New Delopments TrisKem - Part 2

UGM - 21/09/2018

Jesus College - Cambridge (UK)

S. Happel

TRISKEM
Expertise in Separation Chemistry

New Resins - domains and applications

- Analytical
  - Radiochemistry
    - Environmental monitoring, bioassay, waste monitoring, decommissioning
    - Actinides, fission and activation products, NORM, methods/resins for DTMs, rapid methods,...
      - » **TK100/1, TK200, TBP, CL Resin, TK201/2, TK300, TK-TcScint, Extractive discs,...**
  - Mass spectrometry
    - Isotope ratio determination (universities, petrol industry,...)
    - Sr, Pb, U, actinides, Cu, Sn...
      - » Dating of geological samples :**TK200, TK300, TK400,...**
      - » Food provenancing : **TK100,...**
      - » Nuclear forensics: **TK200, TK400,..**
      - » Biomedical (Cu),... => **CU Resin,...**

Domains and applications

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- Decommissioning/decontamination
  - Treatment of effluents / liquid wastes / environmental waters
    - Removal of radioactive contaminants & heavy metals (Cs, Sr, Ra, I…)
  - Inorganic compounds embedded into PAN matrix
    - **CS Resins, more under development**
  - Polymer-based => **TK202,…**

- Hydrometallurgy
  - Recovery of critical metals
  - Recycling
    - **Mainly functionalized polymers => under development**

Domains and applications

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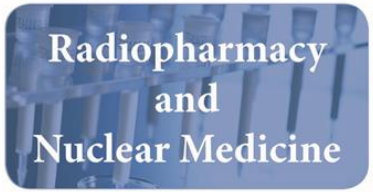

- Radiopharmacy/Nuclear Medicine
  - Radionuclide production
    - Cooperation with cyclotrons & reactors (NL, RN producers,…)
    - Separation of radionuclides from irradiated targets
      - » Diagnostics: Zr-89, Cu-64, Ga-68, Ge-68, Ti-44/5, Tc-99m…
        - **ZR Resin, CU Resin, TK200 Resin, TK400, TK201, TK202,…**
      - » Therapy: alpha emitters, Lu-177, Cu-67, Sn-117m,…
        - **TK400, TK200, TBP Resin, CU Resin,…**

Domains and applications

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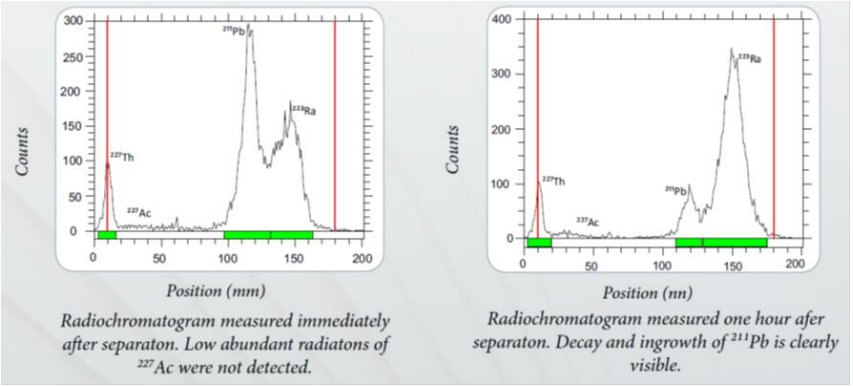
- Radiopharmacy/nuclear medicine
  - Purification of generator eluates => under development
  - Decontamination of contaminated effluents => **CL Resin,...**
  - Quality control
    - Cartridge based methods
    - **DGA sheets** (functionalized TLC, Ra-223, Ga-68, Pb-212,....)



Radiochromatogram measured immediately after separaton. Low abundant radiatons of ^{227}Ac were not detected.

Radiochromatogram measured one hour afer separaton. Decay and ingrowth of ^{211}Pb is clearly visible.

A scheme of chromatographic separaton of mixture of ^{227}Ac and his daugther´s niclides. ^{227}Th remains on start, ^{227}Ac has the retenton factor ca 0.2, ^{211}Pb ca 0.7 and ^{223}Ra ca 0.9.

ZR Resin

- Original scope: Hydroxamate based resin
    - Standard for Zr separation from Y targets
    - Ready to use
    - Facile Zr elution (avoid 1M oxalic acid)
- Zr-89 production via (p,n) reaction from natural Y (Y-89) targets
  - High Zr/Y selectivity necessary
- Fast extraction kinetics: > 99% after 1 min
- Also used for other separations possible (Ti/Sc, Ge/Ga, Ga/Zn)
- Applications in analytical applications (Zr-93, Nb,...)

