Characterization of a TBP Resin and development of methods for the separation of actinides and the purification of Sn

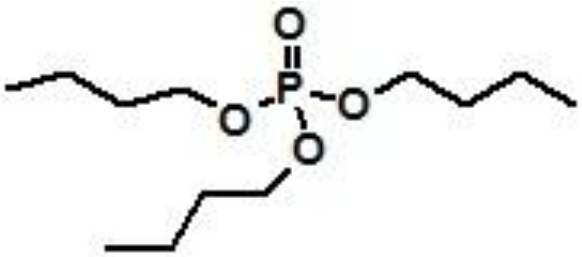
Dirks C.[a], Vajda N.[b], E. Kovács-Széles[c], A. Bombard[d], S. Happel[d]

[a] *Philipps-University, Marburg, GERMANY,* [b] *Radanal Kft, Budapest, HUNGARY,* [c] *Centre for Energy Research, Hungarian Academy of Sciences, Budapest, HUNGARY,* [d] *TrisKem International, Bruz, FRANCE*

- General
- Resin characterisation
- Application I – Pu in drinking water
- Application II – Sn separation

General

- TBP used in PUREX process (LLX)
- TRU Resin (contains TBP) used for Sn separation in geology/archeology
  - Elimination of matrix elements and isobaric interferences
- Determination of long-lived Sn isotopes in rad waste
  - Focus on matrix removal and elimination of isobaric interferences
- Sn-117m separation for use in nuclear medicine
  - Focus on Sn/Cd/Sb separation



TBP (Tributyl Phosphate)

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Resin characterisation

- Determination of D_w values for various elements
  - Multi-element solutions (HCl and HNO_3) for ICP-MS
    - 10 µg/mL of each element: Al, As, B, Ba, Ca, Cd, Co, Cr^{3+}, Cs, Cu, Fe, Ga, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, Th, U, V, Zr
    - 10 µg/mL of each element: B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, Zr
  - Pu(IV), Np(IV), Th(IV) and U(VI) via LSC
  - 50mg resin contacted with 1.3 or 1.5mL solution for ≥ 1h
  - Centrifugation and filtration
  - Dilution with H_2O for ICP-MS measurements (multi-element solutions),
  - Evaporation and dilution in 0.1M HNO_3 for LSC measurements (Pu, Np, Th and U)

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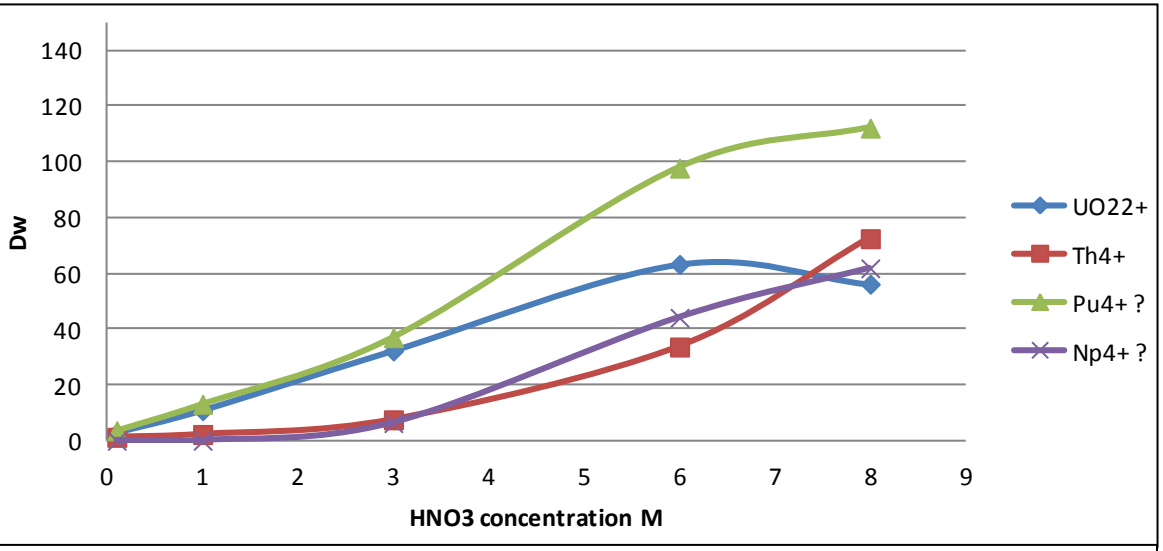
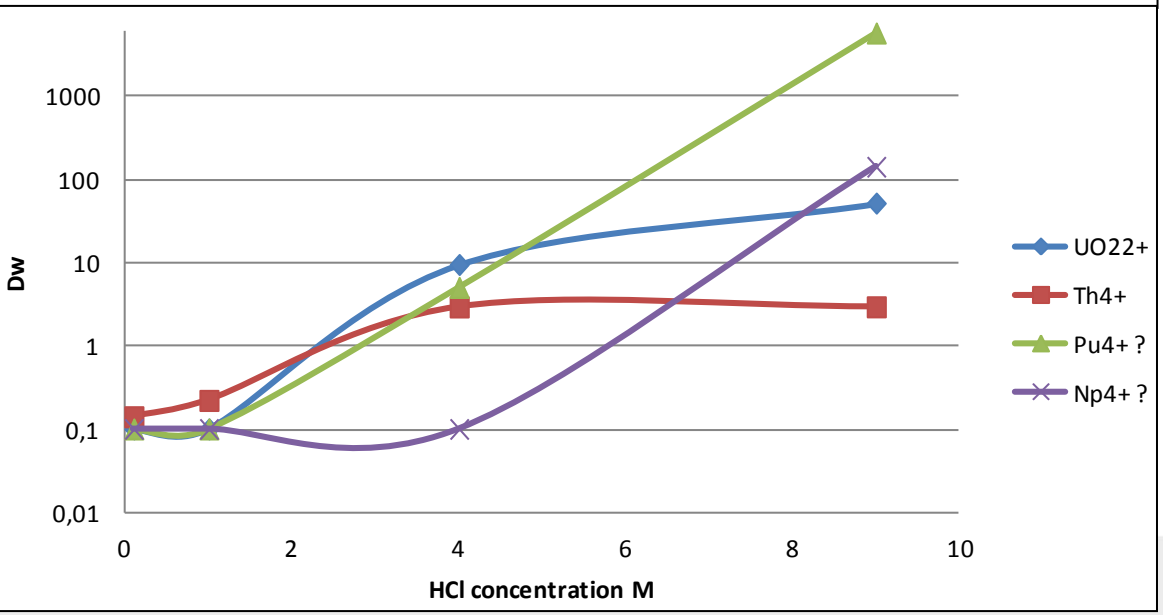
Resin characterisation

