Transforming ENERGY

Hydrogen Contaminant Detector

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Project Goal

- Identify potentially viable commercial or research hydrogen contaminant detector (HCD) technologies
- Verify ability of instrument to detect contaminants to SAE J2719 requirements
- Provide HCD manufacturers with a test platform to demonstrate the performance of their analyzers
- Determine limitations of the HCDs, and develop recommendations for hydrogen contaminant detection at fueling stations
- Integrate HCDs into high pressure hydrogen fueling stations
- Demonstrate near real-time verification of in-line detectors for the SAE J2719 hydrogen quality requirements or a relevant potential subset
- Support development of fuel quality methods and standards for sampling and measurement (e.g., ASTM and SAE Fuel Cell Standards Committee)

Overview

Timeline and Budget

- Project Start Date: 02/22/2019
- FY22 DOE Funding: $350K
- FY23 Planned DOE Funding: $0
- Total DOE Funds Received to Date**: $650K

  ** Since the project started

Barriers

- Hydrogen Storage
  - 3.3.5.D - Durability/Operability
- Hydrogen Delivery
  - 3.2.5.I - Other Fueling Site/Terminal Operations

Partners

- Project lead: William Buttner
- Co-PI: Matthew Post
- Partner organizations: CARB, DOE, California Hydrogen Infrastructure Research Consortium

Potential Impact

- Hydrogen fuel quality (FQ) verification is required for station commissioning.
    - Current Method: Remote laboratory analysis with periodic subsequent verification of fuel quality
- Contaminated H_2 has been dispensed
    - Immediate loss of FCEV performance
- Need for “real-time” FQ verification
    - In-line “Hydrogen Contaminant Detector” (HCD)
    - Provides a possibility to find and mitigate system problems before problematic hydrogen is dispensed
    - Station developers send samples for testing frequently to ensure they will have a passing test performed by regulating entities

Photo by Dennis Schroeder, NREL 34599

An in-line HCD will provide near real-time verification of hydrogen fuel quality

- Current FQ verification protocols may be inadequate
- Out-of-Spec H_2 has been dispensed with adverse impact on FCEV performance

Potential Impact

SAE J2719 *Hydrogen Fuel Quality for Fuel Cell Vehicles* prescribes allowable contaminant levels

Constituent	Limits [ppm]
Water (H_2O)	5
Total hydrocarbons (C1 basis)	2
Oxygen (O_2)	5
Helium (He)	300
Nitrogen, Argon (N_2, Ar)	100
Carbon dioxide (CO_2)	2

Constituent	Limits [ppm]
Carbon monoxide (CO)	0.2
Total sulfur (S)	0.004
Formaldehyde (CH_2O)	0.2
Formic acid (CH_2O_2)	0.2
Ammonia (NH_3)	0.1
Total halogenates	0.05

Source: SAE International, 2020

Probability of Contaminant Occurrence in Hydrogen

Source: Bacquart et al, 2018

Steam methane reforming with pressure swing adsorption	Proton-exchange membrane water electrolysis with temperature swing adsorption	Probability of by-product contaminant presence
CO	None identified	Frequent
N_2	None identified	Possible
CH_4, H_2O and Ar	N_2, O_2 and H_2O	Rare
CH_2O	CO_2	Very rare
He, CO_2, O_2, CH_2O, NH_3, sulfur compounds, hydrocarbons compounds, halogenated compounds	He, Ar, CO, CH_4, CH_2O, CH_2O_2, NH_3, sulfur compounds, hydrocarbons compounds, halogenated compounds	Unlikely

Fuel cell electric vehicle fuel quality requirements are defined by national and international regulations

- SAE J2719 (U.S.) is fully harmonized with ISO 146877 *Hydrogen fuel quality — Product specification*
- Likely contaminants are determined in part by hydrogen production method