ZR Resin - HCl

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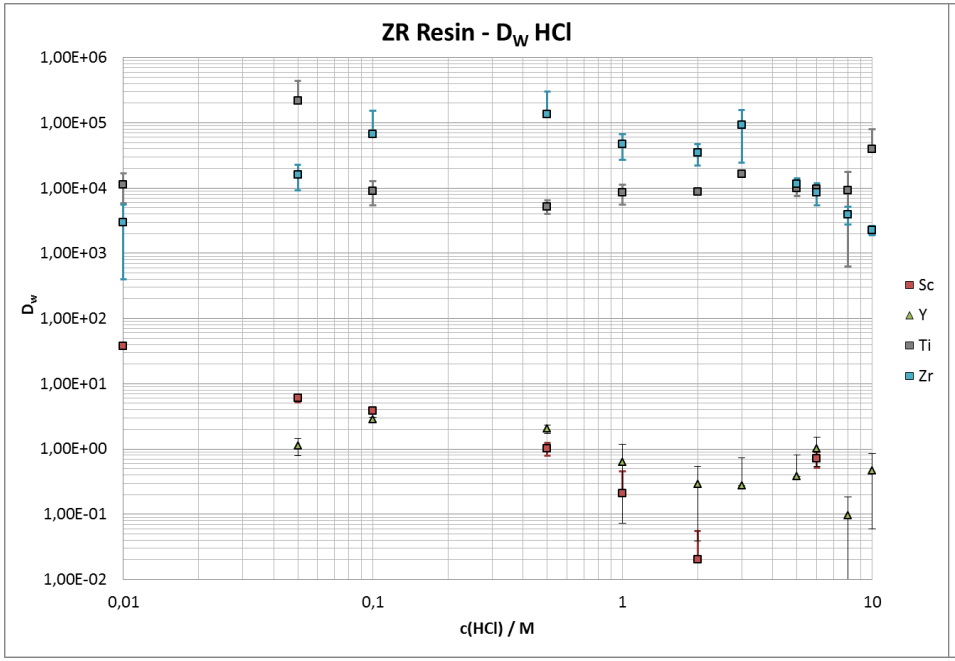
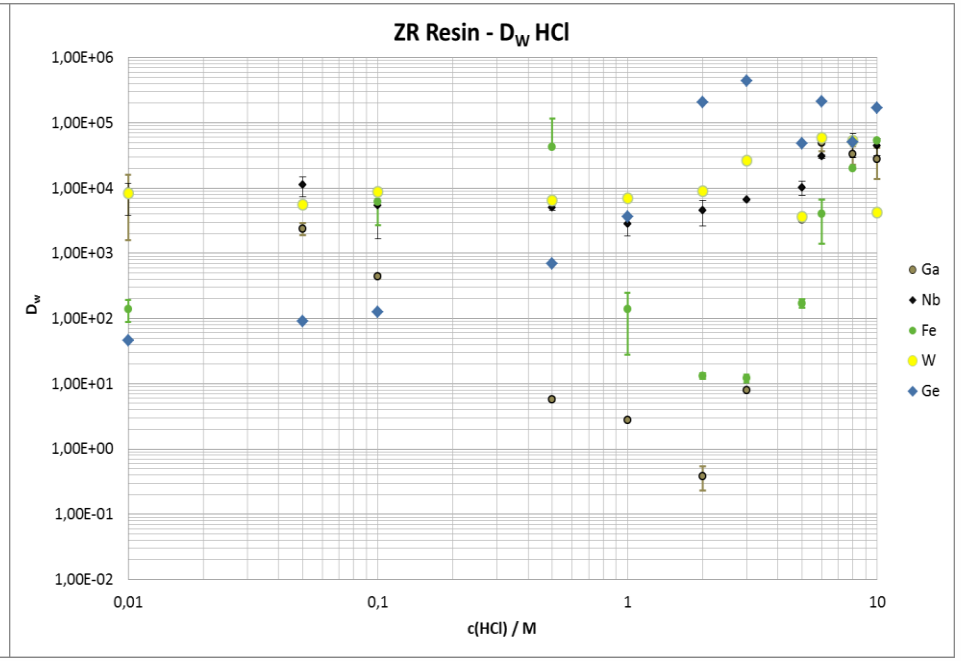
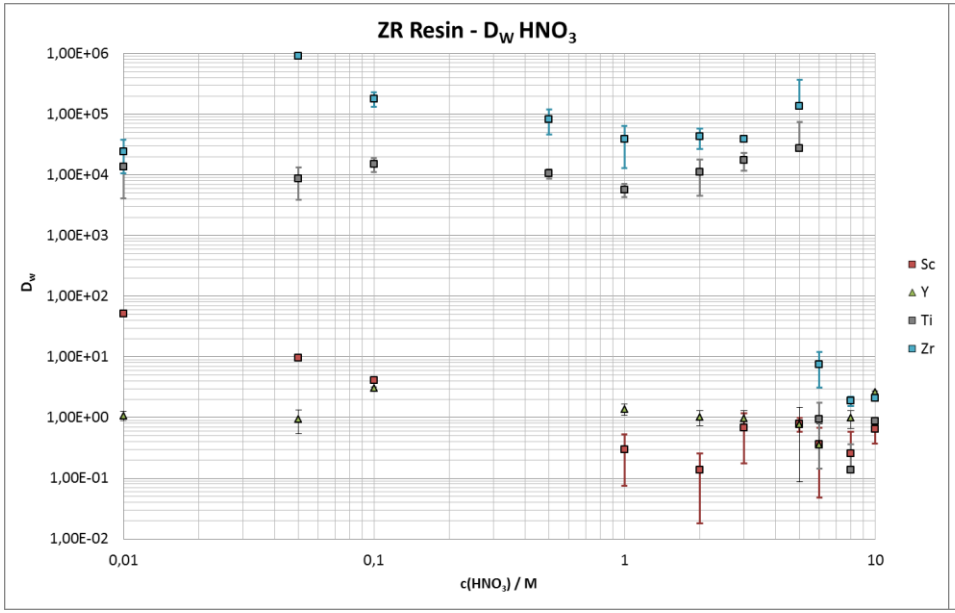
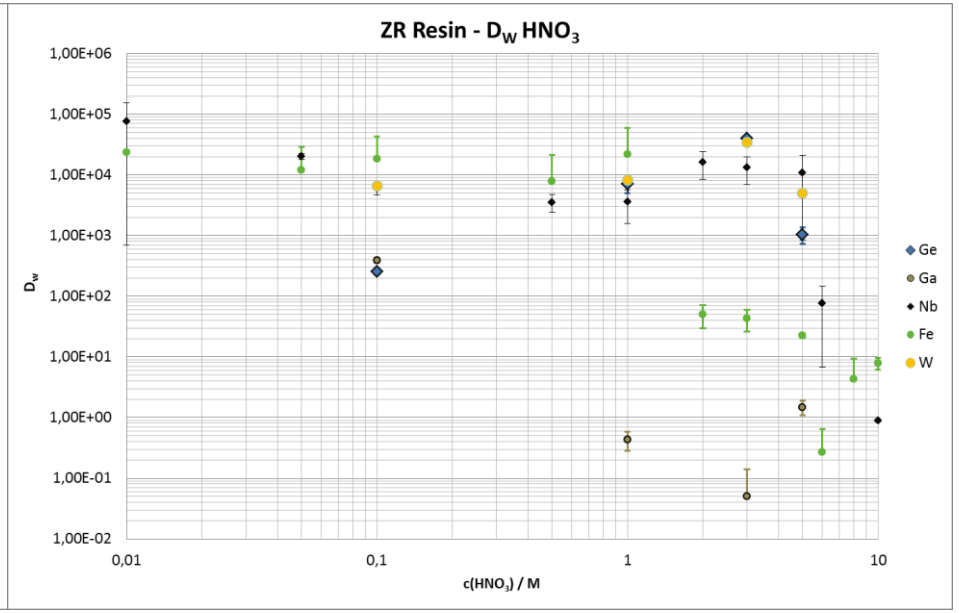




- No selectivity for Y, Sc
- High Ge/Ga selectivity at elevated HCl
- High selectivity for Zr, Ti, Nb, W over wide HCl concentration range
- No selectivity for alcaline and earth alcalines
- Lanthanides are not retained
- Strong Fe retention (dip at 2 – 3M HCl)

