

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

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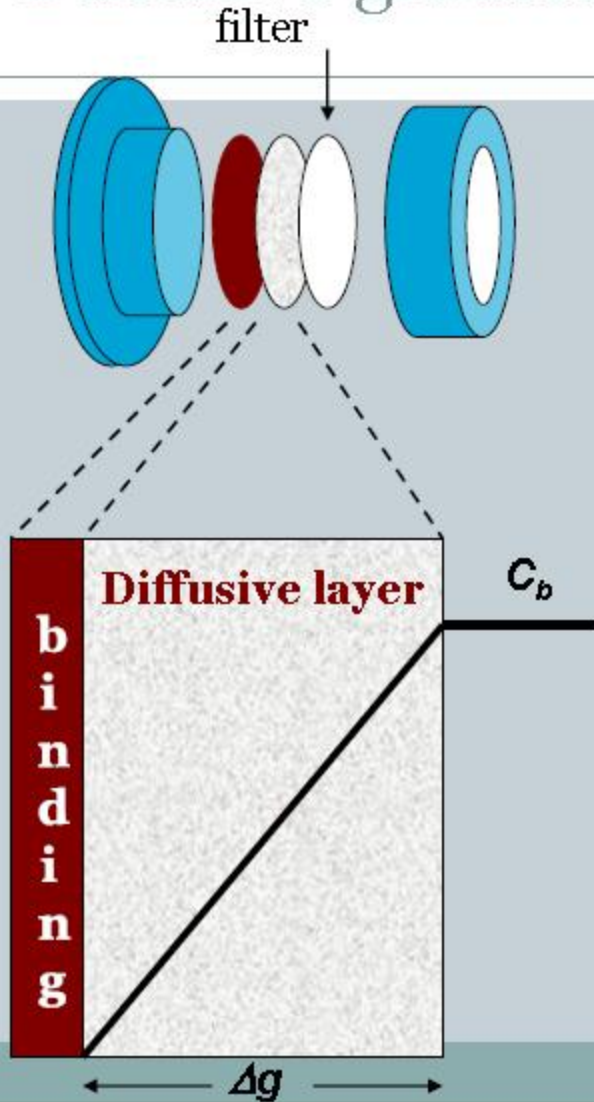
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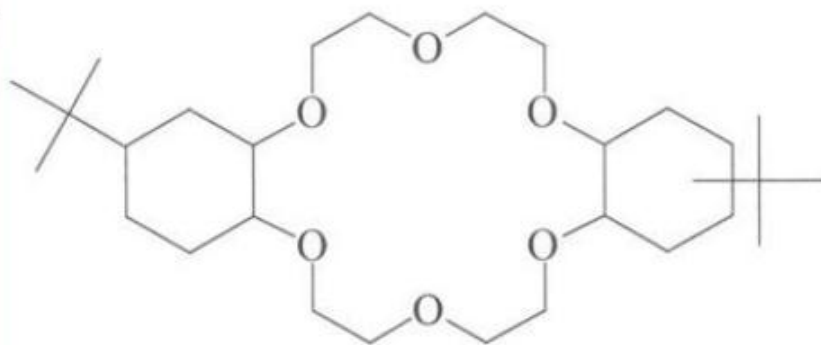
Context

- 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 MnO₂ (resin and Ra Nucfilm discs), U
- Rapid method
 - Concentration and separation on same resin/column
 - Load in batch, disc or column mode

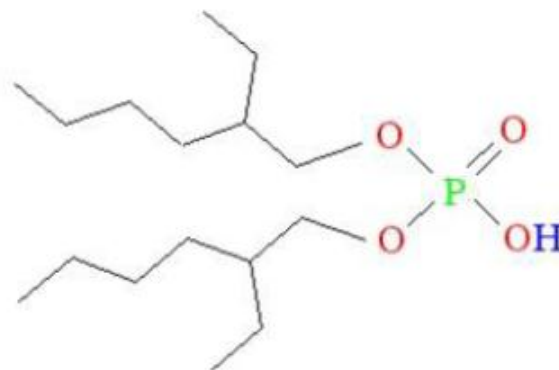
Diffusive gradients in thin-films (DGT)



