

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

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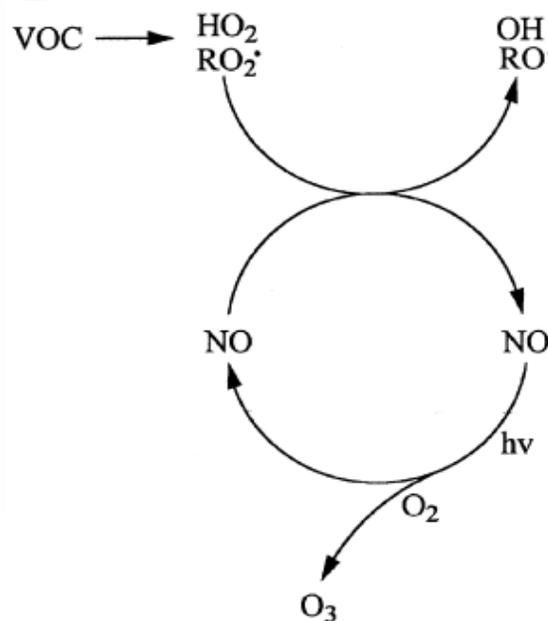
*Initiated under EPA Region IV Project "Community Assessment of Air Toxics in Birmingham, AL and Vicinity"  
Augmented by JCDH and Continued by NOAA NESDIS*

*Presentation Outline*

- Project Motivation
- ECIP-FTIR Instrumentation and Operations
- System Integrations
- Preliminary Results
- Future Plans

**Project Motivation - Chemistry**

- 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



*Project Motivation - Regulatory*

- 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



## *Project Motivation – EPA Compendium Methods*

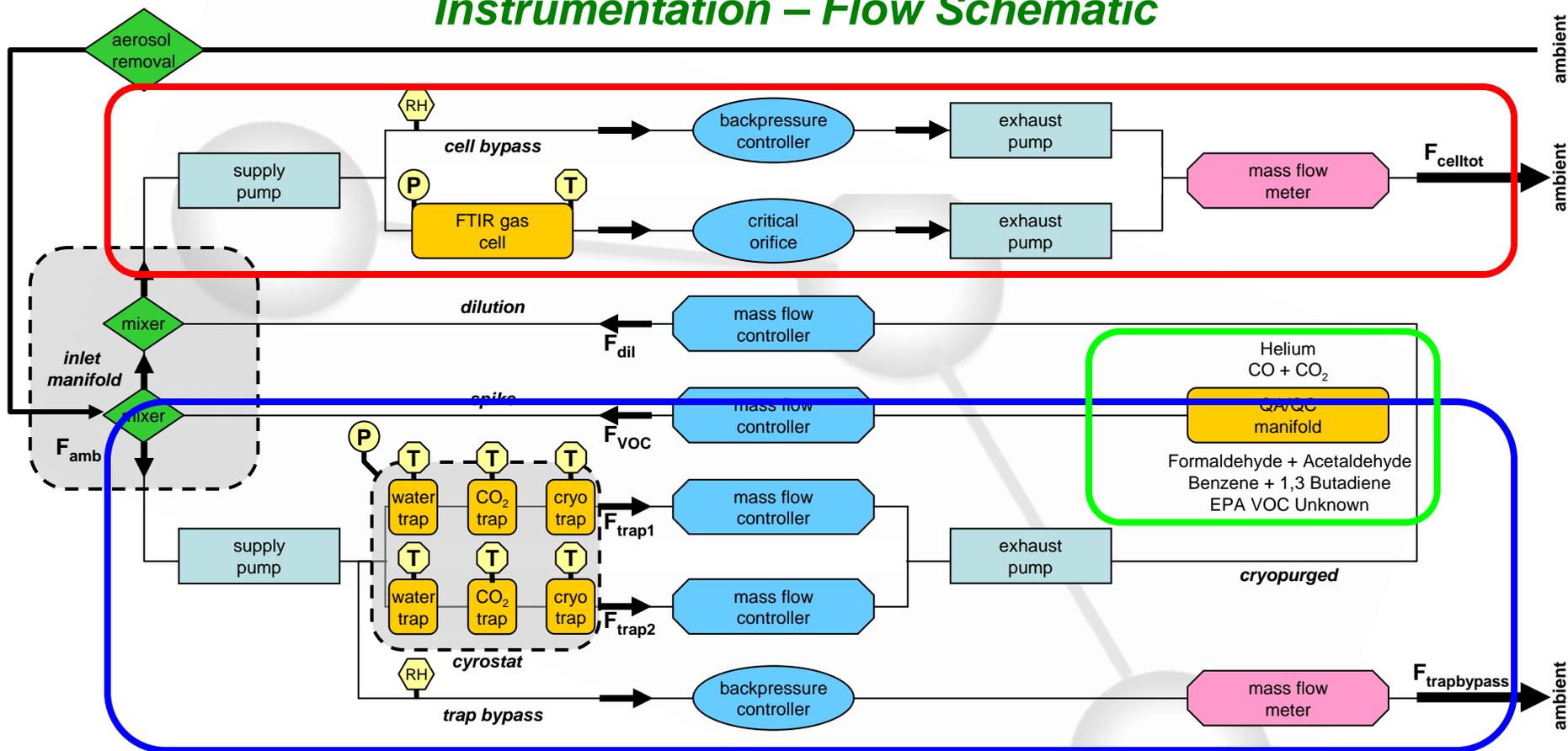
- **EPA currently has 17 methods (Compendia) for measuring organic air toxics**
- **Fundamental similarities**
  - *Collection of ambient samples in the field*
    - Compound-specific sorbent material
    - Reactive sorbent or non-reactive adsorbent filter
    - Low-temperature condensation
    - Evacuated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