Approach – HCD Identification

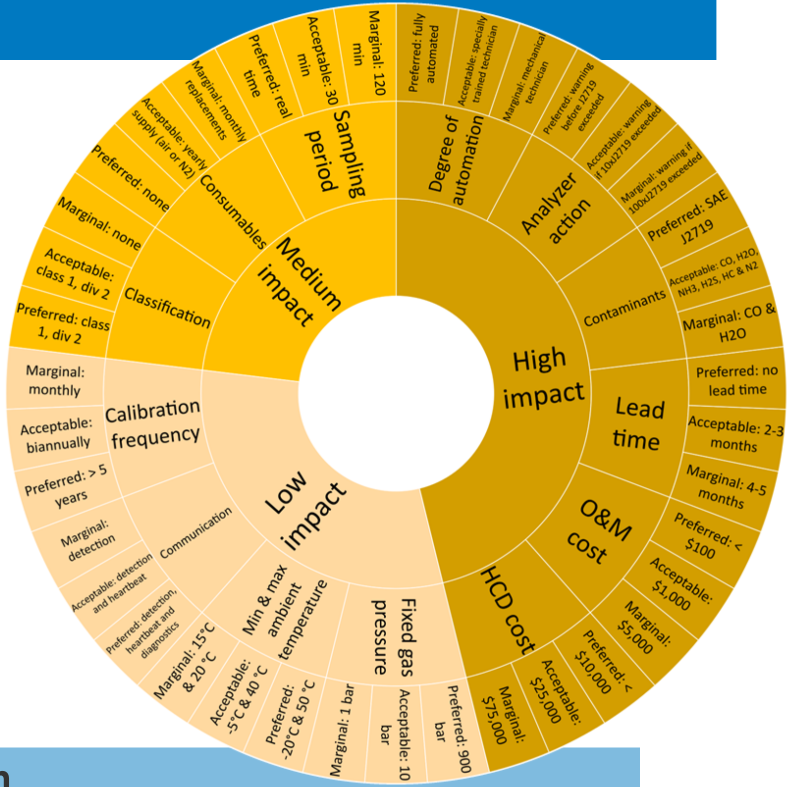
Identify viable commercial or research hydrogen contaminant detector (HCD) technologies

- Select the most promising HCDs using a numerical ranking of prioritized specifications
- Verify instrument capabilities by testing to SAE J2719 standards
- Determine limitations of the HCDs and develop recommendations for contaminant detection at fueling stations

Integrate HCDs into high pressure hydrogen fueling stations

- NREL's Hydrogen Infrastructure and Testing Research Facility (HITRF)
- Forecourt of a California Hydrogen Fueling Station

Provide near real-time verification of hydrogen quality requirements using in-line HCD



HCD Identification

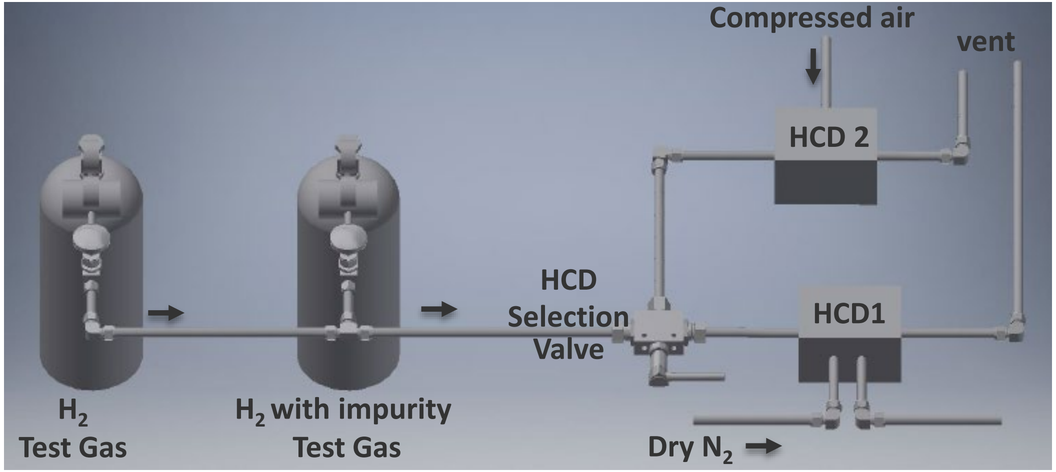
Numerically ranking potential HCDs as per a prioritized list of performance metrics identified two HCDs

- HCD 1 – Fourier Transform Infrared Spectrometer—FTIR (a multi-analyte system)
- HCD 2 – LANL sensor for carbon monoxide

Approach – HCD Characterization

Simplified Test Gas Generation System Block Diagram:

- Two gas lines with flows regulated by mass flow controllers (not shown) to generate precise test gas concentrations
- Pneumatic connection to either of the two HCDs is controlled by a three-way valve
- HCDs are installed in an enclosure designed to achieve Class I Division 2 compliance
- Enclosure is ventilated with an equivalent 6 air changes per minute
- Dry nitrogen purge is supplied to HCD 1 to background remove background moisture
- Compressed air is supplied to HCD 2 to actuate pneumatic valve



The Test Gas Generation System produces a range of contamination levels for HCD validation and calibration

Approach – Dispenser Integration

Hydrogen Contaminant Detector Integration at Fueling Station: Concept

STEP 1:
A typical FCEV refueling includes a hose vent so the nozzle can be decoupled. This vented H_2 can now be automatically sampled by the HCD-I for HCD analysis.

