SSSAAP (SES) 2019
Grand Hotel Marriott Resort
Point Clear, Alabama

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A Leading Provider of Environmental Solutions

Emerging Technology
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Difficult to Measure Compounds at Low Levels (ppb/ppt) Near/Real Time

- Real Need to Measure low levels in ambient air (low ppb) Compliance/Reference Method
- Need to measure low levels in Ambient and Sources (PSD, Expansion, Major Out, Non-Attain., RA and TITLE V MAJOR SOURCES - OUT
  - Formaldehyde in Turbines (single digit ppb)
  - Ethylene Oxide (Stacks/Ducts, Ambient Air) Discuss Interferences
    - FTIR or GC-FID - Ducts - <10 ppb
    - Ambient – Need <150 ppt typically found
  - HRVOCs (1,3 Butadiene)
  - OHAPs
  - BTEX (ambient air geographical – Avg Benzene <0.3 ppb)
  - PFAS/Gen-X (particulate attachment or liquid injection vaporizer

Ambient Benzene

EPA 2010
Proton Transfer Time of Flight Mass Spectrometry (PTR-TOF-MS)

- Proton Transfer Reaction Mass Spectrometry for Real Time VOCs
- Part Per Trillion (PPT) LOD Virtually any C compound
- No Compressed Gases while in Real Time Mode
- EPA Reference Method 18 Compatibility with GC
- Weather Station & GPS
- Mobile GPS and Real Time Capability (1 data point per second)

Typical but not limited reactions:

\[ \text{H}_3\text{O}^+ + R \rightarrow \text{RH}^+ + \text{H}_2\text{O} \]
\[ \text{O}_2^+ + R \rightarrow R^+ + \text{O}_2 \]
Reagents and Molecular Interactions

Water $+$ Proton $\rightarrow$ Hydronium

Water $+$ Water $\rightarrow$ Hydroxide $+$ Hydronium

Proton transfer

Association

Charge transfer
Mobile PTR-TOF-MS Platform
Advantages of PTR-MS

• Mobile Real Time
• Couple to GC for Compliance EPA M18
• Absolute Time and Space
• Real-time, continuous results (1/sec)
• No sample or reagent preparation
• New Reagents all the time
• Single unit can handle multiple sampling ports
• Team with RJ Lee Group for Multiple Mobile Platforms and PTR sensitivities (4000 RJ Lee and 6000 Series Montrose)
Selective Reagent Chemistry for Interferences with Selective Ionization

- Reagent Change in 10 seconds on the fly
- New Reagents being developed
- H2O+ (Hydronium)
  O2+
  NO+
  NH3+ (Nitronium)
  Etc.

Anything above the blue line with NO+
Anything above the green line with O2+
Anything above the red line with H2O+
Anything above the black line with NH3+
GC-PTR-TOF-MS Compliance Methods
EPA Method 18 Direct Interface

▪ METHOD 18—MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

▪ “1.2.1 …gaseous organics emitted from an industrial source. … designed for ppm level sources, some detectors are quite capable of detecting compounds at ambient levels, e.g., ECD, ELCD, and “HID”.

▪ Some other types of detectors are evolving such that the sensitivity and applicability may well be in the ppb range in only a few years.”

▪ We are there now
Direct or Thermal Desorption PTR-TOF-MS Compliance Methods
Analogous to Validated EPA Test Method 8265:

- EPA M8265 Volatile Organic Compounds (VOCs) in Water, Soil, Soil Gas, and Air by Direct Sampling Ion Trap Mass Spectrometry (DSITMS)
- “method uses direct sampling ion trap mass spectrometry (DSITMS) for the rapid quantitative measurement, continuous real-time monitoring, and qualitative and quantitative preliminary screening of volatile organic compounds (VOCs) in water, soil, soil gas, and air.”
- Complementary molecular ion information is obtained in the Chemical Ionization (CI) mode also provides enhanced sensitivity and improved selectivity for certain compounds, including alkyl-aromatics, ketones, and aldehydes.
- NOTE: Other mass spectrometers may be used if they have capabilities and performance specifications appropriate for the intended application.
PTR TOF MS Case Study BTEX Ambient
PTR-TOF-MS – Real VOC and BTEX

200 ppb

100 ppb

0 ppb

Ethanol: Feb 19-20, 2018

February 19, 2018

Ethanol Tanker Deliveries

Entered Monitoring Site

February 20, 2018

Instrument Adjustment

Time of Day

Concentration (ppbv)
Case Study: Process  (Fermentation/Ethanol Plants)

Table I. Time averaged concentrations of six sampling locations in parts-per-billion (ppbv).

