Assessing the Feasibility of Measuring Carbonyls in Ambient Air with a Submillimeter Wave Spectroscopic Sensor
Introduction

• Submillimeter wave (SMMW) spectroscopic gas sensor
  ▪ Developed by Battelle and OSU for DARPA
  ▪ Offers significant gains in sensitivity, selectivity, and speed

• Adaptable to air pollutant monitoring applications
  ▪ Direct detection of formaldehyde, acrolein, NO₂, etc.
  ▪ Simultaneous detection of multiple criteria pollutants
  ▪ Reduced reliance on lab-based sample analysis
Overview

• Advantages of SMMW spectroscopy
• DARPA MACS sensor
• Relevance to gaseous pollutant detection
• EPA/OAQPS feasibility study
• Path forward, technology development roadmap
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

• Laboratory SMMW spectroscopy is very mature (50+ years)
Example Spectra
Advantages of SMMW Sensor

• Technology now available for small (1 ft$^3$) system (100-600 GHz)
• Potential for very high sensitivity (ppt) if incorporate preconcentration
• Very high specificity → Low false alarm rate
• Fast measurement and analysis (sec to min)
• Broad range of target analytes

Disadvantages of SMMW Sensor

• System cost currently high for pollution monitoring applications (> $100k)
  ▪ Continued tech development will drive down cost

• Dipole moment required

• Difficult to detect large/complex molecules
  ▪ Additional research required to incorporate alternative techniques

• Some smaller molecules (NH$_3$, HF, etc.) require high frequency sources (600 GHz)
DARPA Mission Adaptable Chemical Sensor (MACS) Program

- 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
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
Formaldehyde

Spectral data from NASA JPL catalog:
http://spec.jpl.nasa.gov/
Acrolein
EPA/OAQPS Feasibility Study

• Objective
  ▪ Investigation of SMMW detection limits for target air toxic compounds (formaldehyde, acrolein, acetaldehyde)
  ▪ Investigation of preconcentration to enhance the sensitivity of the SMMW sensor for ambient air measurements
SMMW Detection Limits (OSU)

• Test planning
• Spectroscopic measurement of three carbonyls: formaldehyde, acrolein, and acetaldehyde
  ▪ Standard spectrometer
  ▪ Neat and diluted samples
• Estimation of method detection limit (MDL)
  ▪ Assume no preconcentration
  ▪ Correlate with relevant measurement parameters (resolution, detector sensitivity, cell conditions)
Preconcentration Study (Battelle)

- Literature search on preconcentration approaches for carbonyls
- Laboratory characterization of two approaches
  - Based on MACS sorbent characterization effort
  - Standard GC/MS methods
- Concentration efficiency estimation for each identified approach
- Estimation of overall SMMW MDL (spectra + preconcentration)
Status

• Test planning complete (draft QAPP)
• Theoretical calculations of SMMW sensitivity underway
• Literature search for preconc methods complete
  ▪ Cryotrap
  ▪ Semipermeable membranes
  ▪ Carbon Nano Tubes (CNTs), functionalized and non-functionalized
  ▪ Functionalized silicas
  ▪ Sorbents (traditional, emerging, non-traditional)
Future Technology R&D

• Spectrometer cost reduction and miniaturization
  ▪ 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
Sensor Development Roadmap

Current MACS prototype

- Ruggedized SMMW sensor based on MACS (minor optimization)

Continuing R&D activities

- Next generation enabling technology
  - Chip level MW
  - Custom pumps

- Expand large molecule limit
  - Stark modulation
  - Cavity techniques

- Expand spectral library content and optimize sorbent / spectroscopy interplay

Mission-specific miniaturized SMMW sensor (major re-engineering effort)

Field testing

Technology transition

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Conclusion

• SMMW sensor provides flexibility to detect multiple air pollutants simultaneously in near real-time

• Concept proven by meeting performance metrics on DARPA MACS program

• Development of ruggedized, autonomous, inexpensive sensor is feasible

• Can broaden scope of air monitoring, fill gaps in continuous monitoring of formaldehyde and acrolein, offer direct NO$_2$ detection, and reduce lab-based sample analysis costs