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Submillimeter Wave Spectroscopy for Real Time Measurements of Carbonyls in Ambient Air

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THE OHIO STATE UNIVERSITY

Battelle
The Business of Innovation

Introduction

- Submillimeter wave (SMMW) spectroscopic gas sensor
  - Developed by Battelle and OSU for DARPA
  - Offers exceptional sensitivity, specificity, and speed
- Adaptable to air pollutant monitoring applications
  - Direct detection of formaldehyde, acrolein, NO_x, SO_x, etc.
  - Simultaneous detection of multiple air pollutants
  - Can reduce reliance on lab-based sample analysis

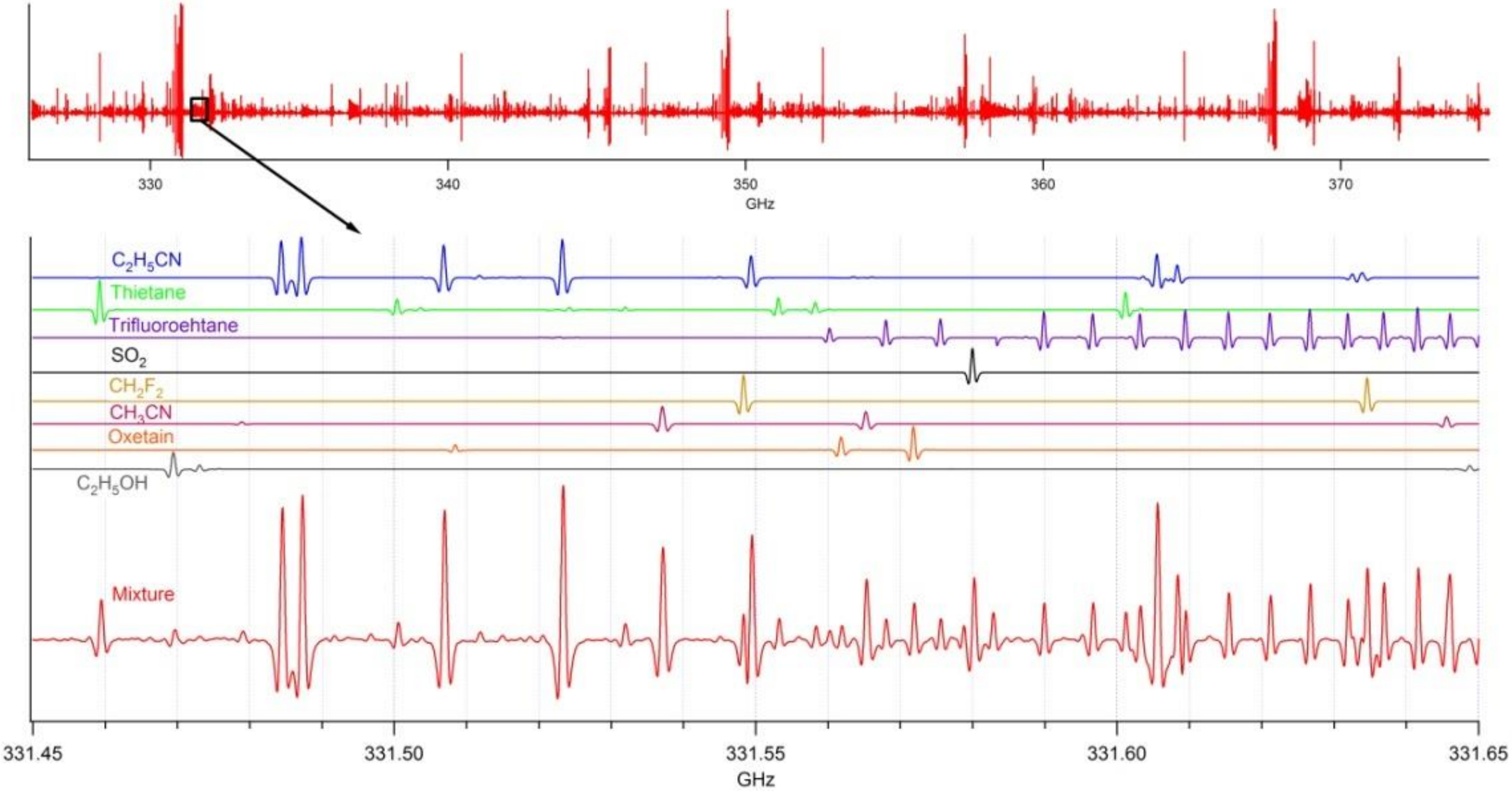
Overview

- Advantages of SMMW spectroscopy
- DARPA MACS sensor
- EPA/OAQPS carbonyl feasibility study
  - Estimate MDL of SMMW spectrometer
  - Investigate MDL gains from preconcentration
- Path forward

SMMW Spectroscopy

- High resolution SMMW spectroscopy exploits molecular rotational transitions
- Uniqueness and redundancy of signatures provide near-absolute specificity
  - Optimal pressure ~10 mTorr - Doppler limit
  - Small number of molecules required for detection
    - Only ~10 mL of ambient air needed to detect formaldehyde at required MDL
- Laboratory SMMW spectroscopy is very mature (50+ years)

