Solid State Mixed-Potential Electrochemical Sensors for Natural Gas Leak Detection and Quality Control

FE0031864

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University of New Mexico, Center for Micro-Engineered Materials

CENTER FOR MICRO-ENGINEERED MATERIALS

SENSORCOMM TECHNOLOGIES

U.S. Department of Energy

National Energy Technology Laboratory

Resource Sustainability Project Review Meeting

October 25 - 27, 2022

Project Overview

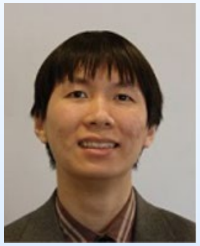
- Funding - DoE FECM.
  - Gov’t Share: $1,498,217
  - Cost Share: $374,555
  - Total: $1,872,772
- Project Performance Dates: 4/1/2020 to 3/31/2023
- Project Participants:
  - University of New Mexico, Center for Micro-Engineered Materials
  - SensorComm Technologies, Inc.
- Overall Project Objectives:

  Development of a portable, field-deployable sensor system for the identification and quantification of natural gas emissions.

Project Team

CENTER FOR MICRO-ENGINEERED MATERIALS

SCT SENSORCOMM TECHNOLOGIES



Lok-kun Tsui (PI)

Research Assoc. Professor (UNM CMEM and CBE)

Fernando Garzon (Co-PI)

Distinguished Professor (UNM CBE) Center Director (UNM CMEM and CBE)

Kannan Ramaiyan

Research Assoc. Professor (UNM CMEM)

Sleight Halley

Graduate Student (UNM CBE + CMEM)

Kamil Agi

President and CEO (SCT), Research Associate Professor (UNM ECE)

Robert Ian

Innovation and Marketing Director (SCT)

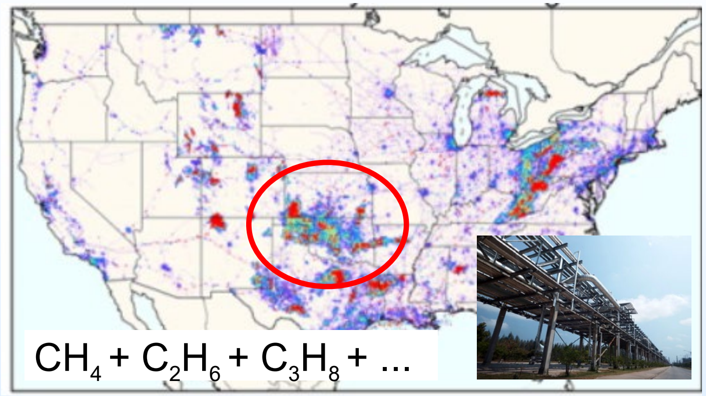
James Smith

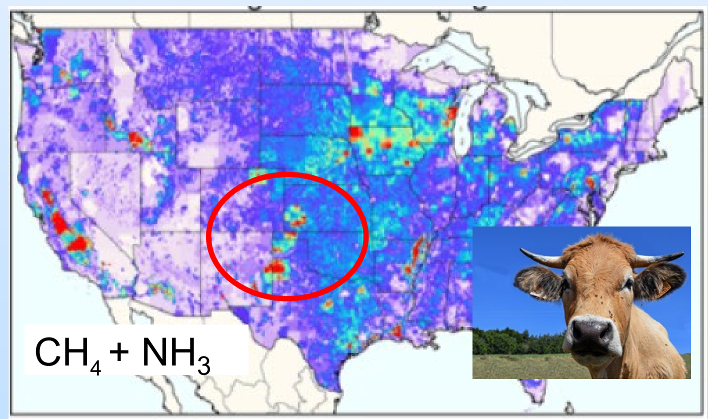
Senior Engineer (SCT)

Motivation

Cost of natural gas leaks

- Economic Cost of Methane Leaks: $ 2 billion dollars per year[1]
- Environmental - CH_4 is a potent greenhouse gas
  - Global warming potential of over 100 years is 28x that of CO_2 (CO2e)[2]
  - Degrades quickly in atmosphere (half life ~ 10 years)[3]
  - Limiting CH_4 emissions could have significant effect on short term climate change
- System Requirements:
  - Robust Field Deployment.
  - Distinguish between natural gas and other man-made and/or naturally occurring methane sources.
  - Limit of detection in the 10-100ppm range for surface level monitoring of buried pipelines – early warning system.



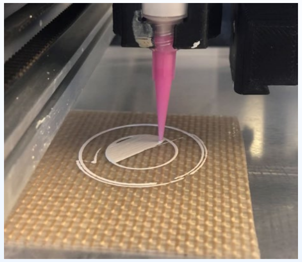


Figures from Maasakkers[4]

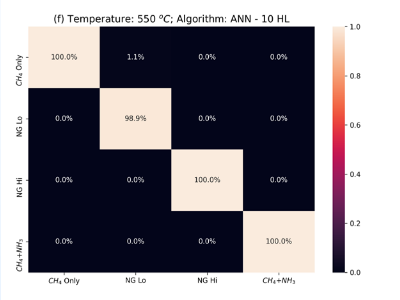
[1] "A.J. Marchese, *et al*. Science. 7204 (2018) eaar7204.
[2] "Global Methane Initiative." https://www.globalmethane.org/ (accessed Mar. 04, 2022).
[3] V. Masson-Delmotte *et al*., Eds., *Climate Change 2021: The Physical Science Basis. on Climate Change*. Cambridge University Press, 2021.
[4] J.D. Maasakkers, et al., Environ. Sci. Technol. 50 (2016) 13123–13133.

Technical Approach & Project Scope

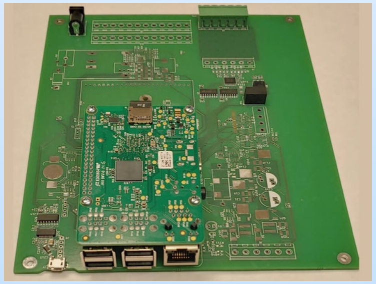
Sensor Additive Manufacturing and Testing
Develop AM methods to prototype sensor materials and designs to achieve 10’s of ppm LoD for natural gas.



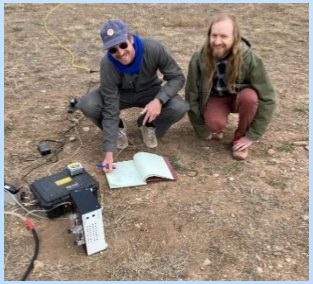
Machine Learning for NG ID and Quantification
Develop field deployable ML methods to identify natural gas and quantify methane concentrations. Target accuracy > 97%.



IoT Technology
Develop IoT platform to record, process, and wirelessly transmit sensor data in a portable package for additional post processing of the data and early warning capability.

