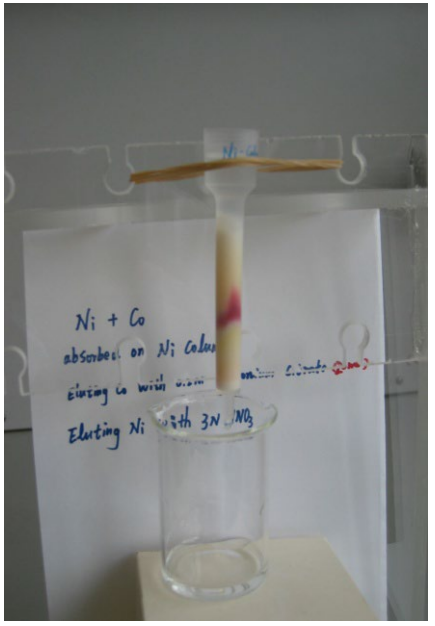
Separation and purification of Ni with Ni resin

The Nickel Resin contains the DMG inside the pores of a polymethacrylate resin. The nickel-DMG precipitate occurs on the resin , where it is held and readily separated from other elements in the supernatant.

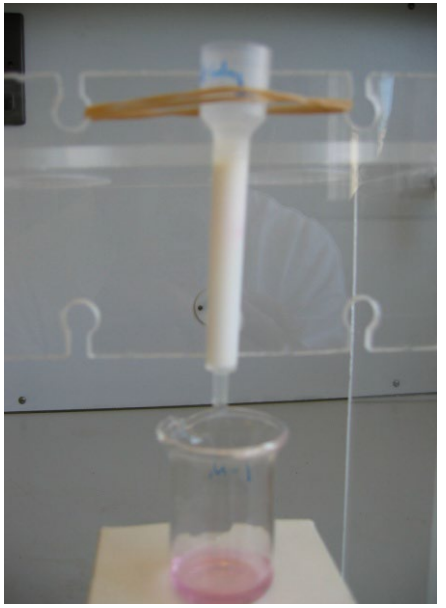
1. Loading of solution



2. Washing with 0.2 M ammonium citrate to remove other elements



3. Eluting Ni using HNO3



4. Evaporte eluted Ni-DMG solution to 0.1-0.2 ml for LSC

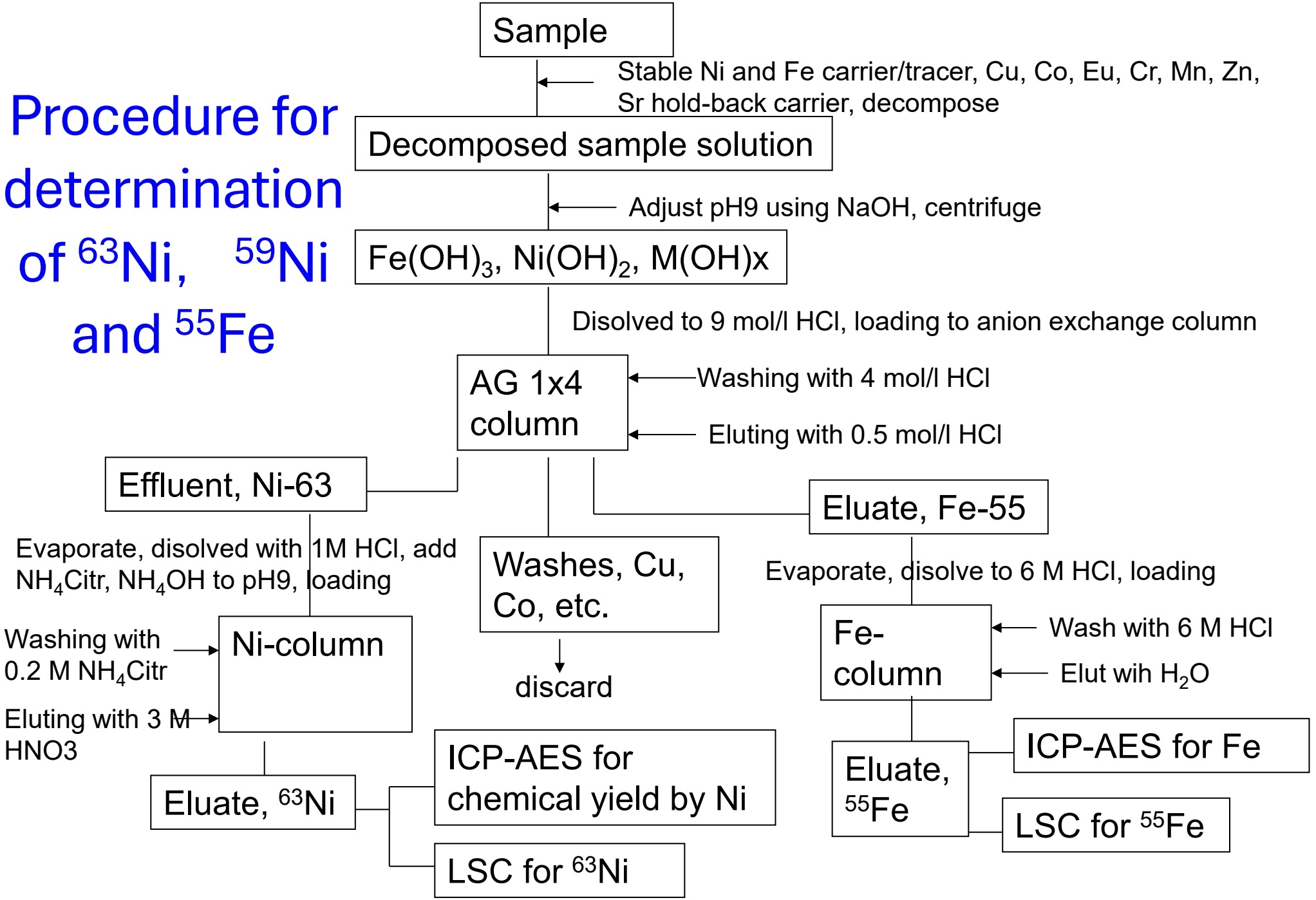
Performance of Ni resin in the separation of Ni

Element	Recovery or decontamination factor
Ni^{2+}	> 98.5%
Fe^{3+}	10^4
Co^{2+}	10^3
Ba^{2+}	10^4
Eu^{3+}	10^4
Cs^{+}	10^4
Sr^{2+}	10^4

Ni specific extraction chromatography has a higher decontamination to most of elements, such as Fe, Co, Cu, Cr. Mn, Ba, Eu, transuranics, etc.

- A higher recovery of Ni can be obtained in the procedure.

