Rapid determination of Pb-210 and Sr-90 in water samples using new crown-ether based extraction chromatographic resins

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Context

- On-going work
- Original project: Rapid extraction and separation of Sr from water samples (pH5–8)
  - « Passive sampling »
    - Use in DGT (Diffusive gradients in thin-films) units
    - Weakly bound/complexed species (« bioavailability »)
    - Technique also used in NORM monitoring
      - Ra-226 via MnO_2 (resin and Ra Nucfilm discs), U
  - Rapid method
    - Concentration and separation on same resin/column
    - Load in batch, disc or column mode

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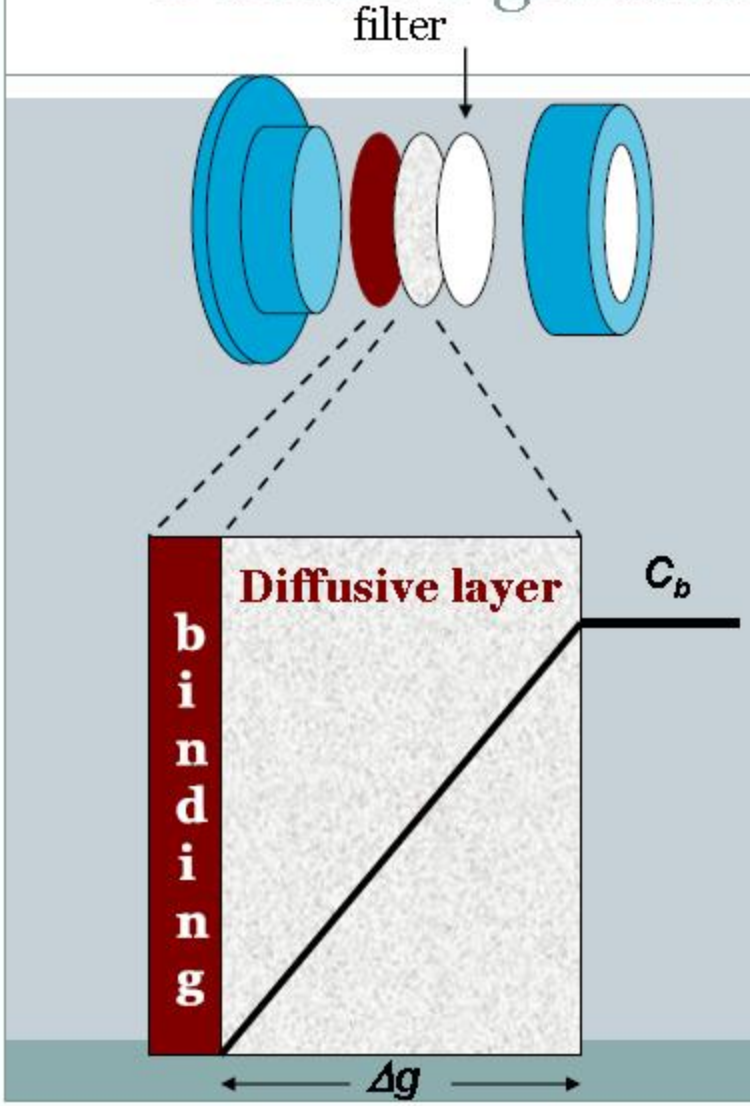
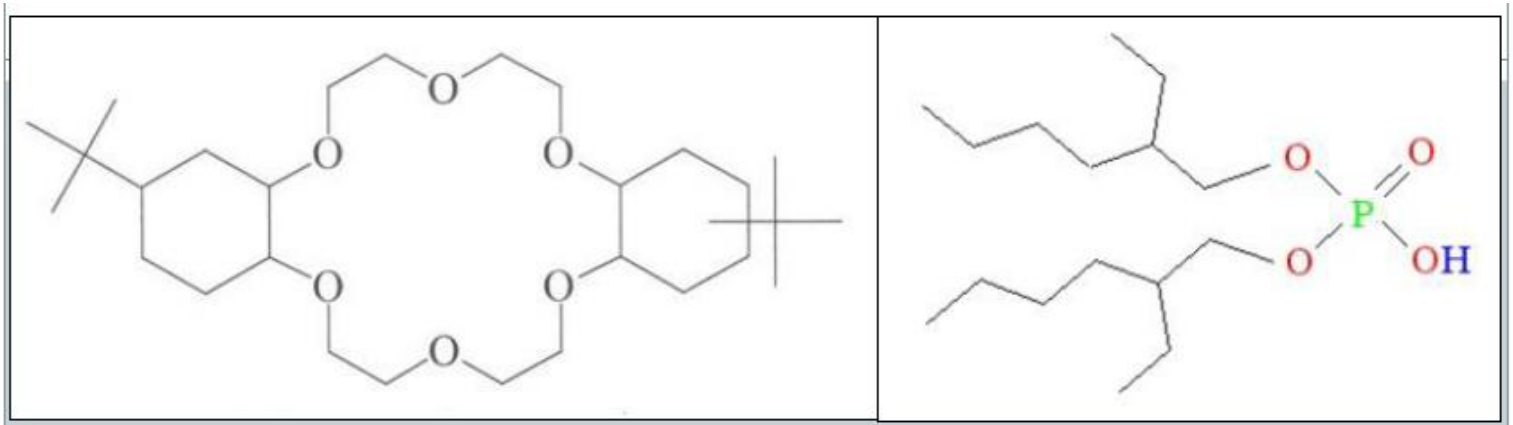
Diffusive gradients in thin-films (DGT)