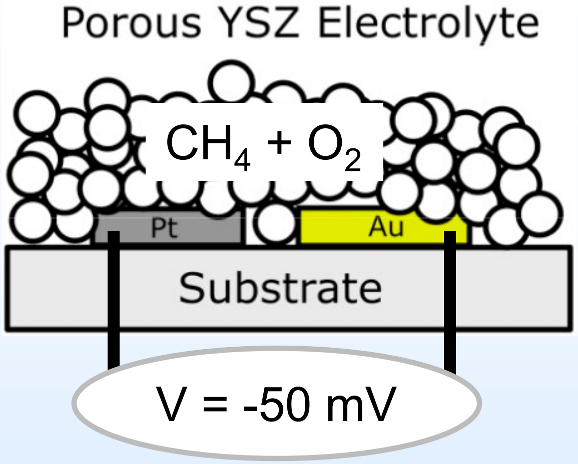


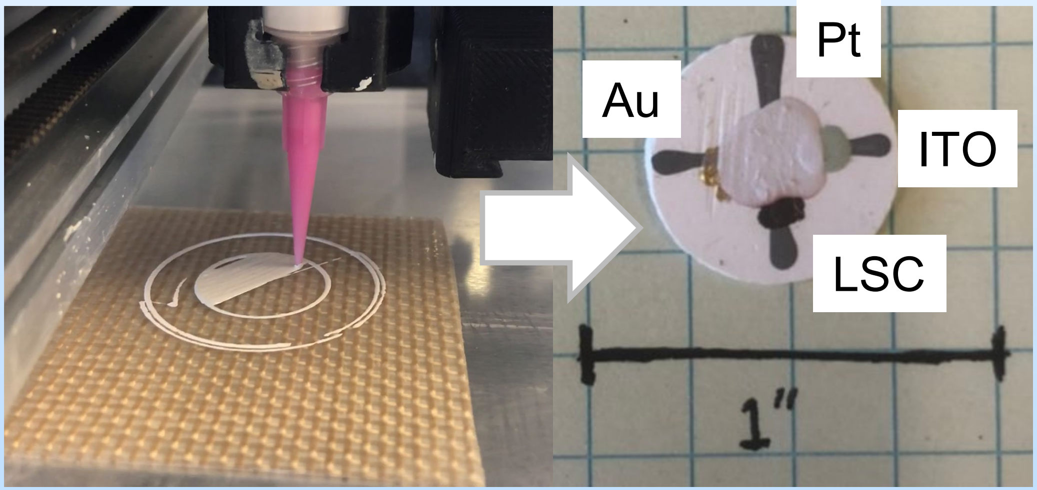
Field Testing
Demonstrate we can detect emissions in real world conditions in a field test.



Mixed Potential Sensors

- **Composition** – Multiple electrodes with different materials embedded in a solid electrolyte.
- **Operating Principle** – Solid state electrochemical device generates difference in catalytic activity between electrodes upon gas exposure generates a voltage.
- **Multi-element array configuration** - CH_4, Heavy HCs, NH_3/H_2.
- Prototyped with ceramic AM at 10s of devices scale.
- Clear transition path to mass production.





Ceramic Additive Manufacturing

Completed Sensor

Technology Comparison

Competing Technologies

Satellites and Aircraft
- Surveys wide areas, but with low spatial resolution
- Very expensive
- Cannot do real-time, continuous monitoring

Optical IR Instruments
- CRDS / IR Spectroscopy / NDIR / Photoacoustic
- High resolution – ppb-ppm CH4
- Limited speciation.
- Need to keep cavities clean.

Semiconductor Sensors
- Sensitive to wide range of species with ppm level resolution.
- Sensor drift is an unsolved problem with SC sensors.

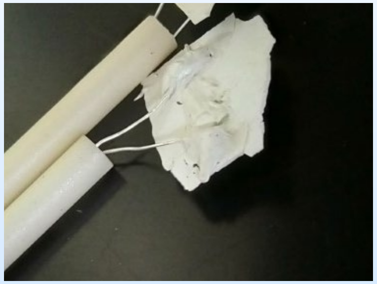
Our Technology
- Mixed potential sensors are sensitive to gases of interest at 10-10000 ppm range.
- Low cost, robust, field deployable.
- Clear transition path to mass production: ceramic manufacturing methods.
- Broad speciation: CH_4, C_2H_6, C_3H_8, NO_x, NH_3, H_2

Our Challenges
- Develop AM processes to prototype these devices
- Develop and integrate ML methods with high accuracy
- Integrate UNM's sensor technology with SCT's IoT platform.

PROJECT PROGRESS SINCE 2021

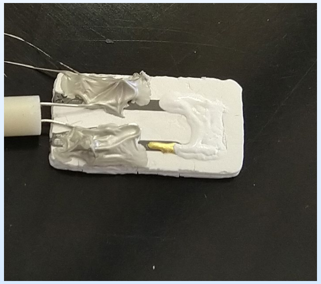
Sensor Evolution (2020 to Present)