- D_W values of the actinides in HNO_3 and HCl





- D_w Pu >100 in ≥ 6MHNO_3/HCl
- D_w U < 100 all acids/acid concentrations

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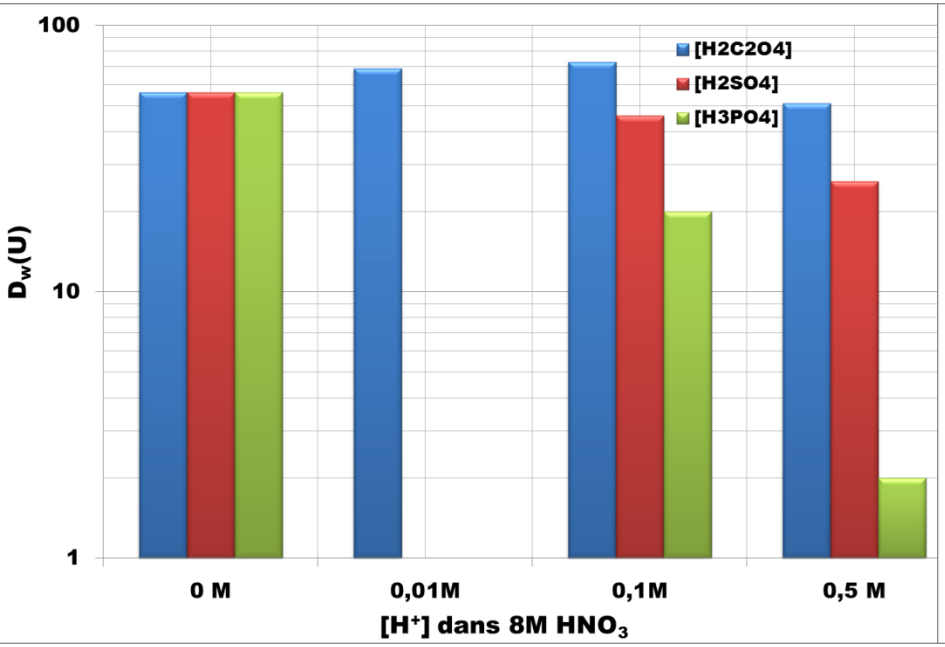
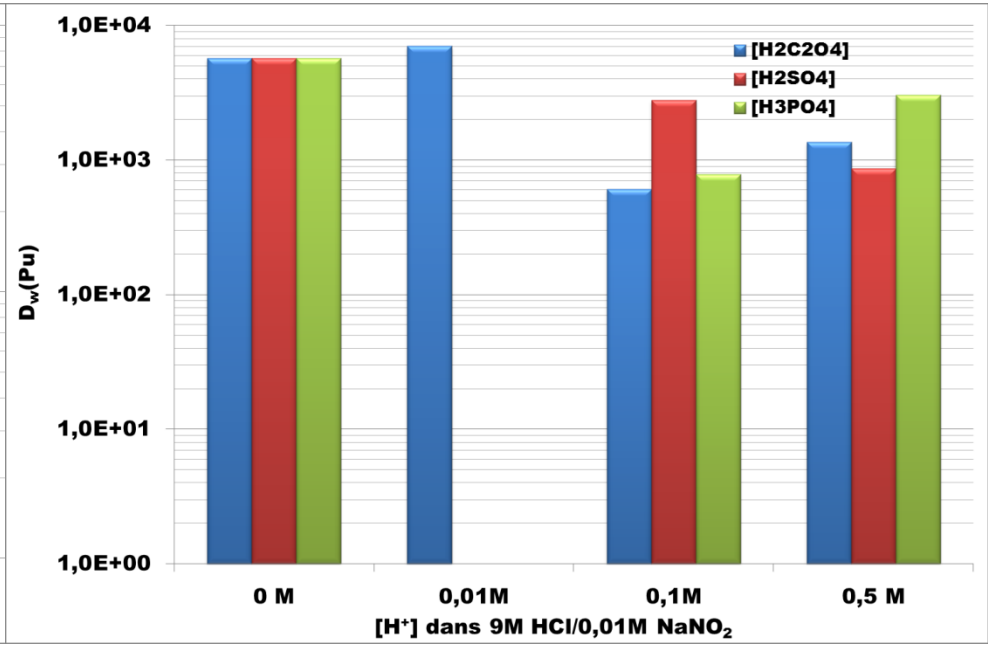
Resin characterisation

