

# Potential of ion-imprinted polymers for studying migration of radioactive contaminants ( $^{226}\text{Ra}$ , $^{137}\text{Cs}$ ) in environment

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# Context

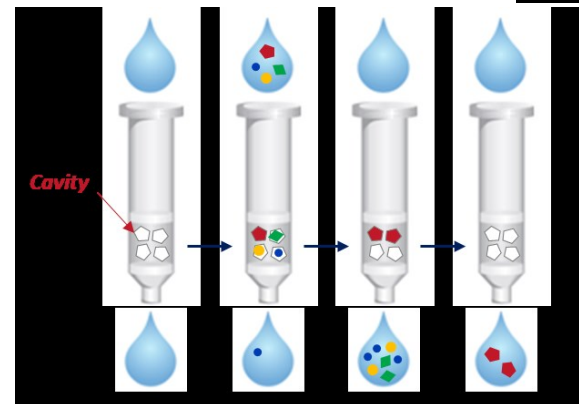


- ❌ Transport mechanisms misunderstood
- ❌ Quantification in transport areas is challenging



Need to predict migration behaviour

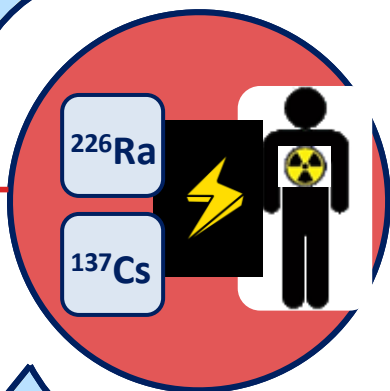
Purification step required before analysis



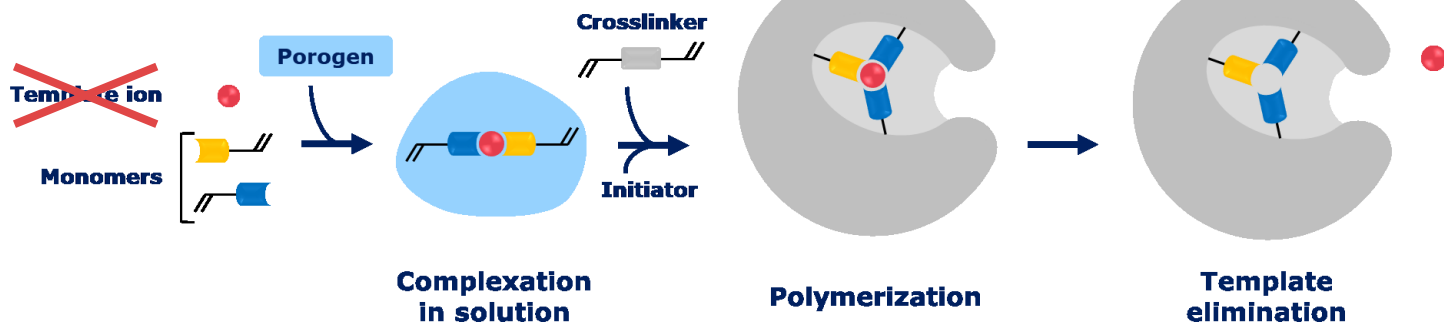
Solid phase extraction (SPE)

- ❌ Lack of specificity of commercial resins
- ❌ Co-extraction of interferents

Two of the most radiotoxic radionuclides



Ion imprinted polymers as specific sorbents

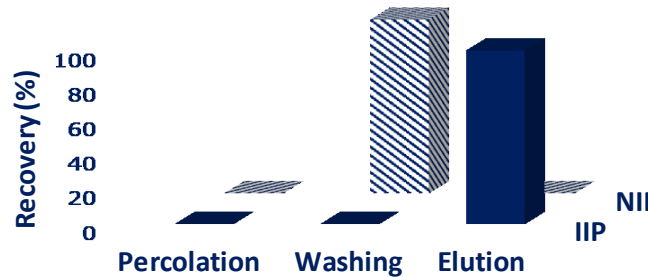


- ✅ Specific recognition sites
- ✅ Non imprinted polymer (NIP) as control polymer