2020 Spring



Hand Prepared

2020 Summer

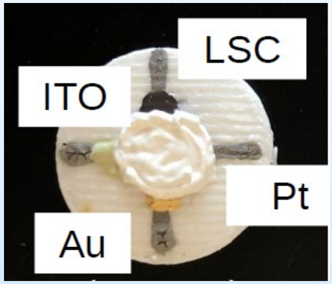


3D Printed

2020 Fall

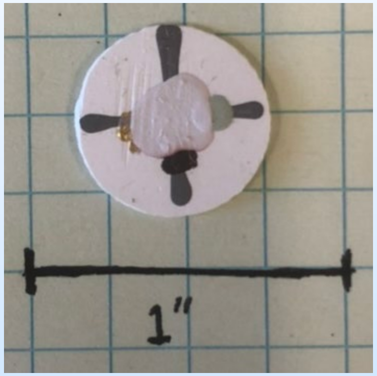
Multi Electrode

2021 Spring



Geometry Refinement

2021 Fall – Present

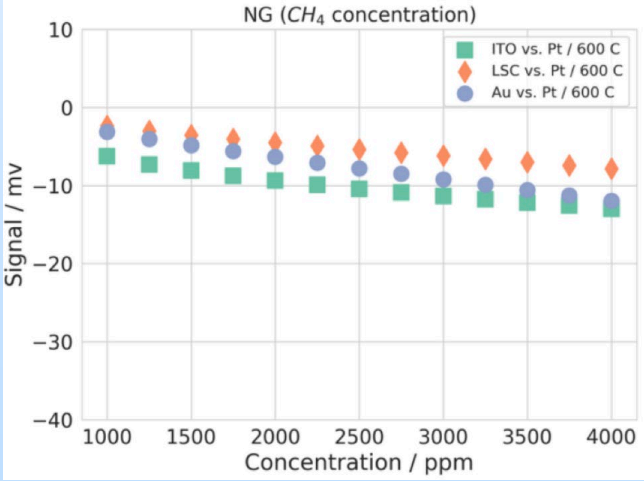


Enhanced Sensitivity

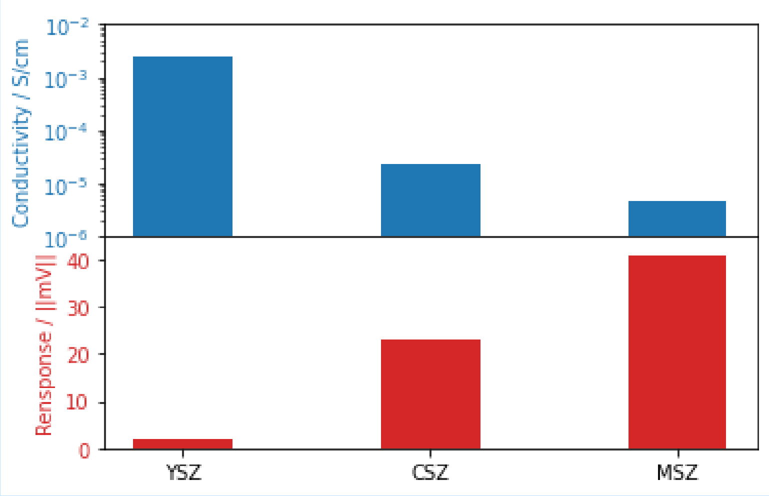
Generation 5 Sensor

Additive Manufacturing – New Generation Sensors

- Previous work achieved < 1000 ppm limit of detection using yttria-stabilized zirconia (YSZ) substrates.
- Desired signals >1 mV for reliable signal-to-noise background on IoT platforms.
- We developed a process with magnesia- (MSZ) and ceria-stabilized zirconia (CSZ) that enhanced the mixed potential signal by providing better ionic isolation of the electrodes.
- Demonstrated a 20x enhancement in sensitivity. Would like 10-100 ppm sensitivity for buried pipeline measurements.



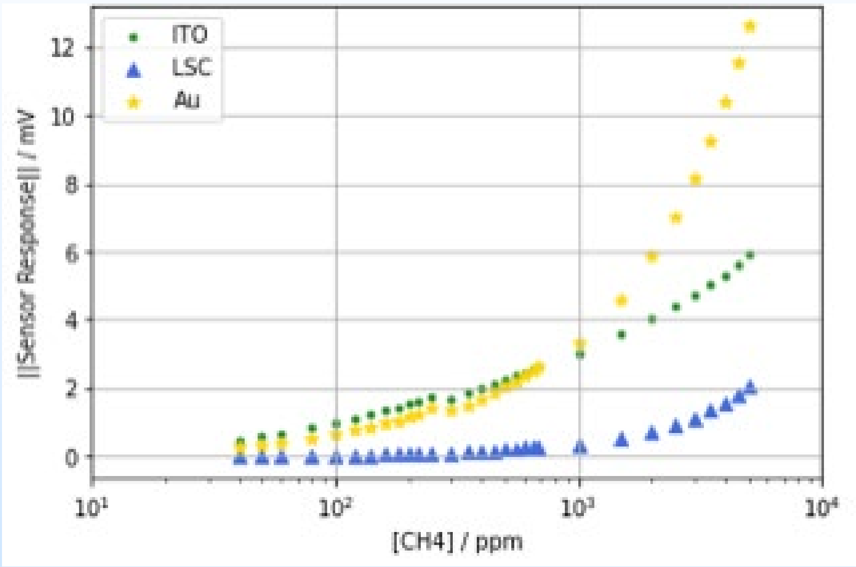
Previous Effort – YSZ Substrate



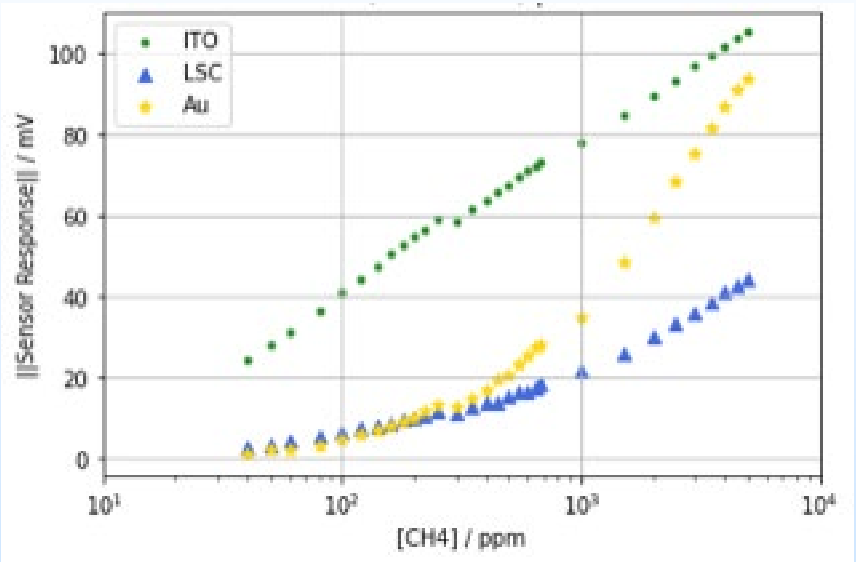
Response to 100 ppm CH_4 in Natural Gas

Enhanced Limit of Detection (LOD)

YSZ Substrate Sensor



MSZ Substrate Sensor

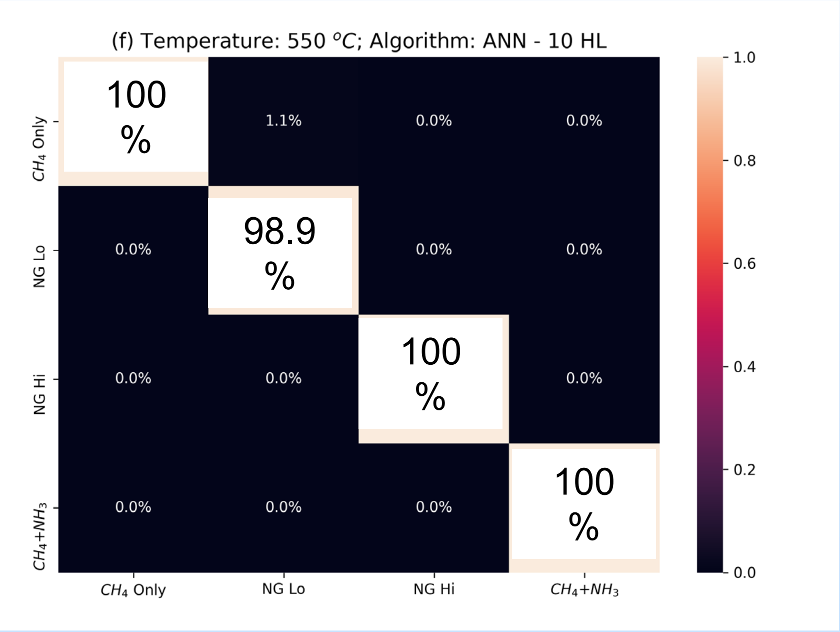


- 40-5000 ppm CH_4 equivalent NG at 550 C was tested with E:M ratio of 0.19
- Sensor response of ITO vs. Pt was linear in log(concentration).
- MSZ substrate-based sensor has >1 mV response on sensor signals.
- LOD likely to be on order of 10 ppm.