TK100 Resin



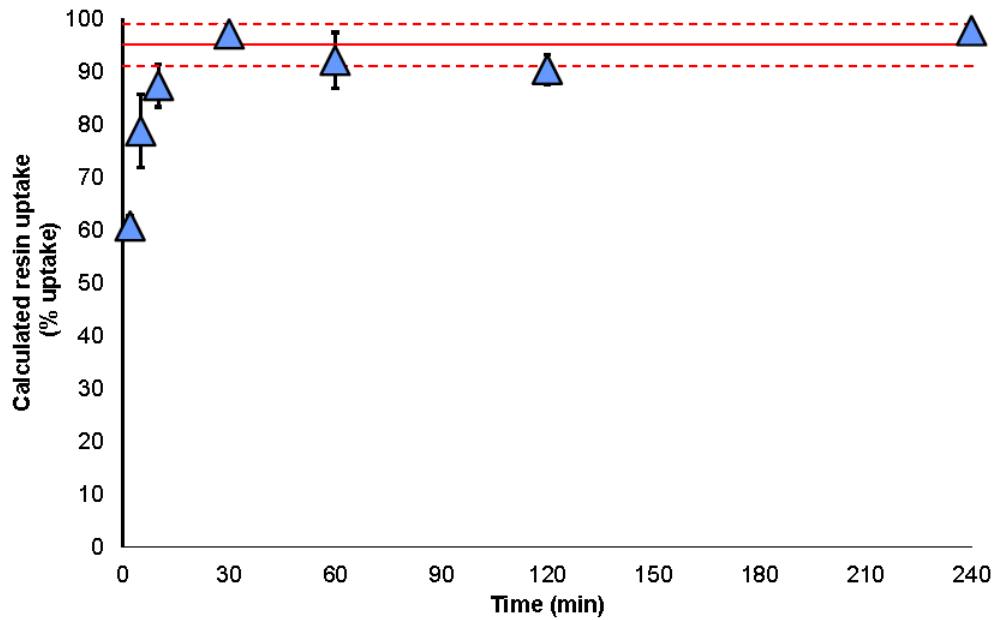
Di-t-butyl dicyclohexyl-18-crown-6



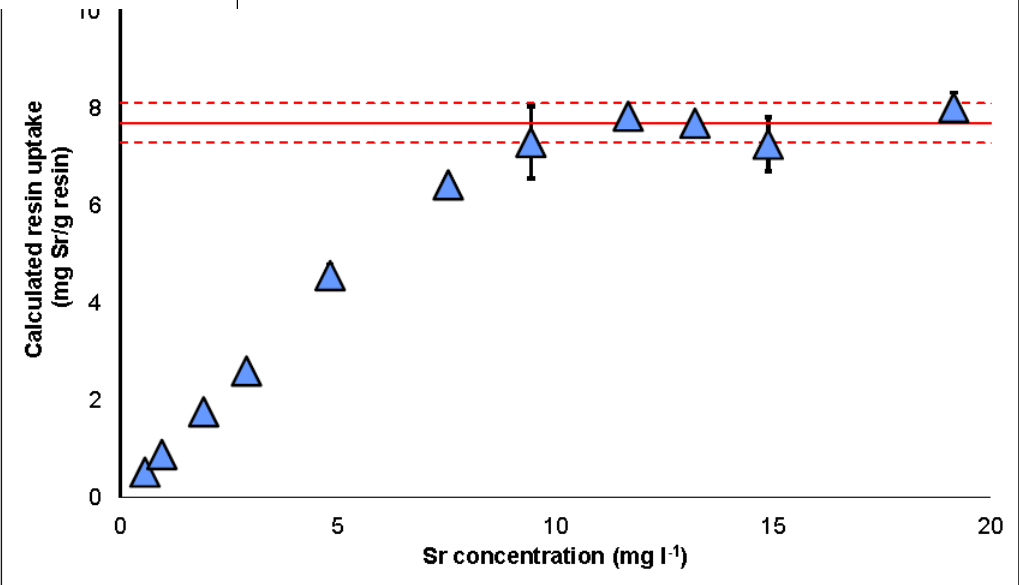
Di(2-ethyl-hexyl) phosphoric acid

- 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

Uptake kinetics

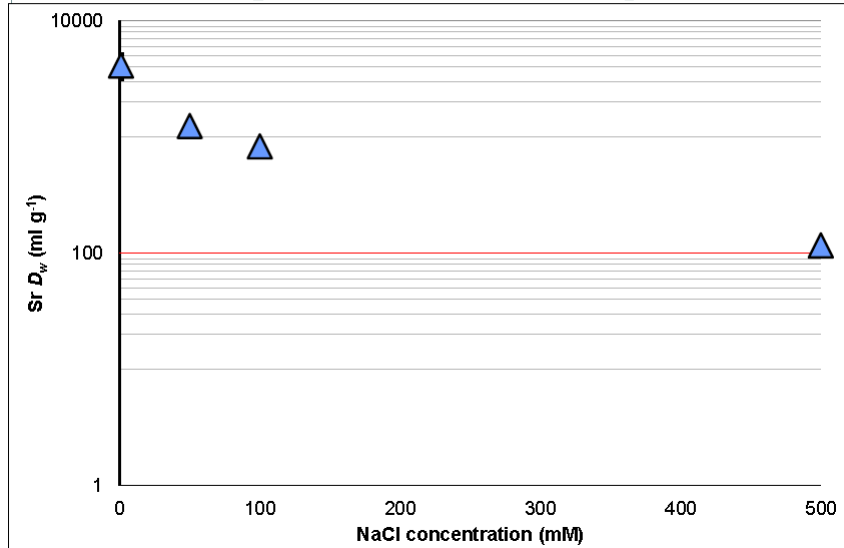


