Hydrogen Contaminant Detector

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Overview

Timeline and Budget#

- Project start date: 02/22/19
- Project end date: 02/22/22
- Total project budget: $400k
  - Total federal share: $300k
  - Partner funding: $100k
  - Additional DOE FY20 AOP funding: $100k
  - Total DOE funds spent*: $276k

Project continuation and direction determined annually by DOE

* As of 03/2020

Barriers

- Barriers addressed
  - Synchronization of hydrogen fueling sampling standards
  - Inline hydrogen fuel quality measurements

Partners

- Partners: CARB, DOE, California Hydrogen Infrastructure Research Consortium
- Collaborators: LANL
- Project lead: William Buttner

Relevance

- Detection of hydrogen contamination will prevent damage to fuel cells electric vehicles

SAE J2719 *Hydrogen Fuel Quality for Fuel Cell Vehicles* Contaminant Level Requirements

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)	0.01
Formic acid (CH_2O_2)	0.2
Ammonia (NH_3)	0.1
Total halogenates	0.05

Source: SAE International, 2019

Probability of Contaminant Occurrence in Hydrogen

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
N2	None identified	Possible
CH4, H2O and Ar	N2, O2 and H2O	Rare
CH2O	CO2	Very rare
He, CO, O2, CH2O, NH3, sulfur compounds, hydrocarbons compounds, halogenated compounds	He, Ar, CO, CH4, CH2O, CH2O2, NH3, sulfur compounds, hydrocarbons compounds, halogenated compounds	Unlikely

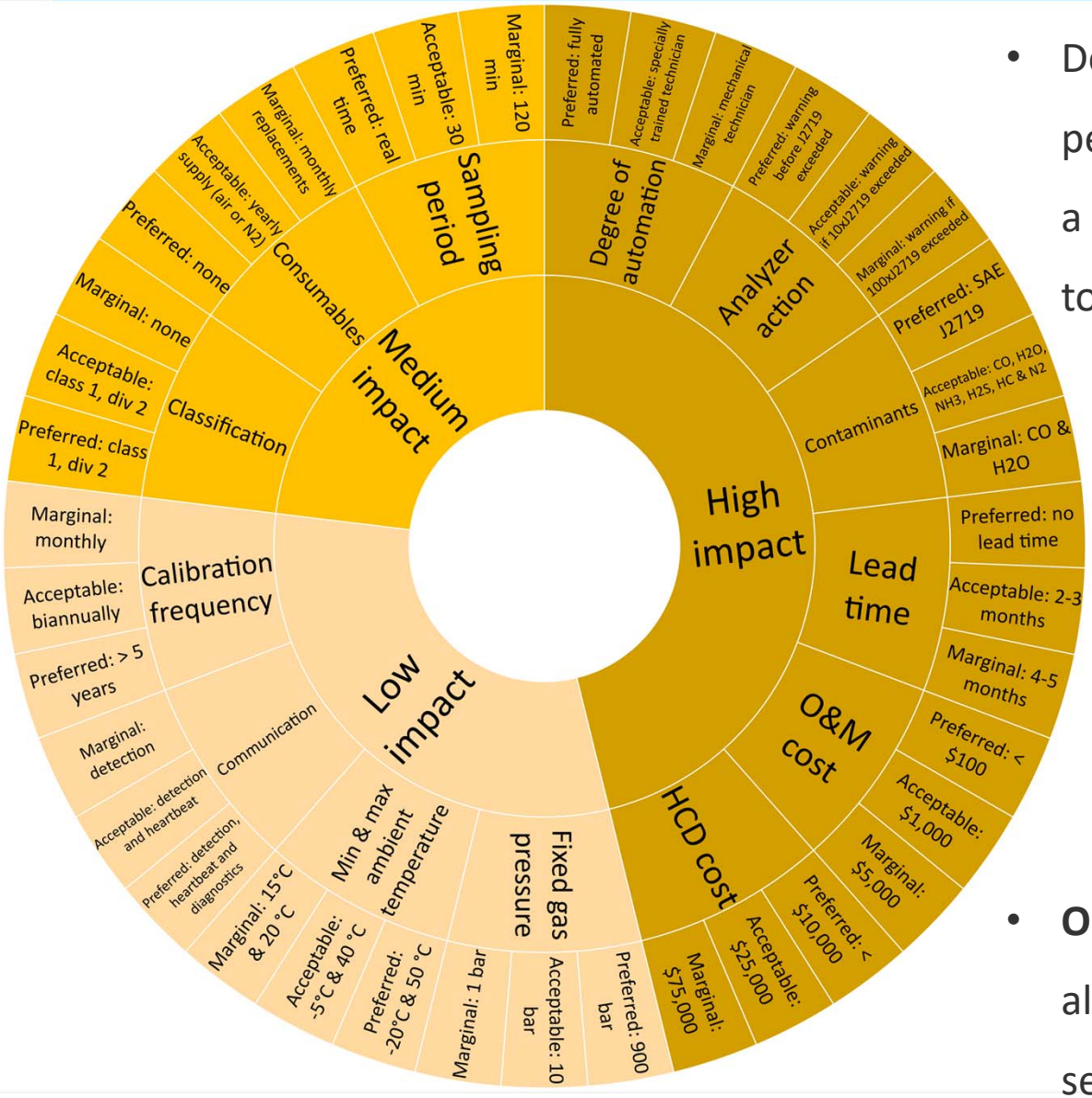
Source: Bacquart et al, 2018

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

Approach and Objectives

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

Methodology



- Developed categorized list of performance parameters each with a **different weight** contributing to a total score
  - **Contaminants, capital and operating cost and lead time** were classified as high impact criteria
  - **Instrument TRL**, expressed as a scaling factor by which the entire score is multiplied
- **Outcome:** numeric ranking that allowed for the selection of two sensors for evaluation