Zr Resin – HNO_3

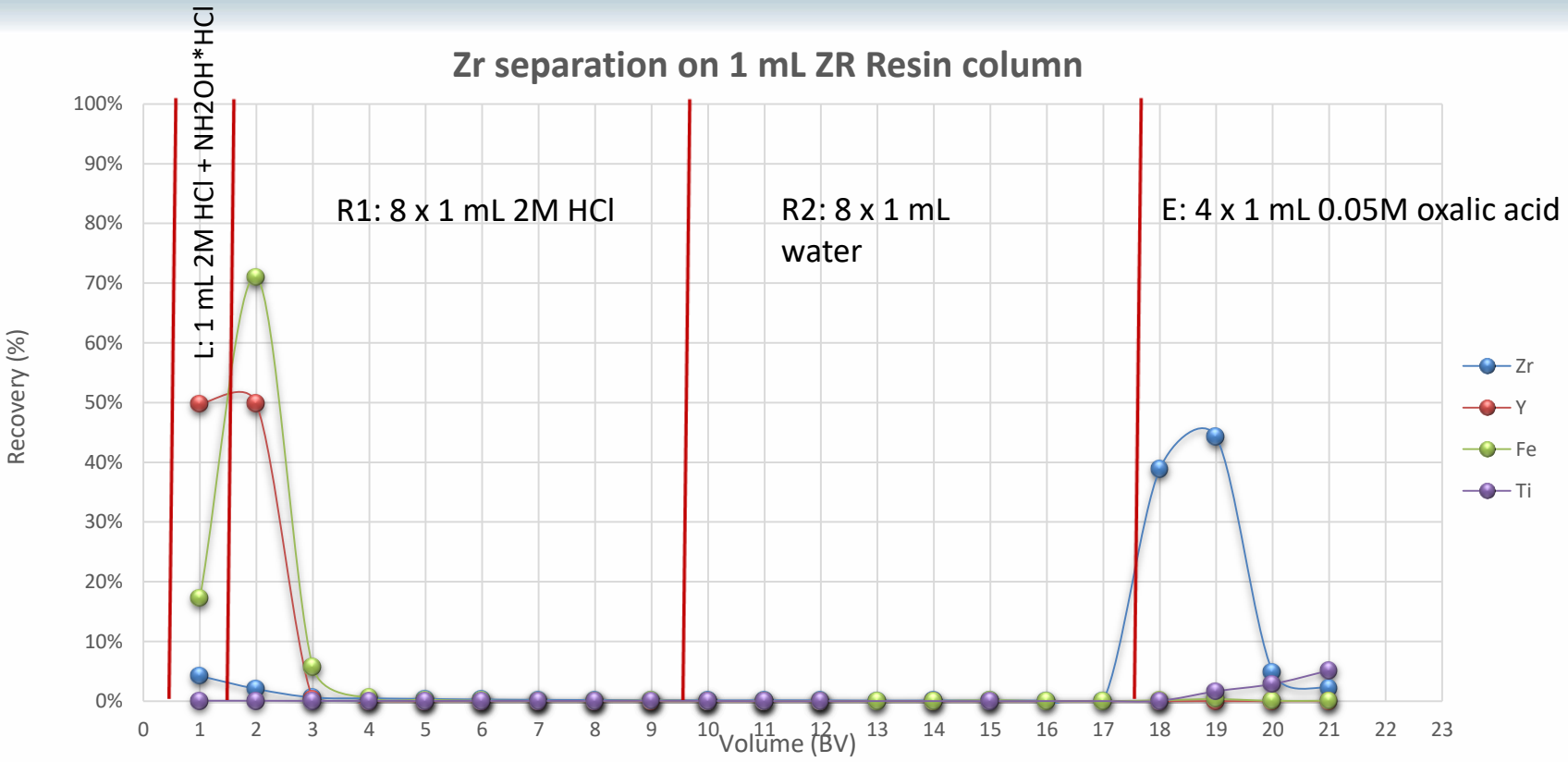




- High selectivity for Zr, Ti, Nb, W over wide HNO_3 concentration range
  - Loss of selectivity at 6M HNO_3

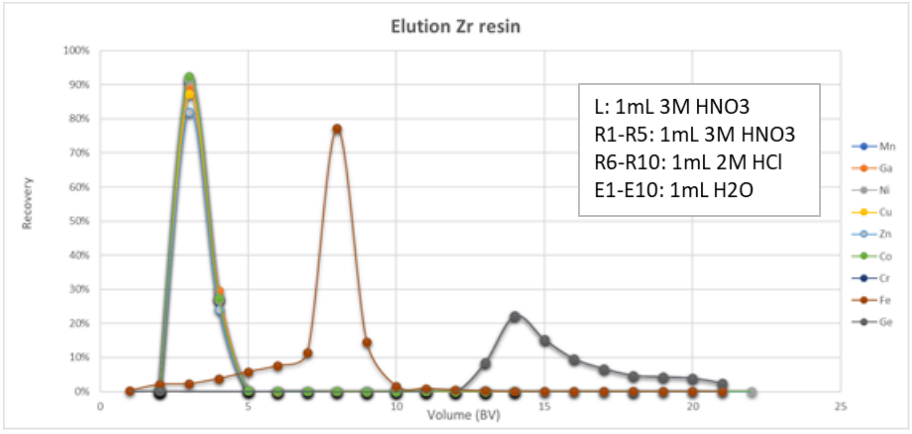
  => Resin shows colour change
- No selectivity for Y, Sc, lanthanides, earth alcalines, most transition metals,...
- High Ge/Ga selectivity at 3M HNO_3

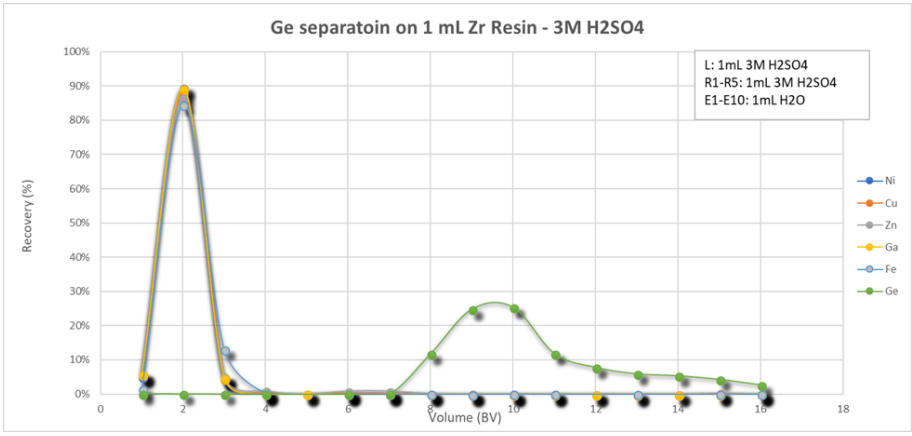
Zr separation incl. Fe removal

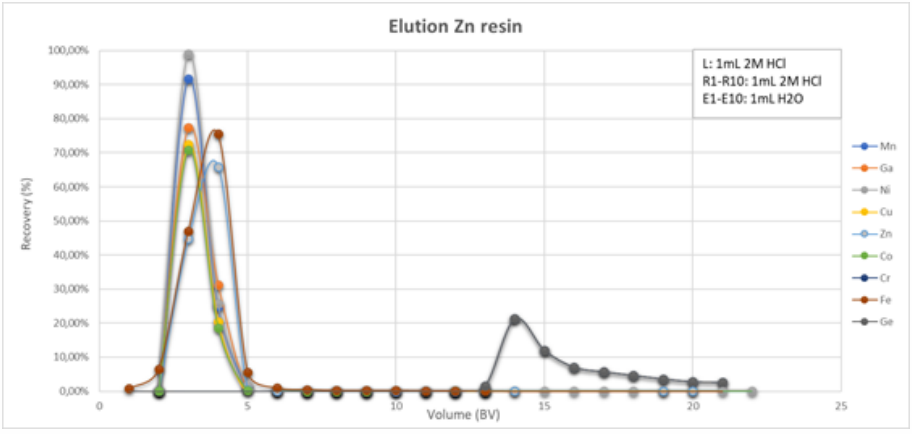


- Load from 2 – 6M HCl
- Rinsing described by Holland can be used
- No activation with acetonitrile
- Quantitative Zr elution in 1.5 - 2 mL 0.05M oxalic acid
- Clean Fe removal