Capacity

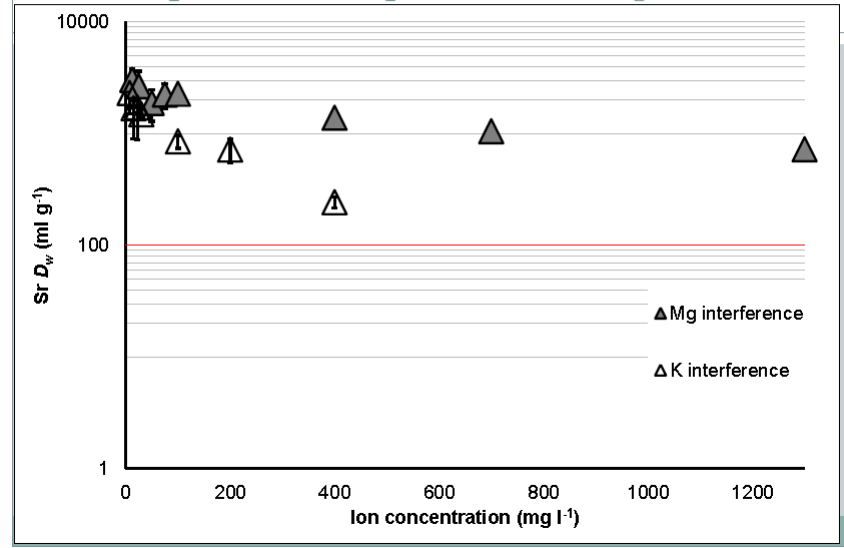


- pH 7
- Batch experiments

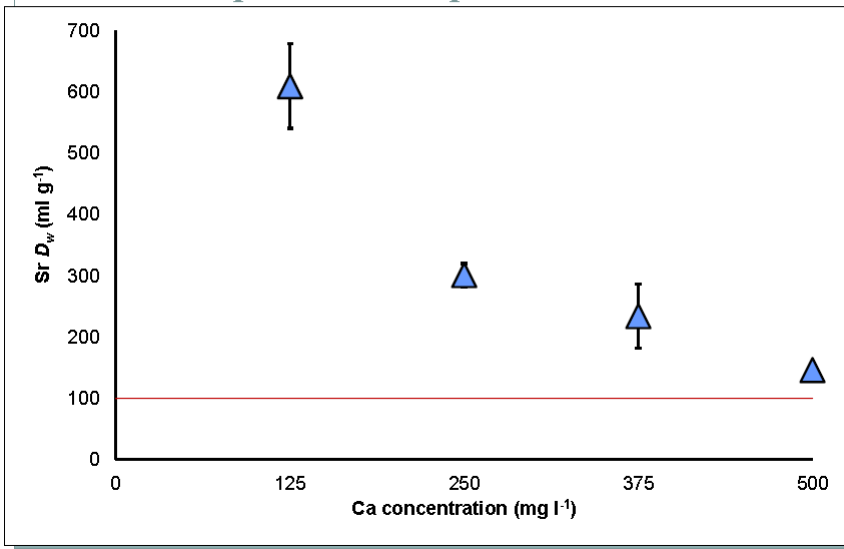
Sr uptake and ionic strength



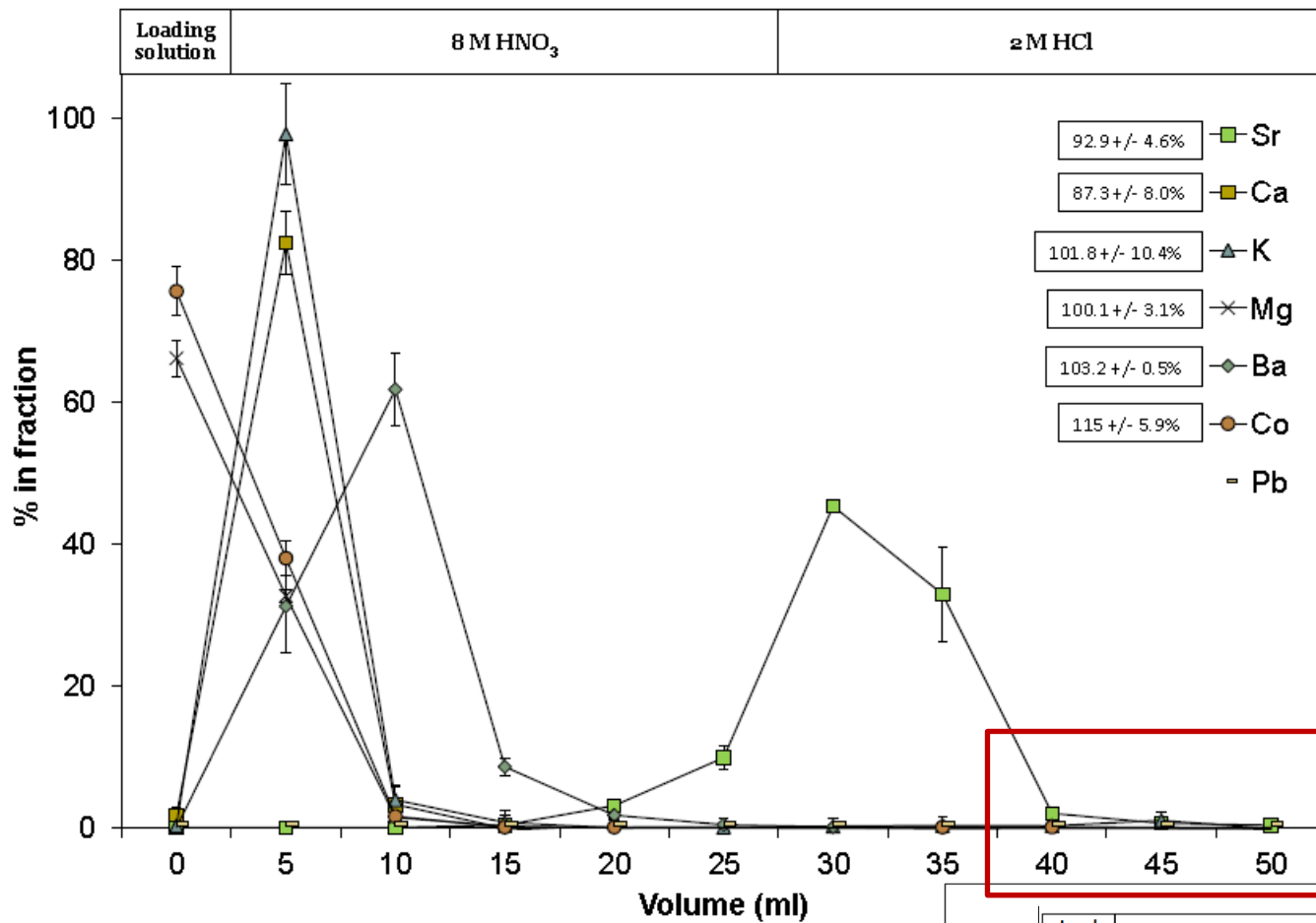
Sr uptake in the presence of Mg and K



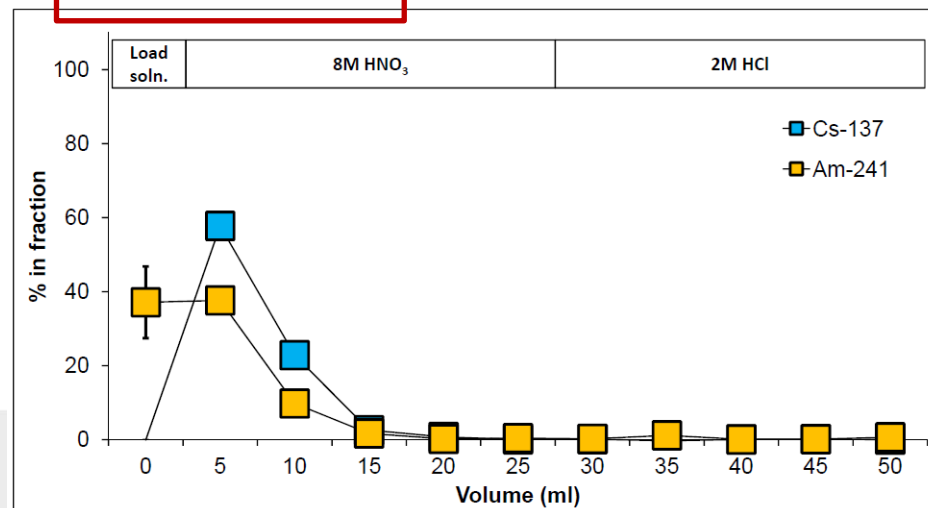