## **Objective: 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*

## Instrumentation – Flow Schematic



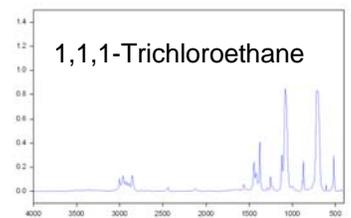
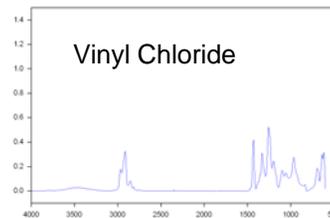
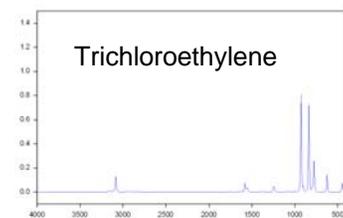
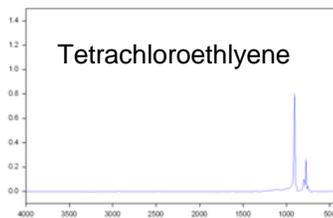
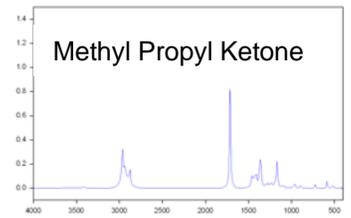
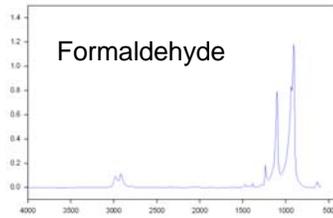
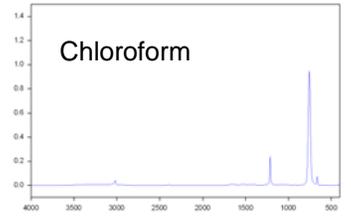
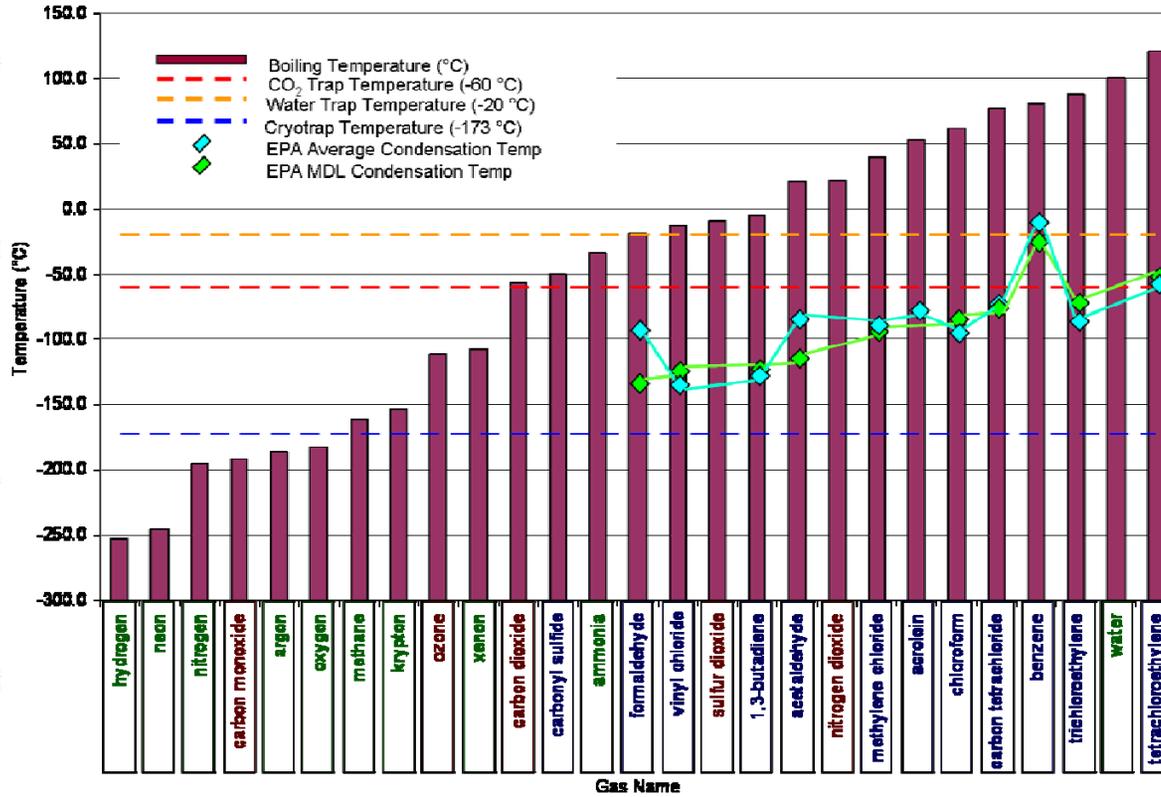
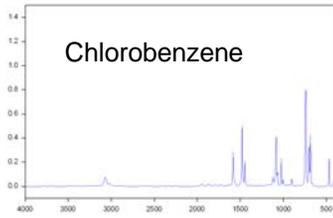
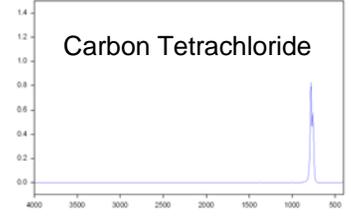
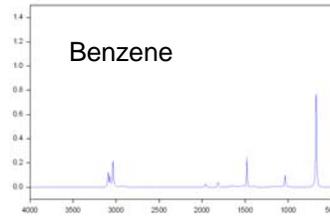
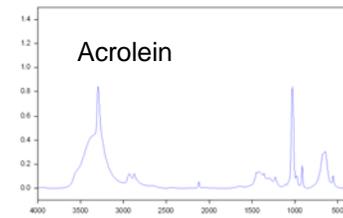
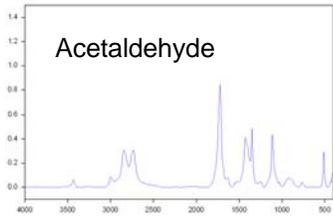
### Onboard QA/QC options:

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

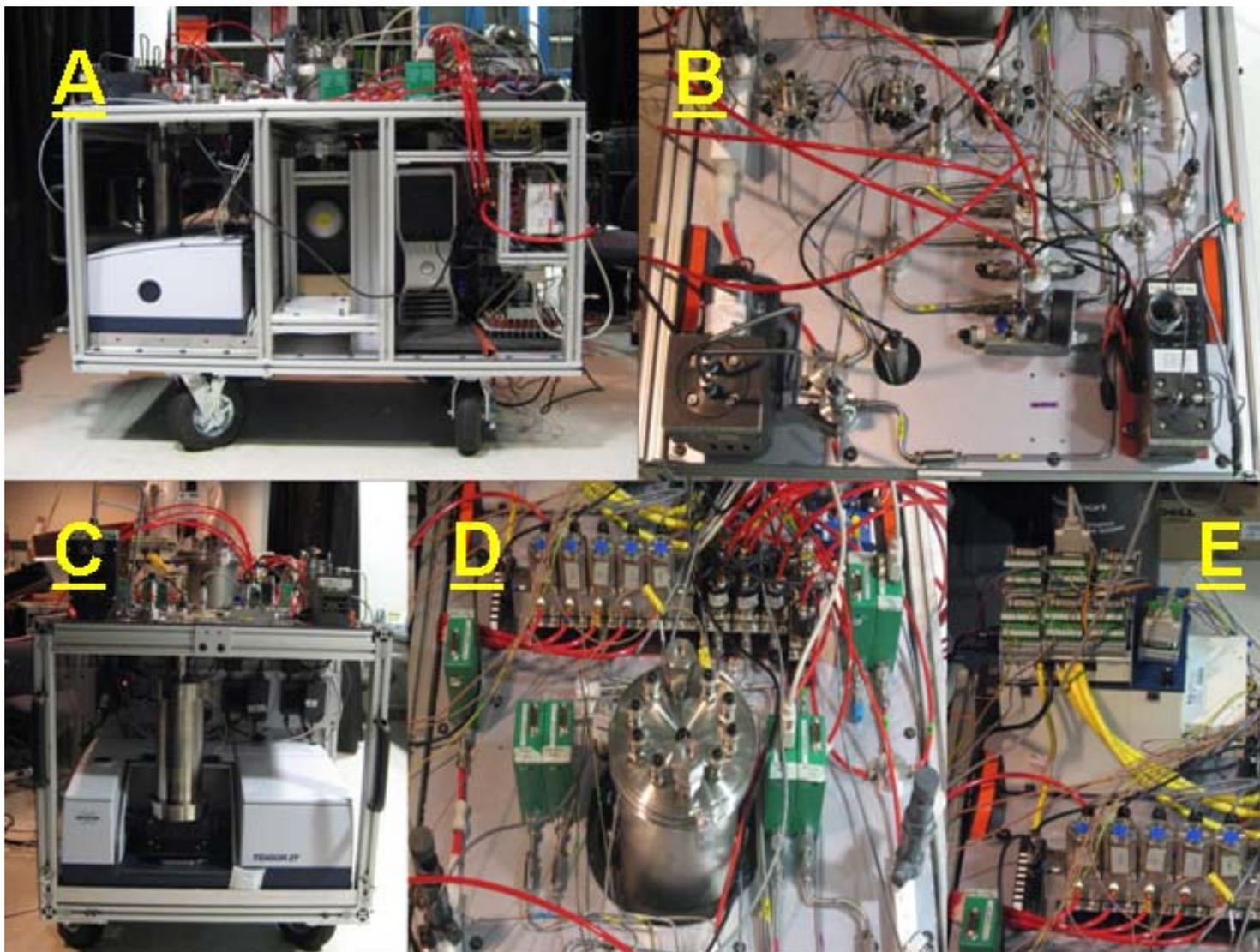
*Unspiked vs. spiked vs. direct shunt to gas cell*

*Replicate: cryotrap vs. cryotrap*

*For simplicity, schematic omits valves, desorption routes, and other flow options*



## *Instrumentation*



## Methodology - Quantification of Complex Mixtures

$$F_{amb} = F_{celltot} + F_{trap1} + F_{trap2} + F_{trapbypass} - F_{dil} - F_{VOC}$$

Volumetric flowrate of ambient analyte at input to spike mixer

*Use this equation only if dilution and/or spike flows are active*

$$C_{amb}^i = \left\{ 1 - \frac{F_{VOC}}{F_{amb}} \right\} \left\{ \frac{V_{cell}}{F_{trap} \Delta t_{trap}} \right\} \cdot \left\{ \frac{1}{L_{cell}} \right\} \cdot \left\{ \frac{AU^i(\bar{\nu})}{k^i(\bar{\nu})} \right\}^{batch} - \left\{ \frac{F_{VOC}}{F_{amb}} \right\} C_{VOC}^i$$

Concentration of  $i^{th}$  ambient analyte, using batch flow through cryogenic trap, thermally desorbed to gas cell