- Anionic interferences





- U in 8M HNO_3:
  - No/little interference from oxalate, interference form sulfates and especially phospates
- Pu in 9M HCl/0,01M $NaNO_2$:
  - Interferences, but D_w(Pu) >500 => little impact on Pu retention

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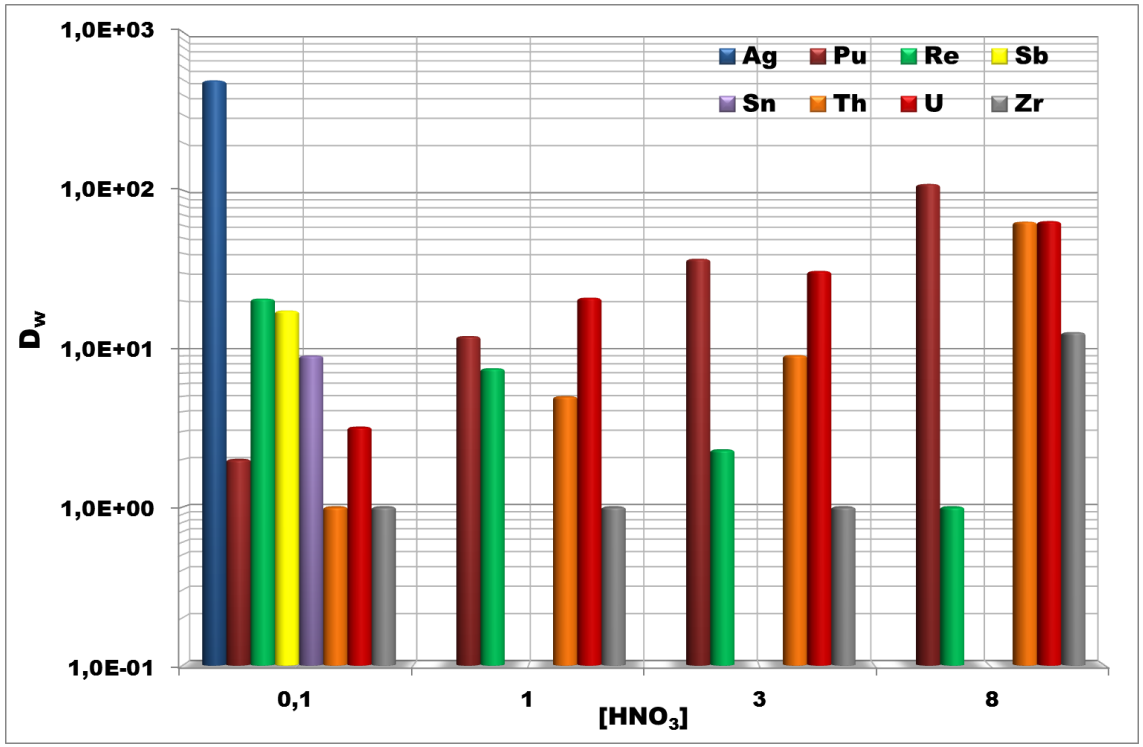
Resin characterisation

