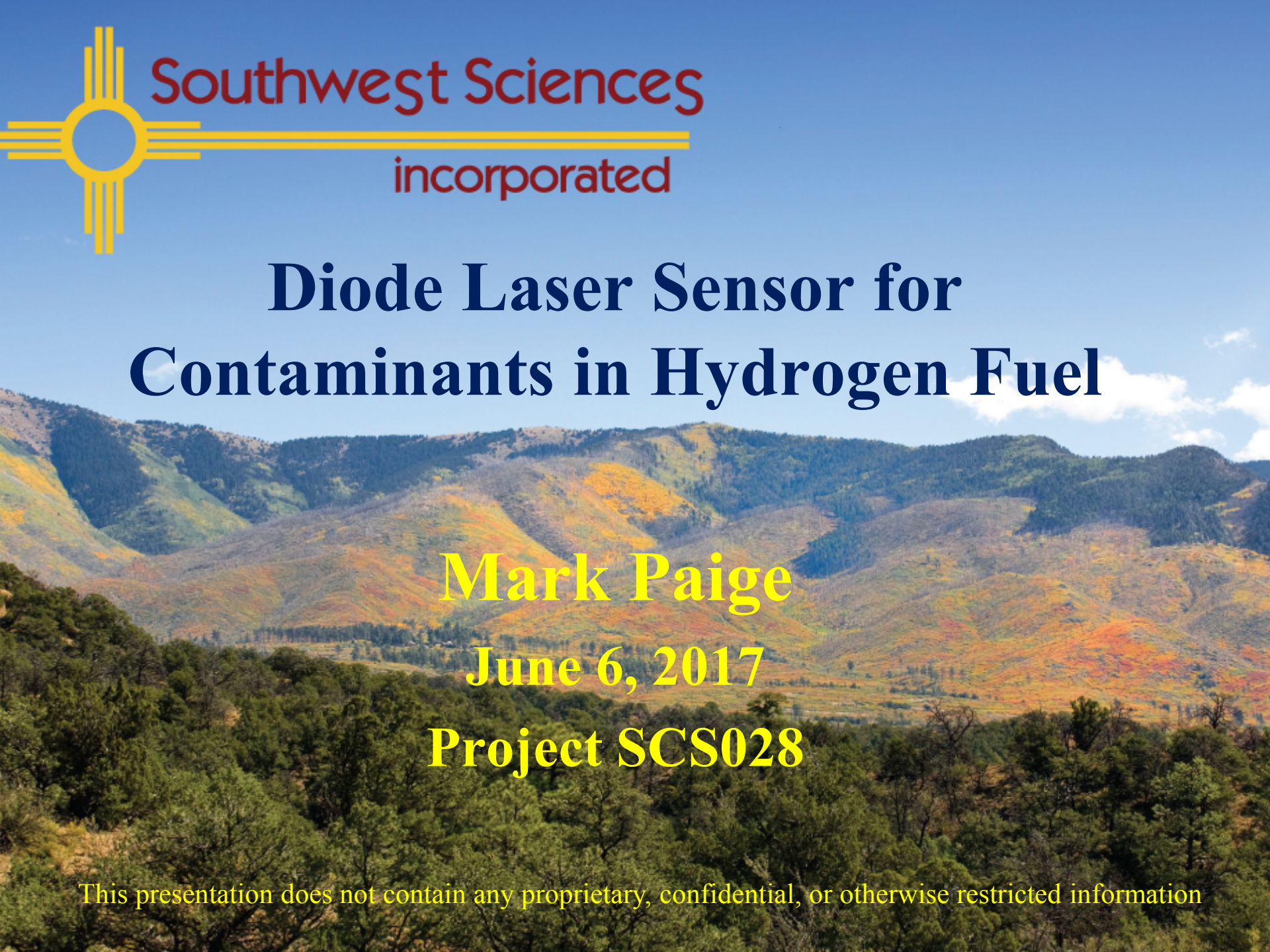

Diode Laser Sensor for Contaminants in Hydrogen Fuel

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June 6, 2017

Project SCS028

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

Project Start Date: 04/11/16
Project End Date: 04/10/18
(SBIR Phase II)

