Update on the Optimization of U.S. EPA Method TO-11A for the Measurement of Carbonyls in Ambient Air

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Acknowledgement

• This work is being performed for US EPA OAQPS under contract number EP-D-13-005.
Background and Motivation

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

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

\[ \begin{align*}
\text{H}_2\text{NH}_2 & \xrightarrow{\text{R}_1, \text{R}_2} \text{H}_2\text{N}=\text{N}=\text{R}_1
\end{align*} \]  

\( R_1, R_2 = \text{H, Alkyl, Aryl} \)
Background and Motivation

• NATTS Network
  ▪ Monitor long-term trends in air toxics concentrations
  ▪ VOCs, carbonyls, PAHs and metals
  ▪ 27 sites around US

• PAMS network
  ▪ Ozone precursors
  ▪ 40 sites across the US
Background and Motivation

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

• Collection efficiency
  ▪ May be less than 100%, especially at longer sampling times
    – May be cause of reported differences between 8 h and 24 h samples
Objectives

• Evaluate the effect of flow rate, ozone, nitrogen dioxide, and water on Method TO-11A for the measurement of formaldehyde, acetaldehyde, propionaldehyde, and benzaldehyde

• Provide updated guidance, as needed, on the implementation of Method TO-11A
Experimental design

• Part 1: Collection efficiency assessment and flow rate selection
  ▪ Carbonyls generated at ~ 5 ppb with a gas-phase standard
  ▪ Both styles of DNPH cartridges, in duplicate, in series
  ▪ Ideal conditions: zero air without particles, NO\textsubscript{2} or O\textsubscript{3}
  ▪ 0.25, 0.5, 0.75, 1.0 and 1.25 L/min @ 25°C, 1 atm
  ▪ 24 hours sampling
  ▪ Tests at 10%, 30%, 65%, and 85% RH @ 25°C

• Goal: investigate trends in CE and select flow rate for future tests
  ▪ Balance maximizing CE with maintaining required MDLs
Part 1 – Test Fixture for Collection Efficiency vs Flow Rate
Experimental design

• Part 2: Evaluate at 4 RHs ozone scrubbers’ capacity and ability to handle short-term high levels of O₃
• Part 3: Evaluate and remediate NO₂ interference, also at 4 RHs
Experimental design

Part 4: Final method evaluation and potential optimization in the presence of co-collected O₃ and NO₂ and investigation of presence of collection interval bias

- 4 humidities (10%, 30%, 65%, 85%)
- 2 cartridge types (Supelco and Waters)
- 2 cartridges each in series (front and backup),
- 2 duplicate trains of each cartridge type
- 4 samples over 24 hours (with 2 sampling durations: 24 h x 1 and 8 h x 3)
- 5 combinations of O₃ and NO₂ (0 ppb, 0 ppb; 150, 0; 0, 100; 70, 50; and 150, 100)
- ~1.5 ppb each carbonyl, at ~22°C, ~1 atm, in zero air w/o particles, with ATEC denuder in line

Total of 640 discrete measurements of four different target carbonyls!

- Plus field blanks and other samples collected to characterize challenge and background levels
Results, Part 1: Assessment of Cartridge Background Contamination and Collection Efficiency vs Flow Rate
Results: Part 1, Cartridge Background Assessment

MDL MQO = 0.065 ppb
5\textsuperscript{th} %ile ambient concentration = 0.61 ppb

MDL MQO = 0.25 ppb
5\textsuperscript{th} %ile ambient concentration = 0.44 ppb

Levels on field blanks are on average > ~3x lower than MDL Measurement Quality Objectives and > ~10x lower than typical measured concentrations!

Values inside bars are values in micrograms per cartridge.
Results: Part 1, Collection Efficiency

- %CEs increase with increasing RH up to 85%, then decrease. %CEs at 85% RH decrease to a greater extent on Supelco vs. Waters.