STEP 2:
The HCD-I is to be installed within the dispenser and is designed to automatically collect & isolate a portion of the hose vent into a pressure regulated buffer chamber.

STEP 3:
The HCD-I then transfers collected hydrogen at low-pressure and controlled flow rate to the on-site HCD for analysis.

Approach – Sample Collection

Hydrogen Contaminant Detector Interface: Method of Operation (slide 1 of 2 slides)

to vent

High-pressure H_2 release

Step 1
Initial venting of high-pressure source

to vent

High-pressure H_2 release

Step 2
Purging of buffer chamber

High-pressure H_2 release

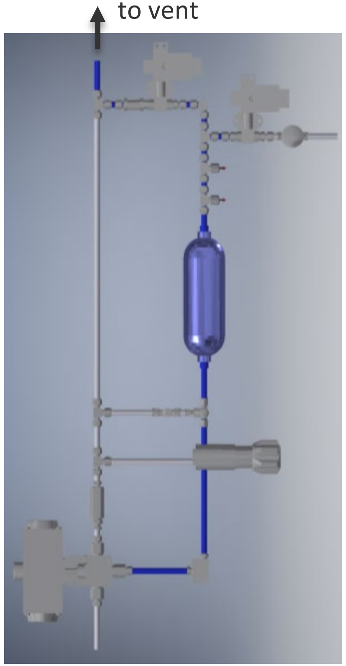
Step 3
Pressurization of buffer chamber

Approach – HCD Identification

Hydrogen Contaminant Detector Interface: Method of Operation (slide 2 of 2 slides)

Step 4
Isolation of buffer chamber; upstream depressurization

Step 5
Sample delivery to HCD at controlled P & Flow



Step 6
Depressurization of buffer chamber

Accomplishments and Progress

Hose Vent Tie-In Point

Vent Continuation
Tie-In Point
(behind dispenser)

- Photo by Dennis Schroeder, NREL 34586

Accomplishments and Progress

Dispenser integration:

- Hose vent line diverted from main dispenser vent manifold.
- Diverted hose vent line connected to sampling valves at the base of the dispenser.
- Further installation work was performed without affecting the dispenser performance.

Vent Sampling Valves

Hose Vent Tie-In Point

Accomplishments and Progress

- Installation of NREL dispenser HCD-Interface is complete
  - All valving and gauges installed
  - Leak checks are complete
  - In-situ hose vent sample capture has been demonstrated
  - Shakedown nearly complete

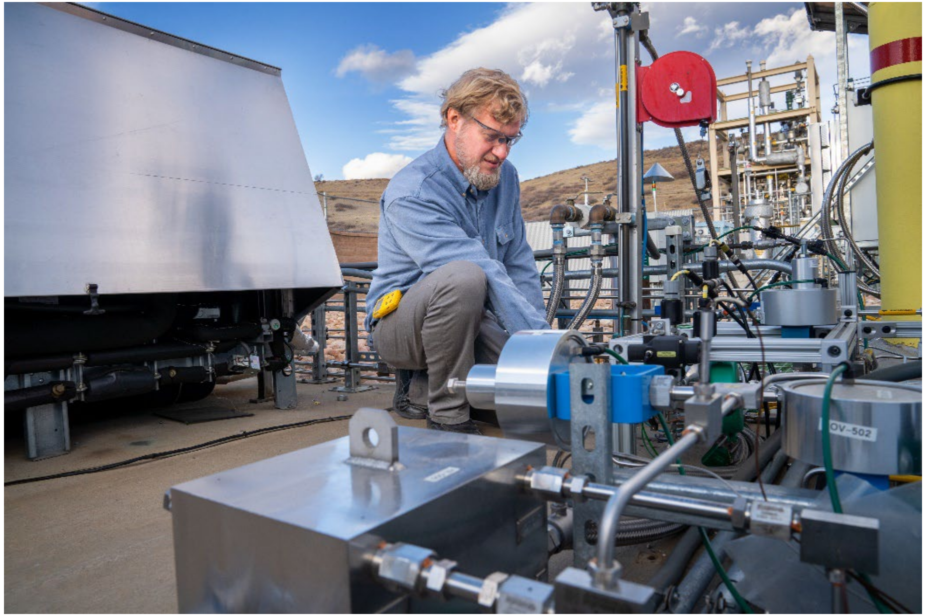


Photo by Werner Slocum, NREL 74358

The NREL dispenser HCD-interface installation is complete, and shakedown is being finalized