Barriers

C. Safety is Not Always Treated as a Continuous Process

G. Insufficient Technical Data to Revise Standards

- No instrument for measurements at fuel stations – samples are sent to a lab

No assurance of clean fuel supply

Budget

Total Project Budget: $1,010,000
Spending as of April 1, 2016:
$404,000

Partners

- DOE Office of Science (funding source)
- NREL
- Los Alamos Nat. Lab

Objectives

Construct & test a portable diode laser H_2 contaminant detector for the lab & fuel station

C. Safety is Not Always Treated as a Continuous Process

- Instrument will perform continuous measurements – 1 sec/contaminant
- Provide real time info

G. Insufficient Technical Data to Revise Standards

Instrument will measure many contaminants - carbon monoxide, ammonia, hydrogen sulfide, water vapor, carbon dioxide, formaldehyde, formic acid, hydrogen chloride, methane

Can be tailored to measure all or as few as needed

Relevance H_2 Contaminant Detector Engineering Requirements[1]

Requirement	Proposed Sensor Specification
Detect H_2O, CO, S, NH_3, & C_xH_x	✓*
<1 minute measurement	10 s
Gas pressure - 900 bar	1 bar
Environmental conditions -20 to 45 C	✓
Calibrate less than 2 times/yr	✓
Sample every fill	✓
Detect contaminants at 10x above SAE J2719 levels	✓
1 ft^3 size	✓
Operable by skilled technician	Automated

*diode laser sensitivity doesn't meet sensitivity levels for S or hydrocarbons

1. H2FIRST Hydrogen contaminant detector task: Requirement document and market survey (NREL, Savannah River NL) https://energy.gov/sites/prod/files/2015/04/f22/fcto_h2first_hydrogen_contaminant_detector_report_april2015.pdf

Detectable contaminants with proposed instrument

Contaminant	Impurity Limit*	Expected Sensitivity
Carbon Monoxide	0.2	0.03
Ammonia	0.1	0.02
Hydrogen Sulfide	0.004	0.3
Water Vapor	5	0.03
Carbon Dioxide	2	0.06
Formaldehyde	0.01	0.2
Formic Acid	0.2	0.04
Hydrogen Chloride	0.05	0.008
Methane	100	0.02

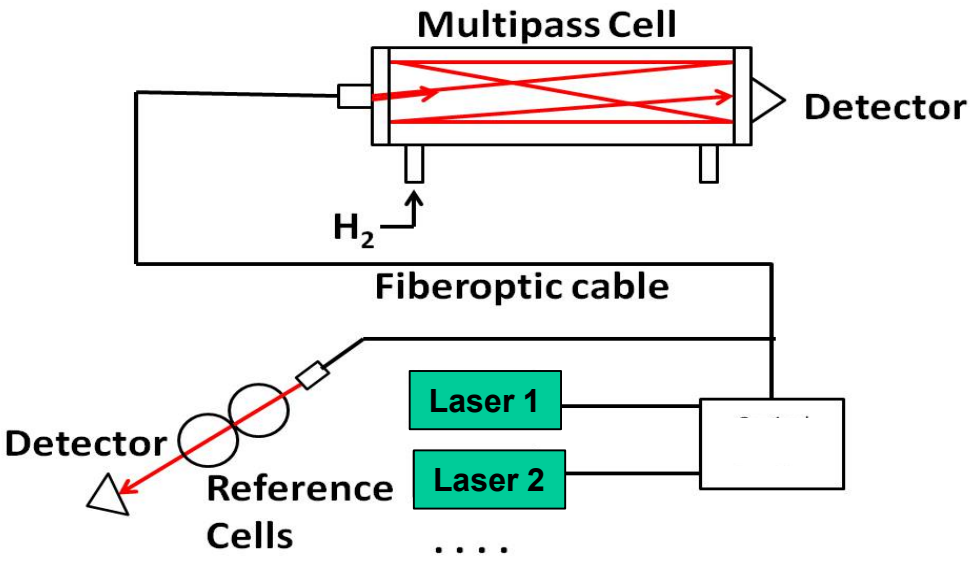
First four contaminants are most common

*Appendix C from MYRD&D Plan (SAE J2719)