Procedure for determination of ^{63}Ni, ^{59}Ni and ^{55}Fe

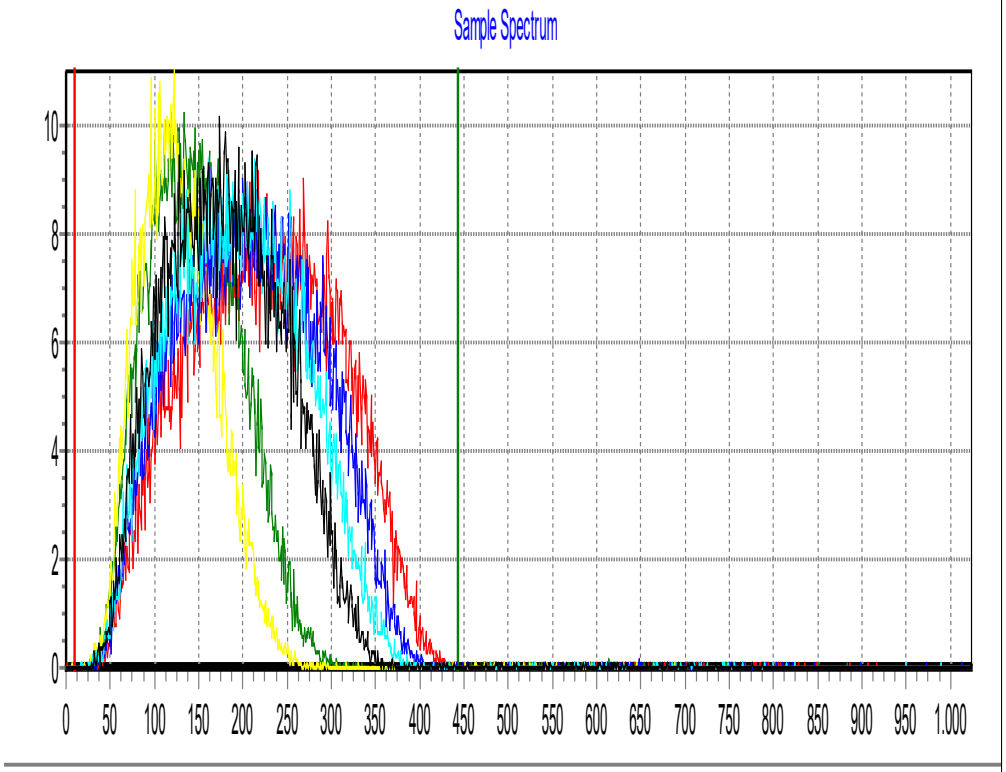


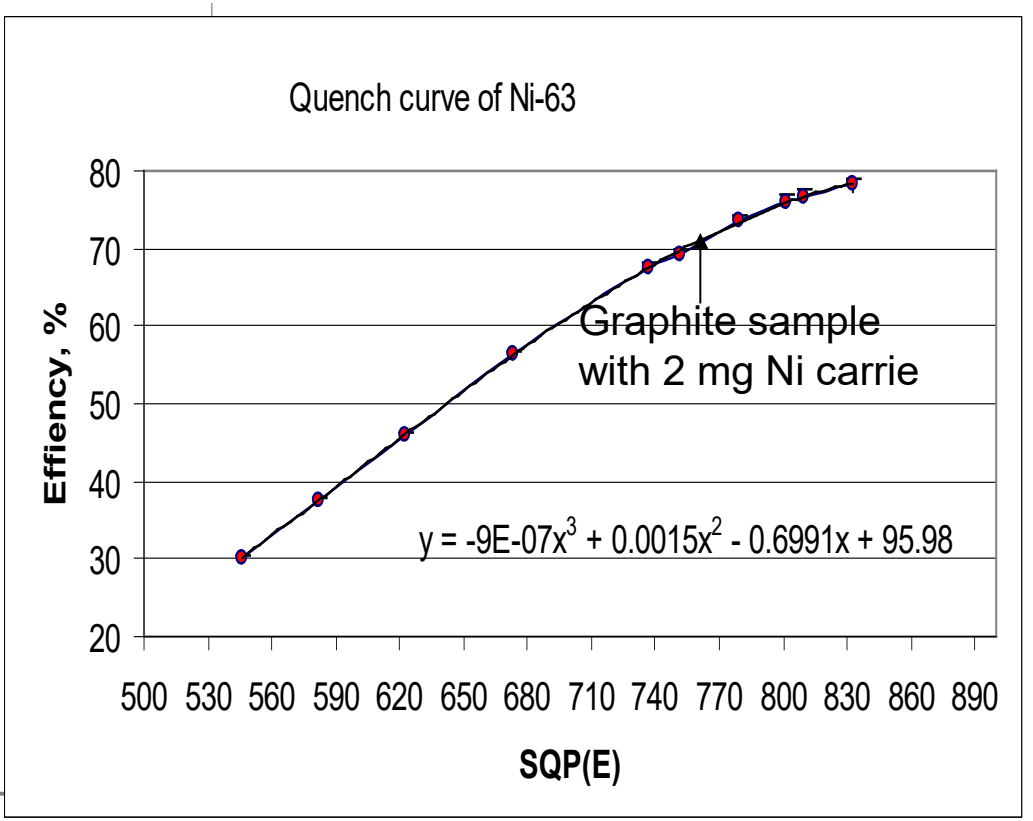
Performance on the separation of Fe and Ni

Interference	Recovery/decontamination factor		Interference	Recovery/decontamination factor	
	Fe fraction	Ni fraction		Fe fraction	Ni fraction
^{55}Fe	85-95%	$>10^5$	^{133}Ba	$>10^6$	$>10^5$
^{63}Ni	$>10^5$	80-95%	$^{134,137}Cs$	$>10^6$	$>10^6$
$^{58,60}Co$	$>10^5$	$>10^5$	$^{89,90}Sr$	$>10^6$	$>10^6$
$^{152,154}Eu$	$>10^6$	$>10^5$	$^{41,45}Ca$	$>10^6$	$>10^6$
^{151}Sm	$>10^6$	$>10^5$	^{36}Cl	$>10^6$	$>10^6$
^{54}Mn	$>10^5$	$>10^6$	^{3}H	$>10^6$	$>10^6$
^{51}Cr	$>10^6$	$>10^5$	^{14}C	$>10^6$	$>10^6$

For all interferring radionuclides, the decontamination factors higher than 10^5.