Accomplishments and Progress

- Installation of NREL dispenser HCD Enclosure Complete
  - All valving and gauges installed
  - Air conditioning unit installed
  - In-situ hose vent sample delivery has been demonstrated
  - Electrical inspection passed
  - Shakedown nearly complete

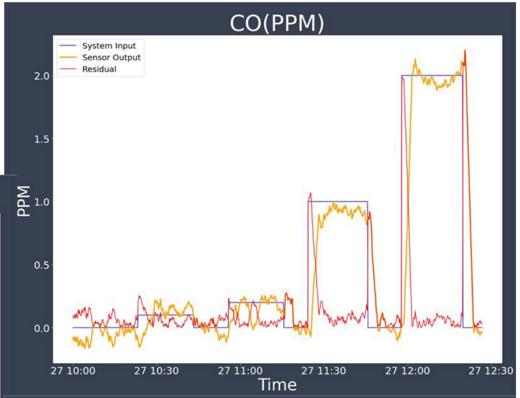
Photo by Werner Slocum, NREL 74360

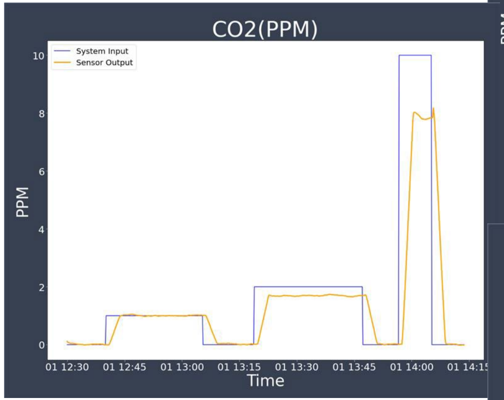
The NREL dispenser HCD enclosure installation is complete, and shakedown is being finalized

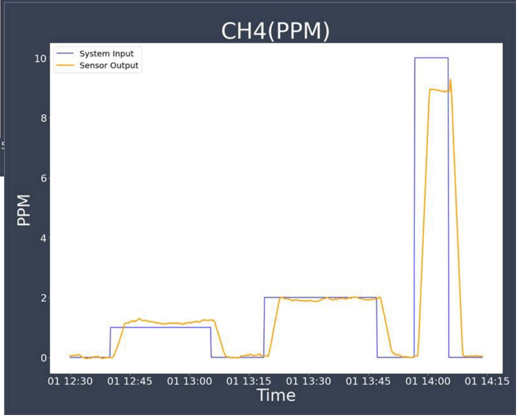
Accomplishments and Progress

HCD advancements

- LANL HCD assessment underway
  - Original sensor has a short and will be replaced
- CIC Photonics HCD
  - All issues fixed and testing underway
  - Initial results obtained
- Additional gas cylinders on order
  - Further studies involving additional contaminant species are planned
- Additional HCDs
  - Water as a target species
  - Electrical classification housing for standalone deployment







FTIR HCD Initial Characterization Plots for CO, CO2, and CH4

Accomplishments and Progress:
Response to Previous Year Reviewers' Comments

- This project has not been reviewed previously

Collaboration and Coordination

Partnership with LANL

- LANL team provided an electrochemical sensor for CO under the auspices of property move agreement (to transfer HCD-2 from LANL to NREL)
- NREL team is evaluating sensor response to CO and different impurities
- NREL team is optimizing operating protocols

Sensor limitations:

- Not commercial but prototypes are available
- Developed for carbon monoxide only
- Sensor may work for other compounds, but methodology is not developed