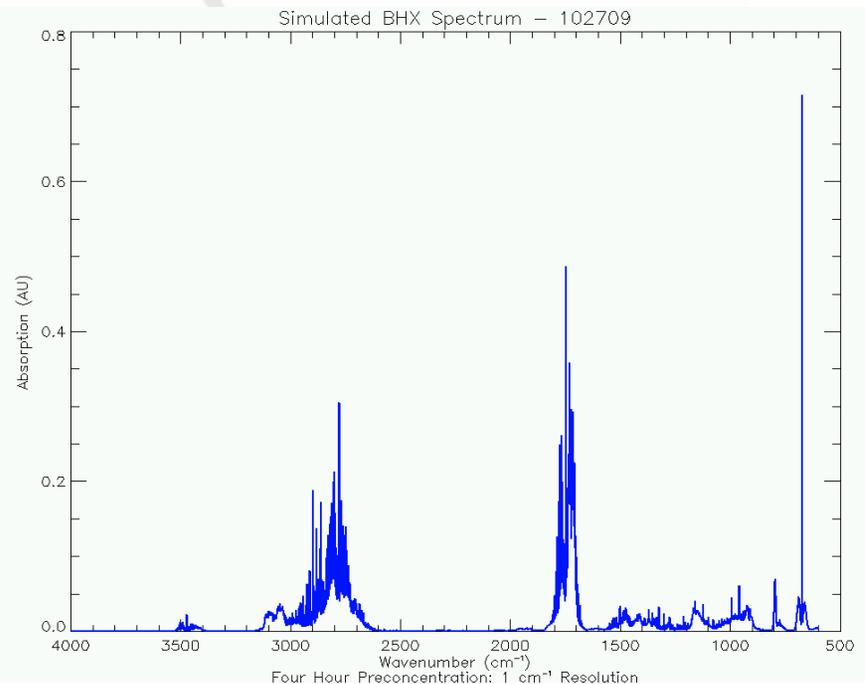
*determined by  
Partial Least Squares  
chemometrics  
same FTIR & gas cell*

$$C_{amb}^i = \left\{ \frac{1 - F_{VOC}/F_{amb}}{1 - F_{dil}/F_{celltot}} \right\} \cdot \left\{ \frac{1}{L_{cell}} \right\} \cdot \left\{ \frac{AU^i(\bar{\nu})}{k^i(\bar{\nu})} \right\}^{cont} - \left\{ \frac{F_{VOC}}{F_{amb}} \right\} C_{VOC}^i$$

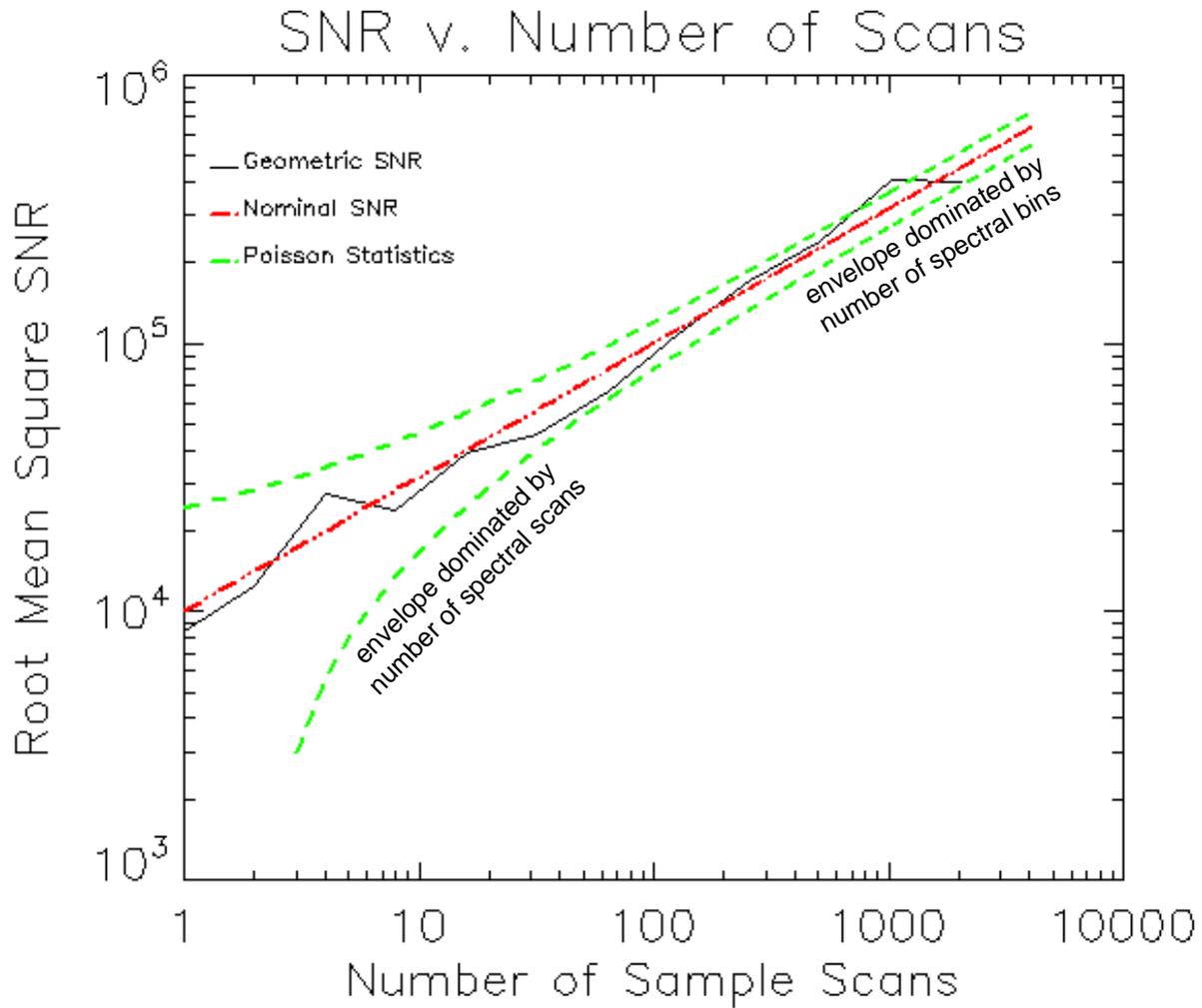
Concentration of  $i^{th}$  ambient analyte using continuous flow through gas cell

