ExTech 2021: XXIII International Symposium on Advances in Extraction Technologies

Assessment of ion imprinted polymers technology for the design of a new radium specific solid phase extraction support

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Context

Radiotoxic radionuclide

Ion imprinted polymers (IIP) as specific SPE support

Purification step mandatory before analysis

Quantification in transport areas → analytical challenge

Commercial supports not specific except AnaLig (10 g = 1940 € excl. taxes → SPE with 50 mg ~ 10 €)

Complex protocols, unsuitable for $V_{\text{sample}} < \text{mL}$

$^{226}\text{Ra}$

Specific cavities

Non Imprinted Polymer (NIP) = control polymer

SPE support

Pore water

Solid Phase Extraction (SPE)

Ion imprinted polymers (IIP)

Template elimination

Complexation in solution

Initiator

Crosslinker

Porogen

Monomers

Terpolymers

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Methodology

Evaluate parameters influence on:
- Retention
- Selectivity IIP/NIP
- Specificity towards interfering ions
- …

Ideal SPE profile
→ SPE protocol optimization (washing)

IIP/NIP synthesized

Target ion
$\text{Ra}^{2+}$

Monomers
Porogen
Template
Crosslinker

Recovery yield (%)
Retention
Selectivity
Specificity towards interfering ions

Ideal SPE profile

IIP
NIP

SPE protocol optimization (washing)

Percolation
Washing
Elution
Screening strategy for synthesis conditions

Key parameters selection

- Monomer(s) with binding properties
- Crosslinker
- Template
- Porogen

- Complexation study by mass spectrometry
  - Ligand(s) nature
  - Metal/ligand(s) ratio
  - Incubation time

- Solubility tests of polymerization mixtures
  - Minimum volume
  - Less dissociating and polar porogen

- Inert toward template ion
  - Excellent pH stability

- Kinetics study by conductimetry in ACN/DMSO 1/1, v/v (Pt electrode with glass rod (In Lab® 720, 0.1-500 µS/cm)

- Analogue ion
  - 2 salts evaluated: Ba(NO₃)₂, BaCl₂

- Orbotrap Q Exactive Plus with HESI source (Thermo Fisher)
  - Infusion in MeOH/water 1/1, v/v

- Ratio Template/DVB/Sty = 1/20/20
Screening strategy for synthesis conditions

- **Monomer(s) with binding properties**
- **Crosslinker**
- **Porogen**

**5 Ba(II)-IIP synthesized**

- **Complexation study by mass spectrometry**
  - Ligand(s) nature
  - Metal/ligand(s) ratio
  - Incubation time

- **Key parameters selection**
  - Ligand(s) nature
    - Infusion in MeOH/water 1/1, v/v
  - Metal/ligand(s) ratio
  - Incubation time

- **Solubility tests of polymerization mixtures**
  - Minimum volume
  - Less dissociating and polar porogen

- **Kinetics study by conductimetry**
  - in ACN/DMSO 1/1, v/v (Pt electrode with glass rod (In Lab® 720, 0.1-500 µS/cm)
  - 24 h

- **Inert toward template ion**
- **Excellent pH stability**

- **Analogue ion**
  - 2 salts evaluated: Ba(NO$_3$)$_2$, BaCl$_2$

- **Orbitrap Q Exactive Plus with HESI source (Thermo Fisher)**
  - Infusion in MeOH/water 1/1, v/v

- **DVB**
  - Styrene
  - Ratio Template/DVB/Sty = 1/20/20

- **2 salts evaluated:**
  - Ba(NO$_3$)$_2$, BaCl$_2$

- **No complexation**

- **Inert toward template ion**

- **Excellent pH stability**
Illustration of the behavior of synthesized Ba(II)-IIP/NIP

**Selected conditions after SPE procedure optimization**

- **Percolation conditions:**
  - Bis-tris buffer, 25 mM pH 7
  - MOPS buffer, 10 mM pH 7

- **Washing conditions:**
  - Decreasing pH

**C** 3 mL NH₃ pH 10
**P** 25 ng Ba²⁺ + 25 ng Cs⁺ in 1 mL NH₃ pH 10
**W1** 0.5 mL water
**W2** 0.5 mL HNO₃ pH 4
**W3** 0.5 mL HNO₃ pH 3
**W4** 0.5 mL HNO₃ pH 2
**E** 3 x 1 mL HNO₃ 0.5 M