TK100 Resin



Di-*t*-butyl dicyclohexyl-18-crown-6 | Di(2-ethyl-hexyl) phosphoric acid

- Keep Sr Resin selectivity (crown ether), increase pH range
- 1st approach: Replace 1-Octanol by HDEHP
- Screening of several test resins (varying HDEHP contents)
- Characterisation of best suited resin prototype
- Elution studies and first tests

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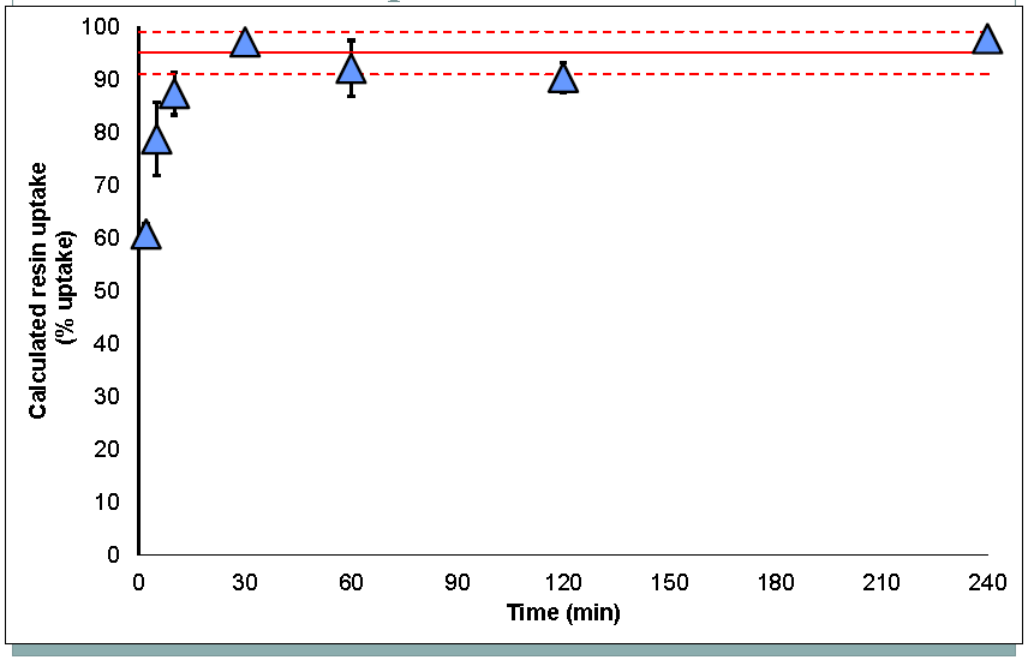
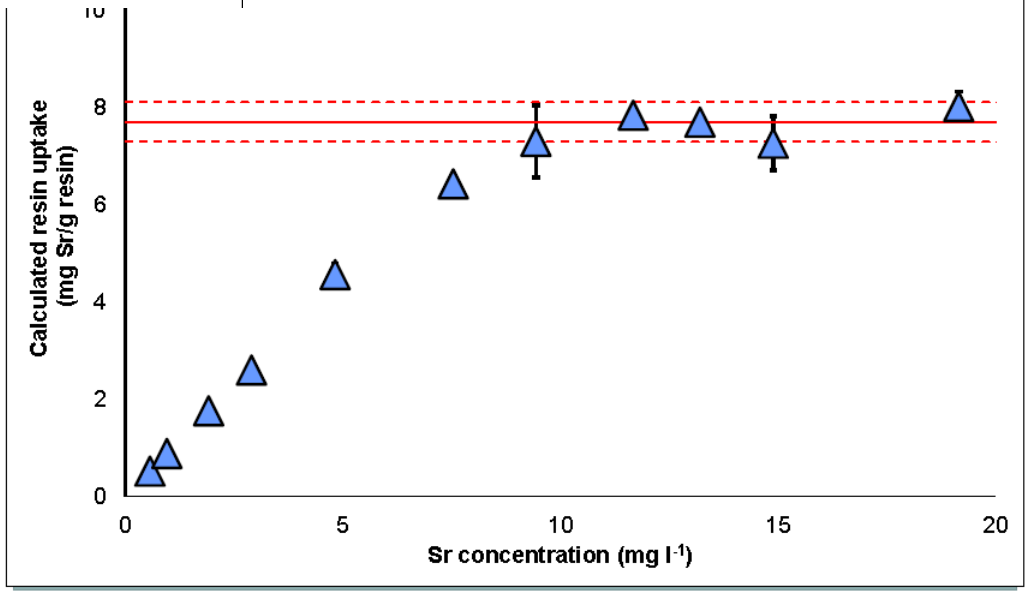
Uptake kinetics