Sr uptake in the presence of Ca



- pH 7
- Batch experiments



Pb remains retained



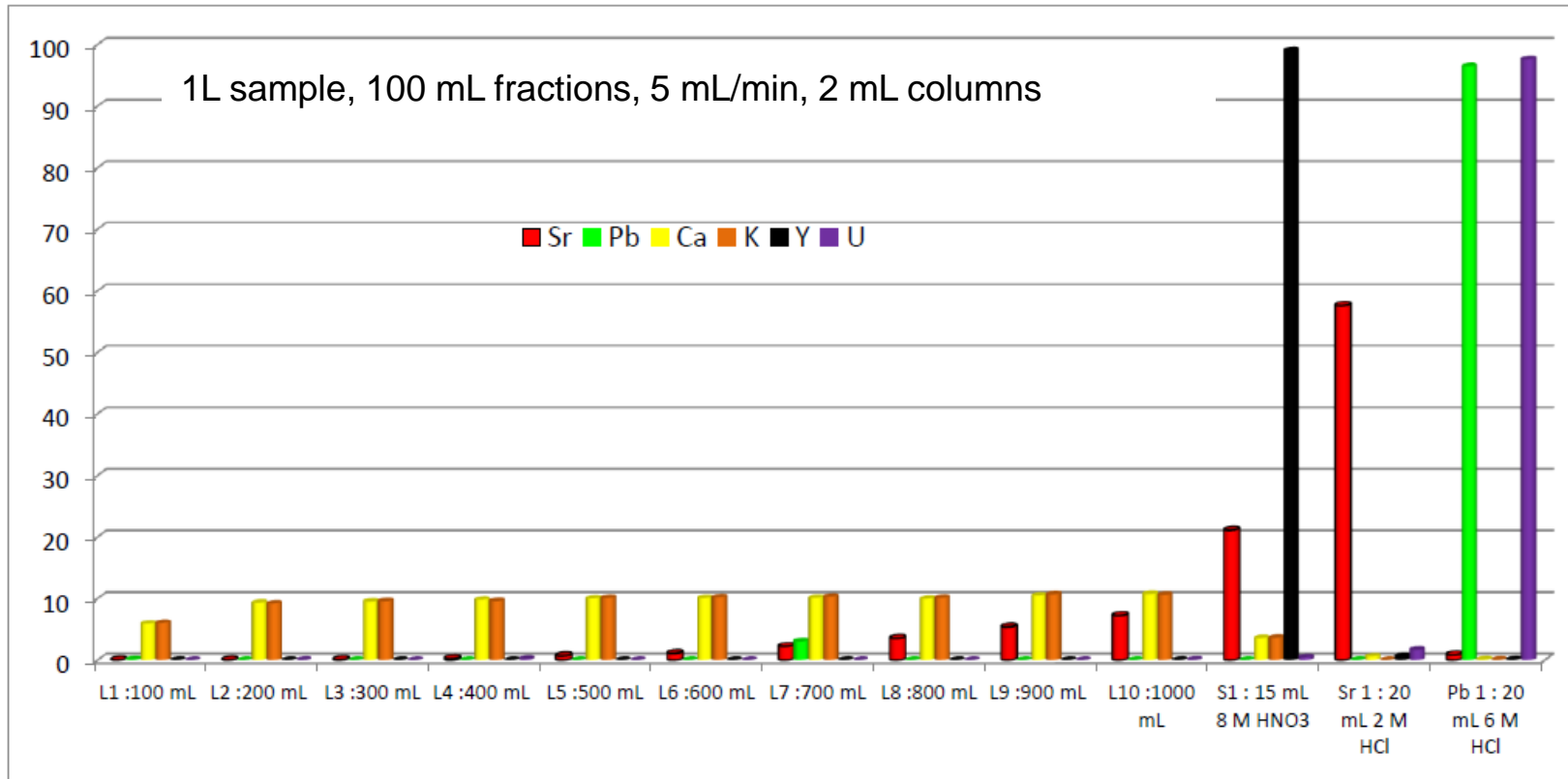
Batch experiment

- 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%

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

Column breakthrough study – direct load