Optical Absorption Spectroscopy

Beer's law: Light absorbed α Conc. × optical pathlength

- Wavelength Modulation Spectroscopy – can detect 1 absorbed photon out of 100,000
- Multipass cell – 20 m optical path in 25 cm base path
- Combine multiple diode lasers with fiber optics



Infrared Measurements

Near IR

- Telecom like (field worthy)
- Less expensive
- Fiber coupled

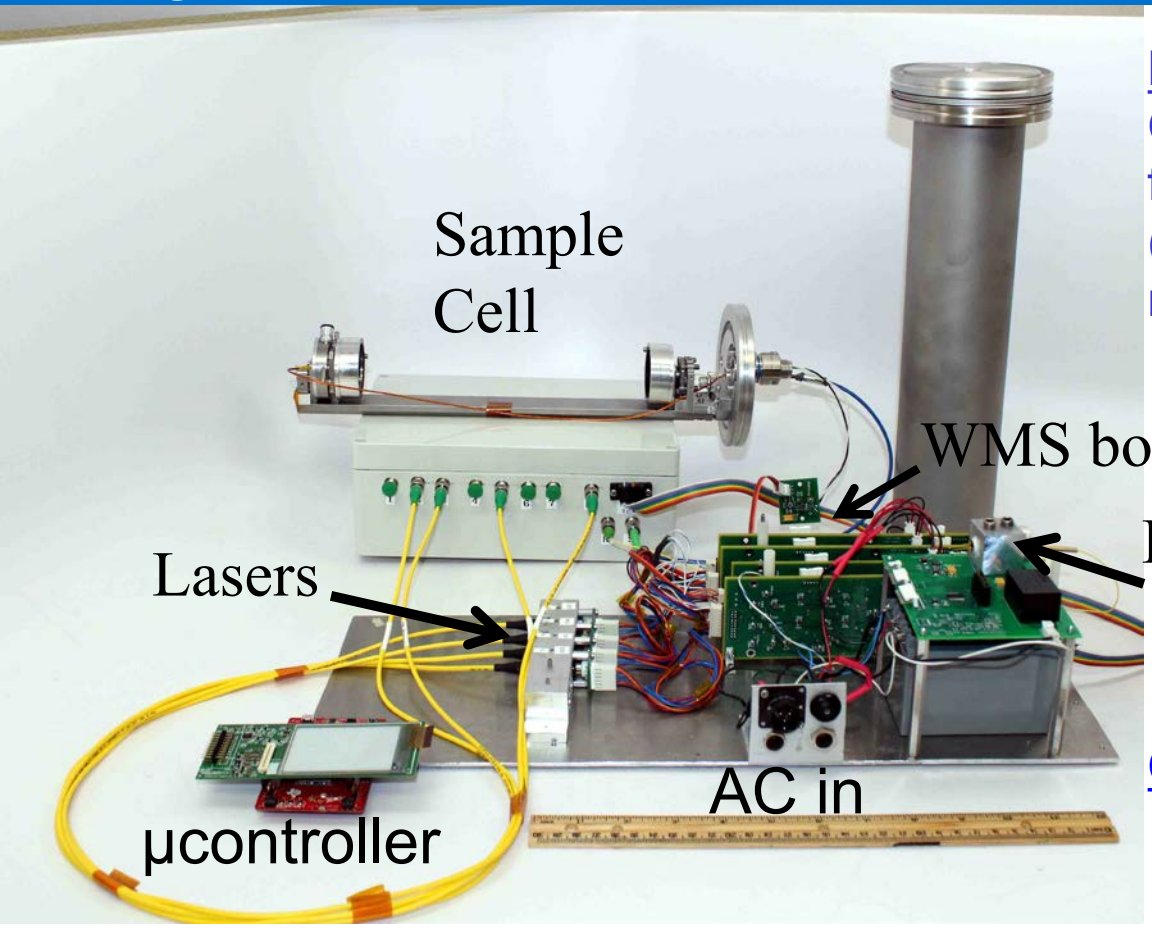
Mid IR

- More sensitive