Futher elution studies Ga/Ge

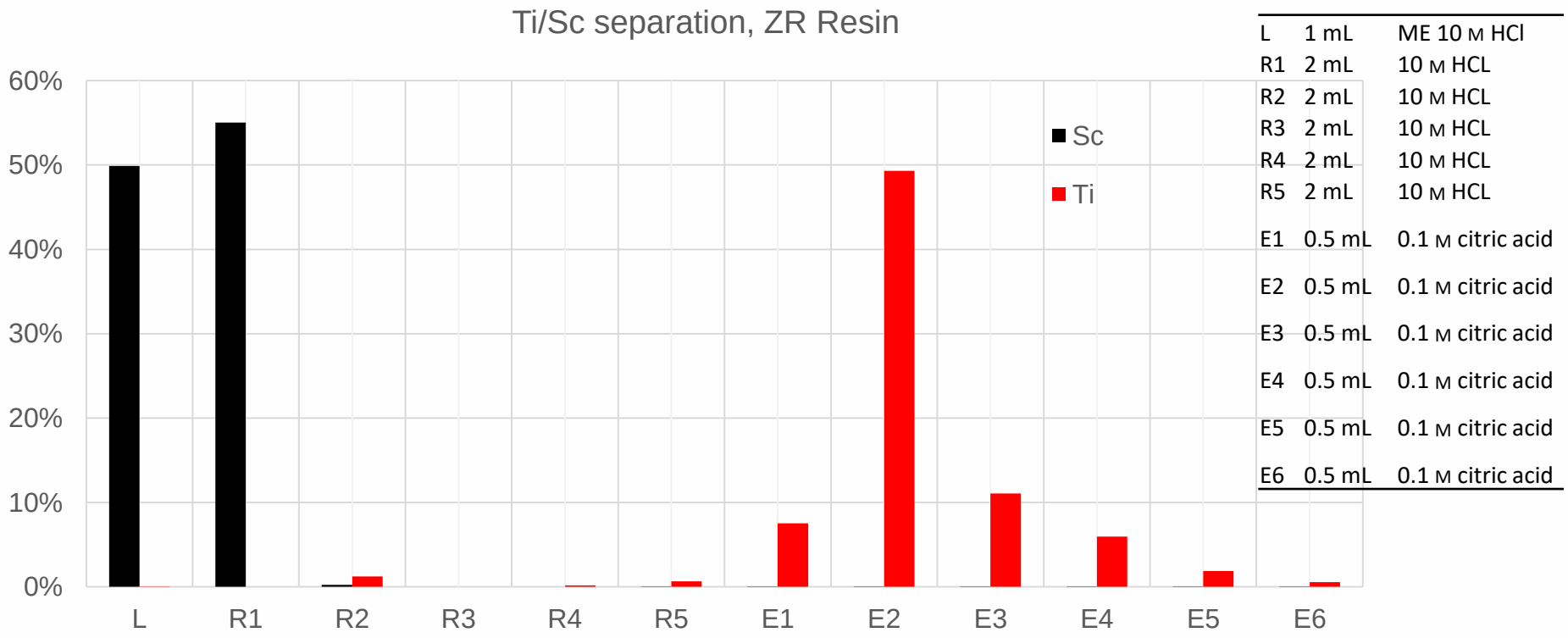






- Ge separation from Ga, GaNi or GaCo for Ge-68 production
- Loading from HNO_3, HCl or H_2SO_4
  - HNO_3 & H_2SO_4 preferred
  - => $GeCl_4$ volatile
- Fe removal with 2M HCl when loading from HNO_3

Ti-Sc Separation



L	1 mL	ME 10 M HCl
R1	2 mL	10 M HCL
R2	2 mL	10 M HCL
R3	2 mL	10 M HCL
R4	2 mL	10 M HCL
R5	2 mL	10 M HCL
E1	0.5 mL	0.1 M citric acid
E2	0.5 mL	0.1 M citric acid
E3	0.5 mL	0.1 M citric acid
E4	0.5 mL	0.1 M citric acid
E5	0.5 mL	0.1 M citric acid
E6	0.5 mL	0.1 M citric acid

- In-house tested up to 50 mg Sc (100 mg ZR Resin)
- Ti retained from 10M HCl, Sc not retained
- Ti elution with 0.1M citric, 0.2M oxalic acid, 0.1M H_2O_2

Ti-44 (LANL)

Separation of ^{44}Ti from proton irradiated scandium by using solid-phase extraction chromatography and design of ^{44}Ti/^{44}Sc generator system

V. Radchenko, C.A.L. Meyer, J.W. Engle, C.M. Naranjo, G.A. Unc, T. Mastren, M. Brugh, E.R. Birnbaum, K.D. John, F.M. Nortier, M.E. Fassbender*

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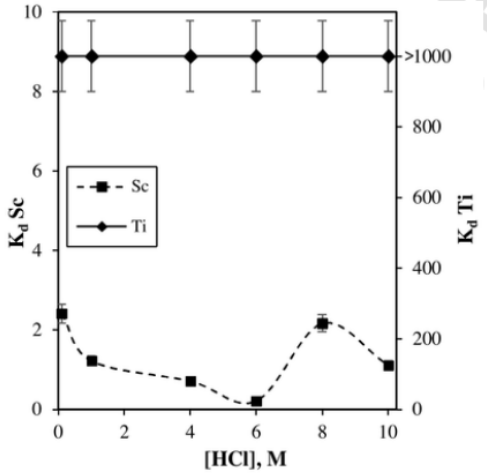


Fig. 3. HCl concentration dependency of K_d for ^{44}Ti/^{46}Sc on ZR hydroxamate resin.

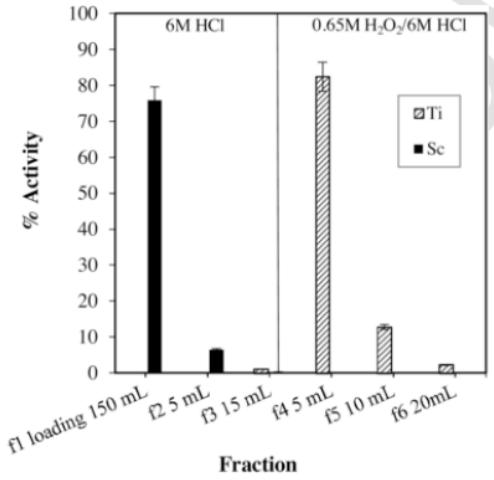


Fig. 5. ^{44}Ti/^{46}Sc elution profile using ZR hydroxamate resin with a load of 4 g of scandium.

- 4g irradiated Sc
- 65.2 MBq Ti-44
- 5 mL Zr Resin
- Ti-44 yield >95%
- D_f(Sc): 10^5