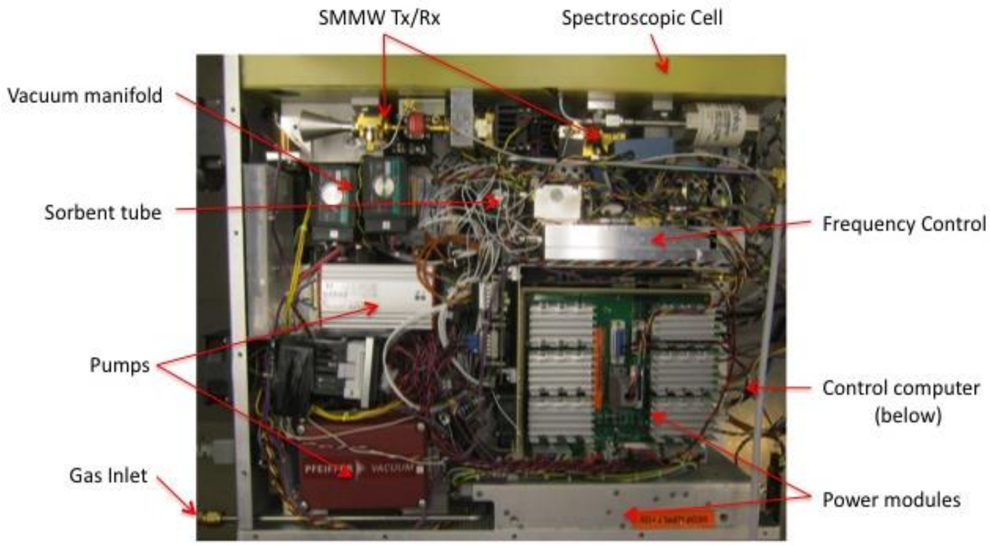
Example Spectra

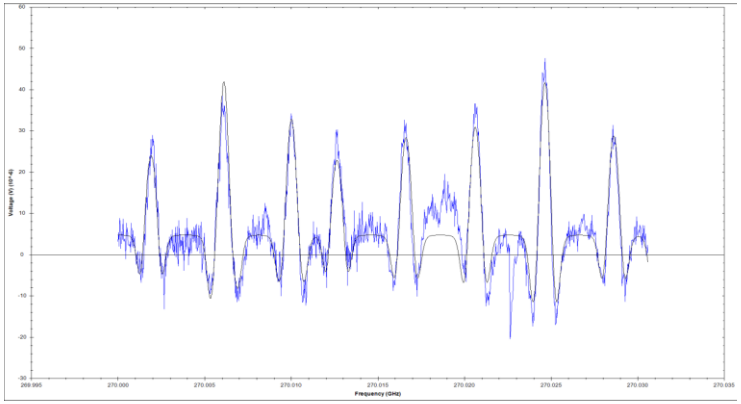


DARPA Mission Adaptable Chemical Sensor (MACS) Program

- SMMW spectroscopy with sorbent preconcentration
- Met or exceeded all DARPA metrics
  - Sensitivity: ~ppt
  - Selectivity: simultaneous detection of 30+ gases
  - False alarm rate: < 10^{-10}
  - Speed: 10 min
  - Size: 1 cubic foot

Neese, et al., *IEEE Sensors Journal* vol. 12, pp. 2565-2574, 2012





Detection of Gaseous Pollutants

- Ability to detect carbonyls, NOx, SOx, etc.
- Simultaneous detection of multiple pollutants
- Sufficient sensitivity for air monitoring (ppb-ppt)
- Near real-time monitoring capability
- Maturation of technology expected to enable development of ~$20k system

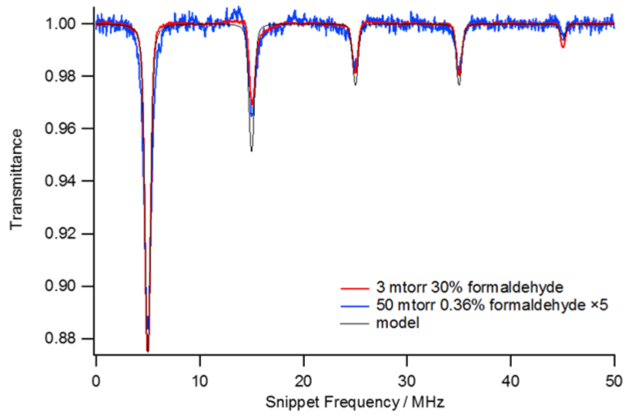