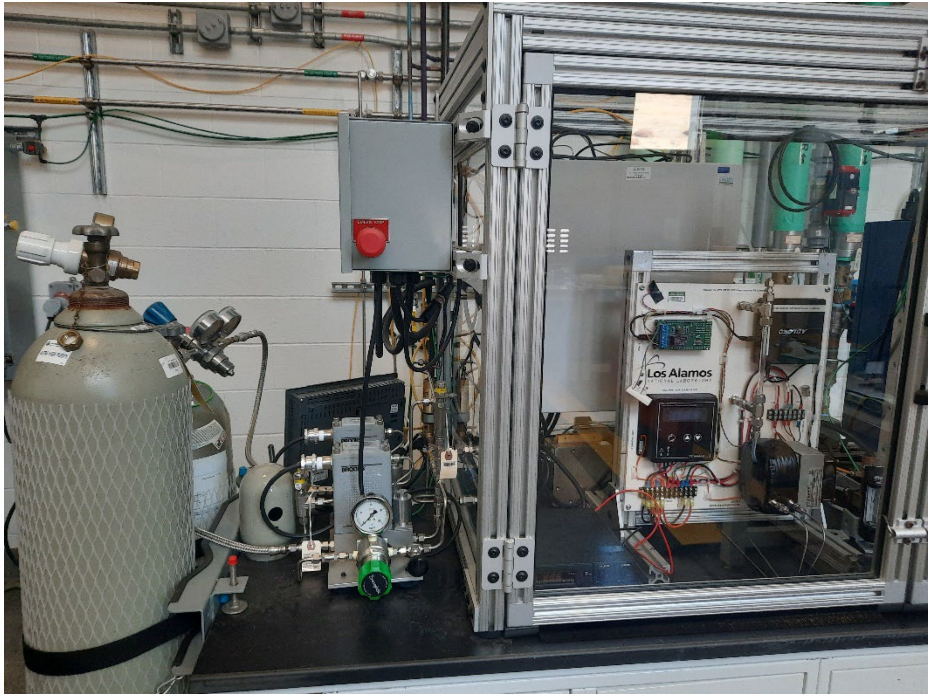


Photo by Matthew Post, NREL 75705

Remaining Challenges and Barriers

- Sample corruption associated with the FTIR sensor with contaminants such as water vapor and ammonia
  - Sulphur and ammonia compounds tends to stick to surfaces (e.g., gas transfer lines)
  - Water vapor in the background gas affects FTIR signal
- Long nitrogen purge times of FTIR sensor to remove moisture in order to obtain accurate water measurements
- No single detector has been identified that can analyze all contaminants at the SAE J2719 limits
- Forecourt demonstration site installation
  - Requires permission from station owner and is yet to be identified
  - Restricted travel for installation by NREL researchers

Proposed Future Work

- Statistical analysis of accuracy, precision, and detection limit of HCD measurement
- Integrating HCD and HCD-interface into a dispenser at NREL Hydrogen Infrastructure and Testing and Integration Facility (HITRF)
- Forecourt demonstration at commercial hydrogen fueling stations
- Keeping abreast with latest detection technologies
- Expanded number of HCDs to be characterized at NREL
- Provide HCD manufacturers with a test platform to demonstrate their analyzers' performance
- Technical Webinar to present the concept to potential stakeholders
- Expand to heavy duty fueling applications (high throughput)

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

Summary

- Detection of hydrogen contamination will prevent damage to fuel cell electric vehicles
- The main project objective is to provide near real-time verification to the SAE J2719 hydrogen quality requirements using in-line detectors
- A multi-analyte FTIR and a CO-targeted electrochemical sensor are being tested against SAE J2719
- NREL is collaborating with LANL on the deployment performance of their CO sensor
- An HCD interface is needed to serve as a pressure reducer, flow regulator and thermal buffer
- Future work includes the HCDs integration into an operating commercial fueling station
- A performance assessment of the HCDs will be documented in a detailed report

Thank You

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Technical Backup and Additional Information

Technology Transfer Activities

- Working with CARB to identify stations for demonstration at a forecourt dispenser.

Publications and Presentations

- Post, Matthew B., William J. Buttner, David E. Pearman, Kevin Hartmann, and Ian Palin. "Assessment and Deployment of Gas Analyzers for In-Line Hydrogen Fuel Quality Verification at Commercial Fueling Stations." Conference Presentation at 2023 Hydrogen & Fuel Cell Seminar, Long Beach, CA, February 8, 2023.
- Buttner, William J., and Matthew B. Post. "NREL Update to the D03 Committee Meeting on Gaseous Fuels." Meeting Update at ASTM D03 Committee Meeting on Gaseous Fuels, Orlando, FL, December 7, 2022.

Reviewer-Only Slides

Methodology

Derivation of Calibration Curves:

- We obtained experimental calibration curves for each of the constituents in the table below
- The test gas concentration ranged from 100% hydrogen (column 1 in table) to 10 times the SAE J2719 limits (column 11 in table), which were generated from a single calibration gas cylinder.
- SAE J2719 limits were 10% of the cylinder test gas concentration.
- Carbon monoxide is the only constituent measured by both HCDs

Tested constituent	Calibration point per constituent [ppm]										
	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11
Carbon monoxide	0	0.1	0.12	0.14	0.18	0.2	0.3	0.4	0.5	1	2
Water vapor	0	2.5	3	3.5	4.5	5	7.5	10	12.5	25	50
Methane	0	1	1.2	1.4	1.8	2	3	4	5	10	20
Carbon dioxide	0	1	1.2	1.4	1.8	2	3	4	5	10	20