Use of ZR Resin as support in Ti-44/Sc-44 generators

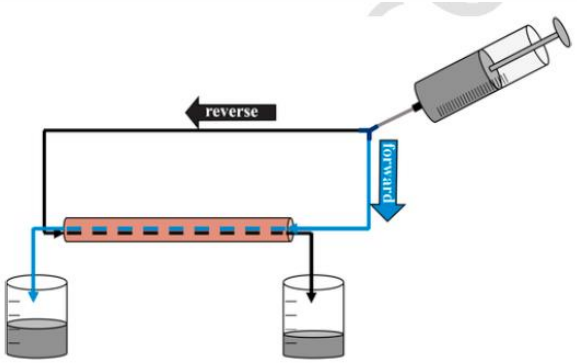
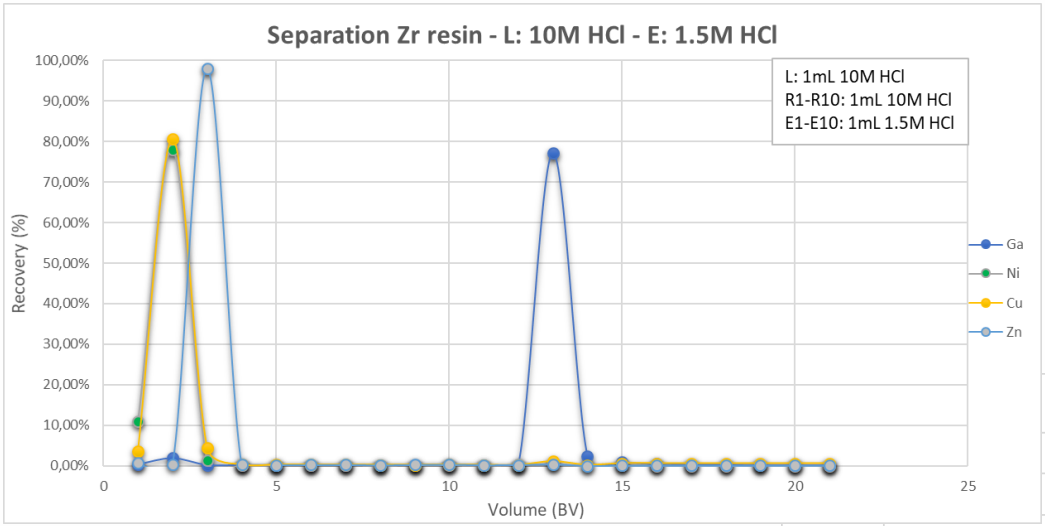


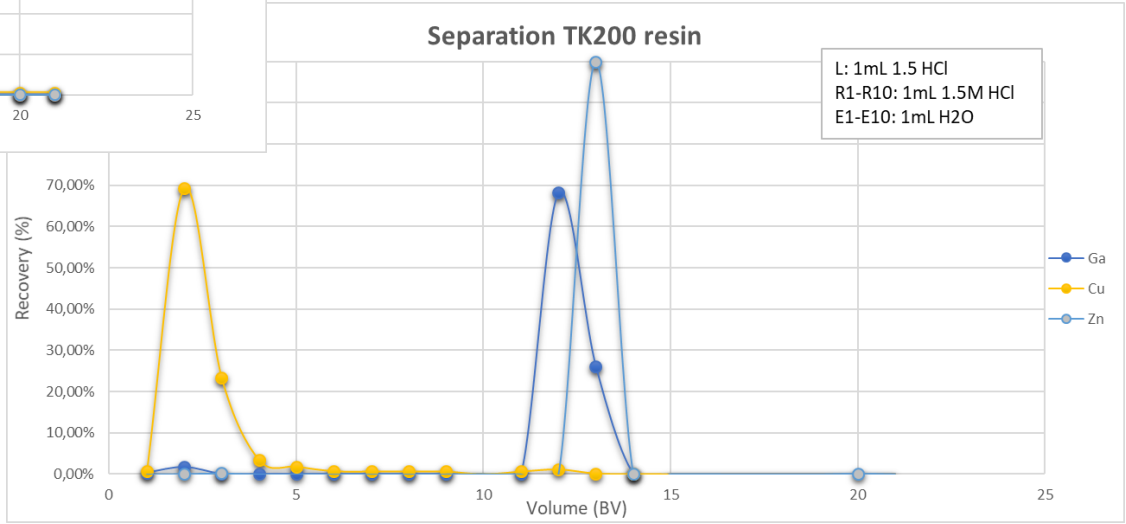
Fig. 1. Schematic concept of a forward/reverse flow radionuclide generator.

- Direct (1 mL ZR Resin) and reverse elution (2 mL ZR Resin)
- 65 column volumes tested up until publication
- High Sc yields, max. Ti-44 breakthrough: 4.1^{E}-4%
- Obtained Sc gave labelling yields > 94%
- Generator has just been set-up at BNL

Ga-67/8 separation from Zn targets



EANM '17: Presentation Gagnon et al.



- Loading from:
  - 0.1M HNO_3 (liquid targets)
  - >6M HCl (solid targets)
- Clean Ga separation on ZR Resin
- Elution with 1.5M HCl
  - Too high for labeling/injection

- Ga conversion step on TK200
- TK200 load from 1,5M HCl, elution in 2 – 3 BV water