- pH 7
- Batch experiments

Capacity



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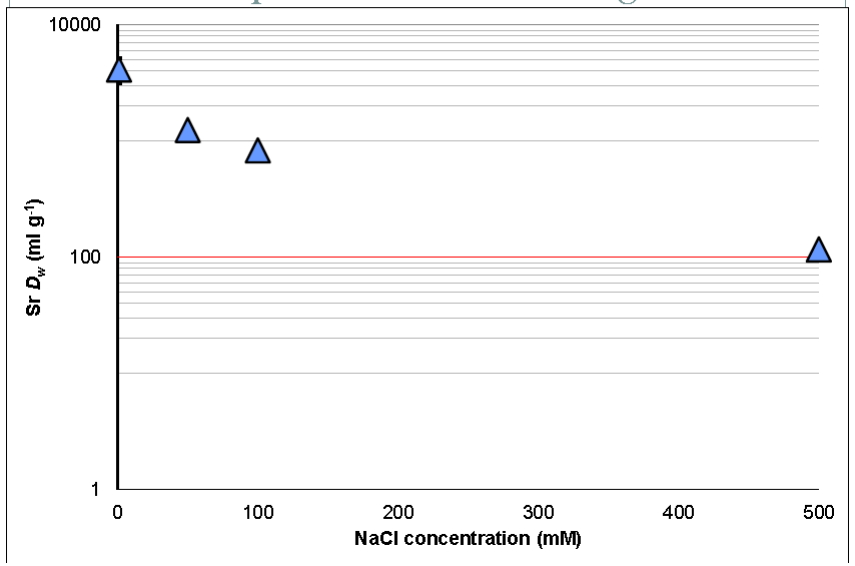
Sr uptake and ionic strength



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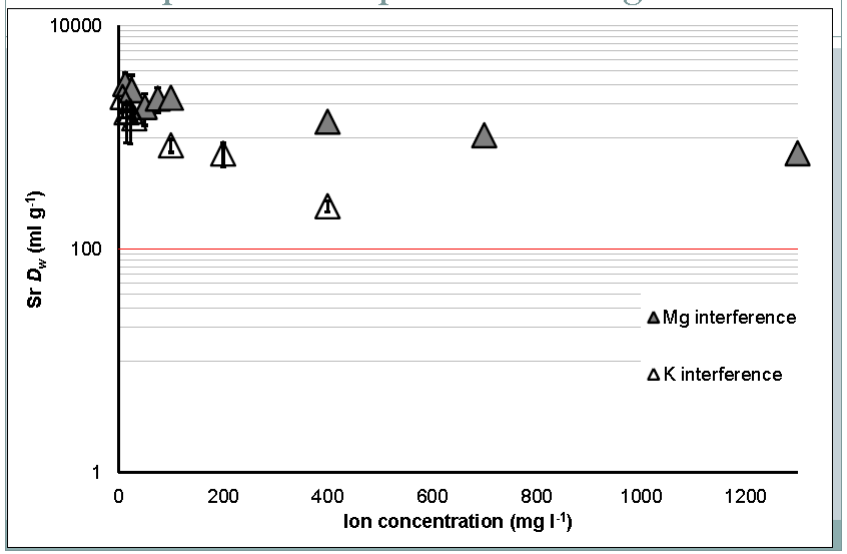
Sr uptake in the presence of Mg and K



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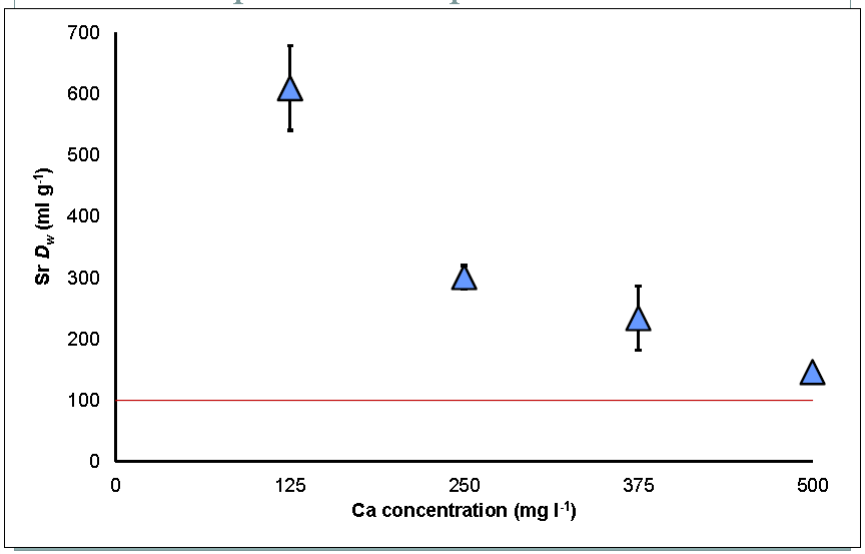
Sr uptake in the presence of Ca