Multigas sensing for > 2 gases – combining beams with fiberoptics is novel approach

Expands usefulness of diode laser sensing

Instrument Development



Modular System
Can switch laser & WMS board for other contaminants
(or reduce number of contaminants measured)

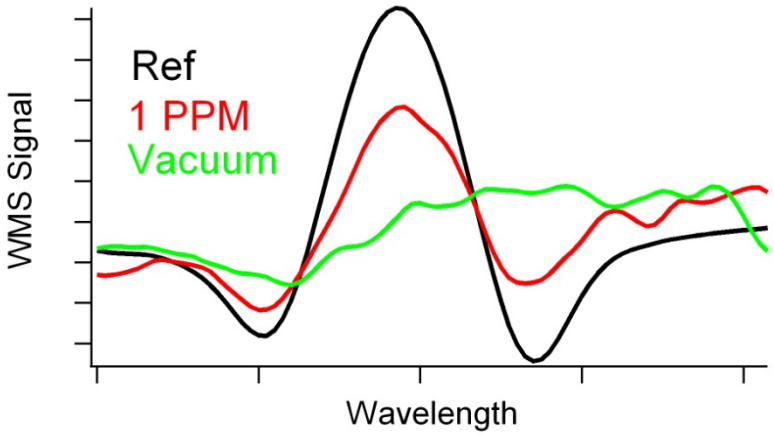
Compact and electrically safe

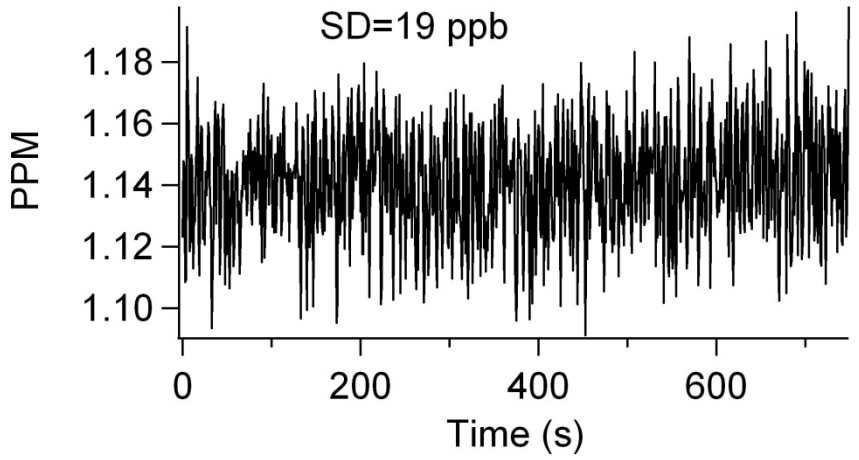
Real time measurements of Carbon Monoxide, Ammonia, Hydrogen Sulfide, & Water Vapor