Machine Learning – Mixture ID

- Task – Distinguish between 4 mixes:
  - CH4 in air
  - Natural Gas – Low Ethane (E:M = 0.02 – 0.05)
  - Natural Gas – Hi Ethane (E:M = 0.19-0.27)
  - CH_4 + NH_3 – Agriculture
- CH_4 content: 300-2500 ppm
- ANN's showed > 98% identification accuracy which meets target milestone accuracy metrics.

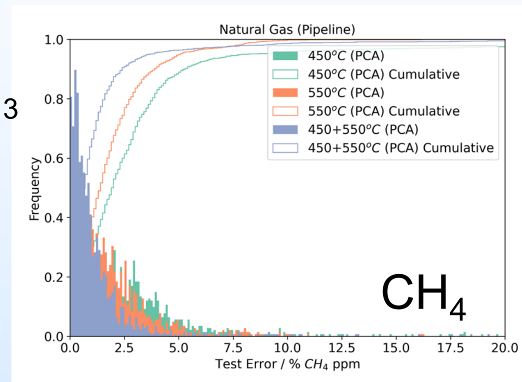
Predicted Labels

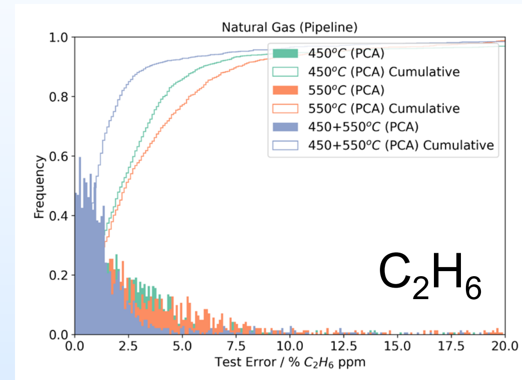


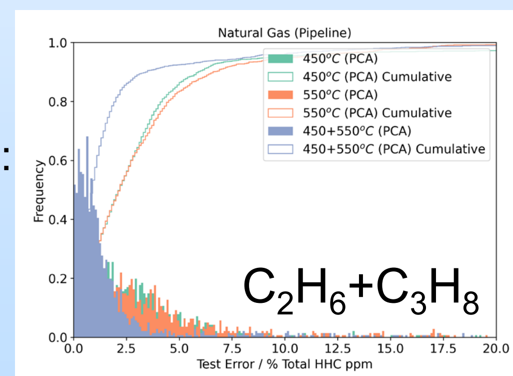
Real Labels

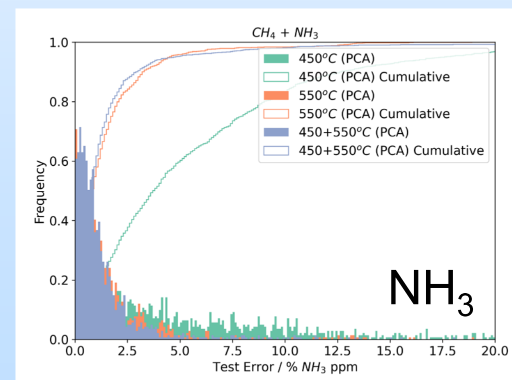
Machine Learning – Quantification

- Quantification was performed for CH_4 in two different natural gas mixtures, CH_4 in air, and CH_4 + NH_3 in 300-2500 ppm CH_4.
- Optimized ANN architecture together with a 10-neuron hidden layer artificial neural networks was found to have the best accuracy.
- **Concentration (ppm) error at 2.5% (~80-90% of test data) milestone target.**
- Demonstrated capability for quantification of secondary species: C_2H_6, total heavy hydrocarbon (C_2H_6+C_3H_8), and NH_3.
- Lower computational-cost methods for identification and quantification under investigation for better integration with IoT platforms.





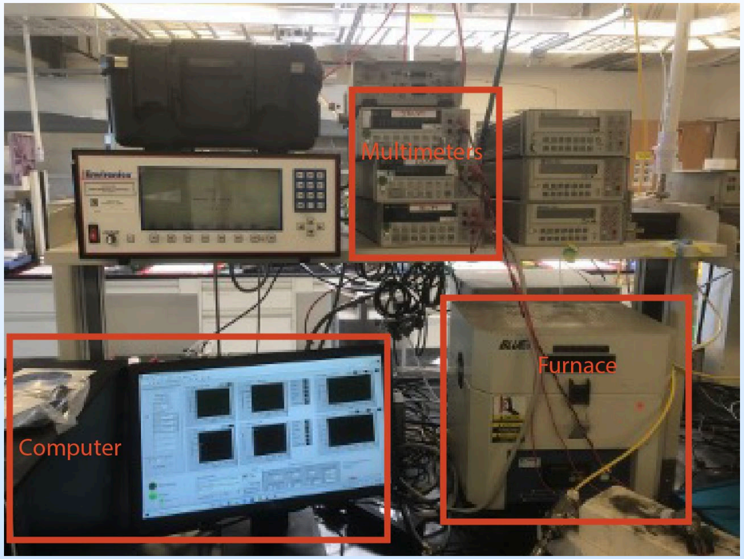




Natural Gas – C_2H_6:CH_4 = 0.04

System Portability Development

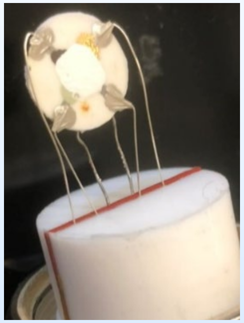
2021



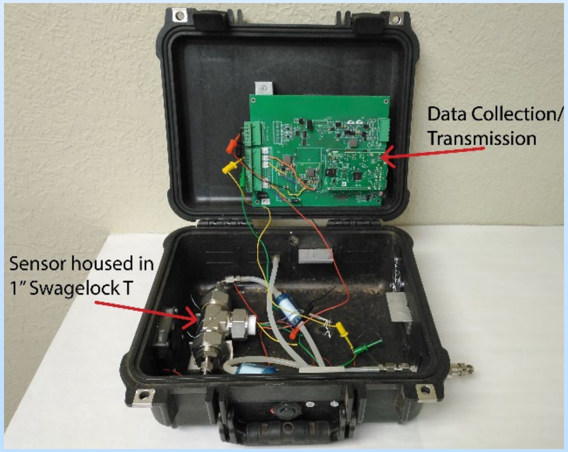
Computer, Furnace, Digital Multimeters.