<table>
<thead>
<tr>
<th>Concentrations (ppbv)</th>
<th>CO₂ Scrubber</th>
<th>DDGS Bag House</th>
<th>RTO Inlet</th>
<th>RTO Out</th>
<th>Syrup Tank</th>
<th>Fluid Out</th>
<th>Detection limit**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>295</td>
<td>322</td>
<td>9300</td>
<td>679</td>
<td>377</td>
<td>540</td>
<td>6.5</td>
</tr>
<tr>
<td>Methanol</td>
<td>828</td>
<td>371</td>
<td>7060</td>
<td>883</td>
<td>5300</td>
<td>906</td>
<td>7.7</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>852</td>
<td>16.0</td>
<td>75.8</td>
<td>50.0</td>
<td>39.5</td>
<td>34.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>12800</td>
<td>718</td>
<td>20400</td>
<td>4228</td>
<td>6070</td>
<td>2840</td>
<td>49</td>
</tr>
<tr>
<td>Formic acid</td>
<td>3900</td>
<td>1110</td>
<td>5000</td>
<td>3930</td>
<td>1160</td>
<td>1230</td>
<td>21</td>
</tr>
<tr>
<td>Ethanol</td>
<td>10400</td>
<td>66.7</td>
<td>11700</td>
<td>146</td>
<td>5910</td>
<td>305</td>
<td>0.4</td>
</tr>
<tr>
<td>CH₄S</td>
<td>953</td>
<td>10.6</td>
<td>245</td>
<td>29.7</td>
<td>142</td>
<td>13.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Acrolein</td>
<td>834</td>
<td>43.5</td>
<td>3996</td>
<td>182</td>
<td>341</td>
<td>52.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Acetic acid*</td>
<td>13000</td>
<td>594</td>
<td>15400</td>
<td>1360</td>
<td>4210</td>
<td>4250</td>
<td>4.9</td>
</tr>
<tr>
<td>C₅H₁₀S</td>
<td>3.6</td>
<td>1.8</td>
<td>308</td>
<td>8.0</td>
<td>8.9</td>
<td>6.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>1160</td>
<td>117</td>
<td>12300</td>
<td>423</td>
<td>399</td>
<td>277</td>
<td>1.6</td>
</tr>
<tr>
<td>2,3-butanedione</td>
<td>93.9</td>
<td>141</td>
<td>10100</td>
<td>276</td>
<td>879</td>
<td>1020</td>
<td>1.6</td>
</tr>
<tr>
<td>C₅H₁₀₅S</td>
<td>114</td>
<td>26.5</td>
<td>293</td>
<td>158</td>
<td>54.3</td>
<td>68.2</td>
<td>2.4</td>
</tr>
<tr>
<td>2-Furaldehyde</td>
<td>24.0</td>
<td>31.8</td>
<td>3010</td>
<td>56</td>
<td>3940</td>
<td>250</td>
<td>0.2</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>14800</td>
<td>85.6</td>
<td>22200</td>
<td>406</td>
<td>250</td>
<td>473</td>
<td>2.2</td>
</tr>
<tr>
<td>Carbonyl sulfide</td>
<td>46.3</td>
<td>6.8</td>
<td>55.1</td>
<td>9.1</td>
<td>10.1</td>
<td>19.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>7.0</td>
<td>5.2</td>
<td>19.0</td>
<td>8.6</td>
<td>13.7</td>
<td>2.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Notes: Data are 5-minute averages of the most appropriate irradiation setting.
Method Development; 1,3 Butadiene, PCCs
Method Dev:
Hard to Measure Compounds- Furans, Nitrosamines

Fast response time – Small to no memory effects

2,5 Dimethylfuran

2,5 Dimethylfuran recovery

Butanenitrile

Butanenitrile recovery
Case Study
Ethylene Oxide/Acetaldehyde Ambient Air

- Mass Spec gives same m/z peak
- Acetaldehyde may be high in Ambient but higher in Combustion
- Similar characteristics make it co-elute – only now new columns coming out
- Typical MS or GC can’t get low enough and concentration needed (50-100 ppt)
- PTR reagent chemistry can do real-time to <100 ppt ambient

Ethylene Oxide

Molar mass: 44.05 g/mol
Formula: C2H4O
Boiling point: 51.26°F (10.7°C)
Density: 882 kg/m³