# Methodology employed

Ideal SPE profile  
obtained by analyzing fractions in ICP-MS

→ Washing step optimization



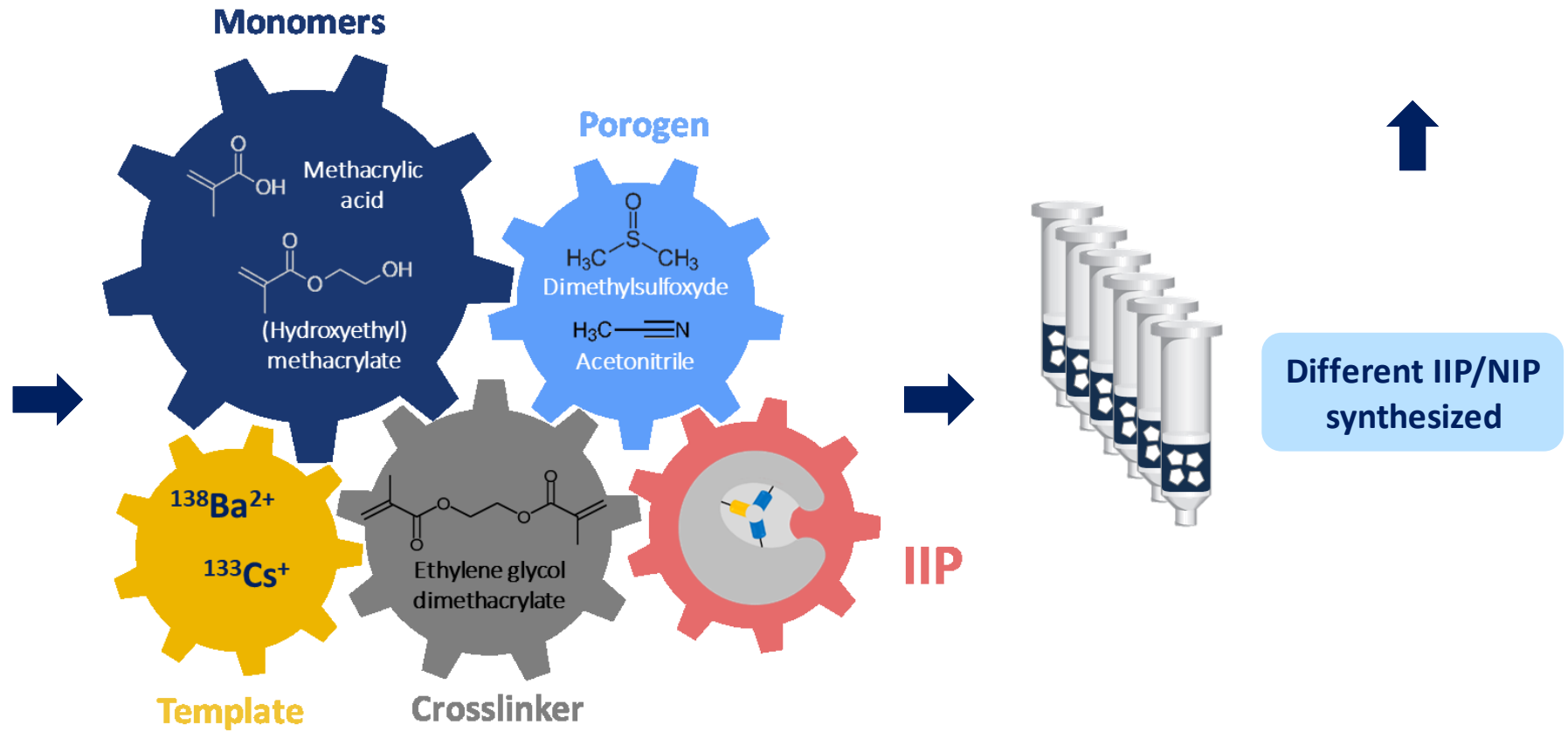
Evaluate parameters influence on :

- Retention
- Selectivity IIP/NIP
- Specificity towards interfering ions

Target radionuclides

$^{226}\text{Ra}$

$^{137}\text{Cs}$



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Abstract  
N° 244

SPE procedure under development  
BUT first results encouraging...

First ion imprinted polymers for  $^{226}\text{Ra}$  and  $^{137}\text{Cs}$  !

...let see the next step...



Thank you for your attention !

