Application of Extractive Cryogenic Preconcentration with FTIR Spectroscopy for Autonomous Measurements of Gaseous Air Toxics: Status and Preliminary Results

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ECIP-FTIR

Presentation Outline

• Project Motivation
• ECIP-FTIR Instrumentation and Operations
• System Integrations
• Preliminary Results
• Future Plans
• Both anthropogenic and natural sources emit volatile organic compounds (VOCs) into the urban atmosphere

• VOCs react with either nitrite radicals at night or hydroxyl radicals during the day to produce reactive organic peroxy molecules

• Increased peroxy molecules result in increased production of ozone (Atkinson, 2000)

• Improved quantification of VOC concentrations will improve predictions of all molecules involved
• The 1990 Clean Air Act Amendments (EPA, 1990) lists 188 VOCs as hazardous air pollutants (HAPs)
• These HAPs are known to have adverse affects on human health (respiratory, cancer, etc.)
• The EPA has placed emissions standards to reduce ambient concentrations of HAPs
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Project Motivation – EPA Compendium Methods

- EPA currently has 17 methods (Compendia) for measuring organic air toxics
- Fundamental similarities
  - Collection of ambient samples in the field
    - Compound-specific sorbent material
    - Reactive sorbent or non-reactive adsorbent filter
    - Low-temperature condensation
    - Evacuated cylinder collection
  - Analysis of collected samples in centralized laboratories
  - Problem: Some volatile compounds degrade during storage causing significant analysis errors (Kelly and Holdren, 1995)
Objectives: Improvement of NATTS Gaseous Air Toxics Sensors

- **Improve Temporal Coverage:**
  - continuous operation, high duty cycle
- **Improve Temporal Resolution**
  - 6-hour required (diurnal coverage), 4-hour design, 1-2 hour goal*
- **Improve Data Latency**
  - Internet-accessible near-real-time data products
- **Improve Chemical Specificity**
  - one sample processor/analyzer for all IR-active trace gases
- **Improve User Interaction:**
  - mobile, autonomous, low-maintenance, no sample handling
  - maintenance, operation, and analysis by non-specialists
- **Reduce Life Cycle Costs:**
  - purchase cost ~ annual cost of one or two conventional sites
  - low annual operating costs
- **Maintain Data Quality:**
  - meet existing EPA MDL’s, random and systematic errors
  - onboard QA/QC, extensive validation against EPA standards
- **Maintain Method Traceability:**
  - EPA-approved physics & chemistry; innovative engineering

*15 minutes or less for transient high-concentration events, using parallel intercalibrated method
**Onboard QA/QC options:**

Parallel: continuous flow without preconcentration vs. batch cryotrap sample with preconcentration

Unspiked vs. spiked vs. direct shunt to gas cell

Replicate: cryotrap vs. cryotrap

*For simplicity, schematic omits valves, desorption routes, and other flow options*
Methyl Propyl Ketone
Chlorobenzene
Acetaldehyde
Benzene
Carbon Tetrachloride

Chloroform
Formaldehyde

Tetrachloroethylene
Trichloroethylene
Vinyl Chloride
1,1,1-Trichloroethane

Acrolein

Sive et al.
Miller et al.
Apel et al.
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Instrumentation
Methodology - Quantification of Complex Mixtures

\[ F_{amb} = F_{cell\text{tot}} + F_{trap1} + F_{trap2} + F_{trap\text{bypass}} - F_{dil} - F_{VOC} \]

Volumetric flowrate of ambient analyte at input to spike mixer

\[ C^i_{amb} = \left\{ 1 - \frac{F_{VOC}}{F_{amb}} \right\} \left\{ \frac{V_{cell}}{F_{trap}\Delta t_{trap}} \right\} \cdot \left\{ \frac{1}{L_{cell}} \right\} \cdot \left\{ \frac{AU^i(\overline{v})}{k^i(\overline{v})} \right\}^{batch} - \left\{ \frac{F_{VOC}}{F_{amb}} \right\} C^i_{VOC} \]