- HNO_3: only elements with D_w >10 shown
- D_W(Ag) ~ 500 in 0.1M HNO_3 and Dw(Pu) ~ 100 in 8M HNO_3
- Other elements show very little affinity in HNO_3



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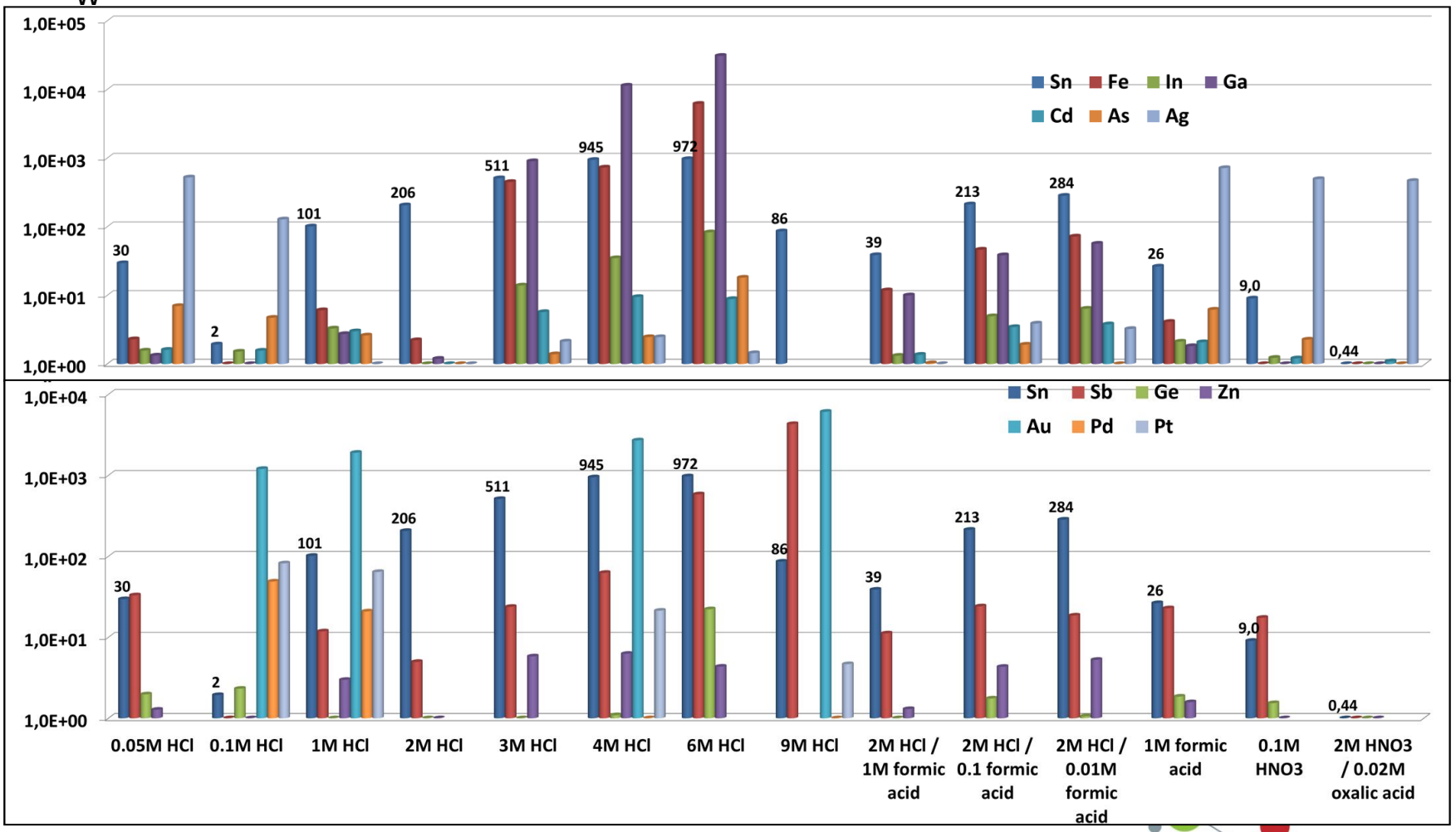
Resin characterisation