Dw values TK200 – HCl
=> product sheet on website

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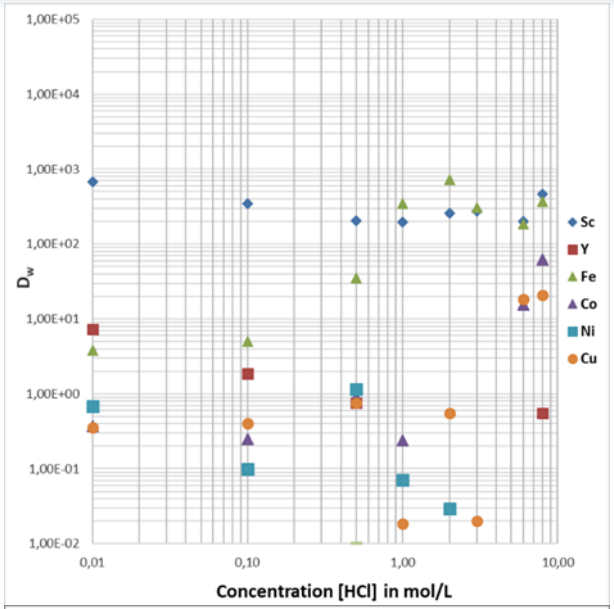
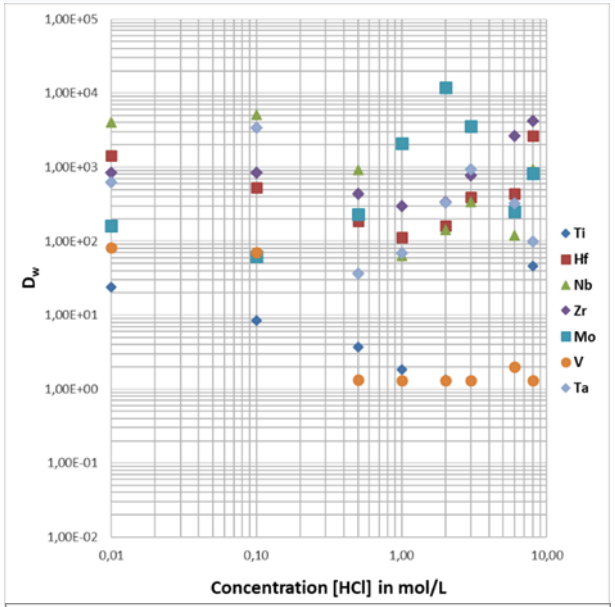
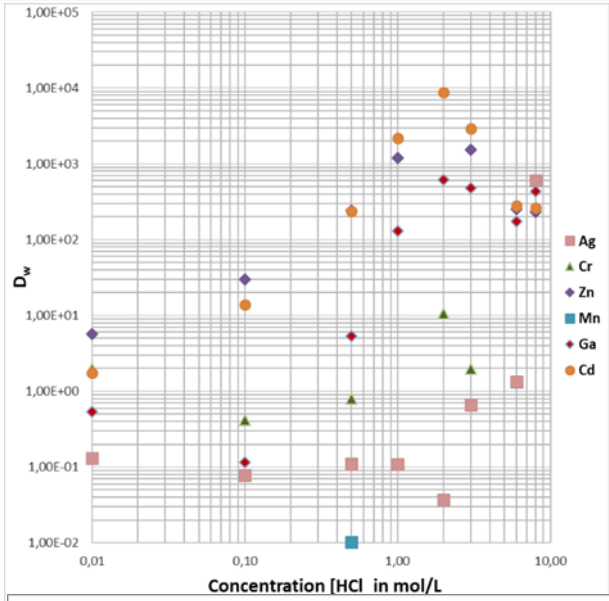
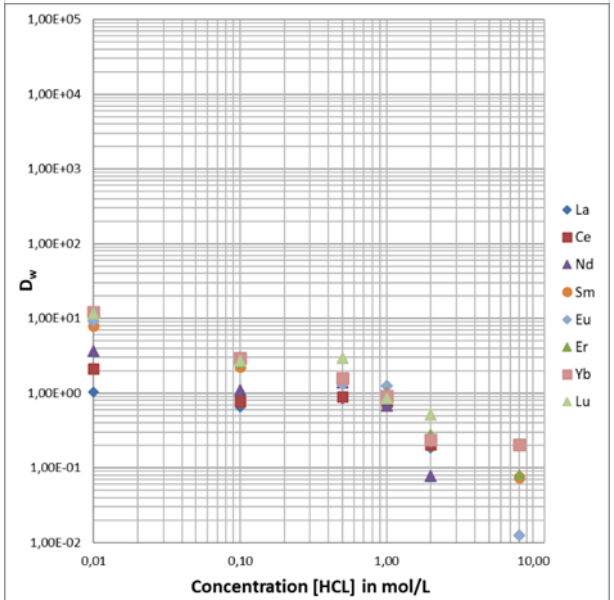
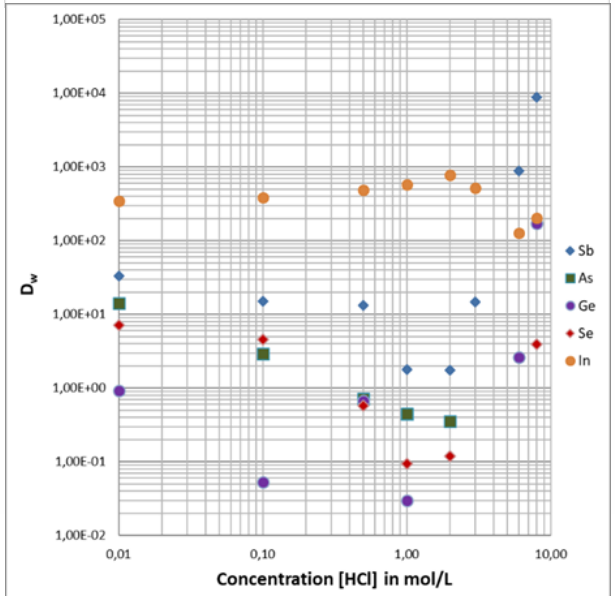
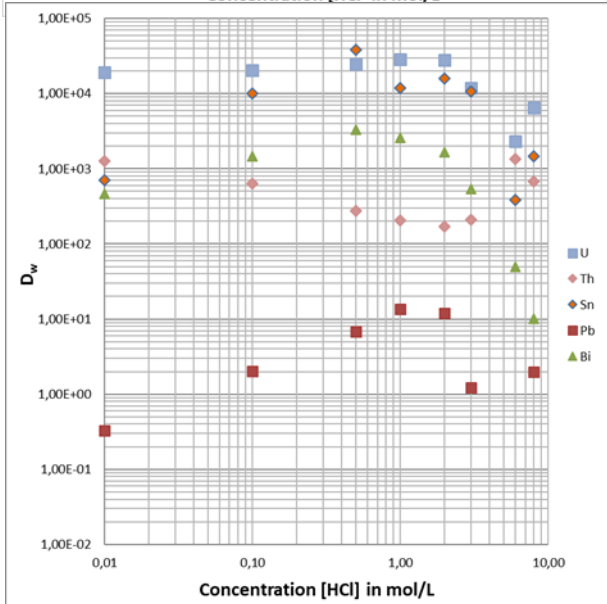






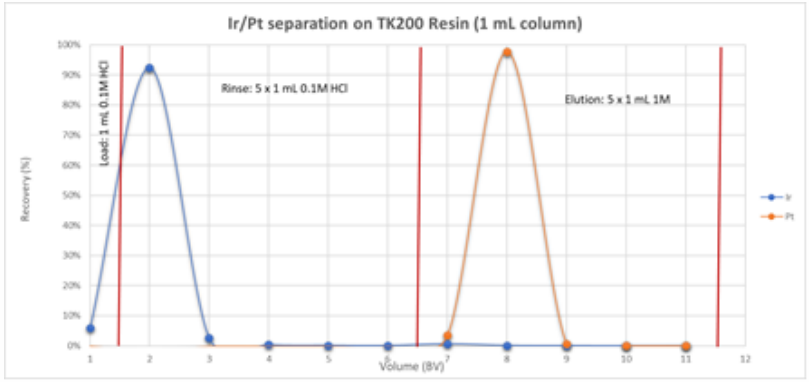




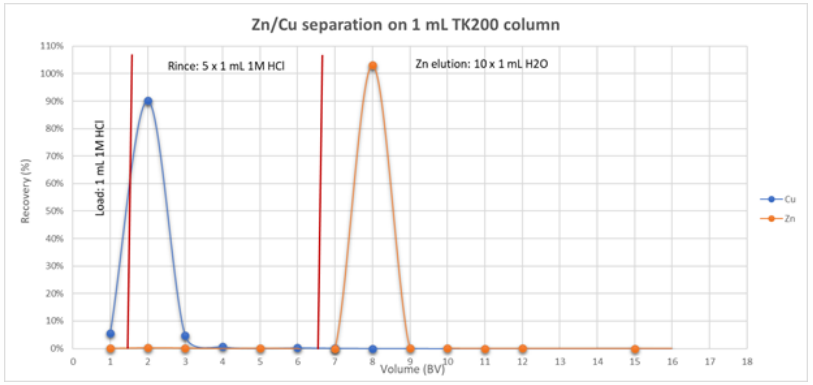


Other examples for separations on TK200

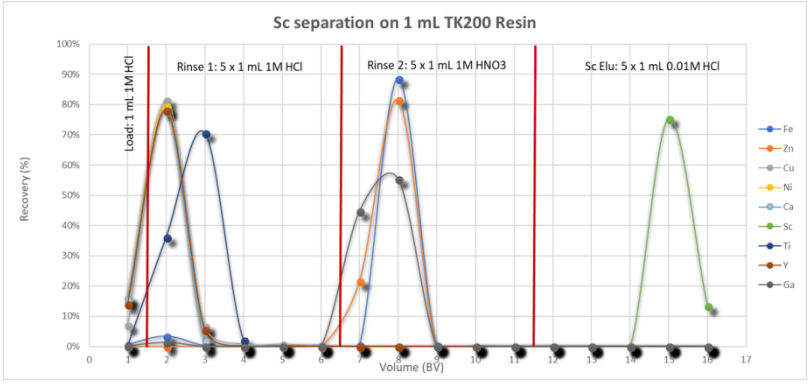
- Pt separation from Ir



- Zn separation from Cu



- Sc from Ti or Ca



More applications under development

Update on CU Resin

- Oxime based resin (very hydrophobic, preferably use as cartridge)
  - Column packing from 20% EtOH
- High selectivity for Cu
- Load from pH >2, elution in high acid
  - Not ideal for solid Ni targets
    - TK201 under evaluation, on its own and combined with CU Resin
  - Very suitable for liquid targets and solid Zn targets (=> Cu-67)
  - High labelling yields
- Typical applications:
  - Cu isotope production from Ni or Zn targets
  - Cu removal (Ni-64 purification)
  - Cu isotope ratio determination by mass spectrometry (=> ESI)
    - Geochemistry, Archaeometry, Biomedical (Wilsons Disease)

Cu-67 at BNL (DeGraffenreid et al.)