Pure hydrogen (#1) **SAE J2719 limit** (#6) **10 x SAE J2719 limit** (#11)

HCD Calibration Curves were obtained from 0 to 10 times the regulated SAE level

Accomplishments and Progress

HCD 1: Features of the Fourier Transform Infrared Spectroscopy (FTIR) HCD:

- Simultaneous multi-component analysis for CO_2, CO, CH_4, H_2O, CH_2O_2, CH_2O
- Designed to detect SAE J2719 limits for targets listed above (to be verified by NREL)

Limitations:

- Does not meet SAE J2719 limits for sulfur, oxygen and inert gases
- Requires large dry nitrogen purge volume to remove moisture from the optical cell

HCD test system with an electrochemical sensor (left) and an FTIR (right) inside an enclosure providing compliance to Class 1 Division 2 operation

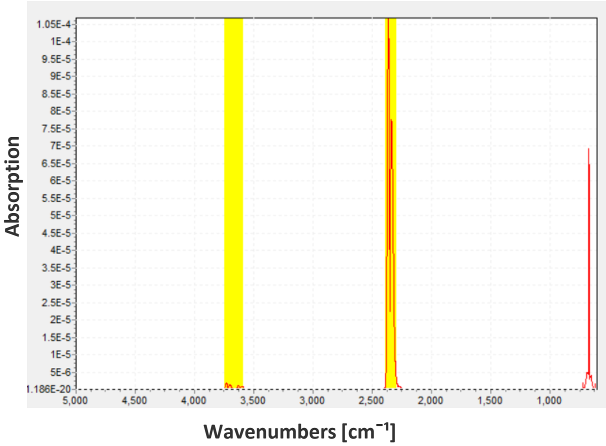
Accomplishments and Progress

Infrared Spectra Obtained by the FTIR HCD:

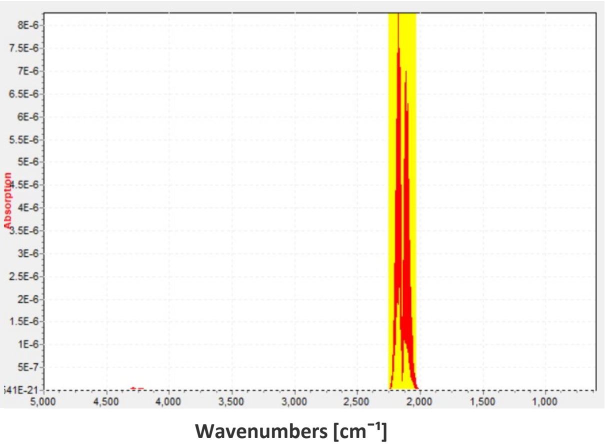
- Unique absorption spectra for each IR contaminant (for selectivity)
- The height of the peaks are defined by Beer-Lambert relationship (for quantitation):

$$Absorbance = molecule\ absorptivity\ \cdot pathlength\ \cdot concentration$$

Absorption spectrum for carbon dioxide



Absorption spectrum for carbon monoxide

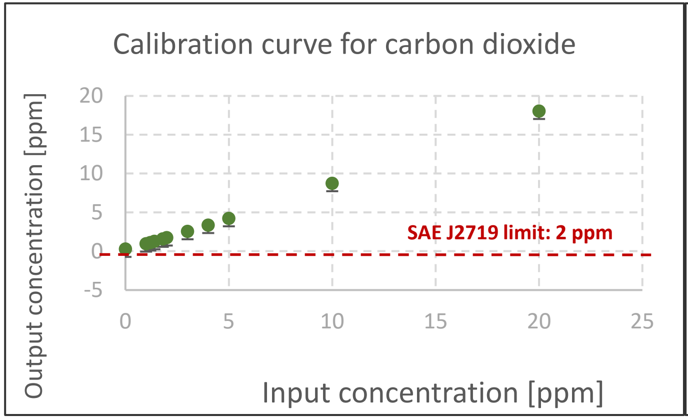


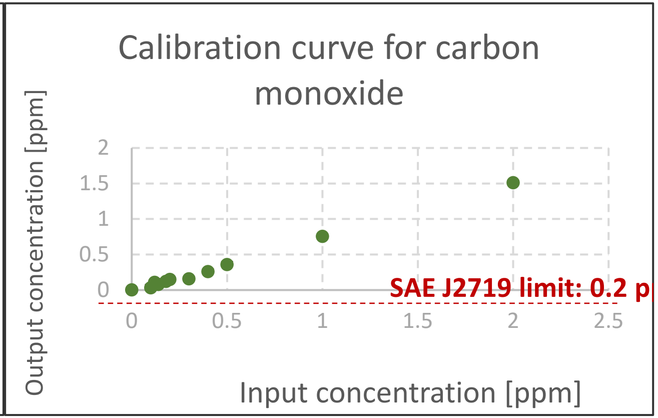
FTIR provides selective quantitation of multiple potential hydrogen contaminants

