Updates on EPA Method TO-11a for the Measurement of Airborne Carbonyls

National Ambient Air Monitoring Conference 2014

Ian MacGregor
Battelle

David Shelow
US EPA OAQPS

August 13, 2014
Background and Motivation

• Carbonyl compounds are important to ambient air quality
  ▪ Formaldehyde
  ▪ Acrolein

• Method TO-11a is the ‘gold standard’
Background and Motivation

• NATTS Network
  - Monitor long-term trends in HAPs concentrations
  - VOCs, carbonyls, PAHs, metals, hexavalent chrome
  - 27 sites around US
Background and Motivation

• Issues with US EPA Method TO-11a
  ▪ Acrolein
  ▪ Interferences with
    – Ozone
    – Nitrogen dioxide
    – Water
  ▪ Potentially poor, or unknown, collection efficiencies
Objectives

- Evaluate the effect of ozone, nitrogen dioxide, and water on Method TO-11a for the measurement of formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde
- Determine optimal collection efficiency for use over a 24 hour sampling period
- Ultimate goal: provide updated guidance on the implementation of Method TO-11a
Experimental design

• Part 1: Evaluate ozone scrubber for capacity and ability to handle O₃ transients
  ▪ 2 types of KI denuders
  ▪ 150 ppb at 1 L/min for 30 days, in duplicate
  ▪ First at ~30% RH
  ▪ Then at ~65% RH
  ▪ Continuous upstream and downstream ozone monitoring
  ▪ Transient high (>200 ppb) levels
Experimental design

• Part 2: Evaluate NO\textsubscript{2} interference and start collection efficiency assessment
  ▪ Carbonyls generated at 1 to 10 ppb using permeation tubes
  ▪ Both style of DNPH cartridges, in series, in duplicate
  ▪ 1 L/min for 24 hours @ 25°C
  ▪ With KI denuder present
  ▪ Modify HPLC method to address DNPA interference, if observed
  ▪ Confirm applicability of modified method at higher humidity

<table>
<thead>
<tr>
<th>Relative Humidity (%)</th>
<th>NO\textsubscript{2} (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 ± 5</td>
<td>0</td>
</tr>
<tr>
<td>30 ± 5</td>
<td>25</td>
</tr>
<tr>
<td>65 ± 5</td>
<td>0</td>
</tr>
<tr>
<td>65 ± 5</td>
<td>25</td>
</tr>
</tbody>
</table>
Experimental design

• Part 3a: Collection efficiency assessment
  ▪ Carbonyls generated at 1 to 10 ppb using permeation tubes
  ▪ Both style of DNPH cartridges, in series, in duplicate
  ▪ Without NO$_2$ or O$_3$
  ▪ ~0.3, ~0.5, ~0.75, ~1.25 and ~1.5 L/min
  ▪ 24 hours sampling
  ▪ 30% RH @ 25°C

• Goal: balance maximizing CE with maintaining required MDLs
Experimental design

• Part 3b: Final method optimization
  ▪ Carbonyls generated at 1 to 10 ppb using permeation tubes
  ▪ Both style of DNPH cartridges, in series, in duplicate
  ▪ 24 hours @ optimal flow rate for maximized CE
  ▪ 25°C, with KI denuder present

<table>
<thead>
<tr>
<th>Relative Humidity (%)</th>
<th>O₃ (ppb)</th>
<th>NO₂ (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First at 30, then at 65</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>25</td>
</tr>
</tbody>
</table>
Timeline

- Begin experimental work in September, results by spring 2015
Acknowledgement

• This work is being supported by US EPA OAQPS under contract number EP-D-13-005.