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Purification of ^{67}Cu and Recovery of its Irradiated Zn Target

A.J. DeGraffenreid[a] , R. Nidzyn[a], B. Jenkins[a], D.E. Wycoff[b], T.E. Phelps[b], A. Goldberg[a], D.G. Medvedev[a], S.S. Jurisson[b], C.S. Cutler[a]
[a]Brookhaven National Laboratory, C-AD/MIRP—Upton, NY (USA)
[b]University of Missouri, Department of Chemistry—Columbia, MO (USA)

Poster presented at ISRS 2017

Cu Resin

- Dissolve irradiated (86.4 µA for 0.79 d) ^{nat}Zn target (13.70 g) in trace metal grade conc. HCl
- Evaporated to dryness and reconstitute into milliQ water (91.5 mL) to give a 312 mg $ZnCl_2$/mL solution
- Ensure pH ≥ 2 with pH paper
- Added ~60.6 mL (18.9 g $ZnCl_2$) to Cu Resin column (2.40 g)
- Quantitative transfer with 2 x 20 mL H_20→ into load bottle
- Rinsed with pH 2 HCl (80 mL)
- Recover radiocopper with 2 x 20 mL 6 M HCl
- Evaporate 6 M HCl to dryness

Cu Resin

Nuclide	EOB Activity (mCi ± 1σ)	Recovery (%) Load w/ Quant. Transfer	pH 2 HCl Rinse	Acid #1	Acid #2
^{64}Cu	4700 ± 200	ND	ND	102	ND
^{65}Zn	41.0 ± 0.8	103	ND	0.04	ND
^{58}Co	63 ± 1	104	0.04	0.1	0.01

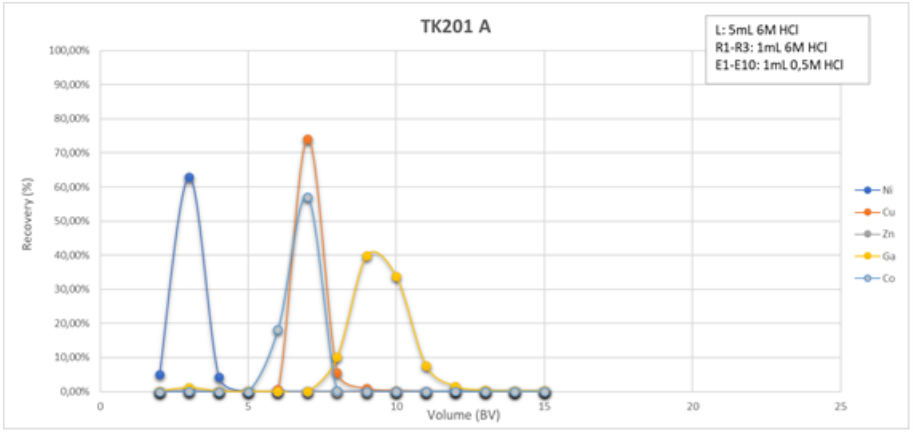
- Produced 143 mCi ^{67}Cu
- Quantitative recovery of radiocopper
- 99.5% radionuclidic purity—single column
- ICP-OES: 132.9 µg Cu and 1.3 mg Zn
  - Anion exchange column still needed to remove trace Zn
- Specific activity ^{67}Cu at EOB: 1.07 mCi/µg

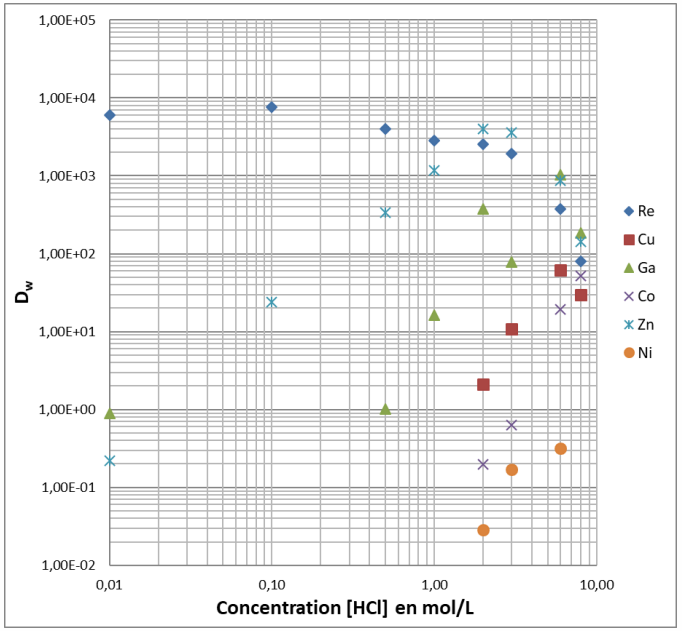
Cu Resin

Robust separation that could shorten the overall processing time to separate co-produced radionuclides and large quantities of Zn from radiocopper
Cation and anion exchange columns still needed to suitably purify radiocopper

Cu separation– conversion on TK201

- Cu conversion from high HCl to more suitable conditions usually done using AIX
- Problem: shrinking/swelling of AIX, insufficient trace Zn removal
- TK201 to be used as replacement?

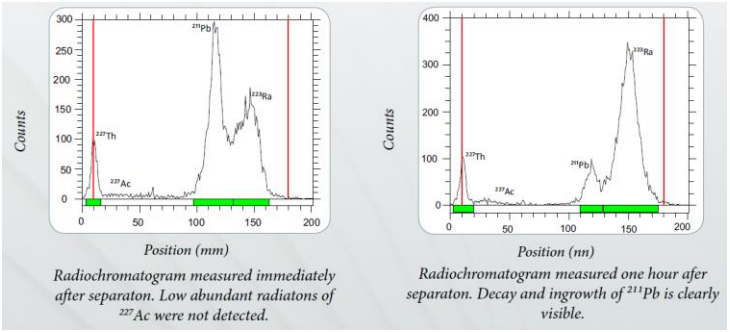


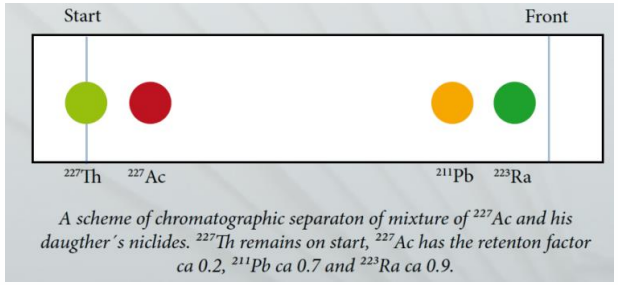


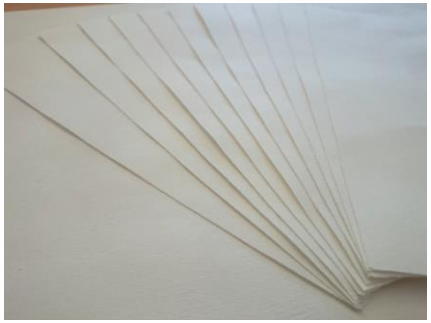
- Removal of trace Ni during load/rinse
- Zn remains retained during Cu elution
- Solid Ni targets: improvement of Ga/Co removal or combination with CU Resin