Same Molecular Weight
Similar boiling points

Acetaldehyde

Molar mass: 44.05 g/mol
Formula: C2H4O
Boiling point: 68.36°F (20.2°C)
Density: 788 kg/m³
Method 18 Compliance – GC-FID or PTR (New Column Found)
EtO/Acetaldehyde

- GC-FID Still not sensitive enough (~10 ppb) for Ambient Air
- Switch to PTR as Detector
Case Study – Try GC-PTR-TOF EtO/Acetaldehyde

- Tried NH+ (Ammonium from Literature) = NG
- Coupled to GC
- Reagent H3O+
- Co-Elution EtO/Acetaldehyde
- Acetone monitored as leak detection (a lot in indoor air)
Case Study – Try GC-PTR-TOF with DNPH Tube (Inlet to GC) 
EtO/Acetaldehyde

- Switch Back to H3O+
- Add Dinitrophenylhydrazine (DNPH Tube)
- Removes 99% Acetaldehyde
  But Sil Gel removes EtO
- DNPH dissolved in acetonitrile
- TO5 DNPH glass fiber cartridge underway

Acetonitrile (Green Line)
Case Study – GC-PTR-TOF-MS
New Column
EtO/Acetaldehyde

- GC-PTR-TOF-MS
- Separation on GC
- PTR-TOF-MS Integrations
- Extremely Reproducible
GC-PTR-TOF-MS EtO Linearity

Ethylene Oxide Calibration Curve

- NIST Traceable
- 1% Accuracy MFCs
- 1000:1 Dilution Capability
- GC Injections each point
- +/-5% diff precision criteria met

Equation: $y = 0.0114x - 0.0134$

$R^2 = 0.9982$
GC-PTR-TOF-MS EtO Detection Limit

- Limit of Detection GC-Integration-PTR-TOF-MS = 350 parts per trillion (ppt) Real Time 100 ppt
- Lower LOD with larger sample loop
- Current ONGOING Real Time Direct PTR-TOF-MS (New Reagent Chemistry) = <100 ppt
- PTR also being retrofitted with new Lens to gain 3x better sensitivity
REAL TIME Mthd Dev - Dioxygenyl Association

Oxonium or Hydronium 18 or 19 amu

Dioxygenyl O2+ 32 & 33 amu

EtO 44 amu

EtO - O2 Association 76 & 77 amu
Optimized method for the detection of EtO

No interferences from isobaric compounds

Mass 76 and 77 EtO
Real Time Mapping

- GPS Coordinates
- Video Corellation
- Wind Velocity - Sonic Anemometer
- Wind Direction
- Montrose Triangulation Platform
Visualization of EtO Dispersion
## EtO and Other Targets Everyday Sources

### EtO & Acetaldehyde

<table>
<thead>
<tr>
<th>Source</th>
<th>EtO and Acetaldehyde</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Concentration (ppb)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2 injection</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Laboratory background</td>
<td>0</td>
<td>2.2</td>
<td>9.5</td>
<td>40</td>
</tr>
<tr>
<td>Breath test</td>
<td>0</td>
<td>6.1</td>
<td>25</td>
<td>96</td>
</tr>
<tr>
<td>Breath test 2</td>
<td>2.5</td>
<td>5.8</td>
<td>23</td>
<td>79</td>
</tr>
<tr>
<td>Korean cabbage kimchi</td>
<td>41.5</td>
<td>0</td>
<td>37</td>
<td>116</td>
</tr>
<tr>
<td>Cigarette smoke</td>
<td>2</td>
<td>150</td>
<td>226</td>
<td>186</td>
</tr>
<tr>
<td>Uniti cigar</td>
<td>0</td>
<td>2.3</td>
<td>6.1</td>
<td>15</td>
</tr>
<tr>
<td>Candle</td>
<td>6</td>
<td>1</td>
<td>5.7</td>
<td>17</td>
</tr>
<tr>
<td>Heated vegetable oil (80% soy)</td>
<td>3</td>
<td>32</td>
<td>7.9</td>
<td>19</td>
</tr>
<tr>
<td>Diesel exhaust (ignition stage)</td>
<td>0</td>
<td>1016</td>
<td>454</td>
<td>475</td>
</tr>
<tr>
<td>De-icer</td>
<td>2</td>
<td>0</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Burning leaves</td>
<td>0</td>
<td>250</td>
<td>108</td>
<td>66</td>
</tr>
<tr>
<td>Breath test 3</td>
<td>0</td>
<td>2.2</td>
<td>6.9</td>
<td>14</td>
</tr>
</tbody>
</table>