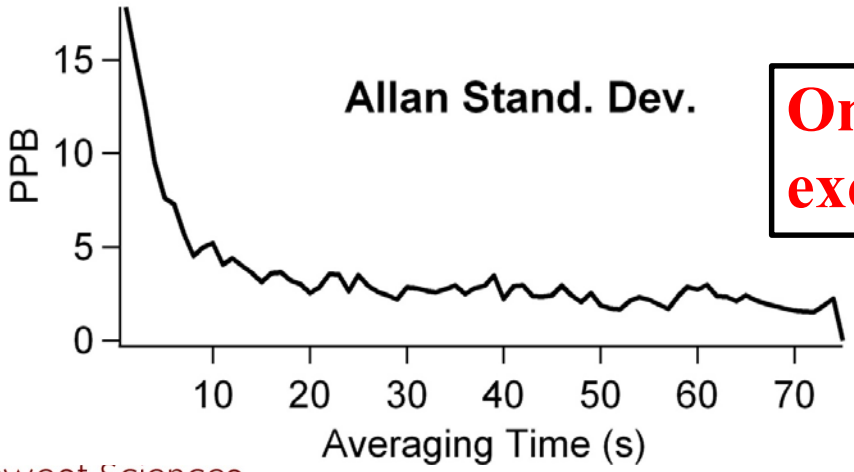
Preliminary Measurements

Carbon monoxide

(0.2 ppm SAE J2719 limit)







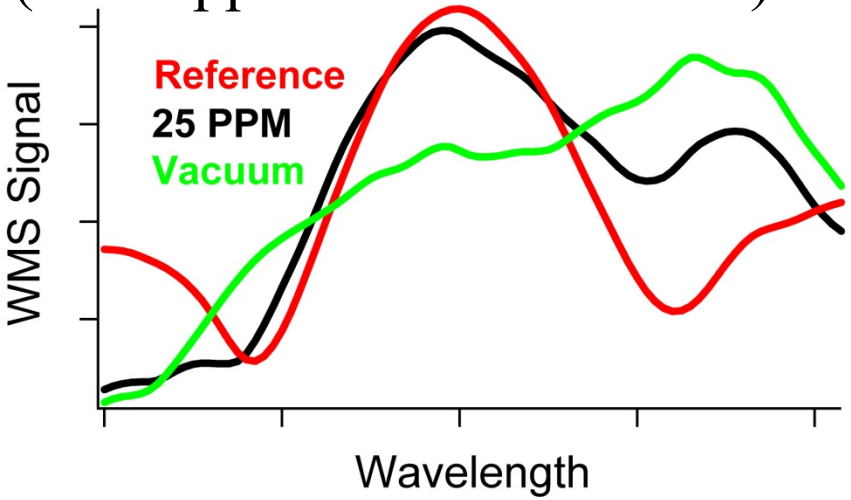
One second detection sensitivity exceeds J2719 standard

Southwest Sciences incorporated

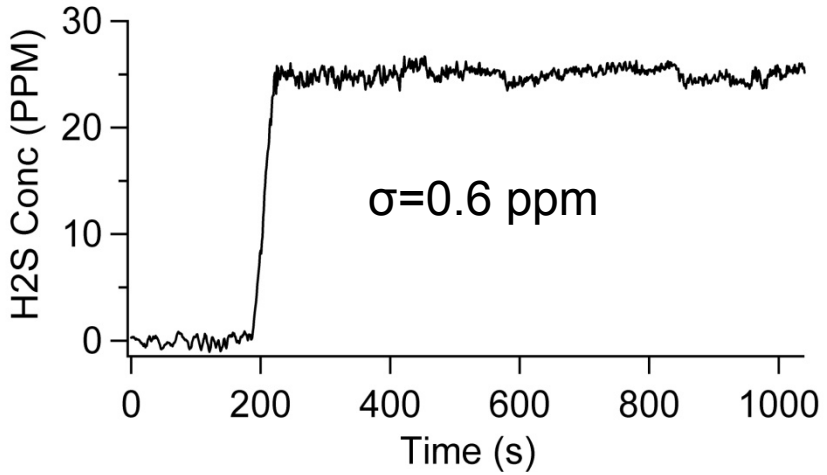
Preliminary Measurements

Hydrogen Sulfide

(0.004 ppm SAE J2719 limit)