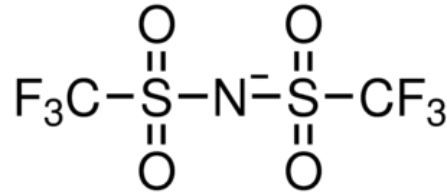
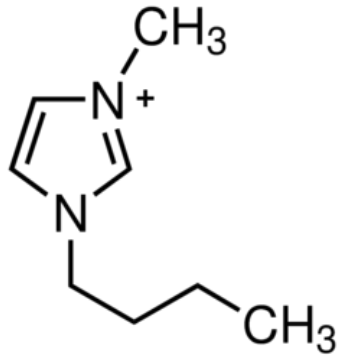
- K and Ca not retained
- Sr breakthrough starts at 600 mL
- Pb fraction:
 - high Pb yield
 - also containing U

Sr Elution study

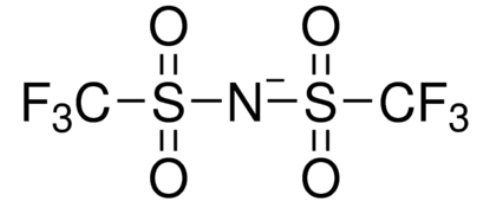
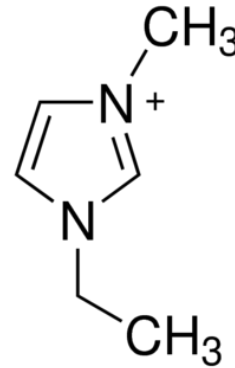
- Elution studies
- 250 mL and 500 mL Spiked tap water samples (pH 2, each N=3))
- Load at 5 – 10 mL/min
- Rinse:
 - 5 mL deion. water
 - 15 mL 8M HNO₃
- Elution with 20 mL 2M HCl
- 250 mL: 95,2 +/- 2,5
- 500 mL: 88,2 +/- 4,3
- Automatisations tests on-going (FZ Jülich)