- pH 7
- Batch experiments

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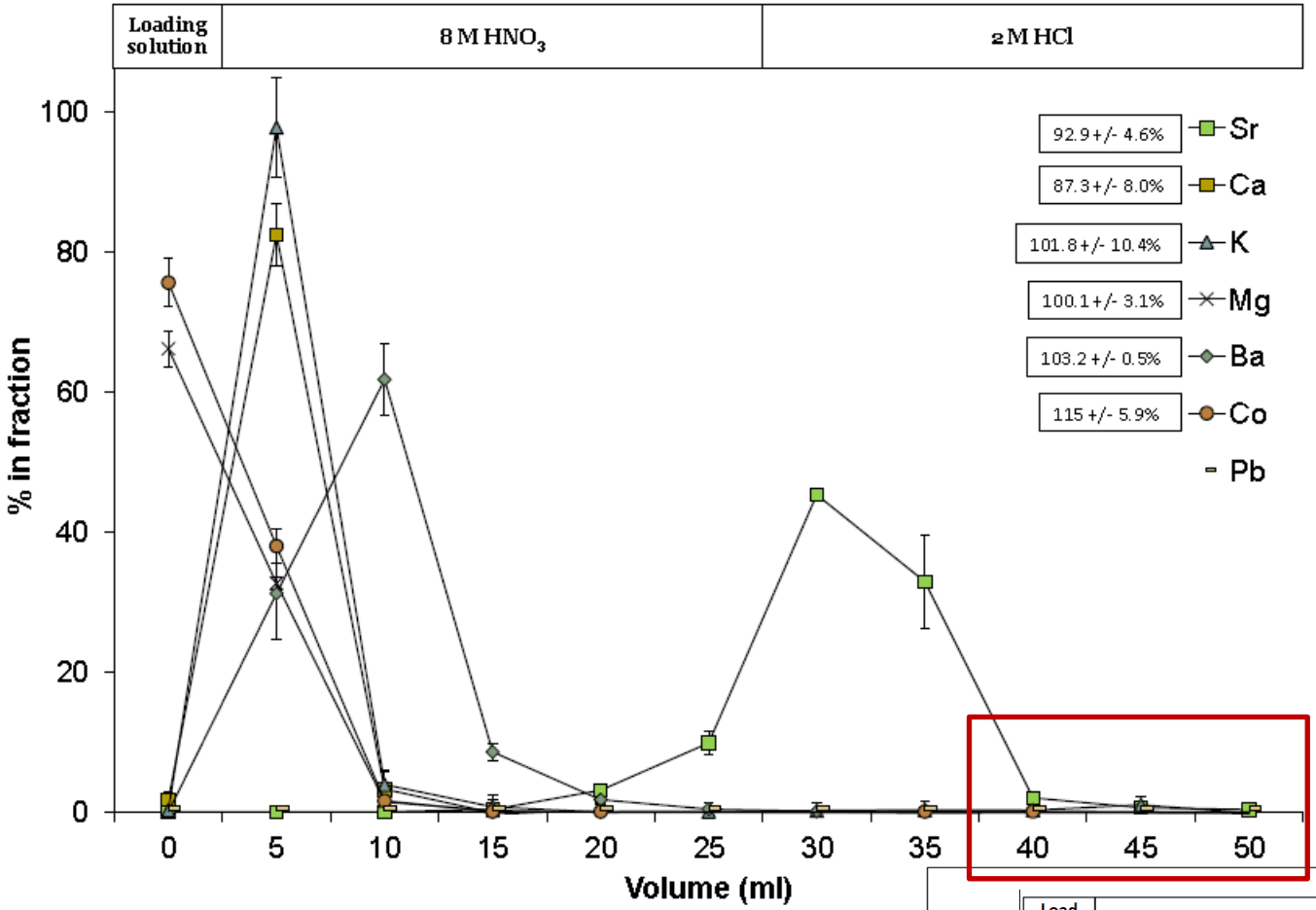
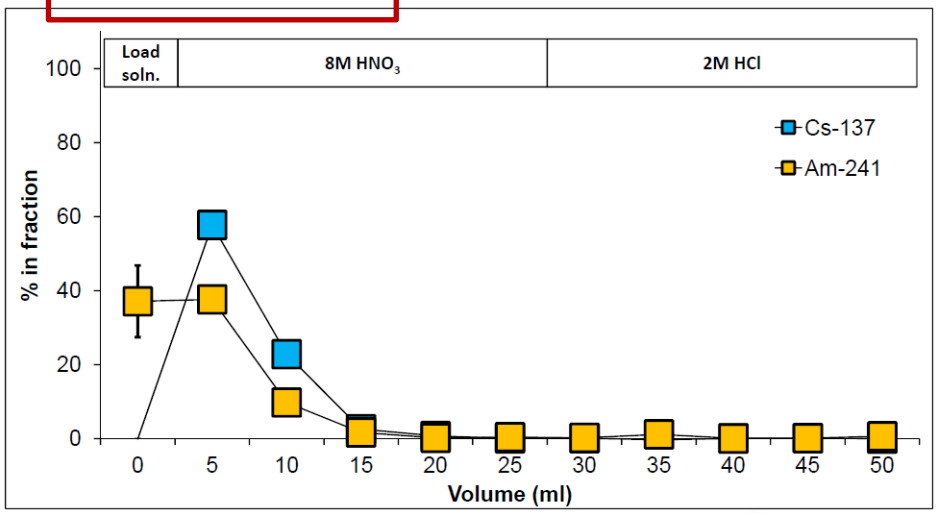