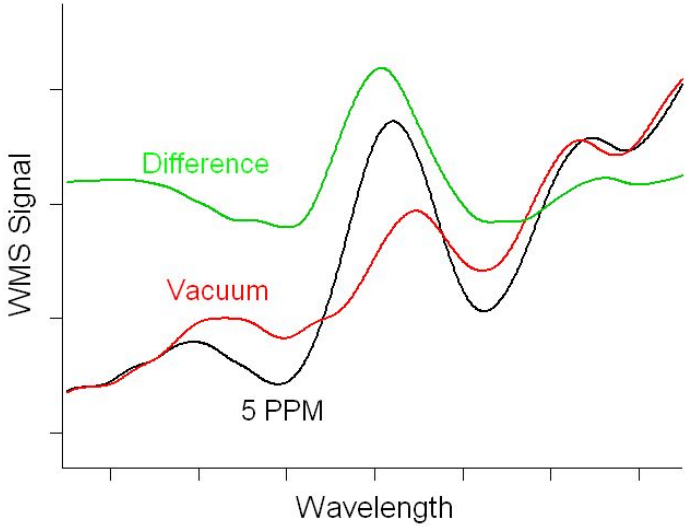


Can detect high levels of H_2S – >> J2719 limit but still useful



Ammonia

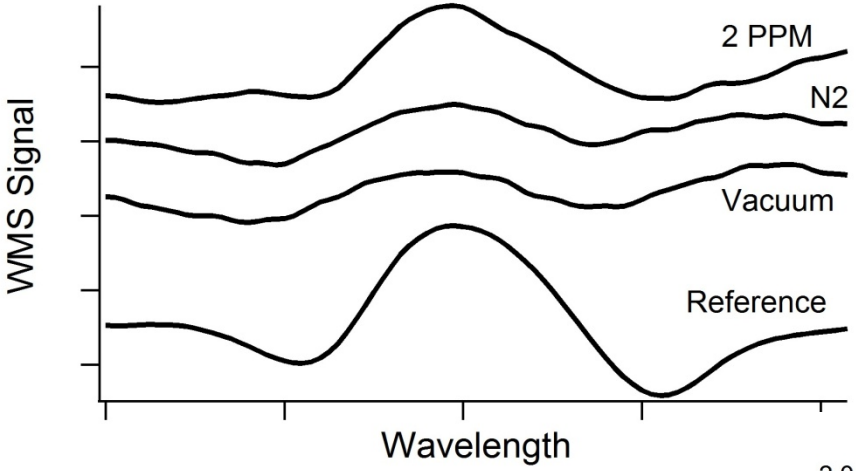
(0.1 ppm SAE J2719 limit)



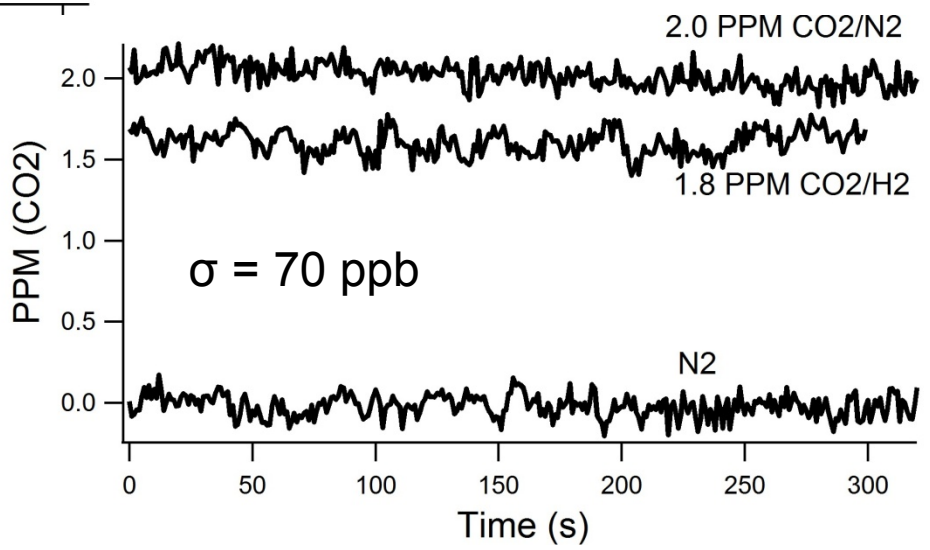
Preliminary Measurements

Carbon Dioxide

(2 ppm SAE J2719 limit)