## 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 H<sub>2</sub>O & CO<sub>2</sub>
  - Absorption spectra for calibration gas
  - Cryogenic preconcentration efficiency

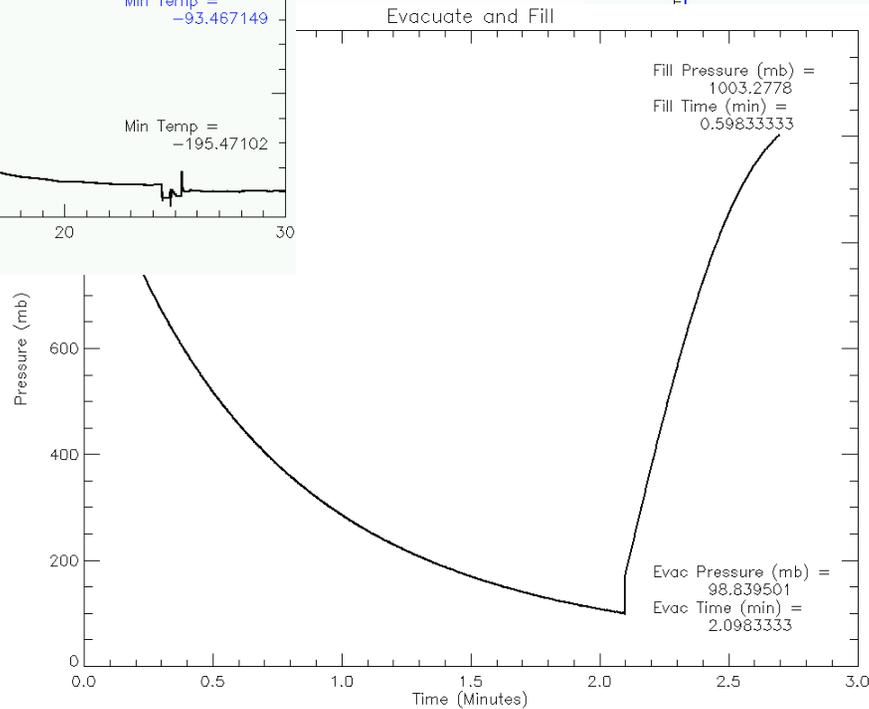
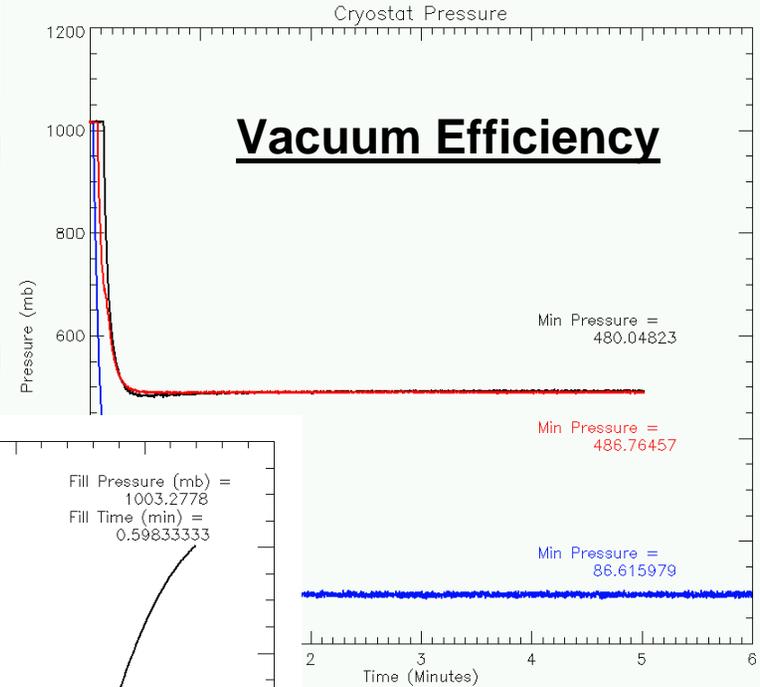
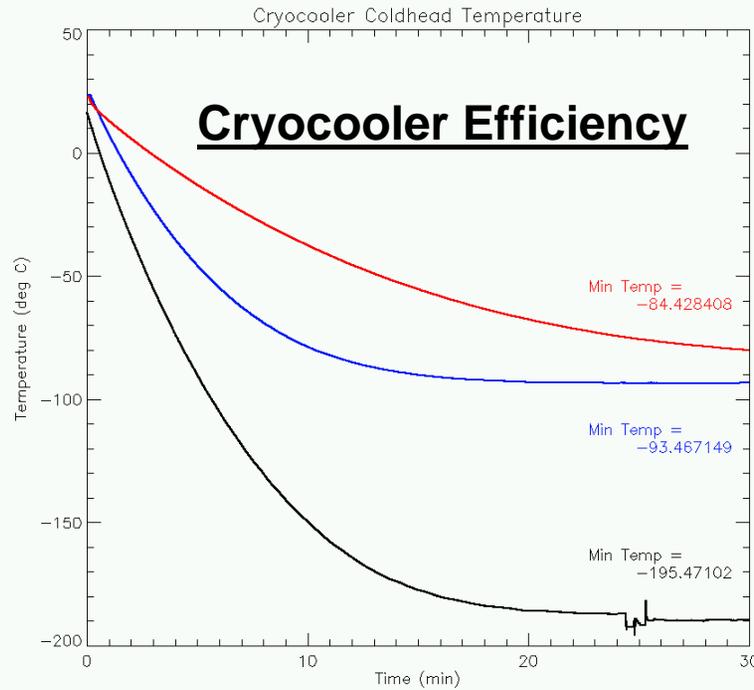