DGA Sheets

- QC of radionuclides and generator eluents (p.ex. Ra-223, Ac-225/Bi-213, Pb-212, Ge-68/Ga-68 …) with TLC scanner or radiometer/LSC after cutting
  - Therapy: alpha emitters
  - Diagnostics e.g. with generator produced Ga-68
- More types of sheets under development (selectivities, geometry)
- 2D TLC under development (with Subatech) => use in decommissioning
  - Quadratic sheet, two runs (90° turn in-between) with different acids => 2D pattern
  - Measurement e.g. with Ai4r Beaver system (high res α/β discrimination counting)

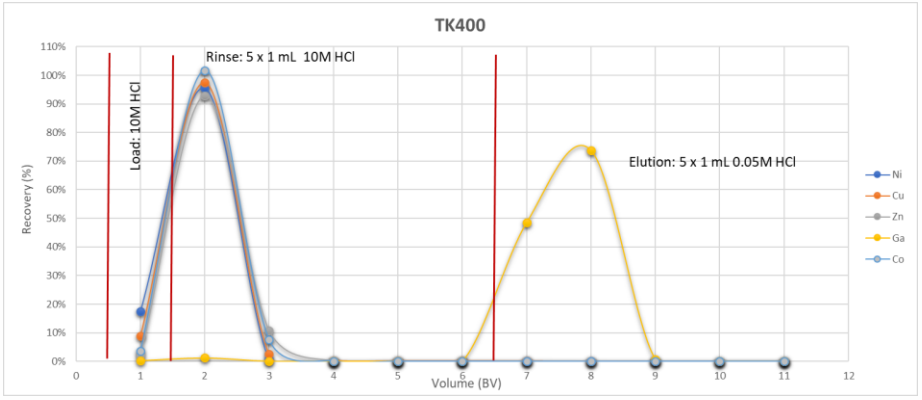


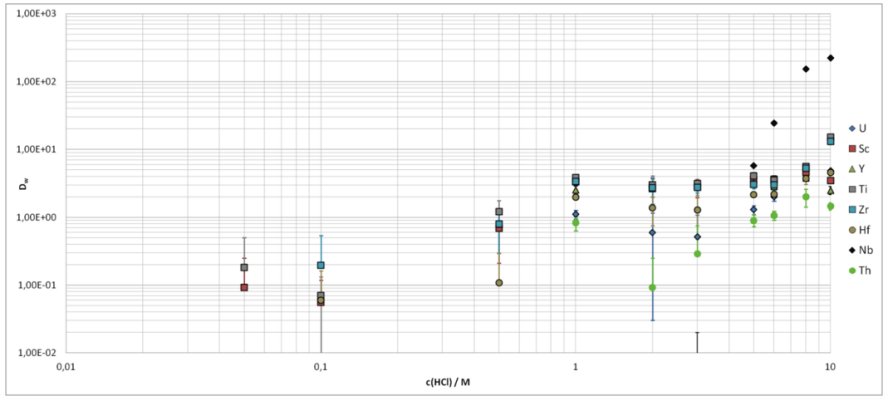




TK400 Resin

- Long chained alcohol
- Main application: Pa separation (Pa-230/1 determination by MS)
  - NPL (no selectivity for actinides, Ac, Ra, Pb,...=> Pa-230 purif.)
  - Also retains Mo, Nb, Po, Ga,...
    - Ga-68 from solid Zn targets under testing
    - Nb separation from Zr (Nb-90)
    - Mo separation for Mo isotope ratio determination
  - At separation from Bi targets to replace dry distillation?





Update CL Resin

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Chromatographic separation of the theranostic radionuclide ^{111}Ag from a proton irradiated thorium matrix

Tara Mastren [a], Valery Radchenko [a, 1], Jonathan W. Engle [a, 2], John W. Weidner [a], Allison Owens [b], Lance E. Wyant [b], Roy Copping [b], Mark Brugh [a], F. Meiring Nortier [a], Eva R. Birnbaum [a], Kevin D. John [a], Michael E. Fassbender [a, *]

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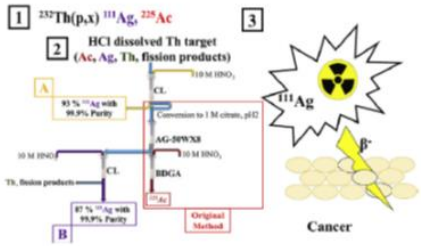
HIGHLIGHTS

- Chromatographic recovery of medical isotope ^{111}Ag from proton irradiated thorium targets.
- First-time measured equilibrium distribution coefficients for silver and ruthenium on CL resin.
- ^{232}Th (p, fission) cross-section data for the formation of ^{111}Ag and ^{110m}Ag.

GRAPHICAL ABSTRACT



ELSEVIER
Applied Radiation and Isotopes
Volume 86, April 2014, Pages 90-96

Accurate determination of ^{129}I concentrations and ^{129}I/^{137}Cs ratios in spent nuclear resins by Accelerator Mass Spectrometry

Emmanuelle Nottoli [a], Philippe Bienvenu [b], Alexandre Labet [a], Didier Bourlès [c], Maurice Arnold [c], Maité Bertaux [a]

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https://doi.org/10.1016/j.apradiso.2014.01.010

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Anal. Chem., 2018, https://pubs.acs.org/doi/10.1021/acs.analchem.8b01380

Separation of protactinium employing sulfur-based extraction chromatographic resins

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- On-going tests for Au, Pd, Hg
- Use in DGT

Iodine removal from effluents

- Decamp et al.: Iodine removal from elevated sample volumes at high flow rates[§]
  - Issues with rad. waste storage
    - Storage as liquid waste challenging
    - Preferably stored as solid waste
  - > 10 L radioactive process effluent (1M HNO_3),
  - Flow rate up to 180 mL/min
  - Mixed-bed columns
    - 3g CL resin (plus 4g XAD-4 resin), iodine uptake: 85 – 95%

[§] C. Decamp (IRE), S. Happel: Utilization of a mixed-bed column for the removal of iodine from radioactive process waste solutions, Journal of Radioanalytical and Nuclear Chemistry, online April 2013, DOI: 10.1007/s10967-013-2503-1

Some on-going projetcs

- C.L.I.P.S. 2020
- Ra Resin(s)
- TK300 Resin for Cs/Rb separation
- Online concentration/separation
- Extractive discs
- Resins based on scintillating beads
  - Uni Barcelona
- Improved Ni Resin
- Li Resin
- Lanthanide separations (e.g. Lu-177 separation from Yb) => new resins
- SE Resin: e.g. Se-72/As-72 generator (piazselenol chemistry)
- Tc-99m separation from Mo (TK201/2)
- DGT (radioelements and heavy metals)
  - Passive sampling/'bio-availability'
- Ga purification (generator) and QC
- At-211 separation (e.g. TK400)
- Ac-225 separation e.g. from Ra-226
- Removal of radiouclides from effluents
- Functionalised polymers/silicates,...
- ...

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Thank you for your participation!

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