One second sensitivity exceeds J2719 standard



Response to Previous Year Reviewer's Comments

This project was not reviewed last year

Collaborations

- Monthly teleconferences with personnel from DOE, Los Alamos, NREL Fuel Cell Programs
- Presentation at DOE Tech Team meeting
- Small business voucher application on alternate status for testing with NREL dispenser system
- Interest at California Measurement Standards Lab & Air Products

Remaining Challenges

- Optimize sample cell
- Instrument operation algorithms for multigas sensing
- Minimizing baseline artifacts associated with optical system
- Examine artifacts with sticky gases - NH_3, H_2O, H_2S
- Establish gas handling procedure

Proposed Future Work

- Complete instrument
- Add capability for other contaminants – CO_2, HCOOH, H_2CO, CH_4, HCl
- Upgrade instrument for outdoor use
- Testing at NREL, Los Alamos, California Measurement Standards Lab

(Project end date 4-11-18)

Any proposed future work is subject to change based on funding levels

Commercialization

In house manufacturing until technology established & stations are built

3 Versions: Lab Portable Station

Licensing to gas supplier or analytical instrument company

Existing Hydrogen Stations

US *	World+
60 + 26 planned	274

120,000 conventional gas stations in US

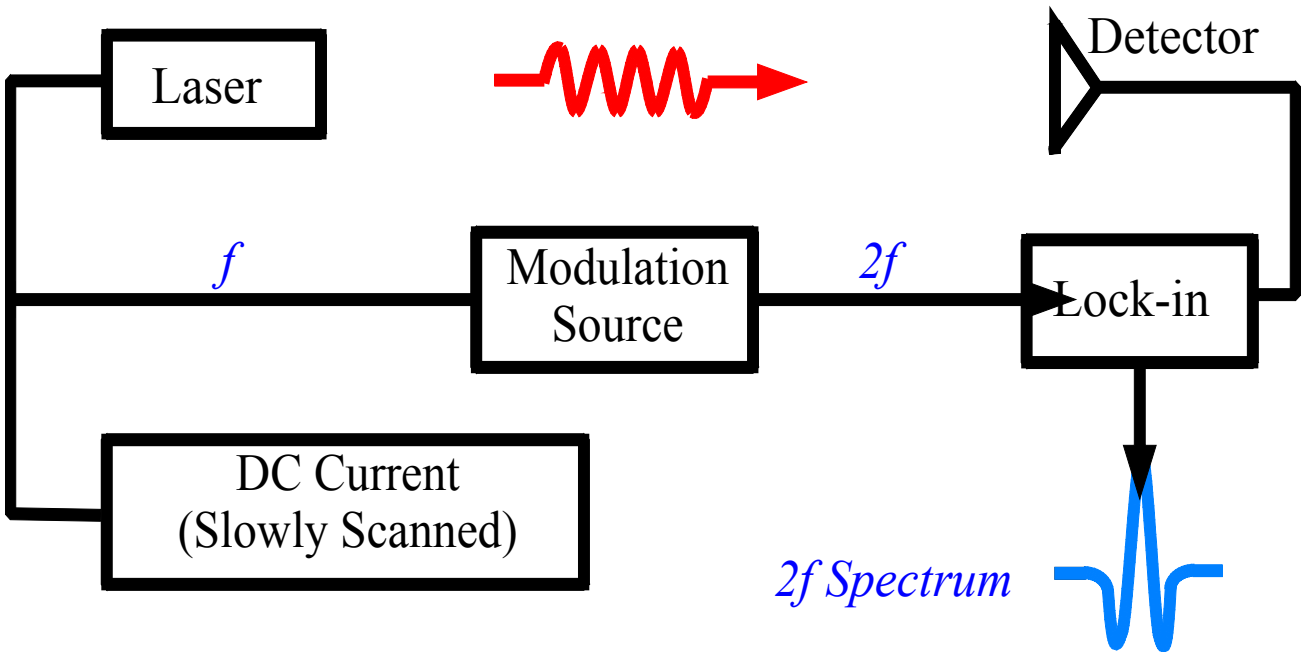
*DOE Alt Fuel website, + H2stations.org

Summary

- Developing diode laser H_2 contaminant detector for real time measurements in fuel station