Improvement of selectivity

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

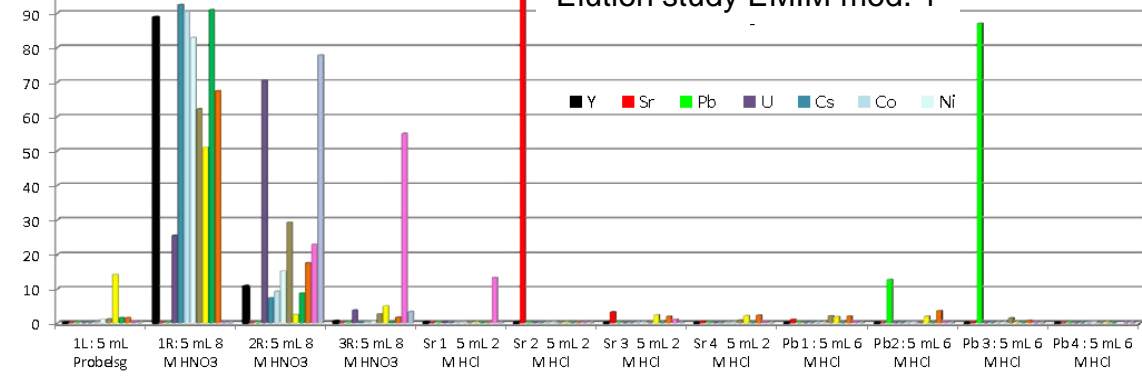


1-Butyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide (**BMIM**)



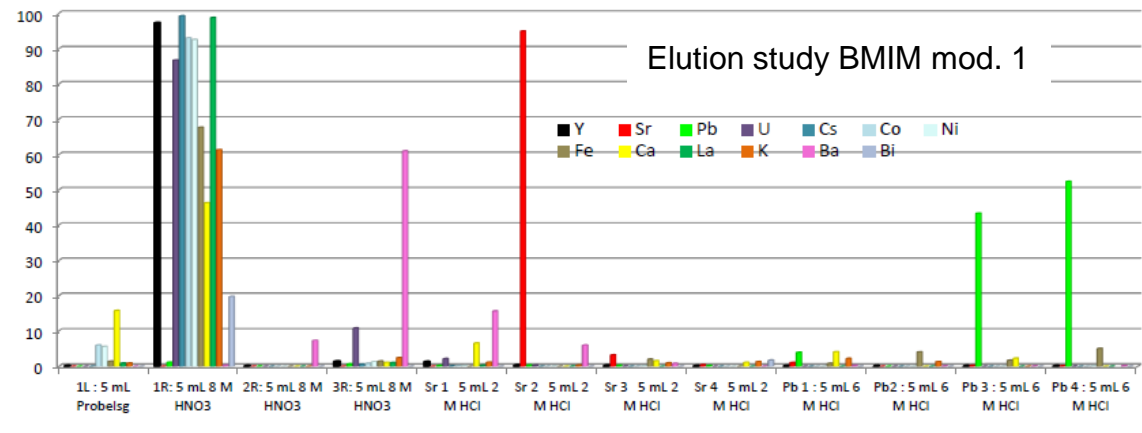
1-Ethyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide (**EMIM**)

