COMPARISON OF TWO POLARITY MEASUREMENTS OF HYDROPHOBIC ORGANIC MATTER FOR THE EVALUATION OF WATER TREATMENT PROCESSES: XAD RESIN AND PRAM

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Three common DOM models

(A mixture of <1k to 10k -15k Daltons molecules)

3-D polymer

Micelle

Supramolecular Assemblage

(Sutton and Sposito, 2005)
Figure 2.3 – Two examples of proposed humic structures (Stevenson, 1994 [68]).
Objectives

• Comparison of PRAM and XAD resin methods for characterization of hydrophobic NOM fraction
  – Correlation between C18 cartridge and XAD-8 at low and ambient pH

• Investigate possibility of more refined characterization of hydrophobic fraction:
  – Use of methods in series:
    UF --> PRAM --> Fluorescence
PRAM Setup

RC (Retention Coefficient) = Percent of UV absorbing material adsorbed by SPE material

RC = 1 - A/A₀
PRAM sorbents

C18

Sorbent

Diol

OH

Sorbent

NH2

Sorbent
XAD resin adsorption

Resin Set-up (Singer et al. 2007)

Water Sample (1L) → pH 2 → Acidification → XAD8 → Acrylic ester → Hydrophobic NOM (Humic Substances) → XAD4 → Transphilic NOM → Hydrophilic NOM
# Polarity Measurements

<table>
<thead>
<tr>
<th>Solid Phase</th>
<th>UV-Criteria (Absorbance)</th>
<th>DOC Criteria (mgC/L)</th>
<th>Clean Time</th>
<th>Sample Run time#</th>
<th>Total Run Time (one run)</th>
<th>Scheme (sample volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XAD Resin</td>
<td>To be determined</td>
<td>&lt;10% bulk</td>
<td>2-4 days</td>
<td>8-12 hours</td>
<td>5-7 days</td>
<td>Series (1 Liter)</td>
</tr>
<tr>
<td>Polarity Rapid Assessment Method (PRAM)</td>
<td>0.0025</td>
<td>&lt;10% bulk</td>
<td>1h-2h</td>
<td>10 min</td>
<td>4-5 hours (Each SPE is run in triplicate)</td>
<td>Parallel (90 ml) (Can be run in series)</td>
</tr>
</tbody>
</table>

# one sample run through XAD-8 and XAD-4, one sample run through six PRAM cartridges
# Structures of Sorbents and XAD Resin

<table>
<thead>
<tr>
<th>Resin</th>
<th>Composition</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>XAD-4</td>
<td>Styrene divinylbenzene</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>XAD-8</td>
<td>Acrylic ester</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>C18</td>
<td>Octadecylsilyl</td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>Diol</td>
<td>Glyceroxypropylsilyl</td>
<td><img src="image4.png" alt="Structure" /></td>
</tr>
</tbody>
</table>
## Column Properties @ pH <2 & fraction of NOM collected

<table>
<thead>
<tr>
<th>Column</th>
<th>pH</th>
<th>Sorbent Structure</th>
<th>m²/g</th>
<th>DOM fraction sorbed</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>XAD-8 (aliphatic, cation exchange capacity &gt;hydrophilic)</td>
<td>&lt;3</td>
<td>Acrylic ester, k’&lt;sub&gt;cutoff&lt;/sub&gt; = 50</td>
<td>140&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Hydrophobic acid fraction (primarily fulvic acids)&lt;sup&gt;c&lt;/sup&gt;, weak hydrophobic acids, hydrophilic bases and hydrophobic neutrals</td>
<td>Aiken et al. (1992) Singer et al. (2007)</td>
</tr>
<tr>
<td>C18</td>
<td>&lt;3</td>
<td>Octadecyl-silyl</td>
<td>527&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Hydrophobic part of DOM molecule, some protonated hydrophilic acids</td>
<td>Rosario-Ortiz et al. (2007)</td>
</tr>
<tr>
<td>C18</td>
<td>7-8</td>
<td>Octadecyl-silyl</td>
<td>527&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Hydrophobic part of DOM molecule</td>
<td>Rosario-Ortiz et al. (2007)</td>
</tr>
</tbody>
</table>
Characterization of hydrophobic DOM fraction

