Comparison of Automated and Manual Methods for Solid Phase Extraction of Endocrine Disrupting Chemicals

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Water Resources Research Conference April 7, 2009
Presentation Outline

- Endocrine Disrupting Compounds
- Solid Phase Extraction Methods
- Instrumentation
- Method Comparison
- Cost Comparison
- Preliminary Results
Endocrine Disrupting Compounds

- Emerging group of contaminants
- Natural and synthetic hormones
- Variety of reproductive abnormalities and physical deformities
Estrogens

Diethylstilbestrol  
MW 268 g/mol

Estriol  
MW 288 g/mol

Estradiol  
MW 272 g/mol

17β-Ethinylestradiol  
MW 296 g/mol

Estrone  
MW 270 g/mol
Solid Phase Extraction

- Extraction of EDCs from environmental matrixes

- Method comparison
  - Manual versus automated
  - EPA 1694 Method: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment and Biosolids by HPLC/MS/MS (2007)
SPE Method Comparison

- HLB Oasis cartridges
  - On-line
  - Single use
- C-8 analytical column (X-Bridge)
- LC/MS/MS (ESI-)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Parent/Daughter (m/z)</th>
<th>Cone/Collision (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estrone (E1)</td>
<td>269.3 / 145.3</td>
<td>50 / 30</td>
</tr>
<tr>
<td>Estriol (E3)</td>
<td>287.1 / 171.0</td>
<td>55 / 35</td>
</tr>
<tr>
<td>Estradiol (E2)</td>
<td>271.3 / 145.3</td>
<td>50 / 35</td>
</tr>
<tr>
<td>17B-Ethinylestradiol (EE2)</td>
<td>295.2 / 145.2</td>
<td>50 / 40</td>
</tr>
<tr>
<td>Diethylstilbestrol (DES)</td>
<td>267.1 / 251.2</td>
<td>40 / 25</td>
</tr>
</tbody>
</table>
Manual SPE Method

- 500 mL to 1000 mL sample size concentrated to 1 mL
- One-time use HLB extraction cartridges
- 8 hour extraction method time
- 16 min instrument run time
- HPLC-MS/MS
# Manual SPE Method

## Approximate Minimum Detection Limits (MDLs)

<table>
<thead>
<tr>
<th>Compound</th>
<th>MDL (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estrone (E1)</td>
<td>5</td>
</tr>
<tr>
<td>Estriol (E3)</td>
<td>5</td>
</tr>
<tr>
<td>Estradiol (E2)</td>
<td>15</td>
</tr>
<tr>
<td>17B-Ethinylestradiol (EE2)</td>
<td>15</td>
</tr>
<tr>
<td>Diethylstilbestrol (DES)</td>
<td>5</td>
</tr>
</tbody>
</table>

![Graph showing intensity over time for various compounds](image)

- **Y-axis:** Intensity
- **X-axis:** Time (min)
- **Legend:**
  - Estriol
  - Estradiol
  - Estrone
  - Ethinylestradiol
  - Diethylstilbestrol
Automated SPE

- AquaAnalysis
  - Parallel on-line sample prep plus separation and detection system
- 20 min extraction and instrument run time
- Reusable HLB cartridges
  - (>4000 injections)
- 5 mL to 20 mL sample size
## Automated SPE Method

### Approximate Minimum Detection Limits (MDLs)

<table>
<thead>
<tr>
<th>Compound</th>
<th>MDL (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estrone (E1)</td>
<td>2.5</td>
</tr>
<tr>
<td>Estriol (E3)</td>
<td>5</td>
</tr>
<tr>
<td>Estradiol (E2)</td>
<td>10</td>
</tr>
<tr>
<td>17B-Ethinylestradiol (EE2)</td>
<td>10</td>
</tr>
<tr>
<td>Diethylstilbestrol (DES)</td>
<td>5</td>
</tr>
</tbody>
</table>

![Graph showing the intensity of different compounds over time.](image)
Cost Comparison

- Capital Costs
  - Instrument Costs

- Operations and Maintenance Costs
  - Labor
  - Consumables
## Cost Comparison – Capital Costs

<table>
<thead>
<tr>
<th>Capital Costs</th>
<th>Total Instrument Costs</th>
<th>Annualized Instrument Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>AquaAnalysis - Automated</td>
<td>$349,000</td>
<td>$47,000</td>
</tr>
<tr>
<td>Alliance/Micro - Manual</td>
<td>$281,000</td>
<td>$38,000</td>
</tr>
</tbody>
</table>

Environmental Engineering

\[
n = 10 \text{ yrs} \\
\]
## Cost Comparison – Operations & Maintenance

<table>
<thead>
<tr>
<th>O&amp;M Costs per Sample</th>
<th>Extraction Columns</th>
<th>Analyst Time</th>
<th>Instrument Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>AquaAnalysis – Automated</td>
<td>$0.084</td>
<td>5 min</td>
<td>15 min</td>
</tr>
<tr>
<td>Alliance/Micro – Manual</td>
<td>$5.30</td>
<td>20 min</td>
<td>16 min</td>
</tr>
</tbody>
</table>
Method Comparison

- **Manual SPE Method**
  - Labor intensive extraction method (8 hours for 24 samples)
  - MDLs of 15 ppt or lower

- **AquaAnalysis**
  - Faster turn-around on samples
  - MDLs of 10 ppt or lower
  - Potential for much lower MDLs with automated cartridge loading
  - Automated with ability to run over night
Discussion on AquaAnalysis

- Contribution to Environmental Engineering
  - Decreases error with all-in-one unit
  - Increases efficiency in sample preparation
  - Eliminates need for large sample volumes
  - Comparable cost to manual extraction with lower O&M costs
  - Potentially lower MDLs
Special Thanks

- Claude Mallet
- Brad Barrett
- Chris Shevlin
- Waters Corporation
Questions?