- %CEs for acetaldehyde and propionaldehyde are most strongly impacted by co-collected moisture.
Results: Part 1, Collection Efficiency

- No clear trend in %CEs with respect to flow rate.
Results: Part 2, Ozone Scrubber Evaluation
Results: Part 2, Ozone Scrubber Evaluation – 65% RH

Plenum Ozone
ERG 5 minute ave
Atec 5 minute ave
Duplicate scrubber monitored
ERG average
Atec average

Ozone, ppb

Date

Results: Part 3, NO\textsubscript{2} Interferences
Results: Part 3, NO₂ Interferences

- NO₂
  - Reacts with DNPH, consuming it and forming derivatives that may coelute with target carbonyls

**DNPH and its NO₂ reaction products**

- **2,4-dinitrochlorobenzene (DNCB)**
  - Chemical Formula: C₈H₇ClN₂O₄
  - Molecular Weight: 202.55
  - CAS #: 97-00-7

- **2,4-dinitrophenylazide (DNPA)**
  - Chemical Formula: C₈H₇N₃O₄
  - Molecular Weight: 209.12
  - CAS #: 4096-88-2

- **5-nitrobenzofurazan-3-oxide (NBFO)**
  - Chemical Formula: C₈H₇N₃O₂
  - Molecular Weight: 181.11
  - CAS #: 18772-11-7

- **2,4-dinitrophenylhydrazine (DNPH)**
  - Chemical Formula: C₈H₄N₂O₄
  - Molecular Weight: 198.14
  - CAS #: 119-26-6

- **2,4-dinitrophenol (DNP)**
  - Chemical Formula: C₈H₄N₂O₅
  - Molecular Weight: 184.11
  - CAS #: 51-28-5
Results: Part 3, NO₂ Interferences
Results: Part 3, NO₂ Interferences

Co-collected NO₂ forms potential interferants but they are resolved chromatographically from the DNPH derivatives of the target aldehydes!
• No trend in %CE of formaldehyde in the presence of co-sampled NO\textsubscript{2} at 4 different humidities on either cartridge type at 1 L/min sampling rate
Results: Part 4, Final Method Evaluation
Results: Part 1 vs Part 4 – Potential Impact of Denuder

• Compared Part 1 results conducted at flow rate of 1 sLPM to Part 4 results over 24 hours and with no introduced O₃ or NO₂
  ▪ Only differences were the addition of the ATEC denuders and the lower carbonyl concentration in Part 4 (~5 ppb in Part 1, ~1.5 ppb in Part 4)
Results: Part 1 vs Part 4 – Potential Impact of Denuder

- %CEs are lower at lower concentrations and in the presence of the ATEC O₃ denuders for both Waters and Supelco (p-values < 0.001 and = 0.091 respectively)
- %CEs decrease similarly on both cartridge types with denuder present
Results: Part 1 vs Part 4 – Potential Impact of Denuder

- %CE decreased at 10%, 30%, and 65% RH (p-value < 0.001 for each comparison), but increased slightly at 85% RH (p-value = 0.12)
Results: Part 4 – Predicted Formaldehyde %CEs

In general:
%CE 8 h > %CE 24 h
And
%CE Supelco > % CE Waters
Results: Part 4 – Predicted Acetaldehyde %CEs

In general:
No trend in %CE by duration and
%CE Waters ≥ % CE Supelco
Summary of Results

• Part 1: Collection efficiency > ~75% on average for all carbonyls at 1 L/min sample rate for 24 h duration at all humidities for both cartridges except for acetaldehyde and propionaldehyde at 85% RH on Supelco cartridges
  ▪ Statistically and practically significant differences in %CEs by cartridge type, especially for acetaldehyde and propionaldehyde
  ▪ Flow rate not statistically significant and observed differences in %CEs were modest

• Part 2: Ozone denuders scrub O$_3$ for 30 days at 150 ppb; > 100,000 ppb-hour capacity, good for 1 year of sampling at 1 L/min at ~70 ppb O3 at 1:6 schedule (all humidities and both types of denuders)

• Part 3: NO$_2$ interferences may be chromatographically resolved from formaldehyde
Summary of Results