LSC spectra of ^{63}Ni in samples of decommissioning waste





Laufende Arbeiten

Ni, Fe, Nb, Mo, Zr (& Tc) Trennschema für Stahlproben

- Fe Abtrennung via TK400 und ZR
- Nb und Mo via ZR

Ni Abtrennung

- NI Resin: ungenügende Cu und Fe Abtrennung
- Zwei modifizierte NI Resins in Verwendung mit höherer Ni Selektivität

Tritium

Easiest case: Tritiated water in liquid matrices

More complicated: total tritium including OBT (organically bound tritium)

Oxidation of matrix and recovery of « HTO »

- Distillation after/during oxidation with MnO_4^- or $Cr_2O_7^{2-}$
- Pyrolyser/Oxidiser

Tritium in water/urine – H3 column

Tritium column

Diphonix Resin

Anion Exchange Resin

Prefilter Resin

Isotope	A before column [Bq/L]	A after column [Bq/L]
Cr-51	2900	< LD
Mn-54	518	< LD
Co-58	4740	< LD
Fe-59	109	< LD
Co-60	392	< LD
Sn-113	230	< LD
Nb-95	4220	< LD
Zr-95	2210	< LD
I-131	14200	< LD
Cs-134	1120	< LD
Cs-137	1320	< LD

***Tab.1** : Radionuclide removal by Tritium columns in smples from a pressurized water reactor (2)*

Isotope	A before column [Bq/L]	A after column [Bq/L]
Cr-51	1990	< LD
Mn-54	5590	< LD
Co-58	4960	< LD
Co-60	5990	< LD
Nb-95	116	< LD
La-140	1550	< LD
Ce-144	203	< LD

***Tab.2** : Radionuclide removal by Tritium columns in smples from a boiling water reactor (2)*

Removal of cations (Diphonix), anions (1X8) and organically bound radionuclides (Prefilter)

Free HTO

Also tested on Procorad samples

Determination of Cl-36 and I-129 in decommisioning samples

Determination of Cl-36 / I-129 using CL resin

- CL resin originally developed for Pd separation
  - ➢ Ag and Pd methods being tested
- Selective for PGE, Ag, Au
- Halogene selectivity introduced by loading with Ag^+
- Sample loading on Ag^+ loaded CL resin
  - ➢ Acidic, neutral or slightly alkaline conditions
    - ▪ Might need to be done under reducing conditions
  - ➢ Original paper[+]: water/effluents and leached solid samples (concrete, soil, filter)
    - ▪ Leaching: 4h, 70°C, 1M NaOH

Analyte	Extraction condition	D_w, $mL.g^{-1}$
Ag	1M H_2SO_4	650000
Ag	Sulfuric acid, pH 3	600000
Ag	Sulfuric acid, pH 5	350000
Cd	1M H_2SO_4	<1
Ce	1M H_2SO_4	4
Co	1M H_2SO_4	<1
Cu	1M H_2SO_4	<1
Fe	1M H_2SO_4	<1
Mn	1M H_2SO_4	<1
Ni	1M H_2SO_4	<1
Pd	1M H_2SO_4	87000
Zn	1M H_2SO_4	25

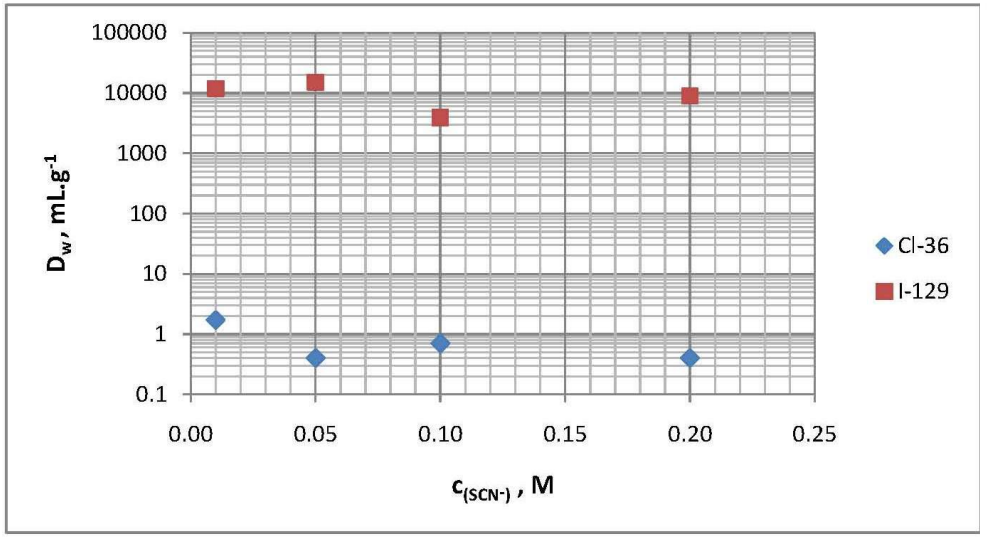
+ A. Zulauf, S. Happel, M. B. Mokili, A. Bombard, H.Jungclas: Characterization of an extraction chromatographic resin for the separation and determination of 36Cl and 129I. J. Radanal Nucl Chem, 286(2), 539-546

Resin characterization – Ag^+ loaded CL resin

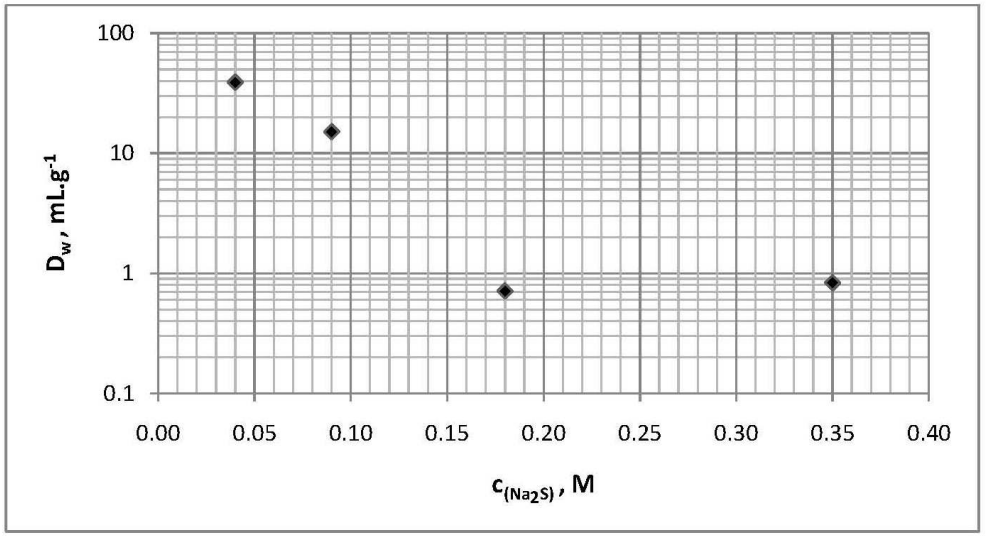
Isotope	D_w retention
Cl-36	1600
I-129	1980

Retention of chloride (^{36}Cl) and iodide (^{129}I) in 1M H_2SO_4

- High uptake of chloride and iodide onto Ag^+ loaded CL-resin in 1M H_2SO_4
- Remark: iodate also retained, chlorate not



D_w of chloride (^{36}Cl) and iodide (^{129}I) on Ag loaded CL resin at pH 7 and varying SCN^- concentrations