- D_W values in various other conditions



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Resin characterisation

- **U capacity**
  - Batch experiments
  - U_{nat}, 50mg resin, 8M HNO_3
  - Filtration, evaporation, dissolution in 0.1M HNO_3
  - Mixed with LSC cocktail (ProSafe+)
  - LSC measurement
- **Results:**
  - capacity =71-76 mg U/g dry resin in 8M HNO_3
    - comparable (although significantly lower) to UTEVA resin

Elution study

- 2mL columns, gravity flow
- Pu-239 (Pu(IV)), U-233 and Th-230
- Presence of Fe(III)
- All eluates collected, evaporated and redissolved in 0.1M HNO_3
- Mixed with LSC cocktail (ProSafe+)
- Elution procedure:
  - Preconditioning: 10 mL 8M HNO_3/0.01M $NaNO_2$,
  - Loading solution (~ 10 mL)
  - Rinse: 2 x 10 mL 8M HNO_3/0.01M $NaNO_2$,
  - Elution Th: 10 mL 9M HCl/0.01M $NaNO_2$,
  - Elution Th+U: 30 mL 9M HCl/0.01M $NaNO_2$,
  - Elution Pu: 20 mL 1M HCl

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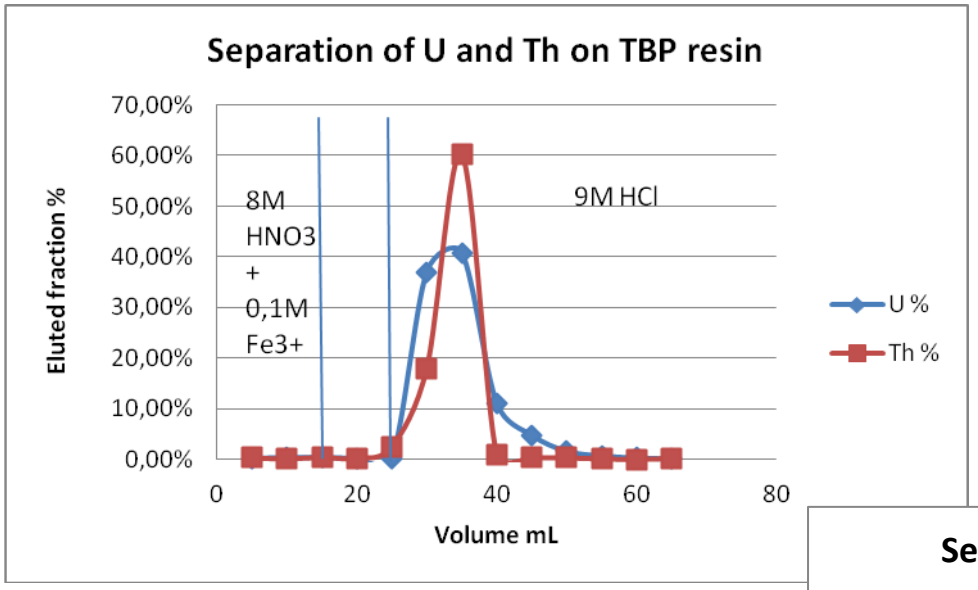
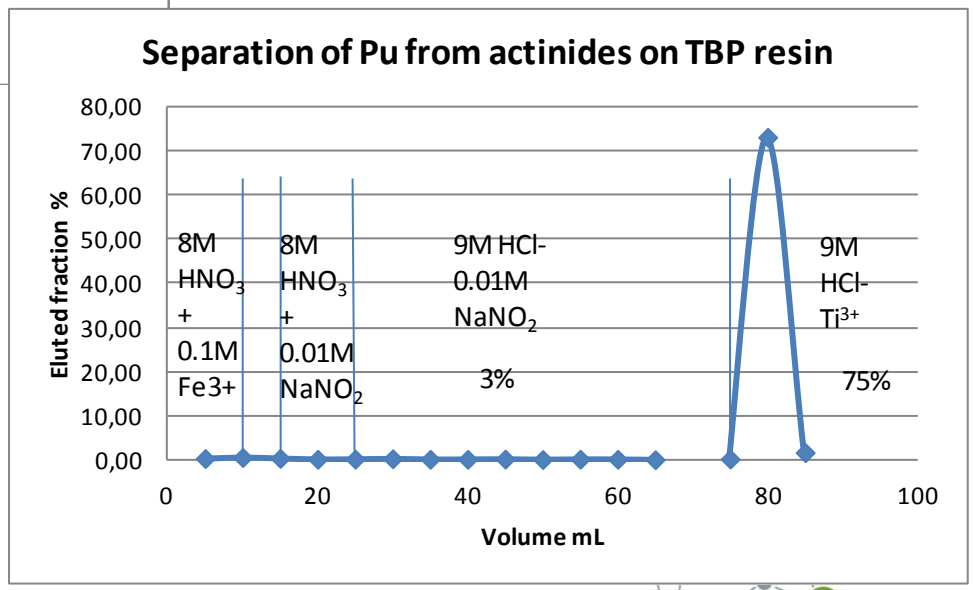
Elution study