Power requirements: ~ 1 kW.

2022



Sensor with portable ceramic disk heater

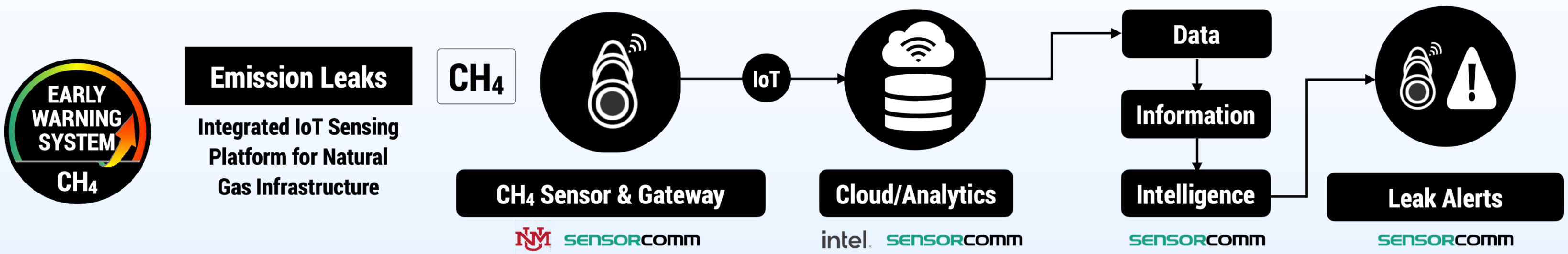


IoT data acquisition system (SCT)

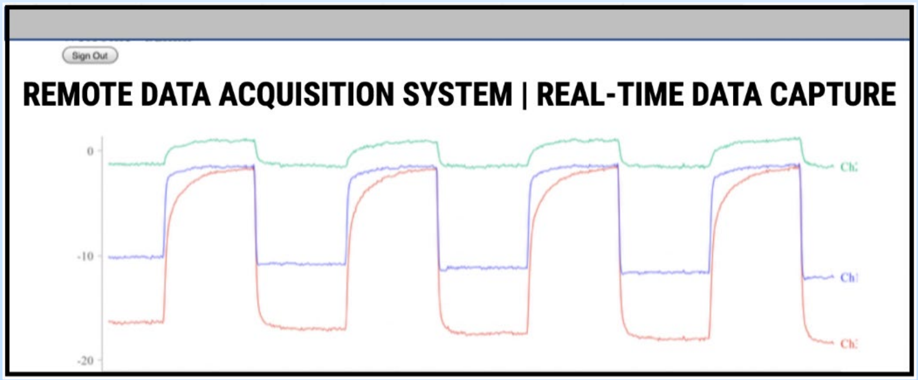
Portable System

Power Requirements ~10's W

IoT Development – SCT



Identifies real-time presence of methane gas. Differentiates livestock, wetland and natural gas infrastructure. Provides analytics for emission leak alerts (early warning system).



Remote Online Dashboard

GOAL: Development of integrated read-out electronics and IoT capability

Key Research Topics:

- Effects of sampling rates
- Noise performance
- Development of read-out electronics
- Integration with IoT capability
- Early warning capability

IoT Development – SCT

1. EVALUATED

Evaluated SCT Prototype Hardware

2. UPGRADED

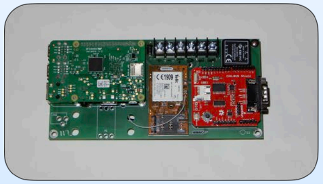
Upgraded Cloud-Based Architecture

3. INTEGRATED

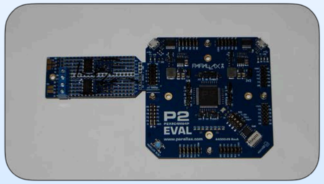
Integrated Readout Electronics with IoT System in Supply Chain Restricted Environment

4. VALIDATED

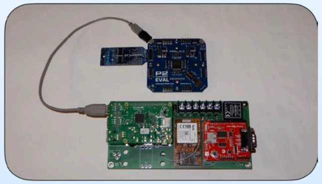
Validated Commercial Need for Early-Warning System Through Customer Discovery



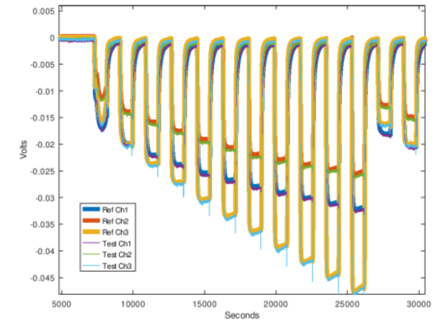
IoT Gateway



Readout Prototype

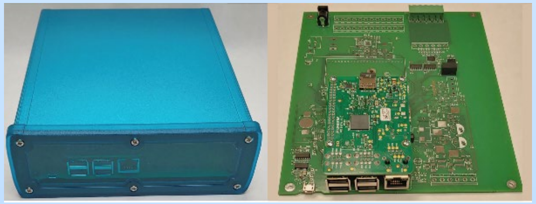


Integrated Prototype

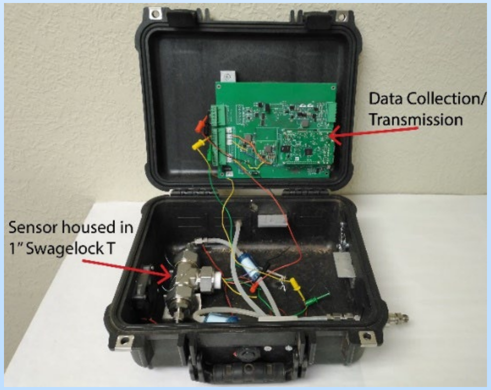


Ref Ch = HP 3478A Multimeter | Test Ch = SCT Prototype

Compare Sequence



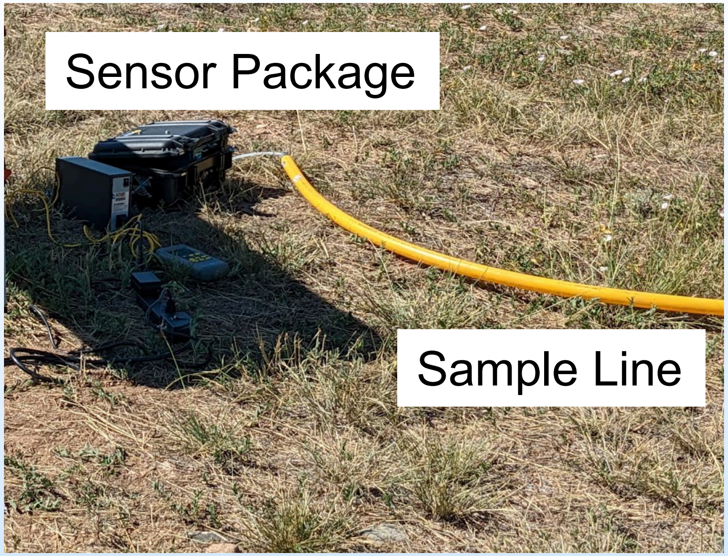
Single Board IoT and readout electronics