• Part 4

- On average there is a 10% percentage point decrease in %CE from the denuder or from the 3x lower challenge concentration
- On average (across cartridges, humidities, and carbonyls), 24 h measurements are lower than the sum of three sequential 8 h measurements; largest differences seen in propionaldehyde
- Recoveries of carbonyls vary with statistical and practical significance with respect to cartridge type, humidity, and sampling duration
  - There may be some a protective effect offered by the additional moisture
- %CEs for different carbonyls are not always higher on a cartridge of the same type
Results and Discussion

• So if am running an ambient air monitoring station, how should I implement this method and what kind of overall performance can I expect?
  - Which cartridge would maximize collection efficiency, and what collection efficiency should I expect to achieve?
Results and Discussion: Estimated Collection Efficiencies (PAMS)

Weights: 0.5 Formaldehyde, 0.3 Acetaldehyde, 0.2 Benzaldehyde (8 hr sampling duration)
Results and Discussion: Estimated Collection Efficiencies (NATTS)

Weights: 0.5 Formaldehyde, 0.5 Acetaldehyde, (24 hr sampling duration)
Backup slides
Part 4 – Test Fixture for Final Method Evaluation
# Experimental design – Part 4

**Final Method Evaluation Test Matrix, T = ~ 25°C**

<table>
<thead>
<tr>
<th>RH %</th>
<th>Duration (hrs)</th>
<th>O₃ (ppb)</th>
<th>NO₂ (ppb)</th>
<th>Carbonyls (each, ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ± 5</td>
<td>24</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30 ± 5</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>65 ± 5</td>
<td>24</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>85 ± 5</td>
<td>24</td>
<td>150</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>0</td>
<td>100</td>
<td>1.5</td>
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<td></td>
<td>24</td>
<td>70</td>
<td>50</td>
<td>1.5</td>
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<td></td>
<td>24</td>
<td>150</td>
<td>100</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>24</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

All concentrations approximate
Background and Motivation

- $\text{NO}_2$ reaction products may (or may not) coelute with formaldehyde

Solid line: analysis at 360 nm; dashed line: analysis at 300 nm
DNPA: 2,4-dinitrophenylazide
FA: formaldehyde
DNCB: 2,4-dinitrochlorobenzene
NATTS PT Samples
Results: Part 3, NO₂ Interferences

• CY2016 QTR3 NATTS PTs spiked w/ and w/o NO₂

• The network wide NATTS mean recoveries versus the nominal for formaldehyde were:
  ▪ Targets + interferences: 85.1%
  ▪ Targets only: 76.9%
  ▪ *That’s a positive bias of ~8%*

• Certain labs are driving the bias and likely have an NO₂ interference issue

<table>
<thead>
<tr>
<th>Lab</th>
<th>Targets + interferences</th>
<th>Targets only</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-01</td>
<td>98.4</td>
<td>78.4</td>
</tr>
<tr>
<td>05-03</td>
<td>95.8</td>
<td>78.2</td>
</tr>
<tr>
<td>10-02</td>
<td>90.8</td>
<td>73.8</td>
</tr>
</tbody>
</table>
Equal weighting applied to Formaldehyde, Acetaldehyde, Propionaldehyde and Benzaldehyde
Results: Part 4 – Predicted Propionaldehyde %CEs

10% RH

- Waters - 8
- Waters - 24
- Supelco - 8
- Supelco - 24

30% RH

- Waters - 8
- Waters - 24
- Supelco - 8
- Supelco - 24

65% RH

- Waters - 8
- Waters - 24
- Supelco - 8
- Supelco - 24

85% RH

- Waters - 8
- Waters - 24
- Supelco - 8
- Supelco - 24

Collection Efficiency (%)
Results: Part 4 – Predicted Benzaldehyde %CEs

- **10% RH**
  - Waters - 8
  - Waters - 24
  - Supelco - 8
  - Supelco - 24

- **30% RH**
  - Waters - 8
  - Waters - 24
  - Supelco - 8
  - Supelco - 24

- **65% RH**
  - Waters - 8
  - Waters - 24
  - Supelco - 8
  - Supelco - 24

- **85% RH**
  - Waters - 8
  - Waters - 24
  - Supelco - 8
  - Supelco - 24

Collection Efficiency (%)