Accomplishments and Progress

Calibration curve for the FTIR HCD (HCD-1):

- We empirically obtained calibration curves for CO_2, CO, CH_4 and H_2O
- Calibration curves for CO_2 and CO exhibit a linear relationship between input test gas concentration and instrument output



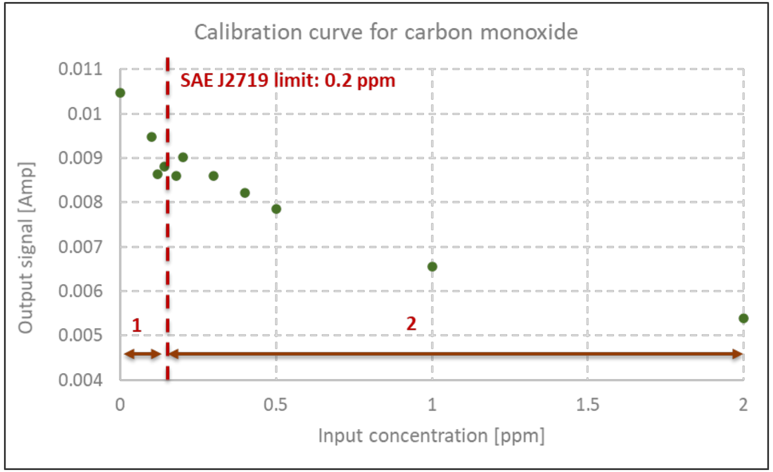


FTIR sensor performs well for the simultaneous CO_2 and CH_4 detection at SAE J2719 limits

Accomplishments and Progress

Calibration curve for the Los Alamos National Laboratory (LANL HCD -- HCD-2):

- HCD-2 is an electrochemical sensor for CO in H_2 developed by LANL
- We empirically obtained calibration curves for CO
- No theoretical conversion transforming sensor signal to test gas CO concentration
- Nonlinear behavior with a quasi-linear range at the SAE limit
- Accuracy of mass flow controllers is compromised in the lower concentration range (≤ 0.2ppm) necessitating corrective experimental methods, e.g. increase in the total flowrate from 120 mL/min to 500 mL/min



1: Total flowrate 500 mL/min

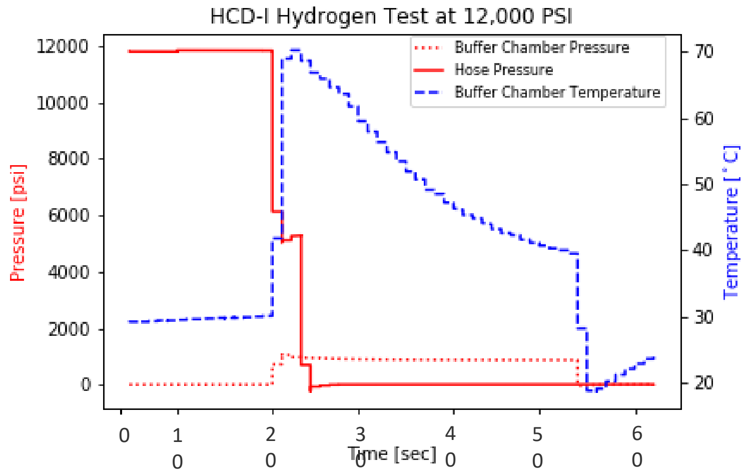
2: Total flowrate 120 mL/min

The LANL Sensor meets SAE J2719 requirements for CO detection

Accomplishments and Progress

Hydrogen Contaminant Detector Interface: Demonstration of Concept

- The solid red line illustrates the dispenser hose high-pressure check and depressurization
- The hydrogen from the hose pressure test is captured in a 1L buffer chamber to an actively-regulated pressure of 1,000 psi (dotted red line)