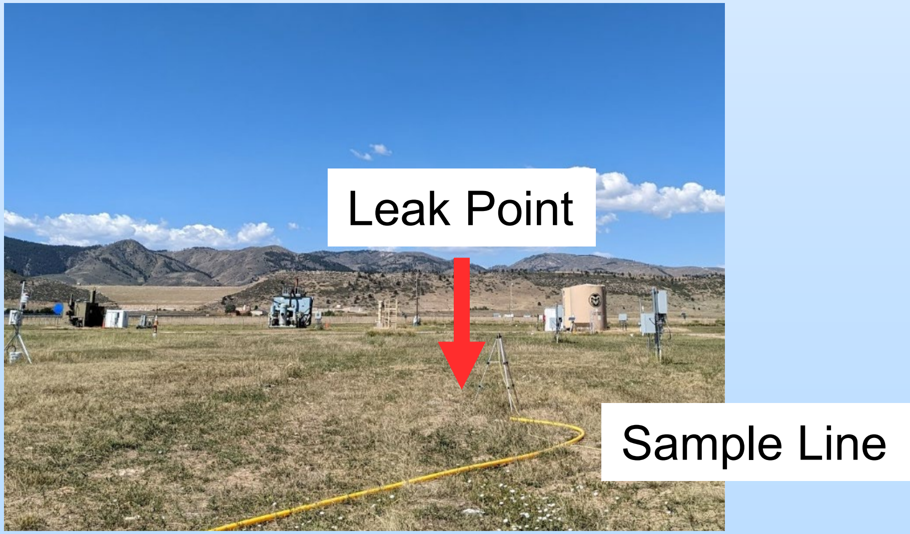


Fully integrated IoT-Sensor Prototype

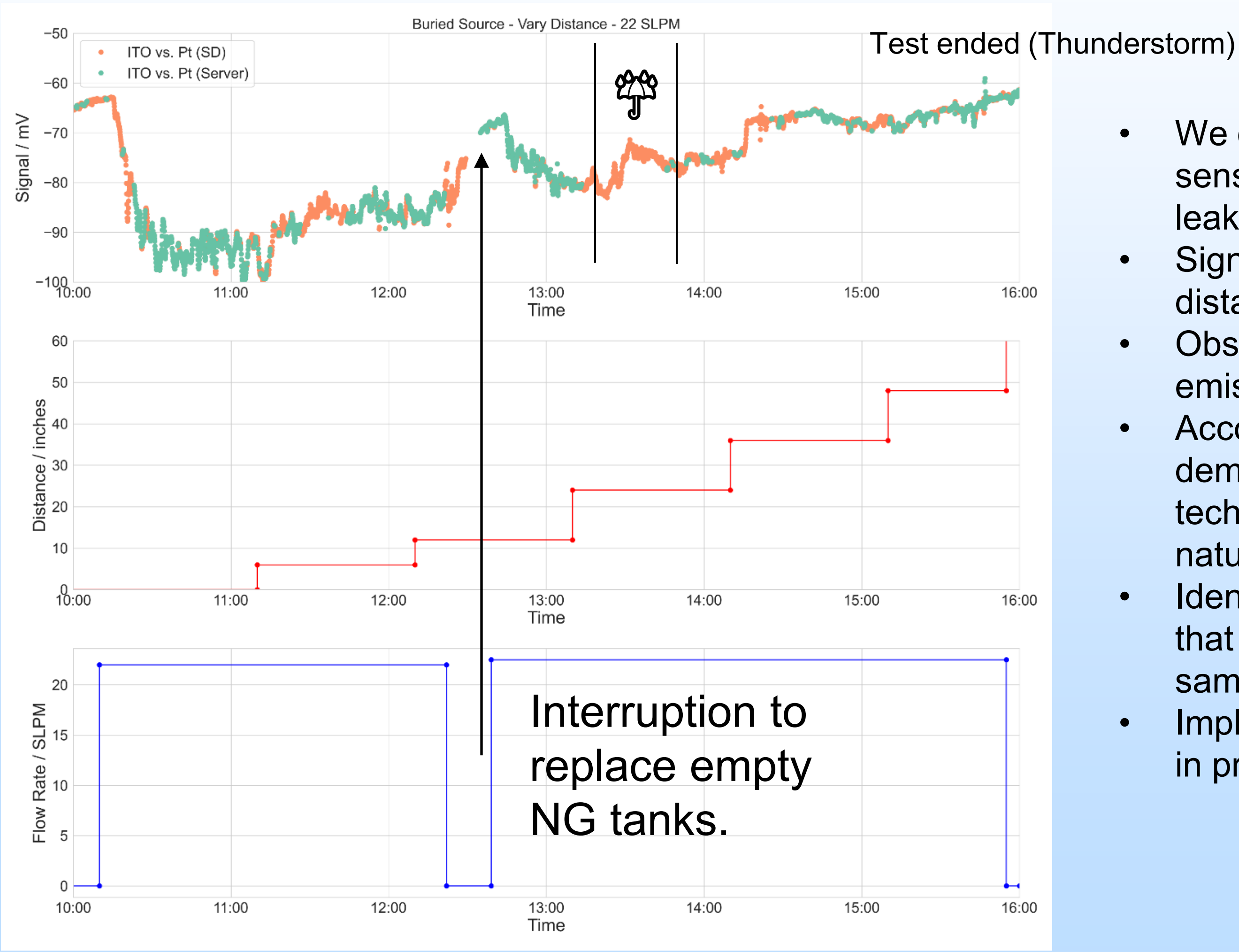
Field Testing – CSU METEC

- Initial round of field testing was completed at CSU METEC on August 22-26th.
- Enables test in real world environment but with programmable leak rates and geometries.
- Examined emissions from a buried pipeline: 2 ft deep using natural mixed soil material.
- Leak rates from 9-40 SLPM were measured.
- Distance from source: 0-50 inches.
- Second round in progress this week.