**FTIR Performance**

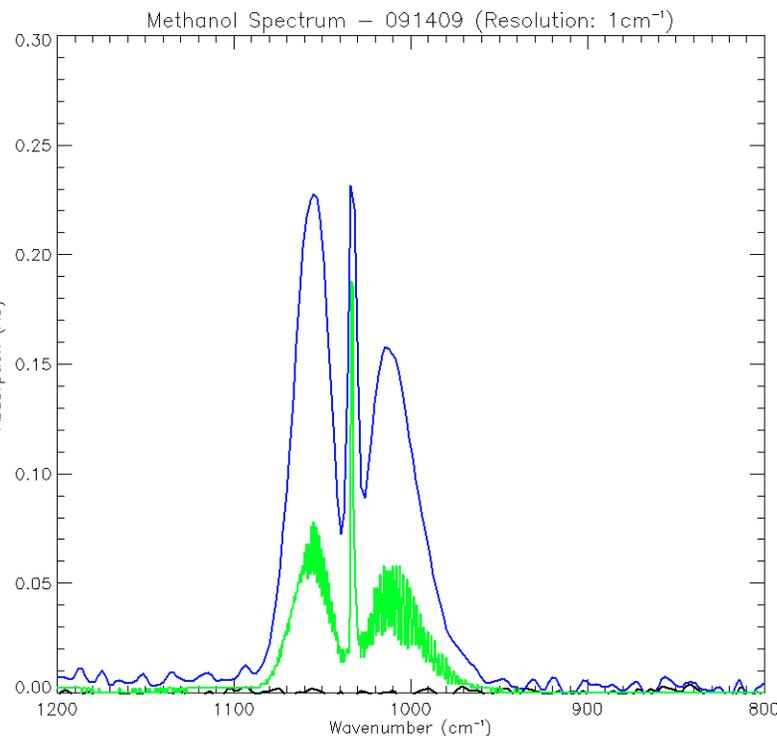
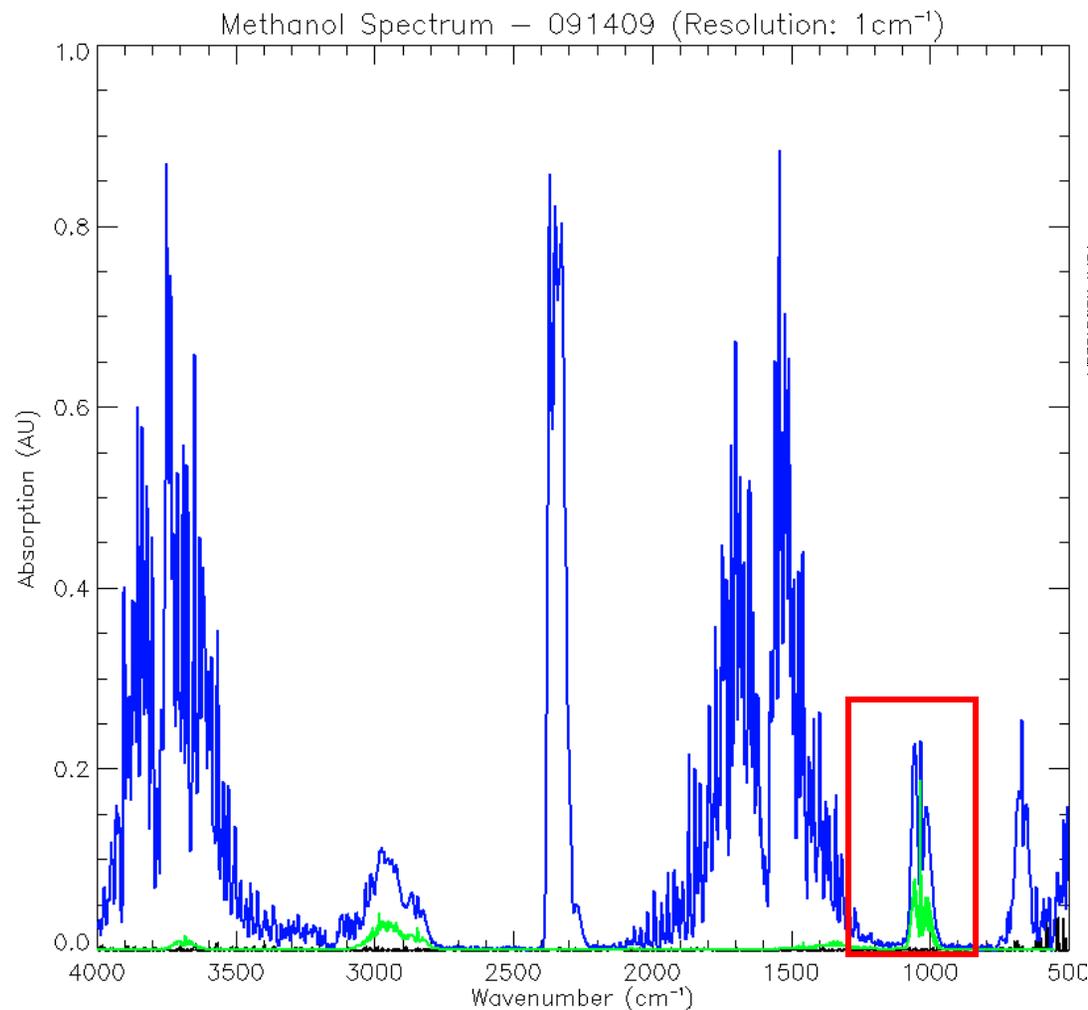