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Application I

- Determination of Pu in drinking water
  - Pre-treatment:
    - 300-500mL water acidified with 2.5mL 1M HNO_3 and spiked with Pu-239, Am-241, Th-230 and U-233 (each 2Bq)
    - 0,5g Mohr's salt
    - 100µL N_2H_4 (Fe reduction)
    - Heating under stirring for 1h
    - $Fe(OH)_2$ precipitation with 2.5mL NH_3 25% (pH 7)
    - Heating, settling over night
    - Filtration 0.45µm
    - Redissolve in 8M HCl
    - Evaporation, redissolve in 3x1mL conc. HNO_3
    - 350µL N_2H_4 + 1 drop conc. HNO_3 (Test SCN^-: Fe^{2+})

Application I

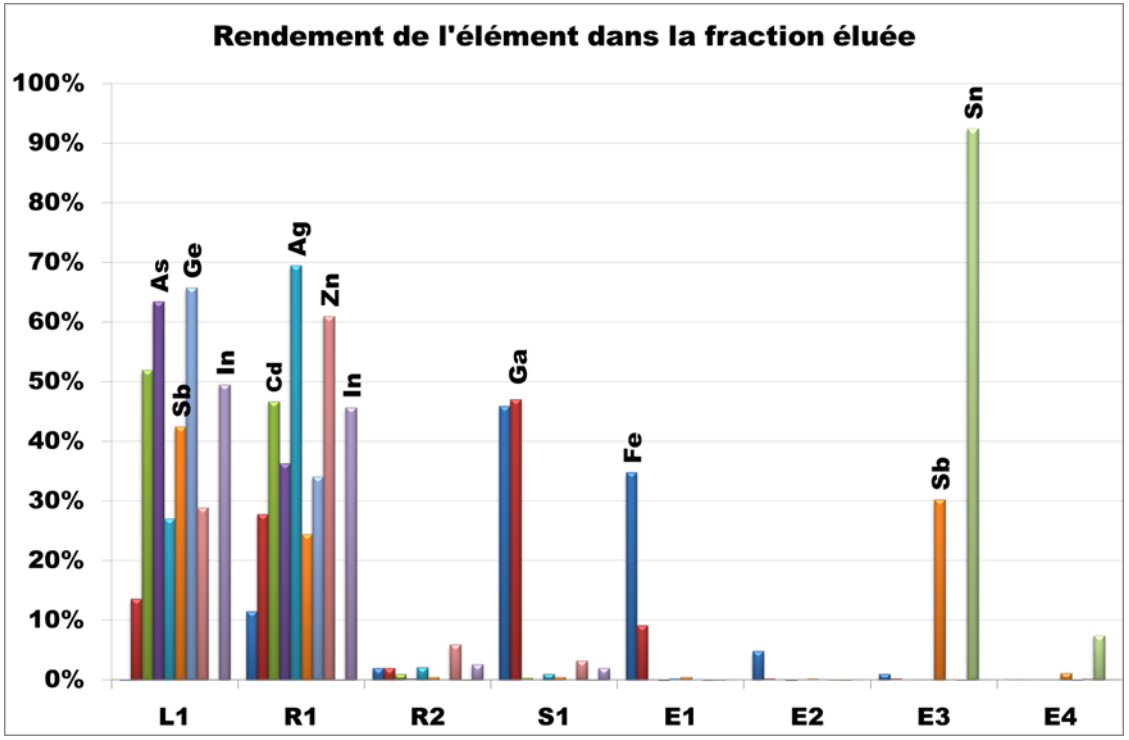
- Determination of Pu in drinking water
  - Pre-treatment:
    - Add 1.5mL conc. HNO_3 to adjust to 4M HNO_3 and heat to boiling (N_2H_4 is destroyed) and
    - Add 1 drop of conc. HNO_3 and allow to cool down to RT
    - Addition of $NaNO_2$ and conc. HNO_3 to adjust to 10mL 8M HNO_3/0,1M $NaNO_2$.
  - Separation as decribed
- Results :
  - Chemical yield for Pu ~ 69%.
  - U contamination in Pu source is <1.4%.
  - No Am or Th found
  - Procedure can be performed in 1 day.

