Imprinted Nanoporous Organosilicas for Selective Adsorption of Nitroenergetic Targets

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Synthesis of Organosilicas

- Surfactant-directed
- Acid-catalyzed condensation
- Tunable characteristics
  - Selection of surfactant
  - Selection of precursors
  - Incorporation of imprint template
Precursors

Bridging

- \((\text{H}_3\text{CO})_3\text{Si}\)
- \((\text{H}_3\text{CO})_3\text{Si}\)
- \((\text{H}_3\text{CO})_3\text{Si}\)
- \((\text{H}_3\text{CH}_2\text{CO})_3\text{Si}\)

Terminal

- \((\text{H}_3\text{CO})_3\text{Si}\)
- \((\text{H}_3\text{CO})_3\text{Si}\)
- \((\text{H}_3\text{CO})_3\text{Si}\)
- \((\text{H}_3\text{CO})_3\text{Si}\)

- Selected to provide structural and binding characteristics
- Combining multiple structures often offers the best compromise
- May also be used to provide sites for post synthesis modifications
Increasing DEB concentration provides enhanced TNT binding capacity.
Trade off is in loss of material surface area and organization.
Also observed is a loss in selectivity upon increase in DEB.
Design of material requires compromise between total capacity, selectivity, and structural characteristics.

**Surfactant**

**Brij 76; Pores ~30 Å**

**Pluronic P123; Pores ~75 Å**

- The surface is structure directing
- Variations provide control of pore size and organizational character
  - Brij®76 - Polyoxyethylene (10) stearyl ether
  - Pluronic P123 - Poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) triblock copolymer
- May be combined with a swelling agent
  - Mesitylene
Imprinting

Surfactant Analog

- Similar to molecular imprinting of polymers
- Template is incorporated into surfactant micelles
- Upon surfactant extraction, provides sites on pore wall that are more favorable to target interactions

Imprinting

Comparison of target binding from single and multi-component solutions

- TNT binding is reduced in mixture for non-imprinted material
- TNT binding is not reduced in imprinted material

Reducing Back Pressure

- Use of Pluronic P123 with swelling agent to produce macropores
  - Mesoporous – pores of 2 to 50 nm
  - Macroporous – pores of greater than 50 nm
- Results in reduced surface area
- Provides the necessary reduction in back pressure to allow application in column formats

TNT/DNT Material

50:50 DEB:BTE imprinted using 12.6% modified Pluronic P123
Hierarchical structure

35 Å mesopores
366 m²/g
0.261 cm³/g

RDX Material

40:50:10 DEB:BTE:PTS
Hierarchical structure

43 Å mesopores
278 m²/g
0.226 cm³/g

Nitrogen Sorption

Pore Size Distribution

Target Binding – Batch Experiments

Imprinted 50:50 DEB:BTE

- Saturation capacity = 50 mg/m²
- Association constant = 2.44e-3 μg⁻¹

40:50:10 DEB:BTE:PTS

- Saturation capacity = 11 mg/m²
- Association constant = 7.69e-3 μg⁻¹


- Equilibrium batch experiments
- Parameters determined based on Langmiur-Freundlich model of a general binding isotherm for identical binding sites
Columns

- Column format using 200 mg of materials
- 4 mL/min flow rates with 3 mL additions of 10 μM target solution

*Johnson et al. In preparation (2008)*
Soil Extraction

- Samples obtained from USAERDC hot and cold grids
- Column format using 25 mg of material
- Gravity driven flow
- Extraction into deionized water
- Elution using methanol

Concentrations Enhanced:
- RDX – 6.25x
- 1,3,5-trinitrobenzene – 1.93x
- 2,4,6-trinitrotoluene – 30.6x

Targets enhanced from non-detectable:
- tetryl
- 2-amino-4,6-dinitrotoluene
- 4-amino-2,6-dinitrotoluene
- 2,4- &/or 2,6-dinitrotoluene
- 2-nitrotoluene


- As extracted and concentrated samples analyzed by HPLC using EPA Method 8330
- Concentration accomplished using Imprinted 50:50 DEB:BTE material
- Data presented here are for sample HO-001; soil taken from an old 2,000 lb bomb crater
Presence of a symbol on the grid indicates detection by the indicated analysis.

*Johnson et al. In preparation (2008)*
# Soil Sample Key

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Description</th>
<th>Grid</th>
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<tr>
<td>HO-001</td>
<td>Old 2,000-lb crater</td>
<td></td>
</tr>
<tr>
<td>HO-004</td>
<td>Old 2,000-lb crater</td>
<td></td>
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<td>HO-006</td>
<td>Old 500-lb crater</td>
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<tr>
<td>HO-018</td>
<td>Low order bomb crater</td>
<td>Hot Grid</td>
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<td>No visible low-order debris</td>
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<td>HO-027</td>
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<td>Cold Grid</td>
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</table>

*Johnson et al. In preparation (2008)*
Current Ongoing Effort

• Incorporate materials inline with electrochemical detection methods

• Extract trace level targets from ground water samples obtained from New Mexico Environment Department, Department of Energy Oversight Bureau

• Compare materials developed for this effort to commercially available materials for nitroenergetic concentration
Acknowledgements

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