• Follow-up of a previous study
  – (Water Science & Technology: Water Supply, 8(6) 725–733)

• Study had evaluated samples for the comparisons of:
  – XAD-8 and C18
  – XAD-4 and Diol

• Study concluded a potential positive correlation of XAD-8 and C18 but not XAD-4 and Diol
<table>
<thead>
<tr>
<th></th>
<th>Rutin</th>
<th>Suwannee (4.9 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydrophobic</td>
<td>Slightly hydrophobic</td>
</tr>
<tr>
<td>R</td>
<td>92</td>
<td>76</td>
</tr>
<tr>
<td>UV</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>P</td>
<td>92</td>
<td>81</td>
</tr>
<tr>
<td>UV</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>R</td>
<td>60</td>
<td>39</td>
</tr>
<tr>
<td>DOC</td>
<td>19</td>
<td>50</td>
</tr>
<tr>
<td>P</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>DOC</td>
<td>14</td>
<td>50</td>
</tr>
</tbody>
</table>

- The C18 and XAD-8 Resins show similar results
- C18 adsorbs less than XAD-8
- The Diol and XAD-4 do not show similar results
- The Diol and Effluent do not show similar results
- Rutin is hydrophobic
Three PRAM analyses at different pH

Comparison PRAM pH <3 and 7 (UV)

- Both cartridges absorb more at the low pH
- Shows the amount of protonated material
Comparison of methods 1/2

\[ y = -0.1768x + 23.882 \]
\[ R^2 = 0.0566 \]

- No correlations between the two methods under respective operational conditions
Comparison of methods 2/2

\[ y = 0.1467x + 32.938 \]
\[ R^2 = 0.0054 \]

correlation C18 (pH 2) and XAD-8 (pH 2) for UV

- No correlations between the two methods at similar low pH
Evaluation of the methods’ differences

• The differences in “hydrophobic” fractions measured by both methods were studied:
  – Use of fluorescence to characterize the effluent from both methods
  – XAD and PRAM at low pH, Raw water at low and ambient pH, PRAM at ambient pH
  – Analysis of two different samples: influent of a treatment facility and a river
• I: Aromatic Proteins
  - Tyrosine-like material

• II: Aromatic Proteins
  - Tyrosine, $\text{BOD}_5$

• III: Fulvic acid-like
  - Humic substances
    soluble at pH <1

• IV: Microbial byproducts
  - Tyrosine, tryptophan &
    protein-like material

• V: Humic acid-like
  - Humic substances
    precipitate at pH <1

All regions are characterized by % Fluorescence Distribution
Differences in fluorescence character of the effluent of both methods

- Differences can be observed in the fluorescent character of the effluent from XAD-8 and C18
- C18 allows region I through (aromatic proteins)
- XAD-8 region IV (microbial by-products)
- No trends in other regions
Study of PRAM hydrophobic fraction

• Following these results it was decided to study a more an in-depth characterization of the hydrophobic fraction as measured by PRAM:
  – Use of PRAM following size distribution analysis by UF membranes
  – Use of three methods in series:
    • UF/PRAM/fluorescence
• The use of PRAM following a size distribution yields more information on DOM functionalities
• Characterization of the size fractions
Use of UF/PRAM/fluorescence in series

- C18 does not collect region I as previously shown. Decreases the relative importance of the other regions
- Size fractions have similar fluorescence character before PRAM but quite different afterwards
- The hydrophobic material from 1K fraction is predominantly in the fulvic and humic regions
Conclusions

• XAD resin adsorption and PRAM are not directly comparable even at pH 2

• The two methods retain different fractions of the DOM
  – C18 cartridge does not collect aromatic type proteins (region I)
  – the XAD does not collect microbial by-product type material (region IV)

• The use of several characterization methods in series (UF for size, PRAM for polarity and Fl for type compound) can help improve understanding of the Hydrophobic fraction of NOM