EPA/OAQPS Feasibility Study

- Objective
  - Explore alternative method (SMMW spectroscopy) to detect carbonyls in air
    - Formaldehyde, acrolein, acetaldehyde
- Procedure
  1. Investigate SMMW spectrometer sensitivity (i.e., MDL with no preconcentration)
  2. Investigate sensitivity enhancement via preconcentration to meet ambient air monitoring requirements (sub-ppb sensitivity)

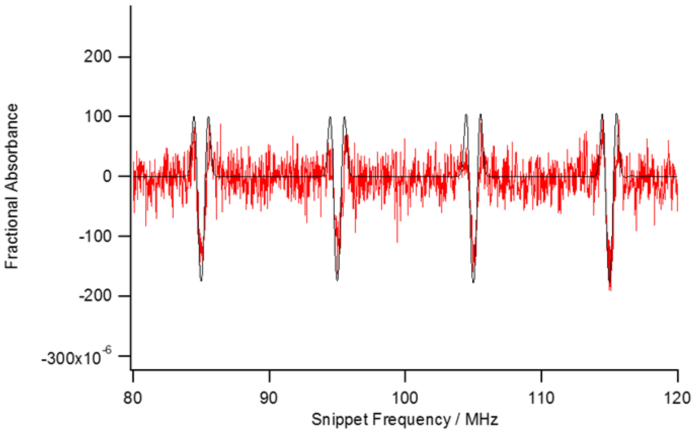
1. SMMW Detection Limits (OSU)

- Estimation of method detection limit (MDL)
  - Standard laboratory-based spectrometer
  - No preconcentration
  - Theoretical calculations
    - *a priori* estimation
  - Experimental measurements
    - Correlate with relevant measurement parameters (resolution, detector sensitivity, cell conditions)