Concentration of \( i^{th} \) ambient analyte, using batch flow through cryogenic trap, thermally desorbed to gas cell
determined by Partial Least Squares chemometrics same FTIR & gas cell

\[ C^i_{amb} = \left\{ \frac{1 - F_{VOC}/F_{amb}}{1 - F_{dil}/F_{cell\text{tot}}} \right\} \left\{ \frac{1}{L_{cell}} \right\} \cdot \left\{ \frac{AU^i(\overline{v})}{k^i(\overline{v})} \right\}^{cont} - \left\{ \frac{F_{VOC}}{F_{amb}} \right\} C^i_{VOC} \]

Concentration of \( i^{th} \) ambient analyte using continuous flow through gas cell

For simplicity, these formulae do not include cryotrap efficiency corrections for the \( i^{th} \) analyte
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Current Status and Preliminary Data

• Assembly:
  – GenI laboratory-ready condition completed
  – Field retrofitting completed for autonomous operation in the laboratory

• Testing:
  – Testing completed for support devices and process software
  – Systems issues resolved: vibration, EMI/RFI, thermal, packaging
  – Testing and optimization in progress for cryogenic subsystem

• Measurements:
  – SNR vs integration time
  – Subsystem analysis
  – Cell purging time and purging efficiency; external H₂O & CO₂
  – Absorption spectra for calibration gas
  – Cryogenic preconcentration efficiency
Nominal SNR should increase with square root of number of scans
Experimental results indicate excellent stability over ~1 hour
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Subsystem Performance

**Cryocooler Efficiency**

- Min Temp = -84.428408
- Min Temp = -93.467149
- Min Temp = -185.47102

**Vacuum Efficiency**

- Fill Pressure (mb) = 1003.3775
- Fill Time (min) = 0.9863333
- Evac Pressure (mb) = 98.839601
- Evac Time (min) = 2.0983333

Evacuate and Fill
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Preliminary Spectra

- Good spectral resolution
- Good sensitivity
- Multi-compound quantification
City of Huntsville retrofitted building interior with air-conditioned room to accommodate ECIP-FTIR

Source: Google Earth

10 km radius

Measuring areal wind field over HSV transportation corridor

expected inlet for ECIP-FTIR sample when high-vols don’t

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Future Work - HSV
Future Work - BHX
Future Work – Additional Applications

• Indoor Air Quality
  – Offices, Schools, Residences
  – Indoor-specific Emission Sources
  – Indoor / Outdoor Interaction
  – Indoor VOC concentrations Up to 5 times higher than outdoor (Solomon et al., 2008)

• Aircraft Cabins
• Rural v. Suburban v. Urban
• High-temporal resolution time series
• Interdisciplinary Studies
## Future Work – Gen II Design Improvements

<table>
<thead>
<tr>
<th>Mechanical</th>
<th>Smaller, lighter, easier compartment access; Could mount in an SUV or small van</th>
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<tbody>
<tr>
<td>Electrical</td>
<td>Modular integrated DAQ and process control; wireless Ethernet</td>
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<tr>
<td></td>
<td>Modular integrated power distribution; lower power consumption</td>
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<tr>
<td>Environmental</td>
<td>Improved isolation from ambient interferents: vibration, EMI/RFI, thermal, and H₂O/CO₂</td>
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<tr>
<td>Optical</td>
<td>FTIR: smaller, lighter, field-ruggedized, splash-proof; Gas Cell: larger L/V, faster purge, automated mirror switching</td>
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<td>Fluid</td>
<td>Expanded use of modular surface-mount plumbing; Improved QA/QC manifold; additional spike routing options</td>
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<tr>
<td>Traps</td>
<td>Improved thermal design; finer temporal resolution; Better handling of minor gases: H₂O, CO₂, and O₃</td>
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<tr>
<td>Cryocooler</td>
<td>Coldhead: remote umbilical, smaller, more cooling capacity; Power: computer-controlled conditioner / motor controller</td>
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<tr>
<td>Systems</td>
<td>Improved modularity, packaging, and integration; Incorporates many features of pre-production prototype</td>
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Questions / Comments?

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