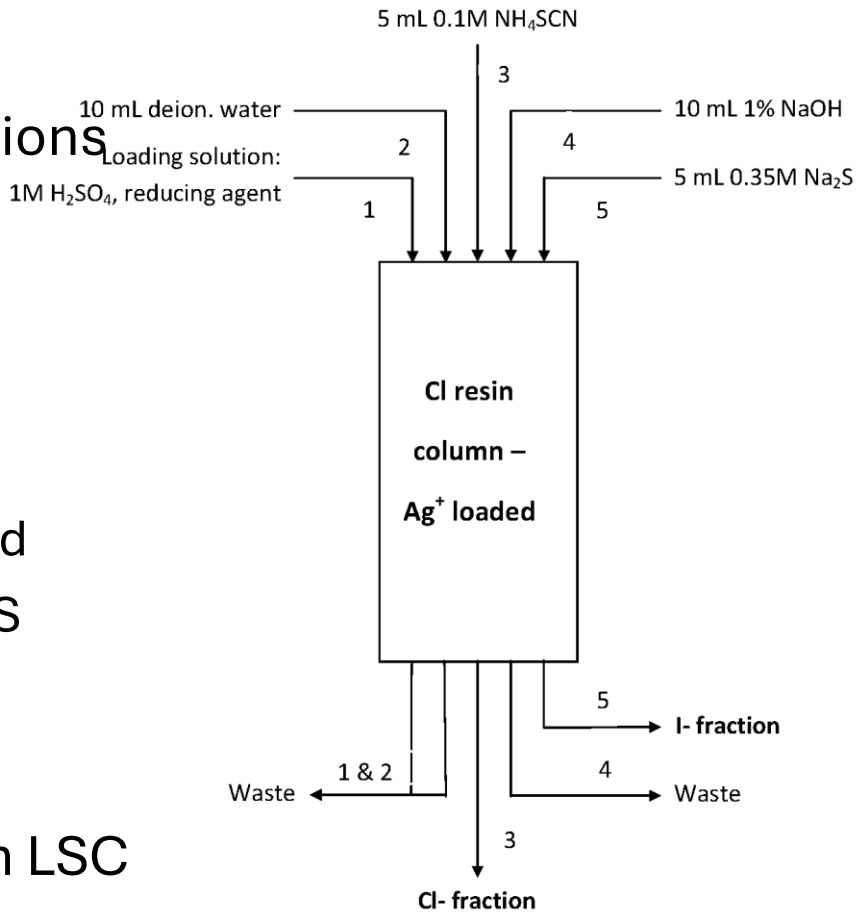


D_w of iodide (^{129}I) on Ag loaded CL resin at pH 7 and varying Na_2S concentrations

- Chloride: very low D_w at all tested SCN^- concentrations
- Iodide: high D_w at all tested SCN^- concentrations,
  low D_w at elevated Na_2S concentrations

Determination of Cl-36 / I-129 using CL resin

- Loading possible over a wide range of conditions
  - Low alkaine to strongly acidic
- Rinse with 10ml of deion. Water
  - ➢ Eliminates matrix elements
- Elute chloride with 5ml of 0.1M SCN^-
  - ➢ Directly mixed with LSC cocktail and counted
  - ➢ Can be replaced by carbonate solution => MS
- Rinse with 10ml of 1% NaOH
  - ➢ Increases iodide yield
- Elute iodide with 5ml of 0.35M Na_2S, mix with LSC cocktail
  - ➢ Fume hood…
  - ➢ Directly mixed with LSC cocktail and counted
- Yields in general > 90 - 100%



Pyrolyser method

- Allows for analysis of large solid samples (several g)
- Thermal decomposition of the samples and desorption of Cl Species in Pyrolyser furnace at 900°C (ca. 2h)
- System flushed with humidified air; samples also humidified (1ml water)
- Decomposition products trapped in bubbler containing alkaline solution
  - 6 mM Na_2CO_3 used (yield > 80%)

P E Warwick, A Zulauf, S Happel, I W Croudace: Determination of 36Cl in decommissioning samples using a Pyrolyser furnace and extraction chromatographic separations. Presentation at the 11th ERA Symposium, 16/09/2010, Chester (UK)

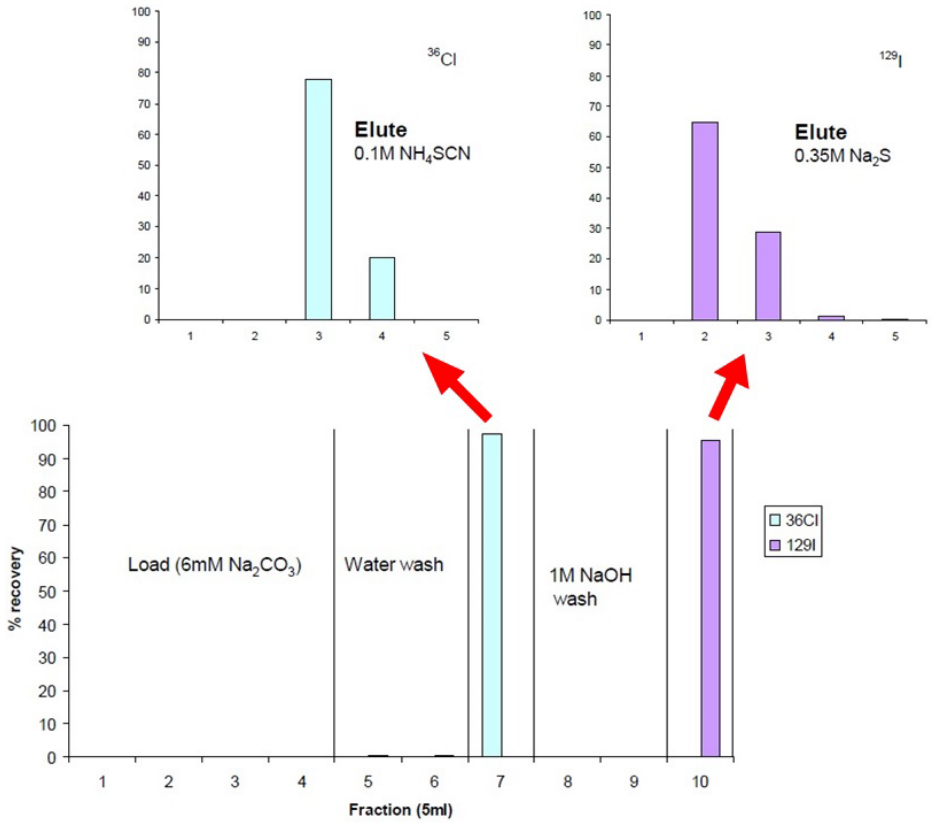
Pyrolyser method

- Bubbler connected directly with furnace via glass connector
  - Avoid losses due to condensation in tubing
- ^{36}Cl separated via Ag^+ loaded Cl resin
  - Separation similar to standard method, but bubbler solution loaded directly onto column
  - When loading column directly from 6 mM Na_2CO_3 additional rinsing with 0.1M H_2SO_4 necessary for improved C-14 decontamination (« modified wash »)
- Similar method currently tested for I-129

Pyrolyser method

Decontamination factors D_f:

	^{36}Cl fraction	^{129}I fraction
^{3}HTO	> 500	> 2000
$^{14}CO_3$	7	5000
^{14}C modified wash	700	
^{35}S modified wash	1500	1000
^{36}Cl		> 2000
^{129}I	1300	



An[illegible]