**Nominal SNR should increase with square root of number of scans**  
**Experimental results indicate excellent stability over ~1 hour**

**Subsystem Performance**

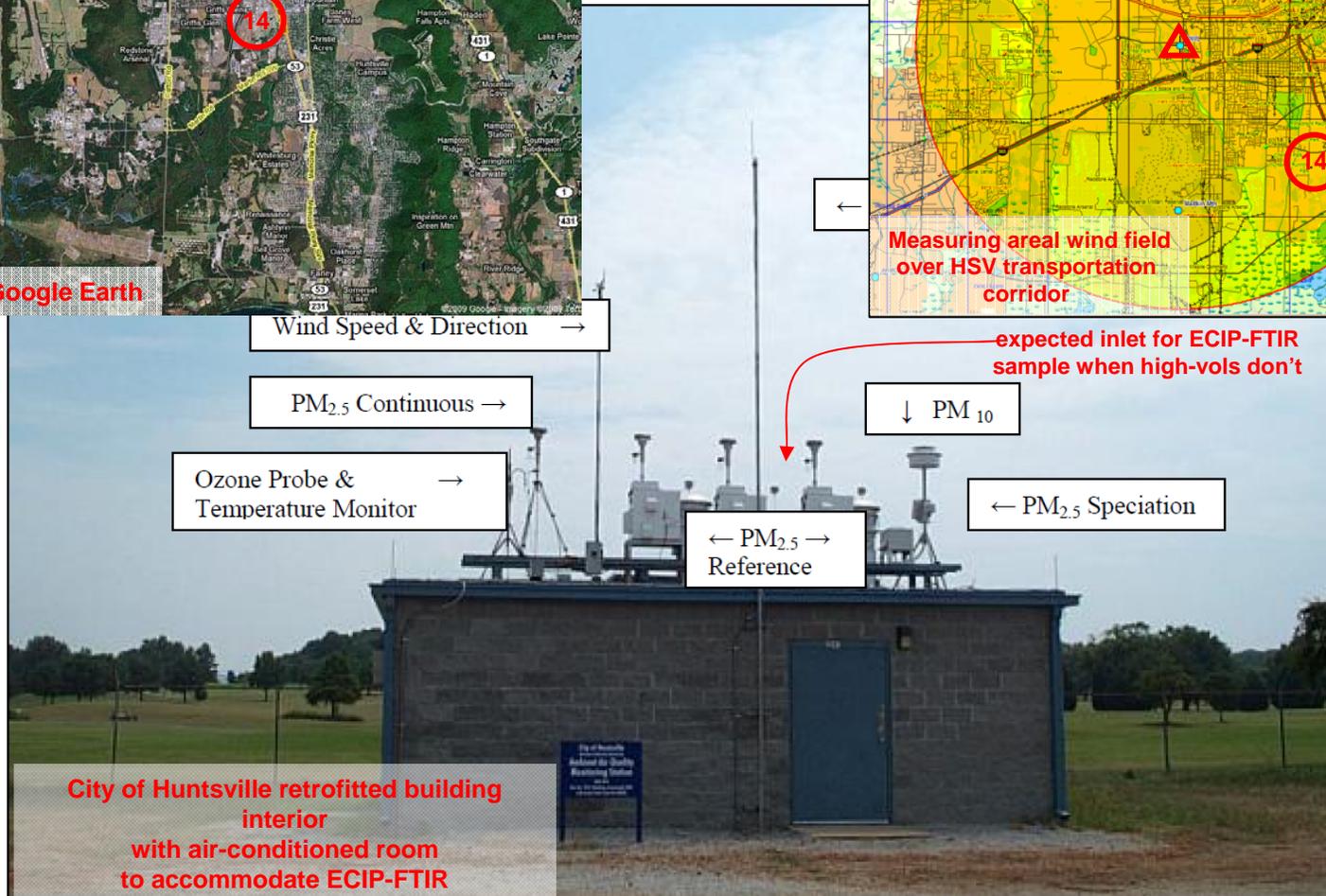
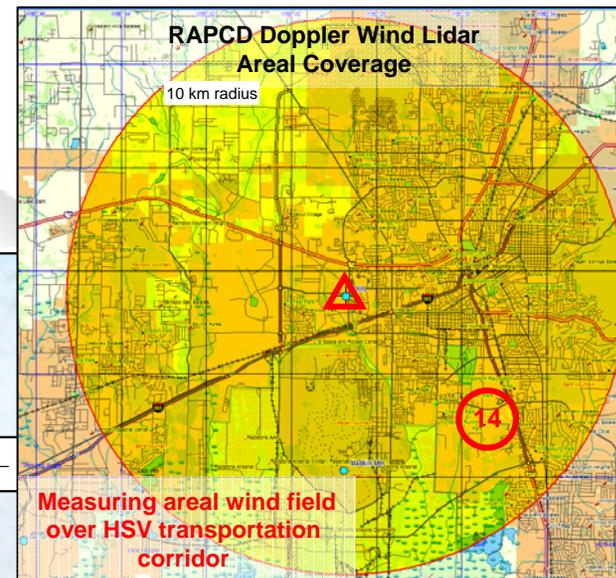