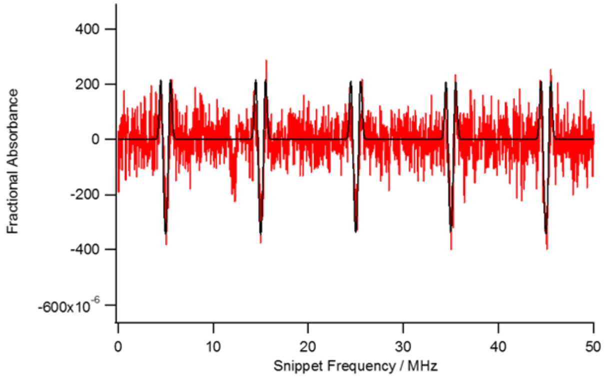
SMMW – Example Spectra



Formaldehyde



Acetaldehyde



Acrolein

SMMW - Results

MDL values in units of ppb

Carbonyl	NATTS MDL MQO	MACS equivalent (0.01 mW, 1 m cell)	MACS with Increased Power (1 mW, 1 m cell)	MACS with Increased Power and Increased cell length (1 mW, 25 m cell)
Formaldehyde	0.065	106	10	0.4
Acetaldehyde	0.25	920	92	4
Acrolein	0.039	570	57	2

- System able to detect 10th percentile concentrations for NATTS
- MDL decreases linearly with increasing cell length
- MDL decreases with square root of increasing power

Detection of carbonyls at ppb concentration is feasible with existing SMMW spectrometer and minor modifications.

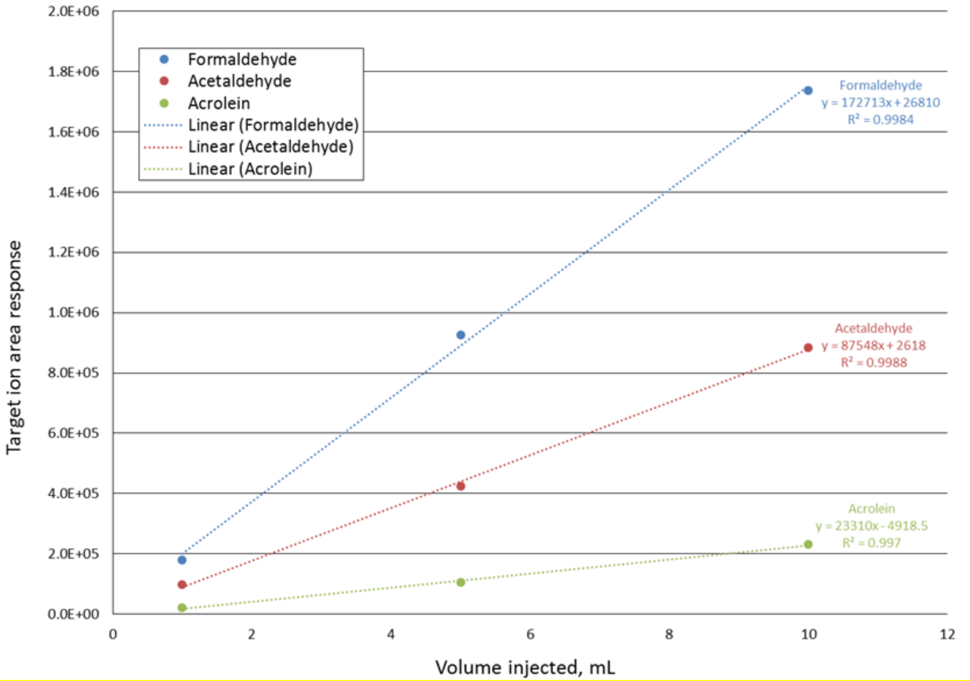
Sub-ppb detection is feasible with longer cell path length (50-100 m) and/or use of preconcentration methods.