Sample type	Expected value	Measured value
Ion exchange resin	4.1 kBq	4.3 ± 0.1 kBq

- High D_f
- Clean Cl-36 / I-129 separation
- Cl-36 separation yield > 95%
- Good agreement

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

I-129 in spent resin via AMS

Nottoli et al.: I-129 in spent resins by AMS

Resin mineralisation by

- microwave digestion (HNO_3/$HClO_4$) or
- oxygen bomb combustion (iodine trapped in NaOH)

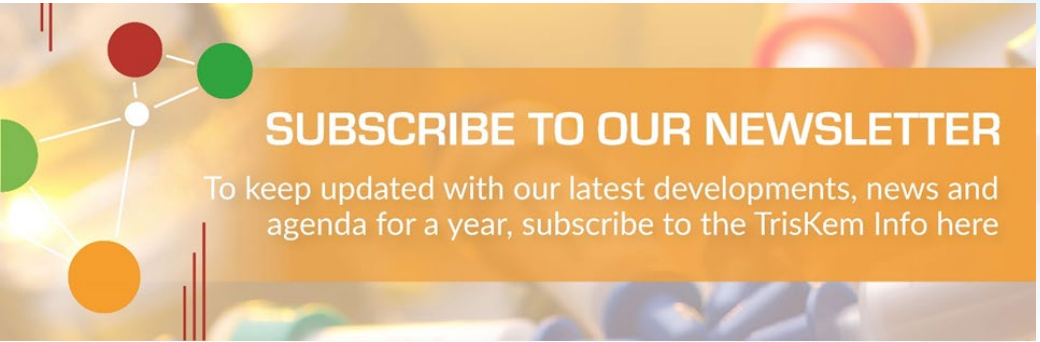
Iodine purified on CL Resin using a modified purification method

- 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.

Thank you for your attention!



TRISKEM
Expertise in Separation Chemistry

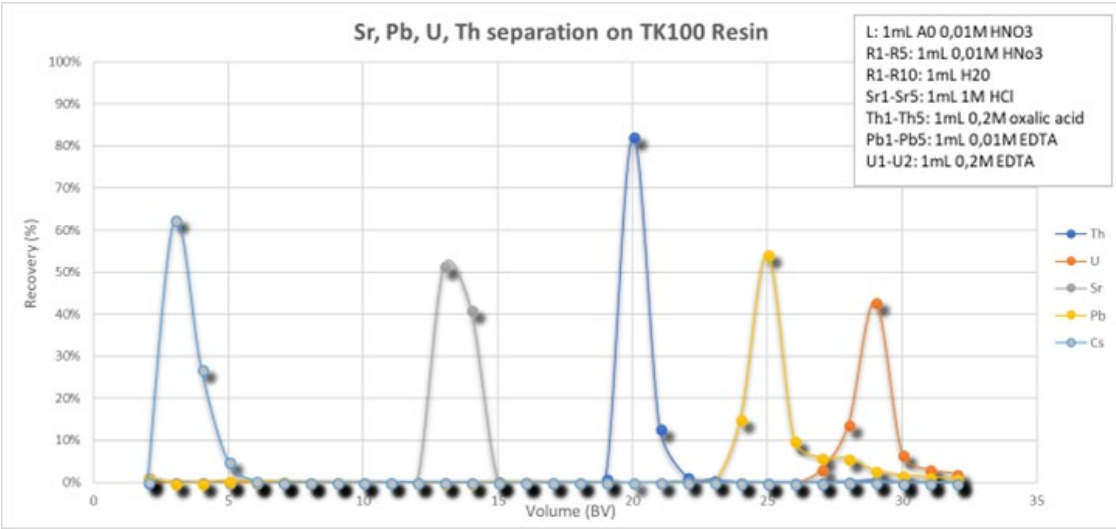
TK100/1

- In case Ra needs to be purified on-column (e.g. dissolved Ra needles)
  - Use of TK101 for Ra retention / purification => test against Chelex, CEX, TK100
- TK100: HDEHP facilitates phase transfer at dilute HNO_3 but also extracts various elements
  - High Ra/Ba retention from dilute HCl / HNO_3
  - preconcentration and sequential separation of U, Th, Pb, Sr, Ba, Ra on-going
- TK101 => similar to TK100 but ionic liquid replaces HDEHP

  Both based on same crownether as SR Resin

  TK100 developed for Sr and Pb uptake also between pH 2 and 7 (DGT)

  ⇒ Wagner et al. TK100 discs



- Replacing HDEHP by ionic liquid (=> TK101 Resin) allows for retention of Pb, Sr, Ba, Ra,… form pH 2 – 7 without extensive extraction of other elements

Ra purification / recycling

Needles and other Ra sources often contain Pt, Ir, Au, Ba besides Ra.

Ra generally present as $RaSO_4$

Suggestion: Work-up following Matyskin et al.

Destruction of the needle, generally cutting (higher losses) or dissolution in aqua regia

Conversion of $Ra(Ba)SO_4$ via heating with Na_2CO_3 solution

- Three cycles at 85°C under reflux, elimination of supernatant after each cycle
- $RaCO_3$ recovered as solid
- Soluble in dilute acid => suggestion: dilute HNO_3 final acidity <0.1M HNO_3

Suggestion:

purification of Ra on column

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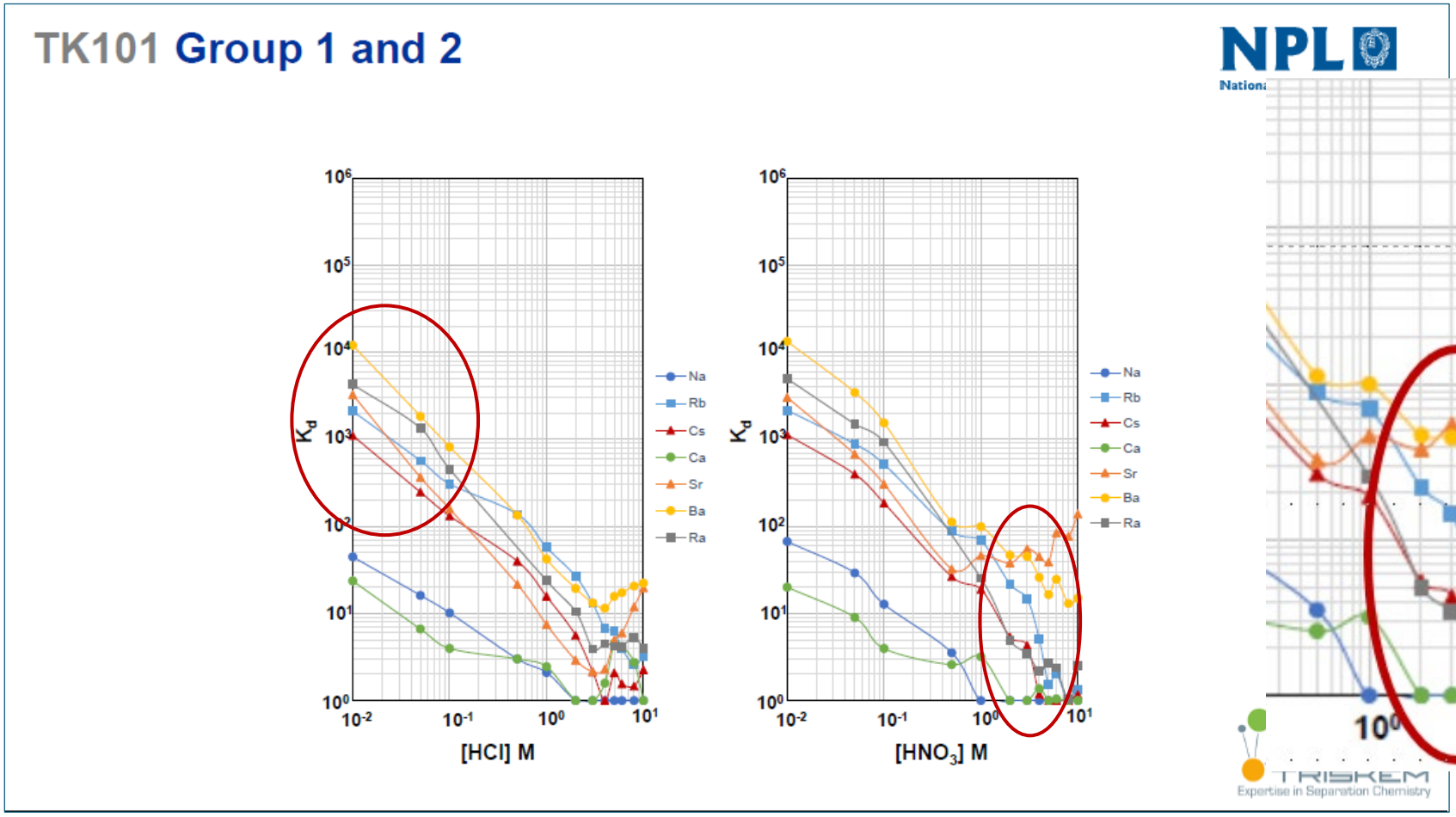
DOI 10.1007/s10967-016-4927-x

Disassembly of old radium sources and conversion of radium sulfate into radium carbonate for subsequent dissolution in acid

Artem V. Matyskin[1] · Burçak Ebin[1] · Mikhail Tyumentsev[1] · Stefan Allard[1] · Gunnar Skarnemark[1] · Henrik Ramebäck[1,2] · Christian Ekberg[1]

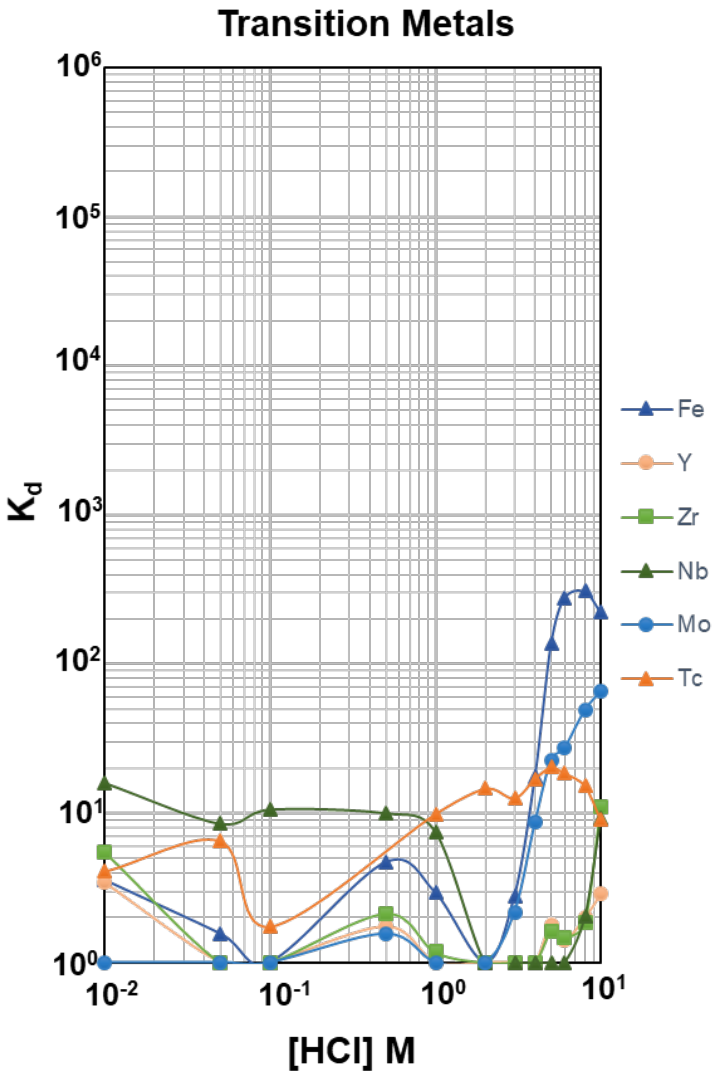
TK101 - Radium

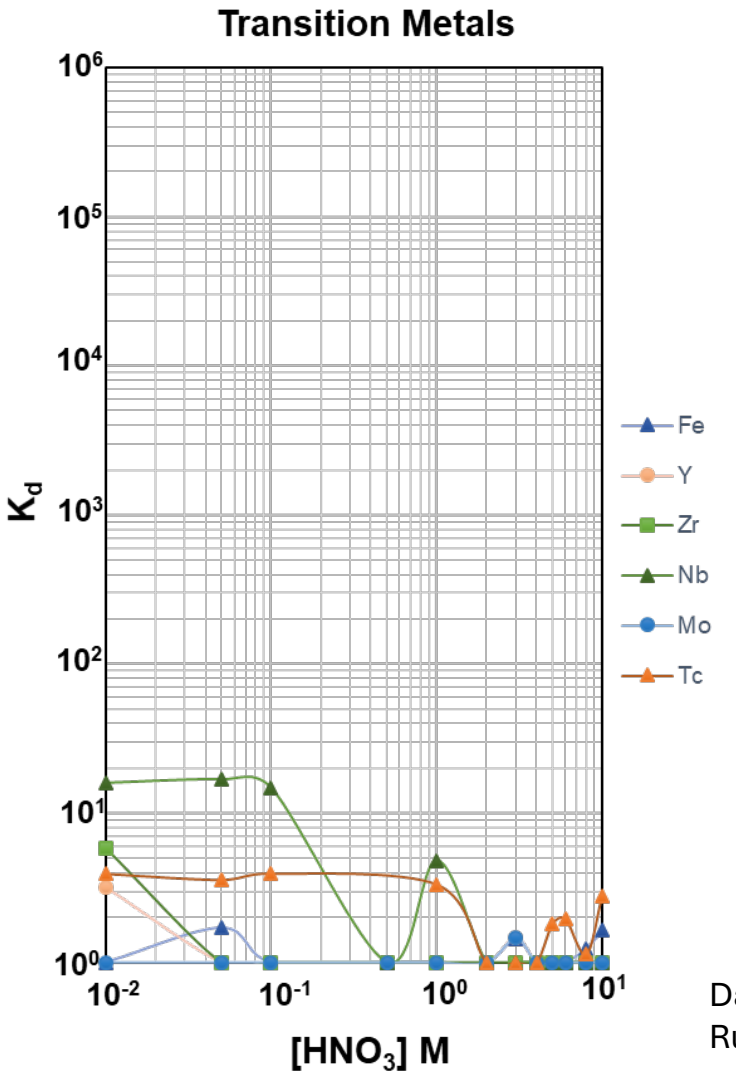


Data provided by Russel et al. (NPL)