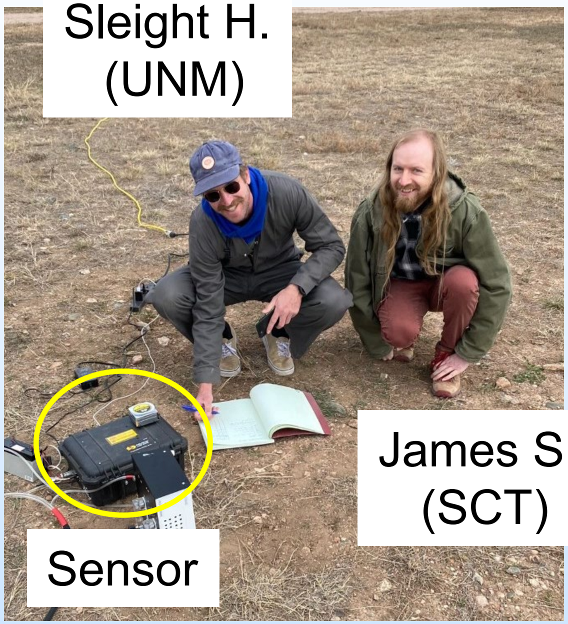


Field Testing



- We observed a clear signal from our sensor in response to a 22 SLPM leak.
- Signal decreases linearly with distance.
- Observed events such as pause in emissions and rain.
- Accomplished first in-field demonstration of MPES-IoT technology outside of laboratory for natural gas emissions detection!
- Identified aspects of test system that need improvement including sampling rate and cell reliability.
- Implemented in 2nd test run which is in progress this week.

Sensor Data Remote Dashboard

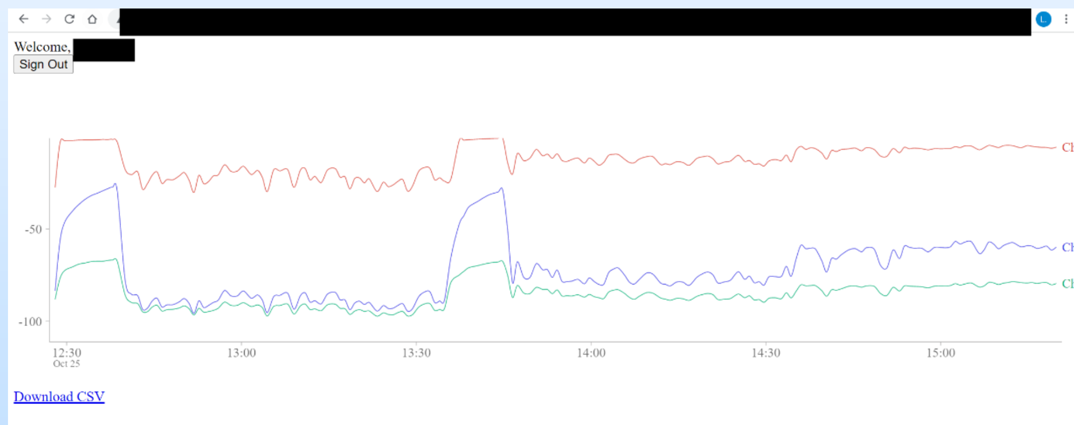


Testing at METEC on Tuesday

Cellular Network

Cloud Server

Remote Monitoring



Data collected at METEC between 12:30-3:30PM EST 10/25

Clipart: irasutoya.com

Plans for future testing/development/ commercialization

- Provisional Patent - “Low Ionic Conductivity Substrates for Multi-Element Mixed Potential Natural Gas Sensor” (Filed 2/27/22)

- Intrinsically Safe Design of electronics (Class 1, Div 1)

- Transition to scale-up
  - Major need for screen printing and tape casting for mass production of MPES sensors.
    - **Oxeon Energy*** (North Salt Lake, UT, USA)
  - Exploring building large-scale manufacturing capacity
    - Manufacturing facility in New Mexico (methane, hydrogen, NOx sensors and systems)
    - Funded through DoE loan program?

*https://oxeonenergy.com/ - Their expertise in fabricating solid-state electrochemical fuel cells and electrolyzers (MOXIE on Mars rover) makes them a promising partner.

Plans for future testing/development/ commercialization

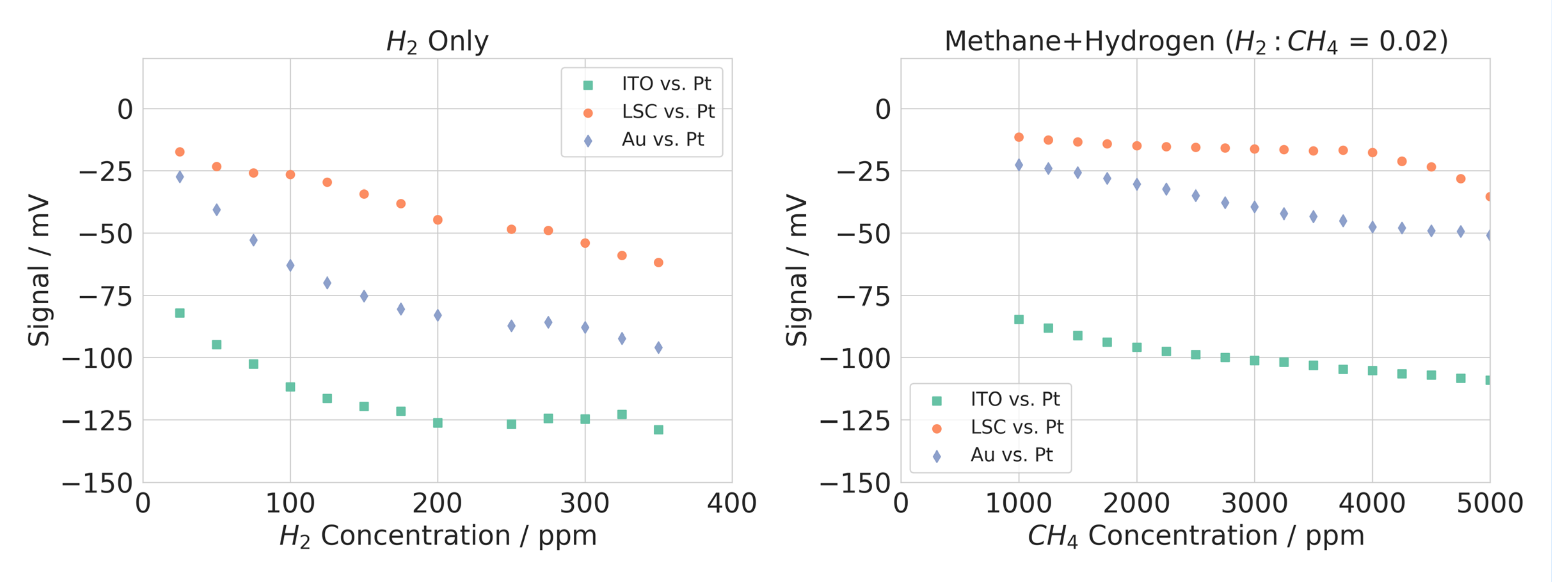
- Funding opportunities for continuation of this research and commercialization(DoE, EPA, Southwest Hydrogen Hub)

- Customer Discovery
  - Potential Pilot Programs: Encino Energy, Sunline Bus Company

- New Applications
  - Hydrogen sensors
  - Hythane sensors
  - NO_x sensors
  - Testing sensors in vehicular applications (e.g. tailpipe)

Future Work - Hythane

- Discussions with DoE program manager have indicated an interest in Hythane (H_2 + CH_4) sensitivity.
- Initial tests in our lab indicate hydrogen can be easily detected in H_2 + CH_4 mixes.
- Further optimization of materials selection could boost selectivity and sensitivity to H_2.



