Challenges and Options for the Analysis of 1,4-Dioxane

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Providing comprehensive scientific resources to environmental clients worldwide.
1,4-Dioxane

Synonyms
- p-dioxane
- diethylene oxide
- 1,4-diethylene oxide
- dioxyethylene ether
- diethylene ether
- ethylene glycol ethylene ether

Formula: C₄H₈O₂
CAS Number: 123-91-1
Molecular Weight: 88.1
Boiling Point: 101.1 °C
Water Solubility - Miscible
1,4-Dioxane

- Primarily used as a solvent stabilizer for 1,1,1-Trichloroethane (TCA) and other chlorinated solvents.
- Prevents breakdown of solvent due to - Light - Heat - Oxygen - Acids
- Also used in lacquers, paints, resins and automotive coolants
1,4-Dioxane

- Sources of 1,4-dioxane are anthropogenic as it does not occur naturally in the environment
- Classified as Class B2 probable carcinogen
- Inhalation and ingestion are the primary routes for human exposure
1,4-Dioxane

- 1,4-Dioxane is listed as a volatile compound under SW-846, Method 8260B. However, until recently (SOM01.2) it was not included in the Target Compound List (TCL) or the Priority Pollutant List (PPL).

- Site investigations may have failed to account for its presence.
An enforceable Maximum Contaminant Level (MCL) has not been established for 1,4-dioxane but several states/agencies have established drinking water guidelines;

<table>
<thead>
<tr>
<th>Region</th>
<th>Value (ug/l)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA (health advisory/RSL)</td>
<td>0.35/0.46</td>
<td></td>
</tr>
<tr>
<td>New Hampshire</td>
<td>0.25 (limit for all public water)</td>
<td></td>
</tr>
<tr>
<td>Massachusetts</td>
<td>0.3 (GW clean-up standard)</td>
<td></td>
</tr>
<tr>
<td>New Jersey</td>
<td>0.4 (GW Quality standard)</td>
<td></td>
</tr>
<tr>
<td>California</td>
<td>1</td>
<td>Notification level</td>
</tr>
<tr>
<td>Florida</td>
<td>3.2</td>
<td>Minimum criteria</td>
</tr>
<tr>
<td>Colorado</td>
<td>3.2</td>
<td>DW criteria (proposed 0.35 ug/l)</td>
</tr>
</tbody>
</table>
Analytical Methodologies

Would like to talk about four that we perform in our laboratory;

- VOC – 8260
- VOC – 8260 SIM
- SVOC – 8270
- SVOC – 8270 SIM
1,4-Dioxane as a Volatile

**SW-846 8260B**

- Water solubility results in poor purge efficiency
- Poor purge efficiency yields elevated reporting limits

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDL</td>
<td>70 ug/l</td>
<td>70 ug/kg</td>
</tr>
<tr>
<td>LOQ</td>
<td>250 ug/l</td>
<td>250 ug/kg</td>
</tr>
</tbody>
</table>
1,4-Dioxane as a Volatile

**SW-846 8260B**

- Poor purge efficiency also results in calibrations with low relative response factors (RRF), typically in the range of 0.08 to 0.11

- Data validators will often reject data with RRFs below 0.1
1,4-Dioxane as a Volatile

**SW-846 8260B**

- **Method Performance/Recoveries**

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Soil</th>
</tr>
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<tbody>
<tr>
<td>LCS</td>
<td>51%-129%</td>
<td>57%-126%</td>
</tr>
<tr>
<td>MS/MSD</td>
<td>43%-131%</td>
<td>39%-180%</td>
</tr>
</tbody>
</table>
1,4-Dioxane as a Volatile

**SW-846 8260B**

**Advantages**
- Can be used with limited sample volume
- Can be cost effective to acquire along with full 8260 list

**Disadvantages**
- High Limits
- Data rejected due to poor RRF
1,4-Dioxane as a Volatile

**SW-846 8260B SIM**

- Use of Selected Ion Monitoring (SIM) allows for better sensitivity for 1,4-dioxane
- Uses isotope dilution (1,4-dioxane d8) so compensates for poor purge efficiency
- Typically see RRFs of 0.9 to 1.1
1,4-Dioxane as a Volatile

SW-846 8260B SIM

- Better Sensitivity than 8260B
  
  **Water**
  
  MDL 0.2 ug/l
  LOQ 0.4 ug/l

- Method Performance/Recoveries
  
  **Water**
  
  LCS 70% - 130%
  MS/MSD 70% - 130%
1,4-Dioxane as a Volatile

**SW-846 8260B SIM**

**Advantages**

- Better sensitivity than regular 8260
- Data will more readily meet typical data quality objectives

**Disadvantages**

- Separate analytical run, so increases cost
- A modified 8260 – not all regulators accept
- Highly contaminated samples can cause interferences
1,4-Dioxane as a Semi-Volatile

**SW-846 8270C**

- Better sensitivity than typical 8260 analysis

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<th></th>
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</tr>
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<tbody>
<tr>
<td>MDL</td>
<td>1 ug/l</td>
<td>100 ug/kg</td>
</tr>
<tr>
<td>LOQ</td>
<td>5 ug/l</td>
<td>330 ug/kg</td>
</tr>
</tbody>
</table>

- Typically see RRFs of 0.5 to 0.8

- **Method Performance/Recoveries**

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<tr>
<th></th>
<th>Water</th>
<th>Soil</th>
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</thead>
<tbody>
<tr>
<td>LCS</td>
<td>45% - 78%</td>
<td>31% - 55%</td>
</tr>
<tr>
<td>MS/MSD</td>
<td>39% - 73%</td>
<td>11% - 59%</td>
</tr>
</tbody>
</table>
1,4-Dioxane as a Semi-Volatile

**SW-846 8270C**

- Waters – solvent extraction with CH2Cl2

**SW-846 3510C**

- Soils – solvent extraction with 1:1 CH2Cl2/Acetone

**SW-846 3550B**

**SW-846 3546**
1,4-Dioxane as a Semi-Volatile

**SW-846 8270C**

**Advantages**
- Better sensitivity than regular 8260
- Technique is more capable of dealing with difficult matrices
- Data will more readily meet typical data quality objectives
- Can be cost effective to acquire with full 8270 analysis

**Disadvantages**
- 1,4-dioxane elutes early in chromatogram – analyst experience
- Best recoveries are in 50% to 70% range
1,4-Dioxane as a Semi-Volatile

**SW-846 8270C SIM**

- Best sensitivity of the techniques discussed

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</tr>
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<tbody>
<tr>
<td>MDL</td>
<td>0.05 ug/l</td>
<td>0.7 ug/kg</td>
</tr>
<tr>
<td>LOQ</td>
<td>0.2 ug/l</td>
<td>1.7 ug/kg</td>
</tr>
</tbody>
</table>

- Typically see RRFs of 0.5 to 0.8
- Method performance/recoveries similar to 8270 full scan
1,4-Dioxane as a Semi-Volatile

**SW-846 8270C SIM**

**Advantages**
- Best sensitivity of the techniques
- LOQ exceeds (lower than) current drinking water guidelines
- Data will readily meet typical data quality objectives

**Disadvantages**
- Separate analytical run, so increases the cost
- Some regulators will not accept 1,4-dioxane as a semi-volatile
Summary

- There are several approaches that can be used to meet new water quality standards without going to unique instrumentation.

- The particular method and application that is best will depend upon:
  - regulator acceptance
  - sample matrix considerations
  - overall project scope considerations ($)

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Questions