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

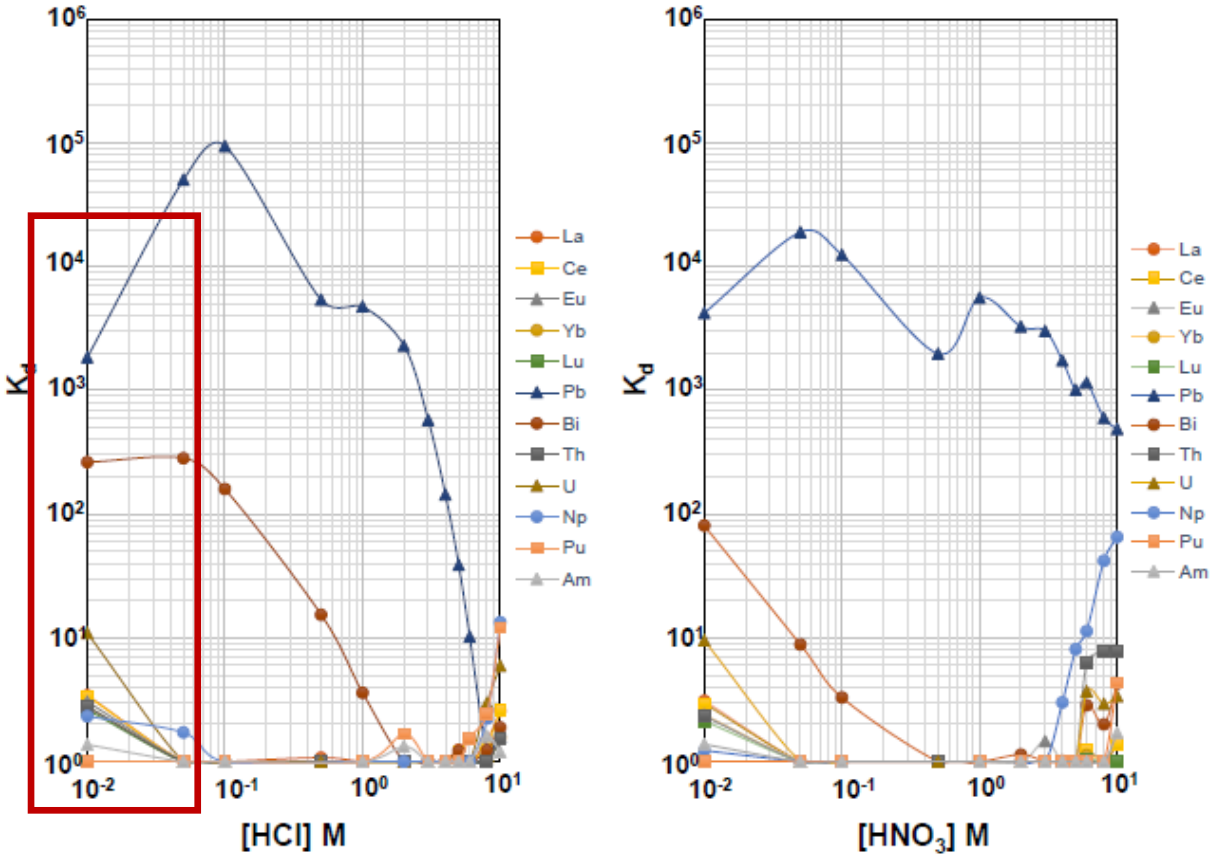
TK101 Transition Metals





Data provided by Russel et al. (NPL)