Application I

- Limits of the procedure:
  - With respect to D_W(Pu) in 8M HNO_3 loading volume has to be <20 mL.
  - Very iron rich (Fe content > 2 g) and/or large samples (>1-2 g of soil) can probably not be treaded on standard 2 mL columns.
  - Pu(IV) valence adjustment time consuming

Application II

- Sn separation:
  - Method development based on D_W values obtained via batch experiments
- Results:



L1: 4mL loading solution: 2M HCl/0,01M formic acid

R1: 5mL 2M HCl/0,01M formic acid

R2: 2mL 2M HCl/0,01M formic acid

S1: 3mL 1M HCl

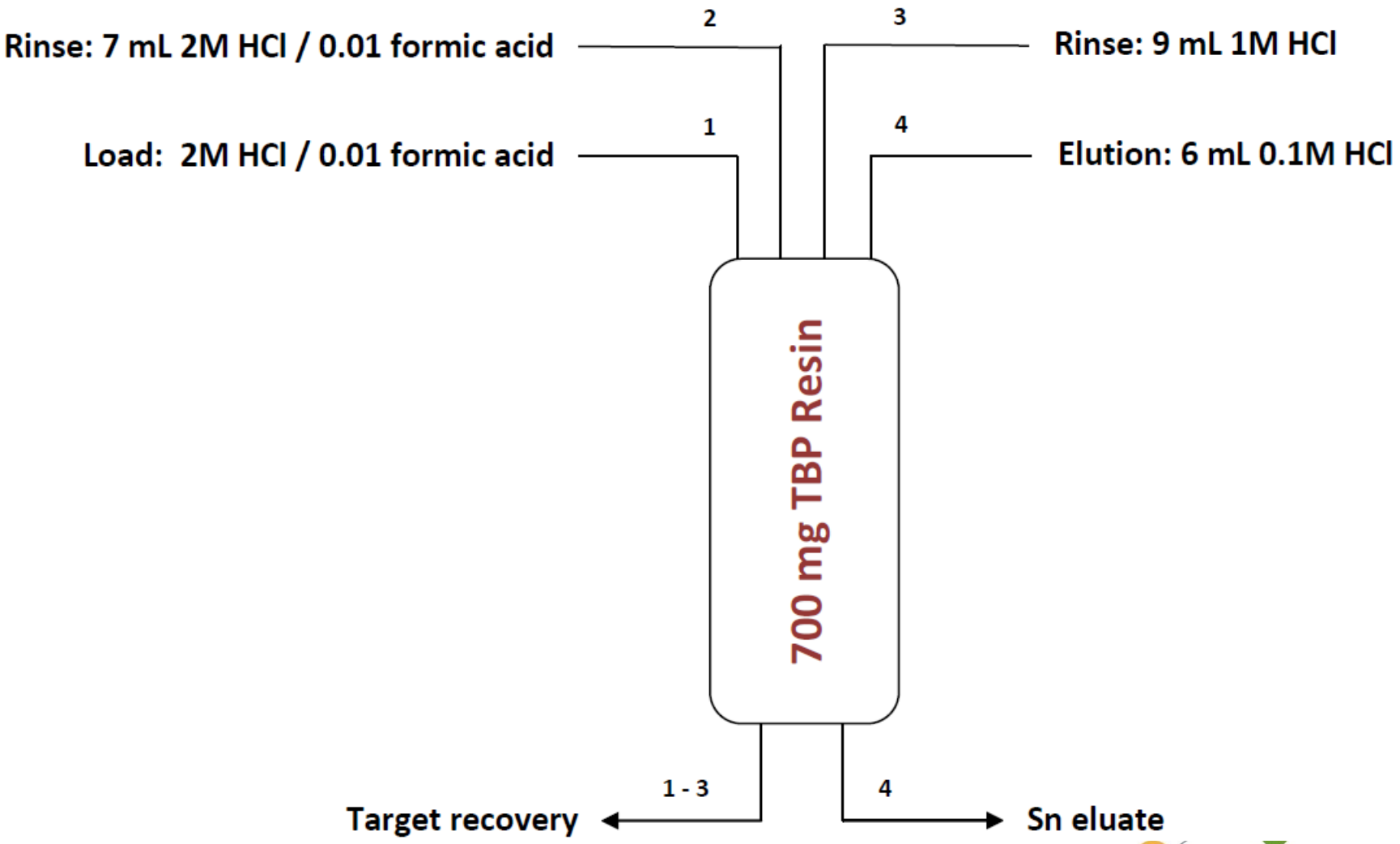
E1: 3mL 1M HCl

E2: 3mL 1M HCl

E3: 4mL 0,1M HCl

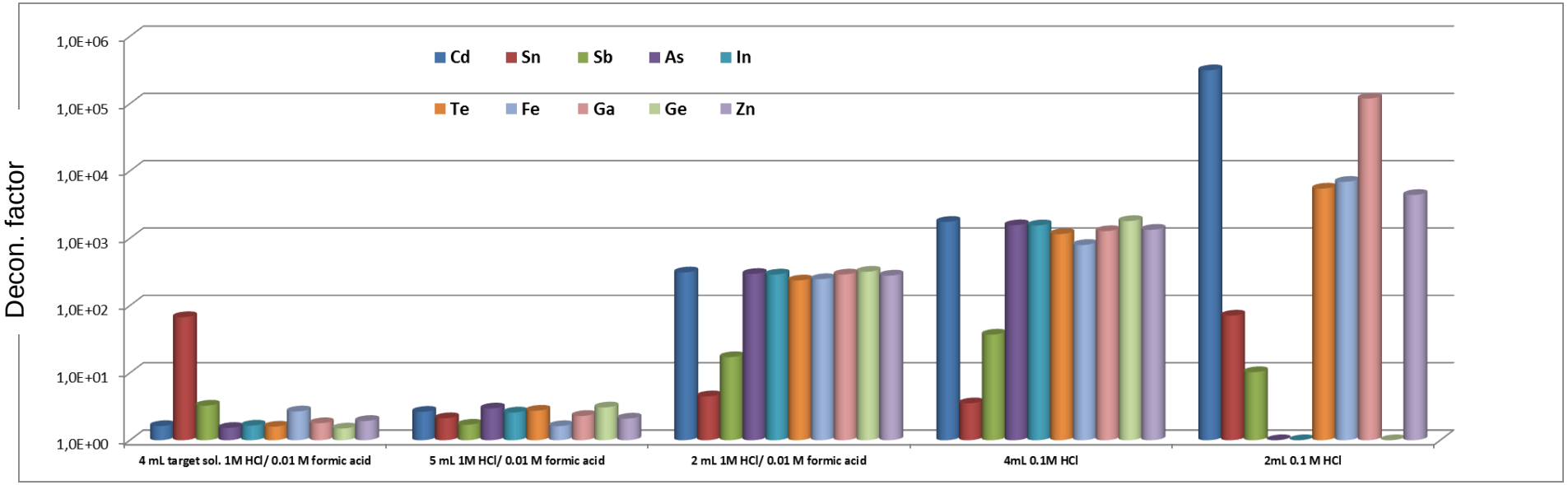
E4:2mL 0,1M HCl

Proposed Sn separation procedure



Application II

- Main isobaric interference for Sn-126 (ICP-MS determination): Te-126
- Decon factor study to verify Sn/Te separation



➢ Te decon.factor in Sn fraction > 1000

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Application II

- Results
  - TBP Resin can be used for the purification of Sn
  - Most elements are eluted during load and first rinse (Cd, As, Ag, Ge, Zn, In, ~70% Sb) => 11mL
  - Fe/Ga are removed with 9mL 1M HCl
  - For Fe rich sample loading under reducing conditions might be necessary
  - >90% Sn eluted in 6mL 0,1M HCl
  - ~ 30% Sb co-eluted with Sn => control of Sb oxidation state
  - Clean Se/Te separation
  - On-going project on Sn-126 determination in rad waste via ICP-MS
    - First step AIX, followed by TBP

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Conclusions

- TBP resin characterized with respect to D_W values of various elements in HNO_3 and HCl, and the influence of selected interferents
- TBP resin is well suited for Sn separation. Optimization of Sn/Sb separation through ontrol of Sb oxidation state (important for work with Sb targets).
- Possibility to seperate and determine Pu in drinking water

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Thank you for your attention!

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Parc de Lormandière Bât. C - Rue Maryse Bastié - Campus de Ker Lann - 35170 Bruz - FRANCE
Tel +33 (0)2.99.05.00.09 - Fax +33 (0)2.99.05.07.27 - www.triskem-international.com - email : contact@triskem.fr