Outreach and Workforce Development Efforts or Achievements

- Outreach:
  - Presented work to New Mexico's US Senator Martin Heinrich (February 2022).
  - Research article published in *J. Electrochem. Soc.*,[1] review published in *Sens. Act. B (invited)*,[2] 2 more papers submitted by end of year (*SNB*, *ECS Sensors Plus*).
  - Presentations at Electrochemical Society Meeting (May & October 2022) and Solid Freeform Fabrication Symposium (July 2022).
  - Total 2 publications and 10 conference presentations to date.
- Workforce Development:
  - Sleight Halley (Ph.D. Graduate Student), expected graduation spring 2023.
  - Donna Koechner (engineer) hired at SCT.

1. "Combined Mixed Potential Electrochemical Sensors and Artificial Neural Networks for the Quantification and Identification of Methane in Natural Gas Emissions Monitoring" S. Halley *et al.* 2021 *J. Electrochem. Soc.* **168** 097506
2. "A review of zirconia oxygen, NOx, and mixed potential gas sensors – History and current trends." S. Halley *et al.* 2022 *Sensors and Actuators B: Chemical* **370** 132363

Summary Slide

- We have developed a multi-electrode mixed potential sensor array with limit of detection of natural gas at 10s of ppm.
- Machine learning methods were successful in identifying and quantifying CH_4 and other subcomponents.
- The sensors were integrated into a portable IoT platform for field deployment.
- We were able to successfully detect the emission from a simulated buried pipeline during a field test.

Future direction: Scale up of sensor systems production, additional in-field testing, taking advantage of new applications in renewable energy economy.

Acknowledgements:

- Aidan Duggan and Dan Zimmerle (CSU METEC) for assistance in development and implementation of field test plan.
- This work was supported by DoE Office of Fossil Energy and Carbon Management through award FE0031864.
- Program Managers: William Fincham (2020-2022); Joseph Renk (2022 – Present)

Contact Information

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SENSORCOMM TECHNOLOGIES

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U.S. DEPARTMENT OF ENERGY

Appendix

– These slides will not be discussed during the presentation but are mandatory.

Organization Chart

CENTER FOR MICRO-ENGINEERED MATERIALS

Subcontract

SENSORCOMM TECHNOLOGIES

PI: Lok-kun Tsui
Co-PI: Fernando Garzon
Accounting: Svetlana Shevkun

Research Assoc. Professor: Kannan Ramaiyan

Graduate Student: Sleight Halley

President and CEO: Kamil Agi

Innovation and Marketing Director: Robert Ian

Electrical Engineer: James Smith

Gantt Chart / Task 1 and 2

Q3 BP3

Task	Assigned Resources	Year 1				Year 2				Year 3			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1.0 Project Management and Planning	UNM / SCT												
Task 1.1 Project Management Plan	UNM / SCT	O											Δ
Task 1.2 – Technology Maturation Plan	UNM / SCT	O											Δ
Task 1.3 – Publication and Presentation of Results	UNM / SCT			O									Δ

Task	Assigned Resources	Year 1				Year 2				Year 3			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 2.0 Sensor Fabrication	UNM												
Subtask 2.1 – Sensor Prototyping	UNM	O			Δ								
Milestone 2.1 – Prototype 2-element sensor	UNM			✓									
Subtask 2.2 – Sensor Element Evaluation	UNM		O			Δ							
Subtask 2.3 – Screen Printed Sensor Fabrication	UNM					O						Δ	
Milestone 2.3 – Multi-Element Sensor	UNM							✓					

Gantt Chart / Task 3

Q3 BP3

Task	Assigned Resources	Year 1				Year 2				Year 3			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 3.0 Artificial Neural Network Development	UNM/SCT												
Subtask 3.1 – Laboratory Collection of Training Data	UNM	O									Δ		
Milestone 3.1 – Initial Training Data Batch				✓									
Subtask 3.2 – Gas Type Identification Training	UNM			O			Δ						
Milestone 3.2 – – Optimized ANN Algorithm for Identification	UNM					✓							
Subtask 3.3 – Gas Species Quantification ANN Training	UNM			O					Δ				
Milestone 3.3 – Optimized ANN Algorithm for Quantification	UNM							✓					
Subtask 3.4 – Deployment of ANN algorithm on Mobile Hardware	UNM/SCT					O							Δ
Milestone 3.4 – ANN on Development Board	UNM/SCT									✓			

Gantt Chart / Task 4

Q3 BP3

Task	Assigned Resources	Year 1				Year 2				Year 3			
Task 4.0 – Development of an Integrated Sensing Platform		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Subtask 4.1 – Sensor Interface Development	SCT	O			Δ								
Milestone 4.1 – 2-Element Sensor Interface Device Completed	SCT				✓								
Subtask 4.2 – Multi-Element Sensor Interface	SCT			O				Δ					
Milestone 4.2 – Multi-Element Sensor Interface w/ wireless transmission Device Completed	SCT							✓					
Subtask 4.3 – Integration of ANN Inference Hardware	SCT						O						Δ
Milestone 4.3 – Completed Sensor Package	UNM/SCT										✓		

Gantt Chart / Task 5

Q3 BP3

Task	Assigned Resources	Year 1				Year 2				Year 3			
Task 5.0 – Field Test and Validation		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Subtask 5.1 – Arrange for Access to Field Test Facility	UNM						O	Δ					
Milestone 5.1 – Field Test Location Selected	UNM									✓			
Subtask 5.2 – Development of Field Test Plan and Completion of NEPA Documentation	UNM/SCT						O		Δ				
Comprehensive Field Test Plan (Decision Point I)	UNM/SCT									✓			
Subtask 5.3 – Field Test	UNM/SCT									O			Δ
Milestone 5.2 – Field Test Results Completed	UNM/SCT												*