2. Preconcentration Study (Battelle)

- Objective: estimate concentration efficiency for each carbonyl
- Procedure
  - Literature search
    - Primary challenge: eliminating water given solubility of target compounds
  - Laboratory methods
    - Commercial gas standard containing all three carbonyls
    - Two sorbents (Tenax TA, Carboxen 1018)
    - Entech 7100 preconcentration system
    - Agilent 6890/5973 GC/MS

Preconcentration – Results

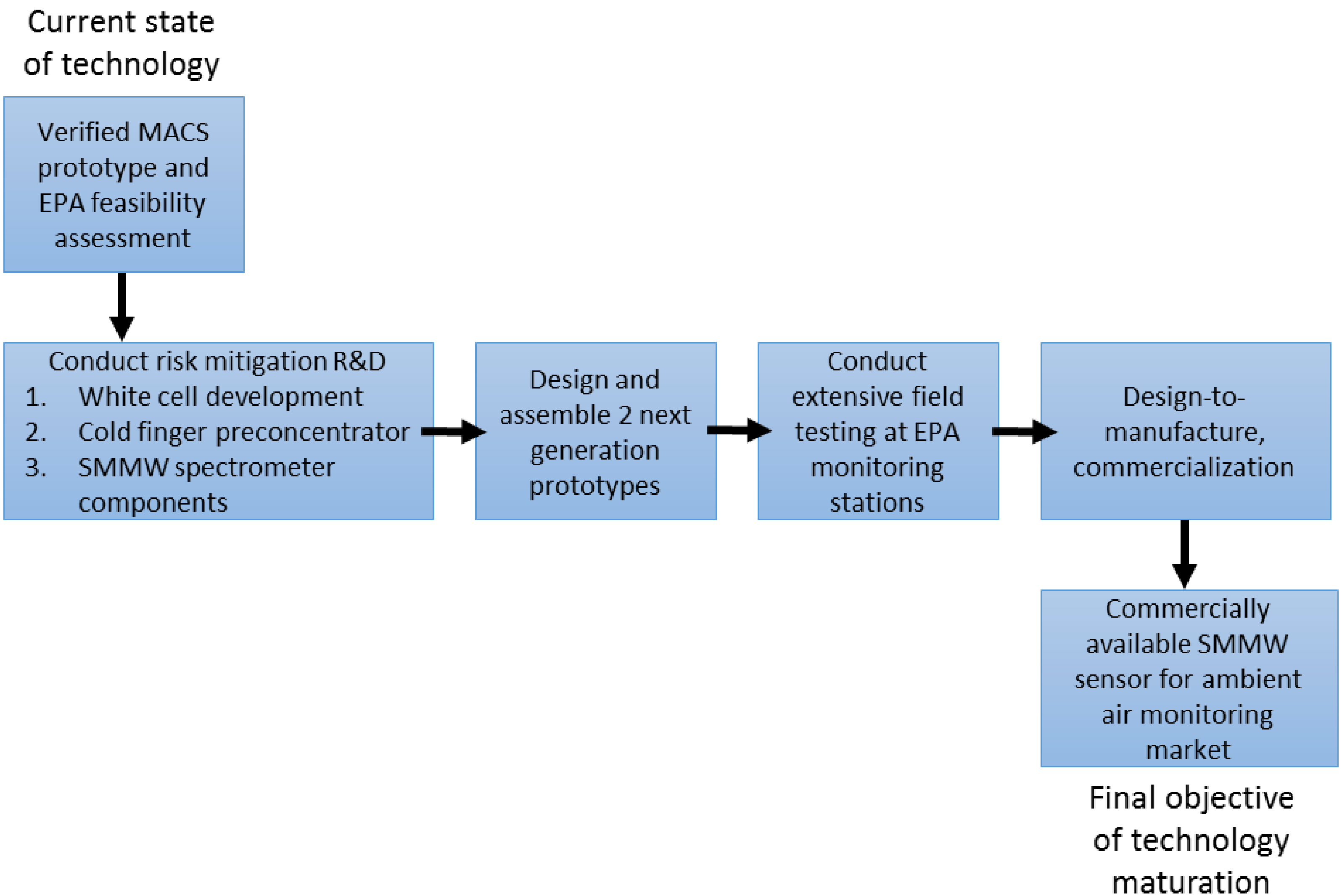
- Tenax TA would not retain formaldehyde and acetaldehyde unless cooled
- Carboxen 1018 retained all carbonyls
  - **Selection factors >200** (vs. N_2, O_2, Ar)
- Some issues with leaks in Entech system, poor water management