**Retention**

**Selectivity (IIP versus NIP)**

**Intrinsic specificity**

**BET analyses intended**
Specificity of IIP Ba(II)-VSDAD in presence of $^{226}$Ra

→ Summary of elements behavior

<table>
<thead>
<tr>
<th></th>
<th>Retained</th>
<th></th>
<th></th>
<th>Not retained</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IIP</td>
<td>NIP</td>
<td>IIP</td>
<td>NIP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkali metals</td>
<td>/</td>
<td></td>
<td>Li,Rb,Cs</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkaline earth metals</td>
<td>Sr, Ba, Ra</td>
<td>/</td>
<td>/</td>
<td>Sr, Ba, Ra</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lanthanides</td>
<td>/</td>
<td></td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transition metals</td>
<td>Co, Ag, Nb</td>
<td>Nb</td>
<td>V, Mo, W</td>
<td>V, Co, Mo, Ag, W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poor metals</td>
<td>Ti, Pb, Bi</td>
<td>Pb, Bi</td>
<td>/</td>
<td>Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metalloids</td>
<td>/</td>
<td></td>
<td>As, Sb</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actinides</td>
<td>Th, U</td>
<td></td>
<td>/</td>
<td>/</td>
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</tr>
</tbody>
</table>

X : element partially eliminated (60 % or more)

Polyatomic interferences at m/z 226 in ICP-MS

<table>
<thead>
<tr>
<th>Radionuclide (atomic mass u)</th>
<th>Interference</th>
<th>Atomic mass u</th>
<th>Required resolution (m/Δm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{226}$Ra (226.25403)</td>
<td>$^{88}$Sr$^{138}$Ba$^+$</td>
<td>225.810855</td>
<td>1,100</td>
</tr>
<tr>
<td>$^{87}$Sr$^{139}$La$^+$</td>
<td>225.815227</td>
<td>1,100</td>
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<tr>
<td>$^{88}$Sr$^{138}$La$^+$</td>
<td>225.812721</td>
<td>1,100</td>
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<tr>
<td>$^{186}$W$^{40}$Ar$^+$</td>
<td>225.916747</td>
<td>2,100</td>
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<tr>
<td>$^{208}$Pb$^{18}$O$^+$</td>
<td>225.975796</td>
<td>4,600</td>
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</tr>
<tr>
<td>$^{209}$Bi$^{16}$O$^+$</td>
<td>225.983123</td>
<td>5,400</td>
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</tr>
<tr>
<td>$^{208}$Pb$^{16}$O$_2$$^+$</td>
<td>225.987201</td>
<td>6,000</td>
<td></td>
</tr>
</tbody>
</table>

...
Influence of the metal/ligands ratio on specificity

1/4

1st synthesis

IIIP
M/L ratio = 1/6

1/8

(8 = Ba and Ra coordination number)

Less retention

Ti, Pb and La separated

Co-extraction

Pb and La separated

Recovery yield (%)

P + W1 + W2
W3
W4
E

P + W1 + W2
W3
W4
E

P + W1 + W2
W3
W4
E

Elements in 1 mL
0.5 mL water + 0.5 mL HNO₃ pH 4
0.5 mL HNO₃ pH 3 + 0.5 mL HNO₃ pH 2
1.5 mL HNO₃ 0.5 M
Influence of the M/L ratio on capacity and breakthrough volume

<table>
<thead>
<tr>
<th>M/L ratio</th>
<th>Capacity</th>
<th>Breakthrough Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 3 mL MOPS 1 mM pH 7</td>
<td>IIP 1/8 B (60 mg)</td>
<td>~ 50 µg/g</td>
</tr>
<tr>
<td>P X µg Ba²⁺ in 1 mL MOPS 1 mM pH 7</td>
<td>IIP 1/6 A (30 mg)</td>
<td>~ 400 µg/g</td>
</tr>
<tr>
<td>W1 0.5 mL water</td>
<td>NIP 1/6 A (30 mg)</td>
<td>~ 400 µg/g</td>
</tr>
<tr>
<td>W2 0.5 mL HNO₃ pH 4</td>
<td>IIP 1/4 (60 mg)</td>
<td>~ 400 µg/g</td>
</tr>
<tr>
<td>E 3 x 1 mL HNO₃ 0.5 M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Applications on mineral waters in progress

Sorption isotherms modeling in progress
Conclusion...

Ion imprinted polymers: a promising technology for specific Ra trapping?

- First Ra(II)-IIPs synthesized using an analogue ion (template = Ba^{2+}) combined to screening strategy (MS, conductimetry, solubility tests)
- Promising IIP synthesized with phosphonate ligand: simple and low-cost synthesis (purchasable reagents), partial specificity, moderate capacity, and high breakthrough volume in pure solution

...and perspectives

- Evaluation of IIP robustness: extraction in different matrices spiked with ^{226}\text{Ra} → quantification by isotopic dilution (^{228}\text{Ra} tracer)
- Comparison with commercial resins
- Miniaturization and on-line coupling to ICP-MS

Thank you for your attention