Elution study EMIM mod. 1



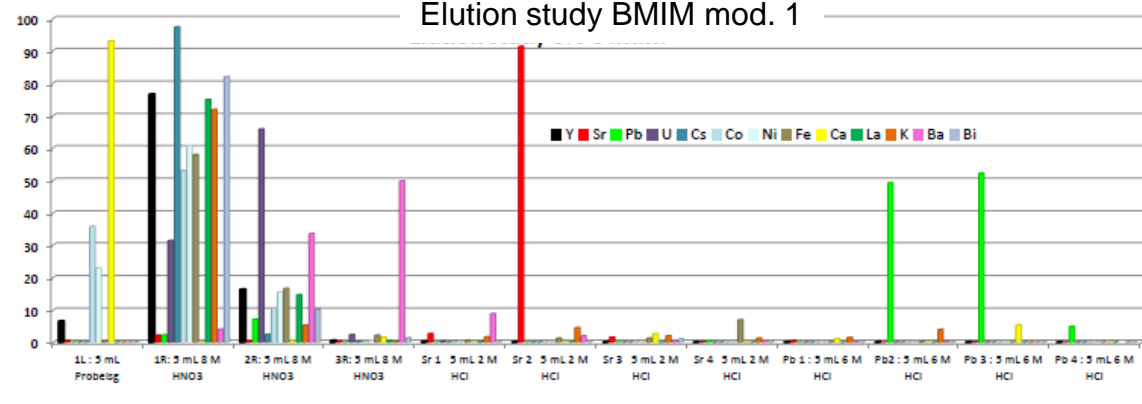
- Load: of multi-element solution at pH 7
- Rinse with 3x5 mL 8M HNO₃,
- Sr elution with 4x5 mL 2M HCl
- Pb elution with 4x5 mL 6M HCl

Elution study BMIM mod. 1



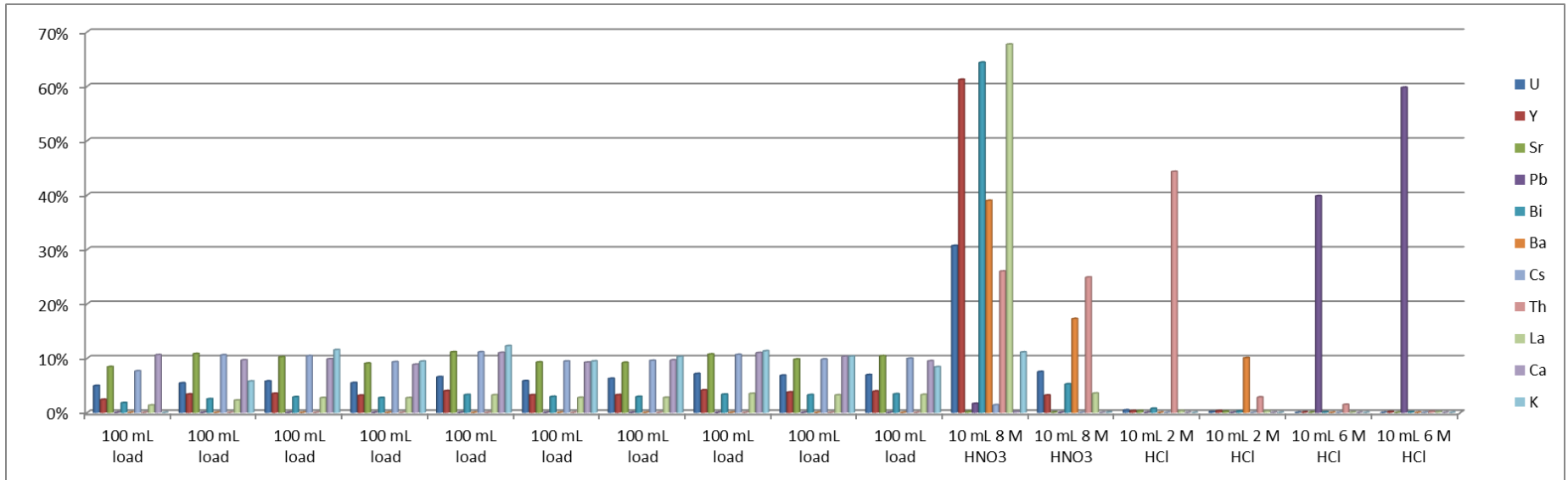
- Similar elution characteristics
- Improved purity of Pb fraction
- Breakthrough experiments on-going (larger volumes)

Elution study BMIM mod. 1



Elution study 1L sample

- 1L sample, pH 2, multi-element spike
- Load in 100 mL steps (all eluates collected and analysed)
- Separation as described before



- No Pb breakthrough
- Most other elements not retained or removed with 8M HNO₃
- Th and trace Ba removed in 2M HCl
- Pb quantitatively eluted with 20 mL 6M HCl
- Automatization tests on-going (FZ Jülich)

Direct LSC counting of 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)

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
- Automated 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

Thank you for your attention!



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