- Ensure fuel quality & provide method of making frequent field measurements providing more data
- Capable of detecting at SAE J2719 levels CO, CO_2,CH_4, and high levels of S. Expect H_2O, NH_3, HCl will be demonstrated at better than SAE J2719 levels.
- Expanding multigas sensing possibilities with diode lasers

Technical Back-Up Slides

Wavelength Modulation Spectroscopy



- High frequency measurements to overcome laser noise
- Derivative like spectrum results
- Detection limit low 10^{-5} absorbance level (10^{-3} for conventional absorption spectroscopy)

Field Measurements

NSF Jet Hygrometer

Commercial Methane Flux

R&D 100 winner

Balloon Measurements

Commercial Natural Gas Leak Detector

R&D 100 winner

Oil Refinery Perimeter Monitor

Rocket Measurements At Mach 7

Southwest Sciences incorporated

Spectral Fitting and Calibration

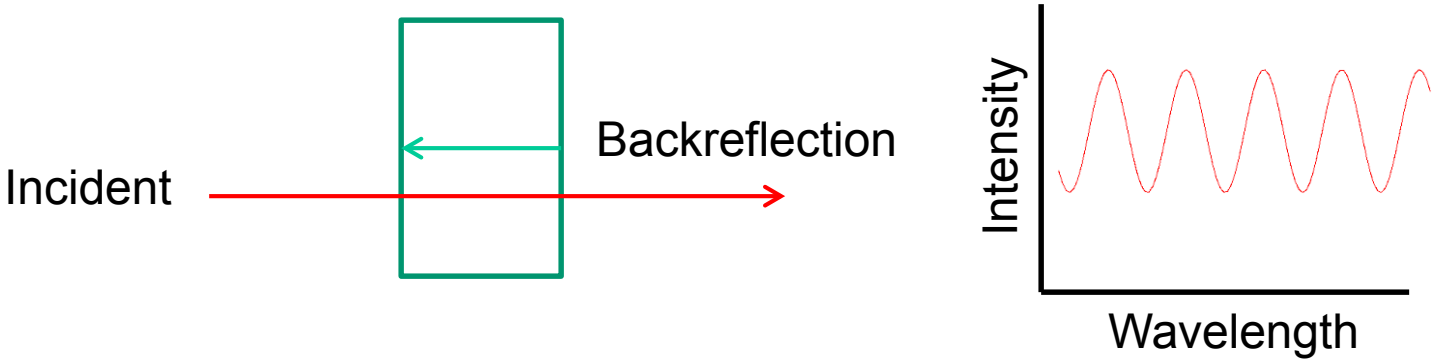
- Reference beam records spectrum in sealed cell
- Sample beam spectrum fit with reference spectrum
- Fit result scaled by calibration with known sample and zero gas

$$C = Fit \times SpanFactor - Offset$$

- Span factor stable indefinitely – no need for cal gas
- Offset drifts with temperature – want offset drift to be small compared to signal level

Interference Fringes

- Result of backreflections from partially transmissive surfaces



- Sources – windows, fiber connections, lens, scattering
- Offset drift – sets detection limit