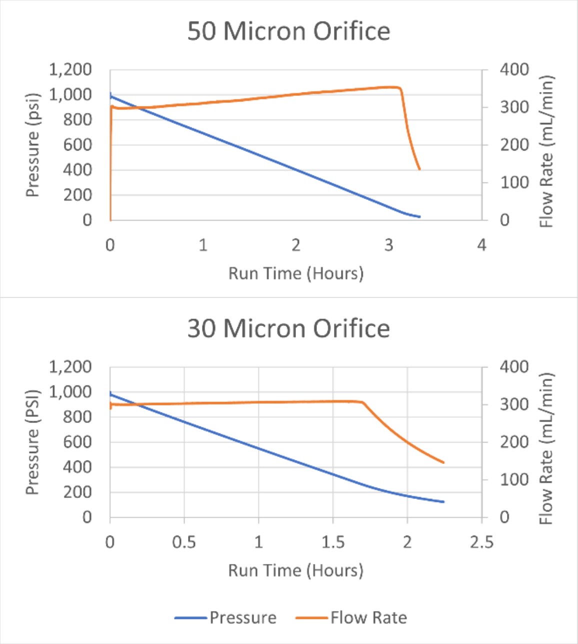


- The buffer chamber gas is then transported to the HCD for analysis under controlled pressure and flowrate
- HCD will be integrated to the HCD-I for automatic analysis

Prototype HCD-interface successfully demonstrated at full pressure operation

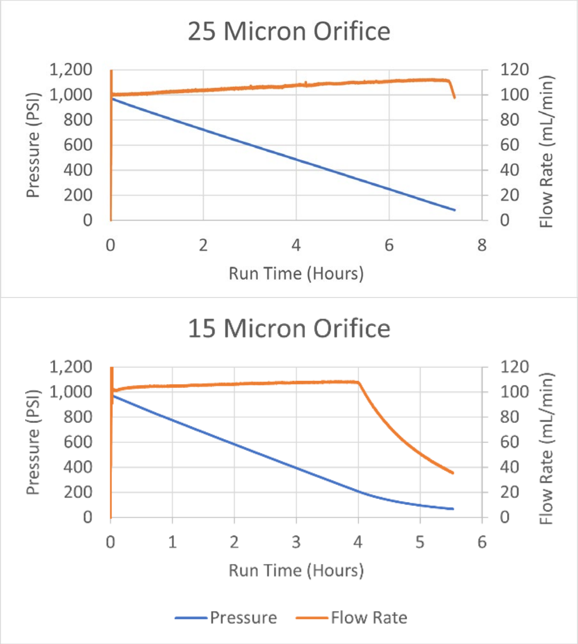
Accomplishments and Progress

300 mL/min Target



Upper: 50-micron orifice sample run
Lower: 30-micron orifice sample run

100 mL/min Target



Upper: 25-micron orifice sample run
Lower: 15-micron orifice sample run

Sample Delivery Characterization Results

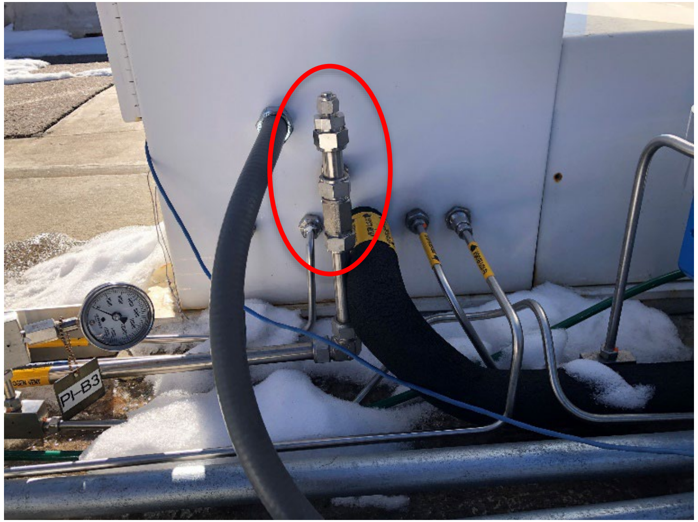
- Larger orifice sizes:
  - Lower pressure required
  - Buffer chamber able to be depleted further
  - Longer sample times
- Smaller orifice sizes:
  - Increased pressure required
  - More stable flow with pressure variations
  - Sample time decreased
- Flow stability influences orifice size more than sample time

Passive flow rate control compatible for HCD operation was achieved using only a regulator and an orifice.

Accomplishments and Progress

Hose Vent Tie-In Point

Vent Continuation Tie-In Point



- Hose vent tie-in point:
  - After each vehicle is fueled, the hose needs to be vented before the nozzle can be removed.
  - The vent valve for this process is located on top of the dispenser and vents into a common vent manifold.
  - This vented sample will be diverted to the HCD-I using tubing rated for dispenser pressures.

- Vent continuation tie-in point:
  - Once a sample is collected from the hose vent, the rest of the hose needs to vent as it would normally.
  - The vent will continue through a tie-in point downstream from the original vent tie-in point.