Pb remains retained



Batch experiment

- 0.5 g of resin added to 1 litre of DI water spiked with ^{90}Sr, shaken for **1** hour
- Supernatant and resin separated, resin loaded onto a column with a 0.4 g ‘guard layer’ of fresh resin to lower Sr breakthrough
- Column washed with 15 ml 8M HNO_3 and 20 ml 2M HCl
- Fractions collected and counted by LSC
- Sr yield ~73%

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Application tests

- Elution study 1L sample (column experiment)
  - pH7, 1 mg Sr, 100 mg Ca, 5 mg K, 0.1 mg Pb, Y, U per sample
  - 1L samples, 100 mL aliquots
  - 2 mL columns (650 mg resin)
  - Vacuum supported separation, 5 mL/min
  - Incl. Pb elution step (6M HCl)
  - ICP-MS measurement of effluents

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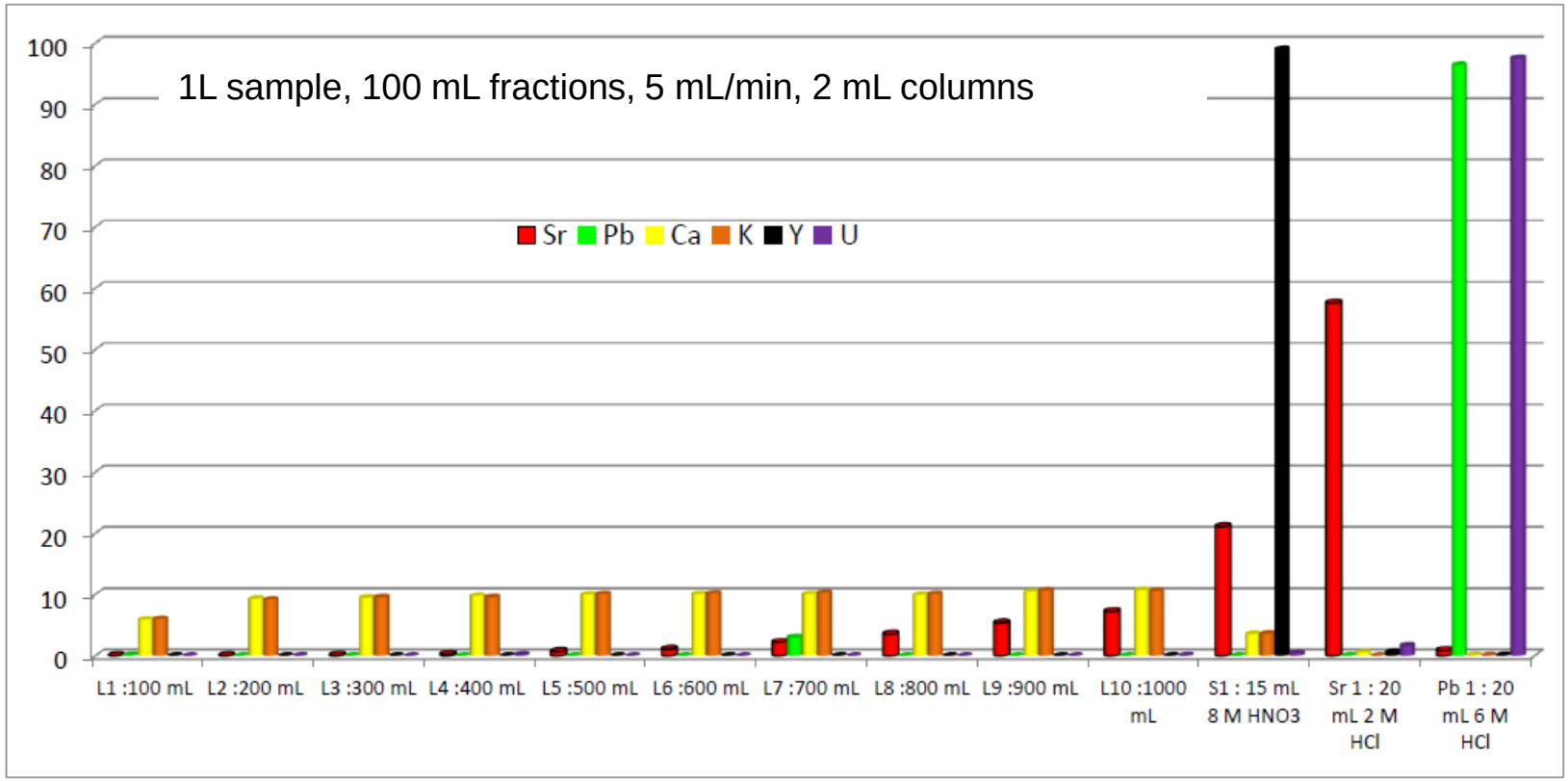
Column breakthrough study – direct load