### Introduction

Radium-226 and Cesium-137 belong to the most radiotoxic radionuclides. Due to chemical properties respectively similar to those of calcium and potassium, they can replace them in biological processes, thus contributing to increase the internal dose. In order to assess the risk of chronic exposure, it is essential to perform environmental radiological monitoring and to have a deeper understanding of processes leading to radionuclides migration in the environment. However, their quantification in environmental samples (e.g., pore waters, plant root) presents many challenges: low sample volumes available (<10 mL), complex matrices and concentrations below instrumental detection limits. Regardless of the analytical technique used (radiometry or mass spectrometry), conventional sample treatment methods are often multi-staged, time-consuming, not suitable for small sample volumes and they lack of selectivity. The objective of this work is therefore to develop new sorbents showing high selectivity for these two radionuclides, in order to allow their analysis by inductively coupled plasma mass spectrometry (ICP-MS), in small volumes of complex samples. To this end, synthesis of ion-imprinted polymers (IIPs) has for the first time been proposed in extraction and preconcentration processes of Ra and Cs.

### 1. Development of ion imprinted polymers (IIPs)

#### 1. Principle of IIP synthesis

- Bulk polymerization and monomers incorporation by chemical immobilization approach
- Specific recognition sites -> complementarity in size, shape and complexing groups
- Non imprinted polymer (NIP) synthesized in parallel but without template ions

#### 2. Screening of synthesis conditions

- Evaluation of the influence of monomer(s) and porogen's nature on selectivity
- Stable isotopes of cesium and barium (radium chemical analogue) used as template ions

IIP/NIP model	IIP Cu-MHEAD	IIP Cu-MHEAD	IIP Cu-MHEAD	IIP Cu-MHEAD	IIP Cu-MHEAD	IIP Cu-MHEAD	IIP Cu-MHEAD	IIP Cu-MHEAD	IIP Cu-MHEAD
Template (T)	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl
Monomers (M)	MMA	MMA	MMA/HEMA	MMA	MMA	MMA/HEMA	MMA/HEMA	MMA/HEMA	MMA/HEMA
Crosslinker (CL)	EDMA	EDMA	EDMA/HEMA	EDMA	EDMA	EDMA/HEMA	EDMA/HEMA	EDMA/HEMA	EDMA/HEMA
Porogen (P)	DMSO	DMSO	DMSO/THF	DMSO	DMSO	DMSO/THF	DMSO/THF	DMSO/THF	DMSO/THF
Complexation time	2h	2h	2h	2h	2h	2h	2h	2h	2h

Temperature and time of polymerization: 24 h, 60°C / Initiator: azobisisobutyronitrile (AIBN)

#### 4. Characterization by solid phase extraction (SPE)

Expected SPE profile

### 2. SPE profiles in spiked pure aqueous solutions

#### 1. Study of the retention of template ion

##### Percolation in Bis-Tris buffer

##### Recovery of Cs-133 on Cs<sup>+</sup> based IIPs

- No retention for Cs-133 -> Cationic buffer Bis-Tris may form complexes with Cs such as with Hg and Cu<sup>2+</sup> and thus be responsible for losses during percolation and washing steps [1] Fernex et al., RSC Adv., 2015, 5, 20898

##### Percolation at basic pH

##### Recovery of Cs-133 on Cs<sup>+</sup> based IIPs

- Cs-133 strongly retained and totally eluted from their respective polymers
- R=100% : no leakage of template ions

##### Effect of pH on selectivity

##### Recovery of Cs-133 on Cs<sup>+</sup> based IIPs

- Better recoveries for Cs-133 on NIPs MHEAD and HEAD compared to their respective IIP
- No selectivity visible for Cs-133 on IIPs MHEAD and HEAD in these conditions

Other washing conditions to try :

- By using pH between 3 and 2
- By using a complexing agent (e.g. EDTA)
- By playing on ionic strength
- By using DMSO for percolation or washing steps

##### Recovery of Ba-138 on Ba<sup>2+</sup> based IIPs

- Ba-138 strongly retained
- R=100% : no leakage of template ions -> High efficiency of the template ion removal step

##### Recovery of Ba-138 on Ba<sup>2+</sup> based IIPs

- Ba-138 still strongly retained in these percolation conditions
- Optimize the washing step to get selectivity

### Conclusion

Characterizations by SPE showed retention potential for template ions at basic pH for all IIPs synthesized. At the moment, washing conditions experimented using acidic solutions did not reveal a difference in selectivity in favour of IIPs. However, before to conclude too quickly on selectivity properties, other washing conditions have to be investigated: e.g. by adjusting the pH more precisely, playing on ionic strength or else by using a complexing agent or DMSO. In parallel, new syntheses will be carried out by changing either monomers, crosslinker or their ratios. If finally one IIP outperforms the other, it will be then necessary to evaluate its performances in presence of target ions (Ra-226, Cs-137) in pure and real media and to determine its capacity and breakthrough volume. The final objective being to miniaturize IIP showing the best results to make possible small samples handling and study migration processes.

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