Pre-concentration and selective separation of Ra²⁺ from natural waters using a newly developed resin

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General context





Background: Ra separation techniques



- Fractional precipitation RaCl₂
- Ion exchange columns: ammonium citrate/EDTA
- Co-precipitation: BaSO₄/BaCO₃
- Synthetic clay: Na-4-mica (Na₄Al₄Si₄Mg₆O₂₀F₄•xH₂O)
- MnO₂ (resin, disks, fibers): Most common used procedure





Alternative approach

MRT: Molecular Recognition Technology

Non-ion exchange process, using specially designed organic chelating agents.



Our developed Ra resins



- Ra ion radius ≈ 1.7 Å: adapted cavity
- Chelating agent choice
 - Ra hard Lewis acid: Oxygen donor
 - Ra coordination sphere : 8-12 (solid phase)
 - → Chelating agent: Ether crown derivative



- Solid Support: SiO₂ 100 mesh.
- Spacer: short alkyl chain.



- Solid Support: aliphatic polymer (acrylic ester)
- Solvent: fluorinated alcohol

Resin applicability conditions: effective pH range





- No sorption was detected for $pH \leq 3$ (Grafted resin), $pH \leq 4$ (Impregnated resin),
- Maximum adsorption is reached over pH 5 (grafted resin) and over pH 6 (impregnated resin)
 - In acidic conditions the extractive molecule is protonated and no neutral complexes can be formed in the presence of Ra²⁺
 - With the organic solvent, the deprotonation is delayed.

Grafted Ra-Resin: kinetics behavior investigations



Ra uptake (pH=7)



 \rightarrow > 80% of ²²⁶Ra²⁺ adsorbed after 10 min of contact.: **Rapid kinetics**

Ra desorption (pH<0)



→ Rapid desorption and reversible process:

Starting material Regeneration

Application: results from French mineral waters





Ra uptake tests using different spiked chosen waters





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- For "classical" waters brands (i.e. Evian, Crystalline and Auvergne), the retention is good showing no competition effects with major cations,
- ✤For Hépar, a strong decrease is noticed which can be well reproduced by the modelling → high sulfate content
- As the Rozana water is the only carbonated water among those tested, the carbonate content of the water and the value of the constant between Ra and HCO³⁻ in PHREEQC are two possible explanations to investigate
- Sea water → high concentration of Na (Fengqi XU theses)





Sorption of Ra on grafted resin in salty waters. (A) Effect of the type of salt and its concentration; $pH=7.0\pm01$; m/V of 1g.L⁻¹. (B) Effect of the pH; m/V of 1g.L⁻¹.

Conclusion



- A new grafting resin specific for Ra is presented. It is very effective in the field of classical pH natural waters (~6-8),
- On the other hand, its application is limited to waters with a low salt content.
- The impregnated resin has a clear advantage: the synthesis method is very fast, the quantity of ligand introduced is greater
- The impregnated resin is still under process improvement in order to enlarge its pH field

To be continued...





Thank you for your attention