- K and Ca not retained
- Sr breakthrough starts at 600 mL
- Pb fraction:
  - high Pb yield
  - also containing U

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Sr Elution study

- Elution studies
- 250 mL and 500 mL spiked tap water samples (pH 2, each N=3)
- Load at 5 – 10 mL/min
- Rinse:
  - 5 mL deion. water
  - 15 mL 8M HNO_3
- Elution with 20 mL 2M HCl
- 250 mL: 95,2 +/- 2,5
- 500 mL: 88,2 +/- 4,3
- Automatisation tests on-going (FZ Jülich)

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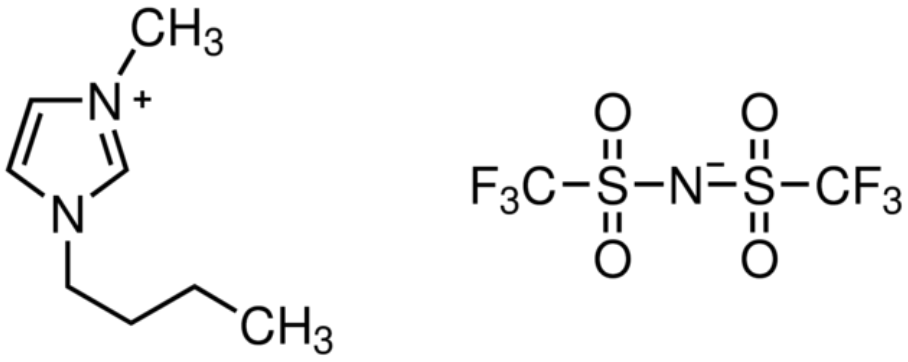
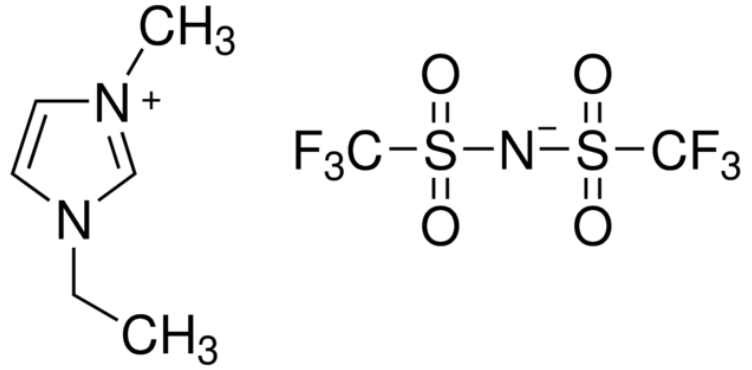
Improvement of selectivity

- Use of room temperature liquids (RTILs) instead of HDEHP



1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**BMIM**)



1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**EMIM**)

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Influence of Room Temperature Ionic Liquids (RTILs) on Sr extraction by crown-ethers

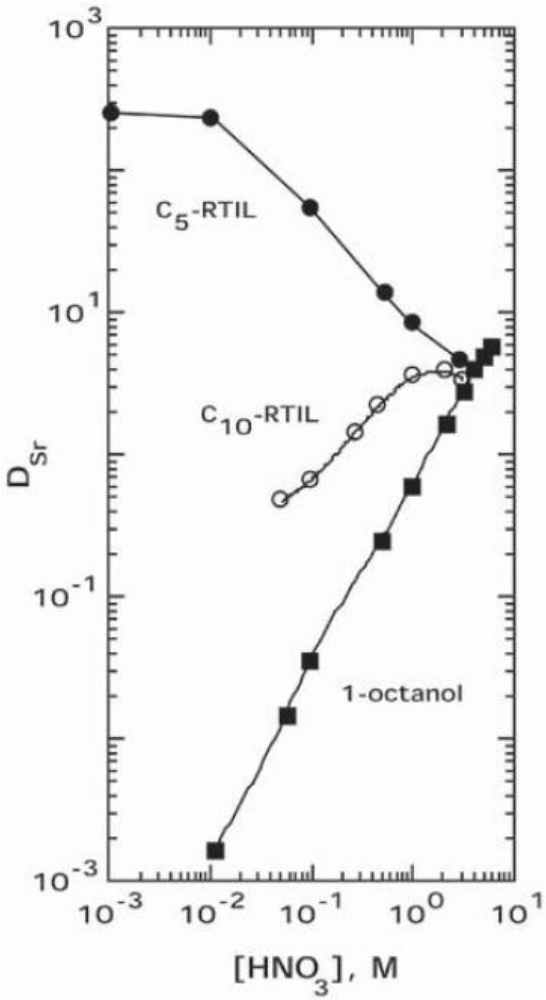

Fig. 1 Nitric acid dependency of D_{Sr} for DCH18C6 (0.10 M) in 1-octanol, $C_5mim^+Tf_2N^-$, and $C_{10}mim^+Tf_2N^-$. (T = 23 °C).