### EtO Alone

<table>
<thead>
<tr>
<th>Sources</th>
<th>Concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EtO</td>
</tr>
<tr>
<td>Kimchi cabbage</td>
<td>10</td>
</tr>
<tr>
<td>Cigarette combustion</td>
<td>176</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>199</td>
</tr>
<tr>
<td>Gas exhaust</td>
<td>0</td>
</tr>
<tr>
<td>Diesel exhaust</td>
<td>1.3</td>
</tr>
<tr>
<td>Diesel exhaust no catalytic converter</td>
<td>2.5</td>
</tr>
<tr>
<td>Diesel exhaust from an older truck</td>
<td>26</td>
</tr>
<tr>
<td>Cigarette breath</td>
<td>12</td>
</tr>
</tbody>
</table>

“-“ identifies materials that were not measured for Ethylene.
Industry Defense Studies 2 – Real Time
## EtO Statistics and Wind Roses

<table>
<thead>
<tr>
<th>location</th>
<th>start time</th>
<th>stop time</th>
<th>average</th>
<th>stdev</th>
<th>min</th>
<th>max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Road 176</td>
<td>11:22</td>
<td>11:54</td>
<td>0.78</td>
<td>1.04</td>
<td>&lt;0.42</td>
<td>5.02</td>
</tr>
<tr>
<td>Highway 41</td>
<td>11:54</td>
<td>12:02</td>
<td>0.64</td>
<td>0.90</td>
<td>&lt;0.42</td>
<td>3.80</td>
</tr>
<tr>
<td>Road 120</td>
<td>12:02</td>
<td>12:16</td>
<td>0.61</td>
<td>0.75</td>
<td>&lt;0.42</td>
<td>4.30</td>
</tr>
<tr>
<td>Road 83</td>
<td>12:17</td>
<td>12:23</td>
<td>0.48</td>
<td>0.53</td>
<td>&lt;0.42</td>
<td>2.14</td>
</tr>
<tr>
<td>Road 176</td>
<td>12:23</td>
<td>12:31</td>
<td>0.54</td>
<td>0.59</td>
<td>&lt;0.42</td>
<td>2.02</td>
</tr>
<tr>
<td>Montrose stationary measurements</td>
<td>12:32</td>
<td>13:51</td>
<td>&lt;0.42</td>
<td>--</td>
<td>&lt;0.42</td>
<td>3.70</td>
</tr>
<tr>
<td>S. Main St.</td>
<td>13:52</td>
<td>13:57</td>
<td>&lt;0.42</td>
<td>--</td>
<td>&lt;0.42</td>
<td>1.16</td>
</tr>
<tr>
<td>ORD</td>
<td>15:32</td>
<td>15:57</td>
<td>&lt;0.42</td>
<td>--</td>
<td>&lt;0.42</td>
<td>4.50</td>
</tr>
<tr>
<td>Road 72</td>
<td>15:57</td>
<td>16:06</td>
<td>&lt;0.42</td>
<td>--</td>
<td>&lt;0.42</td>
<td>2.69</td>
</tr>
<tr>
<td>I-90</td>
<td>16:06</td>
<td>16:12</td>
<td>0.47</td>
<td>0.79</td>
<td>&lt;0.42</td>
<td>4.78</td>
</tr>
<tr>
<td>Road 53</td>
<td>16:12</td>
<td>16:20</td>
<td>&lt;0.42</td>
<td>--</td>
<td>&lt;0.42</td>
<td>0.50</td>
</tr>
<tr>
<td>Highway 12</td>
<td>16:25</td>
<td>16:42</td>
<td>&lt;0.42</td>
<td>--</td>
<td>&lt;0.42</td>
<td>2.17</td>
</tr>
<tr>
<td>S. main St</td>
<td>16:42</td>
<td>16:53</td>
<td>&lt;0.42</td>
<td>--</td>
<td>&lt;0.42</td>
<td>3.36</td>
</tr>
</tbody>
</table>
Visualization of EtO Ambient Dispersion
Summary

- PTR-TOF-MS may be used to measure ultra-low real time detection limits for hard to measure compounds (Methodologies developing quickly) in real time
- Other Test Method (OTM) may be developed for sources with EPA approval
- Integrated GC-PTR-TOF-MS represents legally defensible EPA Reference Method 18 Direct Interface if all QA/QC in Method followed
- GC Integrated or Direct Real Time PTR-TOF-MS is a cost effective solution – Same as a typical FTIR test (Pay by day) - Reasonable Rates