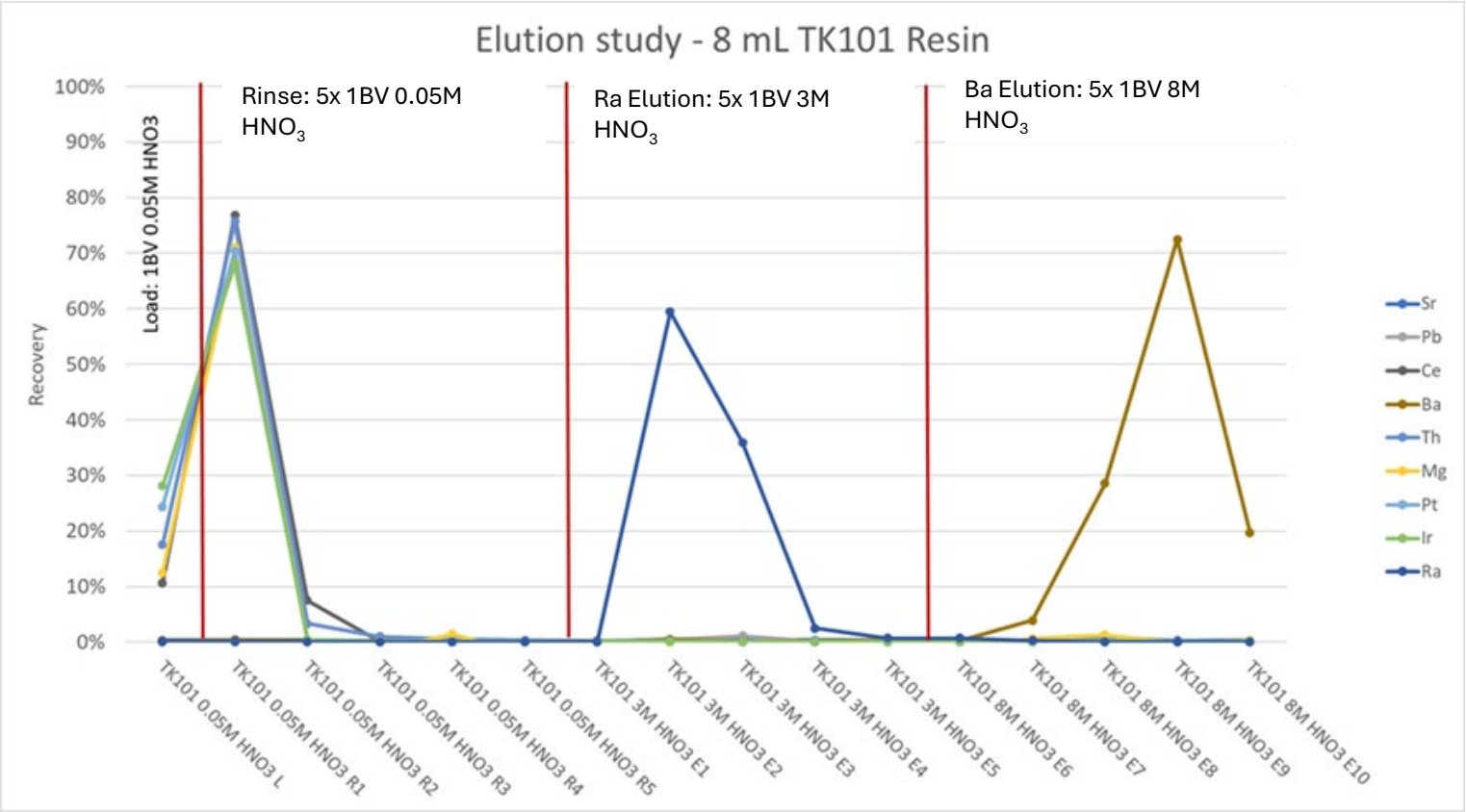
TK101 - Ra



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

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

No retention of U, Th, Pt, Ir,...

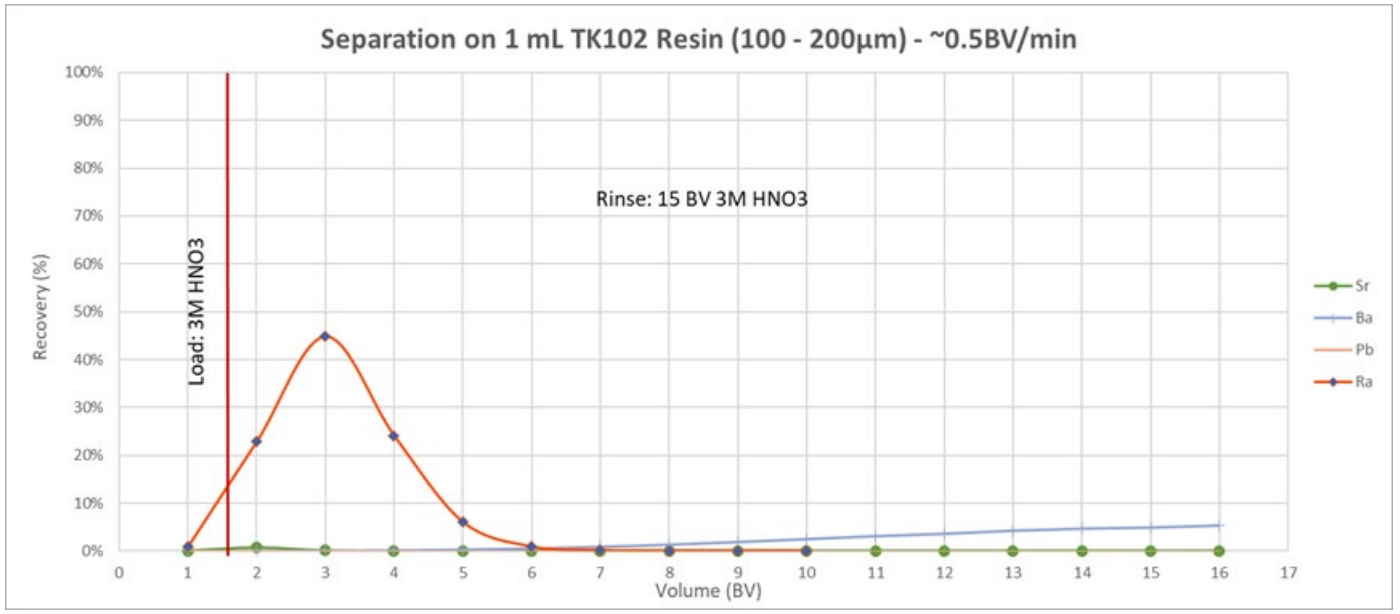
Bi partially retained from 0.05M HNO_3/HCl

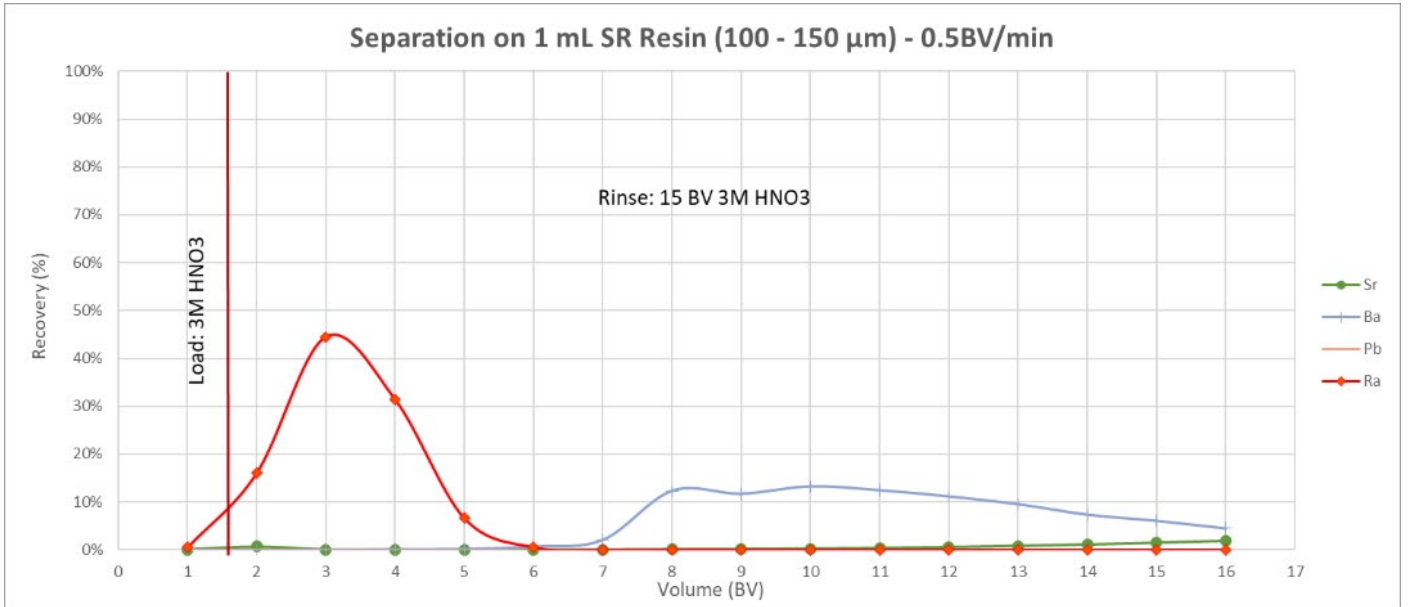
Ra eluted in 3M HNO_3

Further Ba removal via TK102 possible

Tl and Ba eluted in 8M HNO_3

TK102 - Ra purification / recycling





- SR Resin: high Ba breakthrough starts after 7 – 8 bed volumes
- TK102 Resin: significantly lower Ba breakthrough
- TK102 shows less bleeding than SR Resin