- Dietz et al. 2003:
- Short-chain RTIL:
  ion exchange mechanism
- Long-chain RTIL and octanol:
  extraction of neutral species

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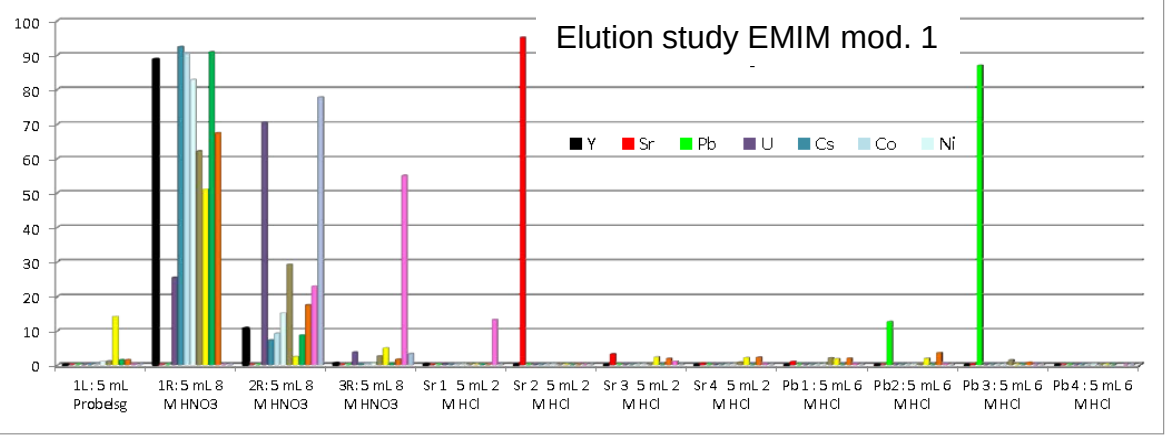

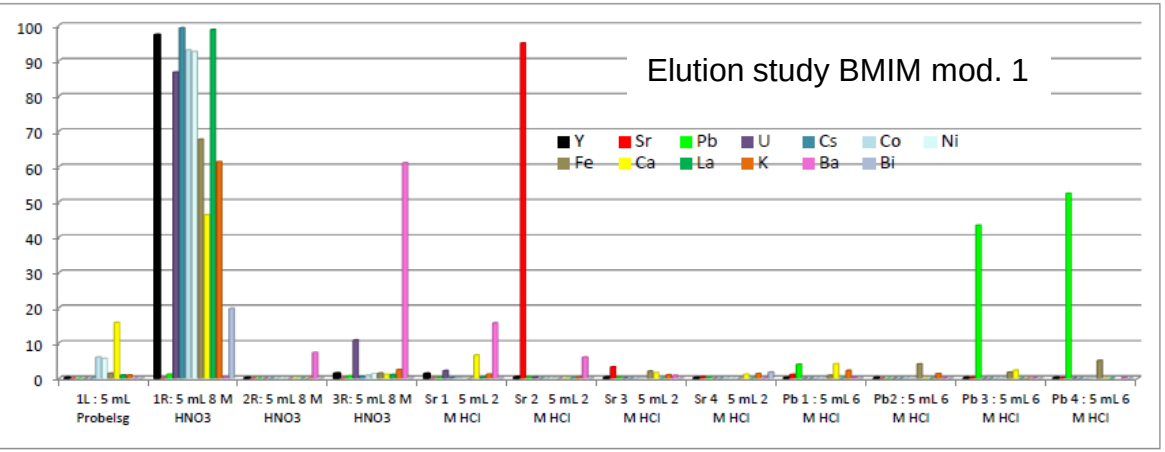

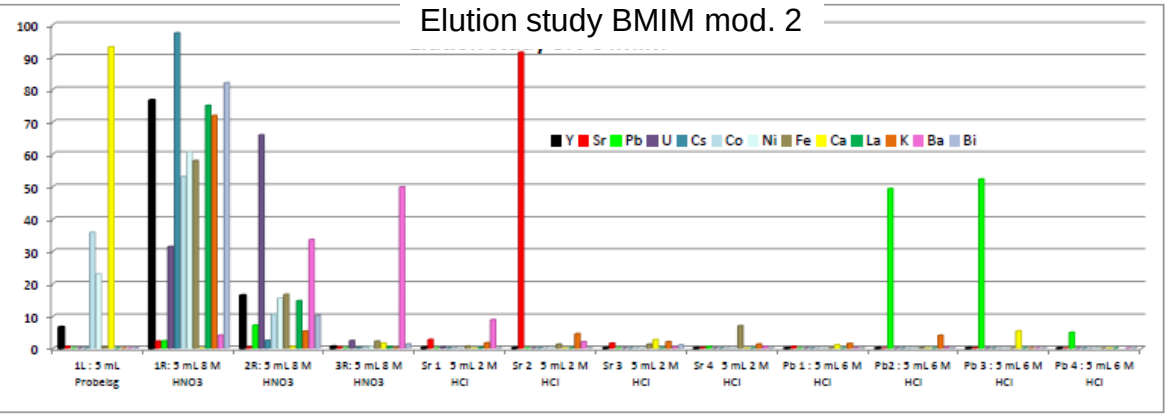

- Load: of multi-element solution at pH 7
- Rinse with 3x5 mL 8M HNO_3,
- Sr elution with 4x5 mL 2M HCl
- Pb elution with 4x5 mL 6M HCl