EPA Study Conclusions

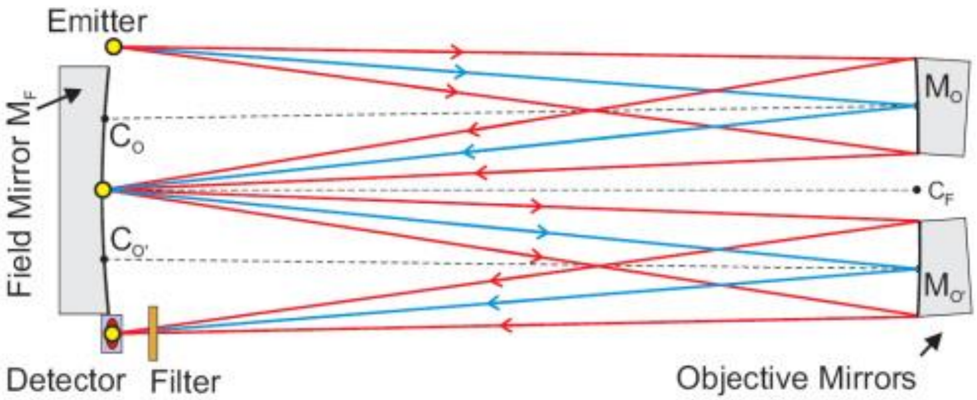
- SMMW sensor based on MACS system can detect carbonyls at ppb level
- Additional preconcentration expected to gain at least a factor of 200 to enable sub-ppb detection
- Very small volume of air needed to achieve high sensitivity
  - 10 mL ambient air sufficient to meet NATTS MDL requirement assuming co-collected gases can be removed

Sensor Development Roadmap



SMMW White Cell Development

- Objective: maximize SMMW sensitivity by increasing optical path length
- Plan: explore multi-pass cells (also known as "White cells")
  - Conduct bench experiments to address potential diffraction issues
  - Design and assemble "White cell"
  - Integrate, align, and characterize cell performance



Cold Trap Preconcentration

- Objective: Explore elimination of sorbent-based preconcentration
- Plan: increase SMMW sensitivity via cold finger trap preconcentration
  - Prepare target analytes, measure baseline response of TD-GC/MS
  - Design and assemble cold trap packed with glass beads and held at -10C by use of Peltier (thermoelectric) cooling
  - Characterize concentration factor of cold trap system
  - If additional sensitivity is needed, assess performance of Carboxen 1018 sorbent trap
  - Assess adequacy of cold trap system in context of SMMW sensitivity gains from White Cell and MDL requirements for ambient air monitoring

SMMW Component Cost Reduction

- OSU continuing to monitor development of SMMW enabling technologies in telecomm industry
  - Current MACS technology uses robust commercial MMW multipliers and amplifiers that cost ~$70K
  - Advances in wireless communications technology moving toward chip-level devices that can produce 100 GHz and cost ~$100
  - Leveraging advances in CMOS technology funded by Semiconductor Research Corp
  - Following advancements at IBM to extend current Tx/Rx of 60 GHz to ~240 GHz

Conclusion

- SMMW sensor can detect multiple air pollutants simultaneously in near real-time
- Concept proven by meeting performance metrics on DARPA MACS program
- SMMW can provide real-time ambient air monitoring capability for various carbonyls at sub-ppb concentrations
- Development of ruggedized, autonomous, inexpensive sensor is feasible
- Immediate applicability at 27 NATTS and proposed 40 Core PAMS sites nationwide