*Preliminary Spectra*

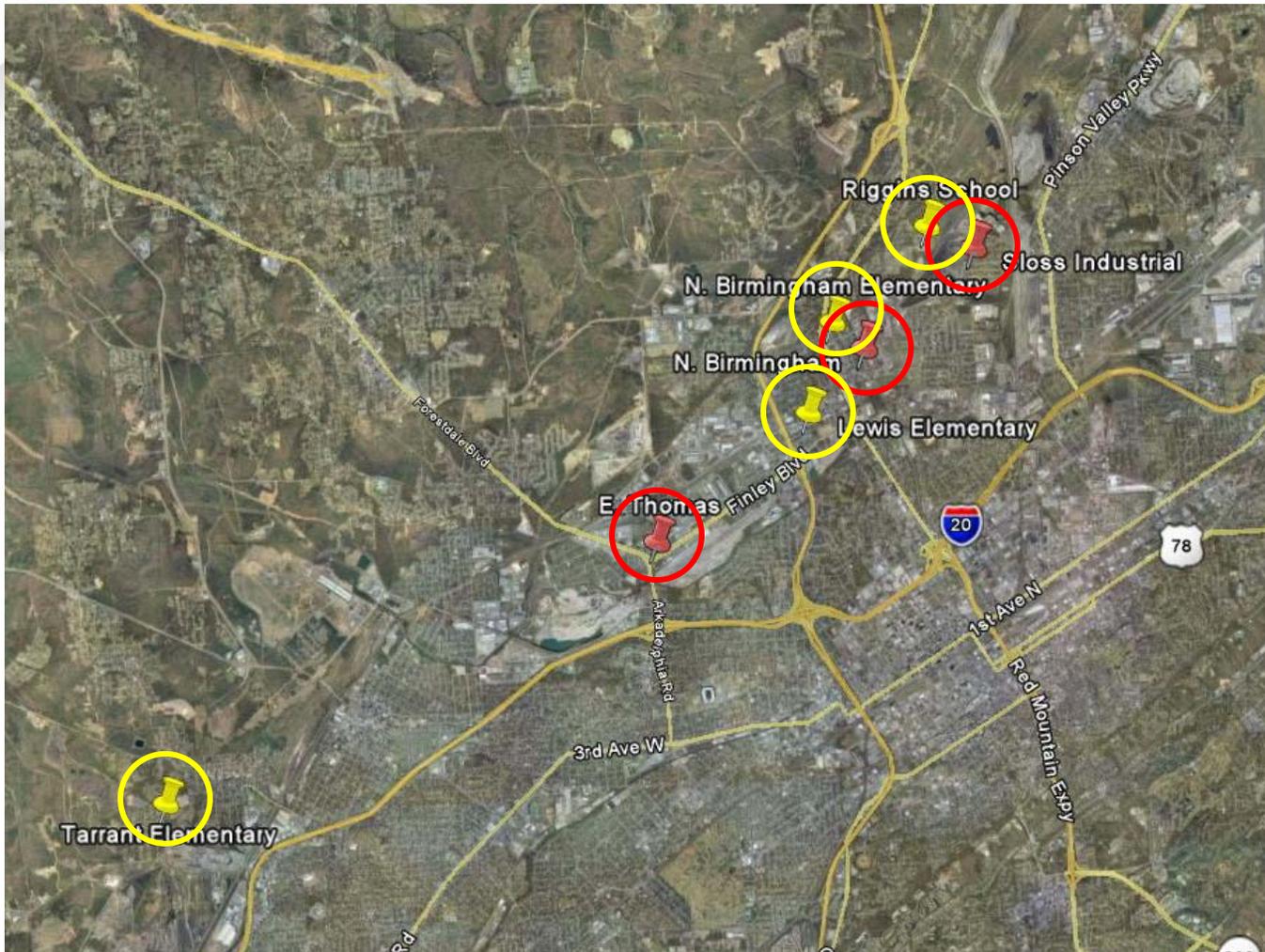


- ***Good spectral resolution***
- ***Good sensitivity***
- ***Multi-compound quantification***

**Future Work - HSV**



## Future Work - BHX



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*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 – GenII Design Improvements*

<b>Mechanical</b>	Smaller, lighter, easier compartment access; Could mount in an SUV or small van
<b>Electrical</b>	Modular integrated DAQ and process control; wireless Ethernet Modular integrated power distribution; lower power consumption
<b>Environmental</b>	Improved isolation from ambient interferents: vibration, EMI/RFI, thermal, and H <sub>2</sub> O/CO <sub>2</sub>
<b>Optical</b>	FTIR: smaller, lighter, field-ruggedized, splash-proof; Gas Cell: larger L/V, faster purge, automated mirror switching
<b>Fluid</b>	Expanded use of modular surface-mount plumbing; Improved QA/QC manifold; additional spike routing options
<b>Traps</b>	Improved thermal design; finer temporal resolution; Better handling of minor gases: H <sub>2</sub> O, CO <sub>2</sub> , and O <sub>3</sub>
<b>Cryocooler</b>	Coldhead: remote umbilical, smaller, more cooling capacity; Power: computer-controlled conditioner / motor controller
<b>Systems</b>	Improved modularity, packaging, and integration; Incorporates many features of pre-production prototype

## Questions / Comments?

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