- Similar elution characteristics
- Improved purity of Pb fraction

- Breakthrough experiments on-going (larger volumes)

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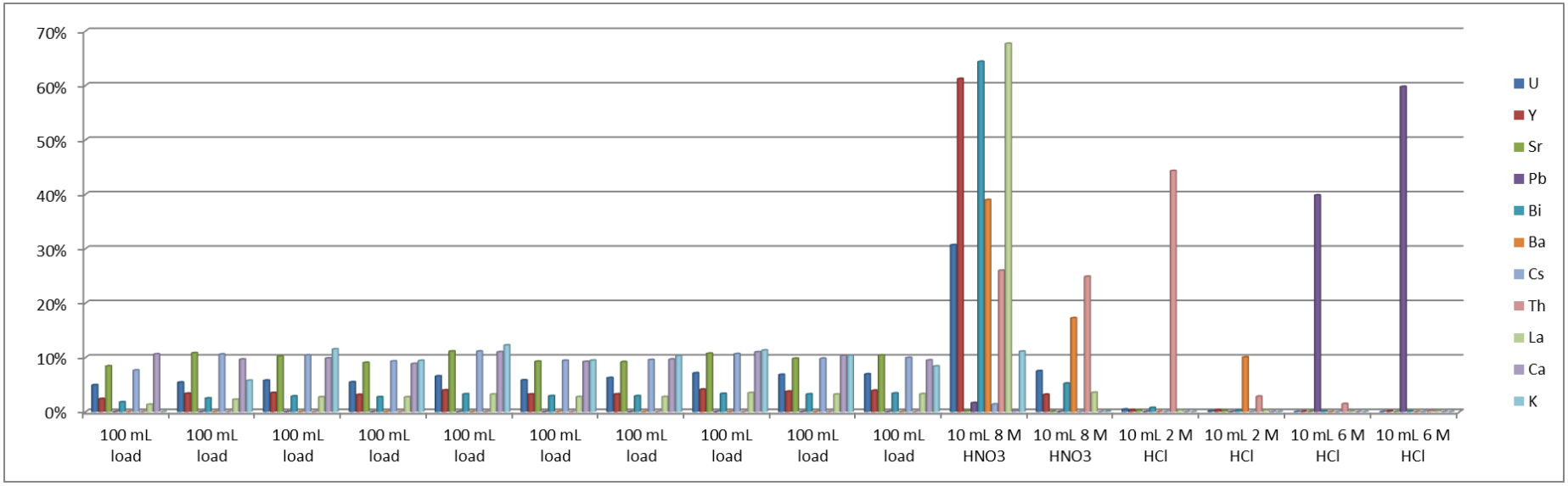
Elution study 1L sample

- 1L sample, pH 2, multi-element spike
- Load in 100 mL steps (all eluates collected and analysed), 5 – 10 mL/min
- Separation as decribed before



- No Pb breakthrough
- Most other elements not retained or removed with 8M HNO_3
- Th and trace Ba removed in 2M HCl
- Pb quantitatively eluted with 20 mL 6M HCl
- Automatization tests on-going (FZ Jülich)

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Extractive disc

- Aim: Direct LSC measurement of discs
  - Sample load and rinse (incl. additional rinse with water to remove trace acid)
  - Drying with vacuum
  - Transfer disc in LSC vial
  - Addition of 2 mL water and 16 mL LSC cocktail (ProSafe HC+)

➢ First tests on LSC counting

- Low increase in blank count rate
- Count rate is not depending on orientation of disc in vial:
  - 3 samples prepared (known Pb-210 activity on disc)
  - Each counted four times (90° turns after each measurement)
  - %RSD of count rate < 1% (N=12, k=1, at 100 Bq level)

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Conclusion

- On-going work
- Crown-ether based resins
  - Modification of Sr resin with HDEHP and RTILs results in extended uptake pH range (pH 8 to high nitric acid) for Sr and Pb
- High Pb uptake
- Pb separation possible
  - U/Pb separation to be addressed for HDEHP modified resin
  - Use of RTIL increases Pb selectivity
- Tests in column and disc form
- Automized separation currently being tested
- Discs for increased flow flow rates
  - Direct LSC count of discs: no dependence on disc orientation
  - Rinsing steps be optimized for discs
- DGT tests

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Thank you for your attention!

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