* Number of sensors was defined by programmatic limitations

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

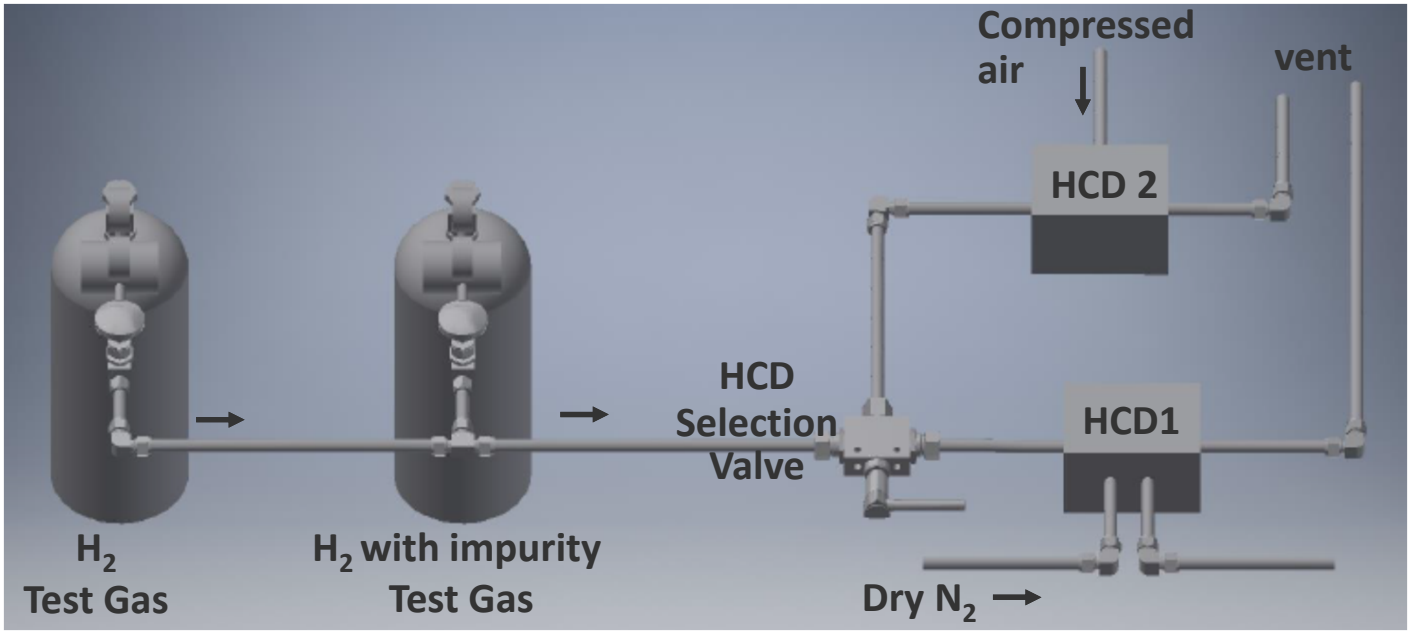
Pure hydrogen **SAE J2719 limit** **10 x SAE J2719 limit**

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

Accomplishments and Progress

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 (see next slide)
- Enclosure is ventilated with an equivalent 6 air changes per minute to achieve Class I, Division 2
- Dry nitrogen purge is supplied to HCD 1 to background remove 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

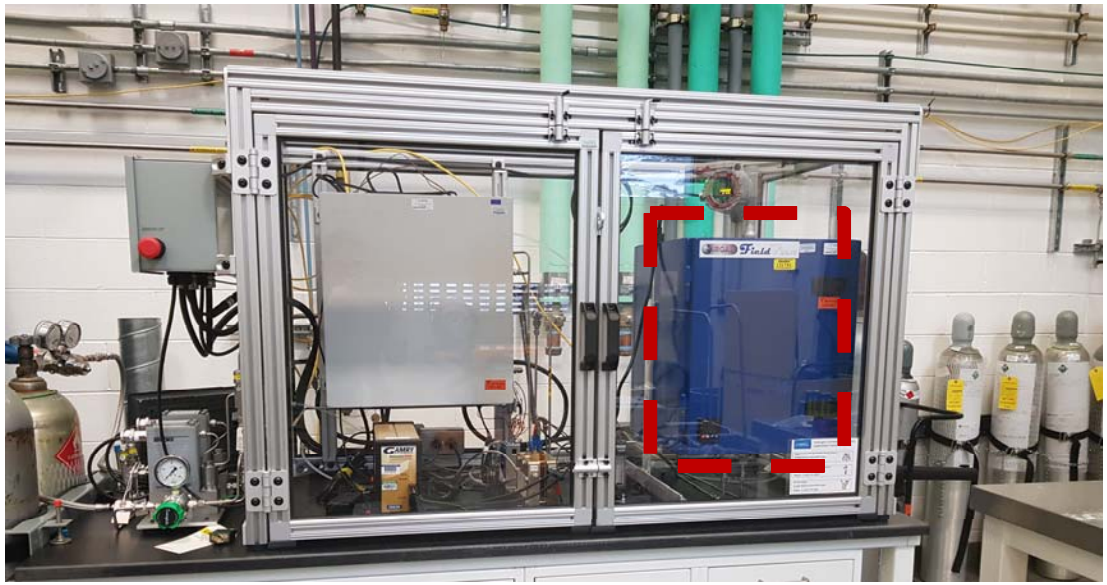
Accomplishments and Progress

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 I, Division 2 operation

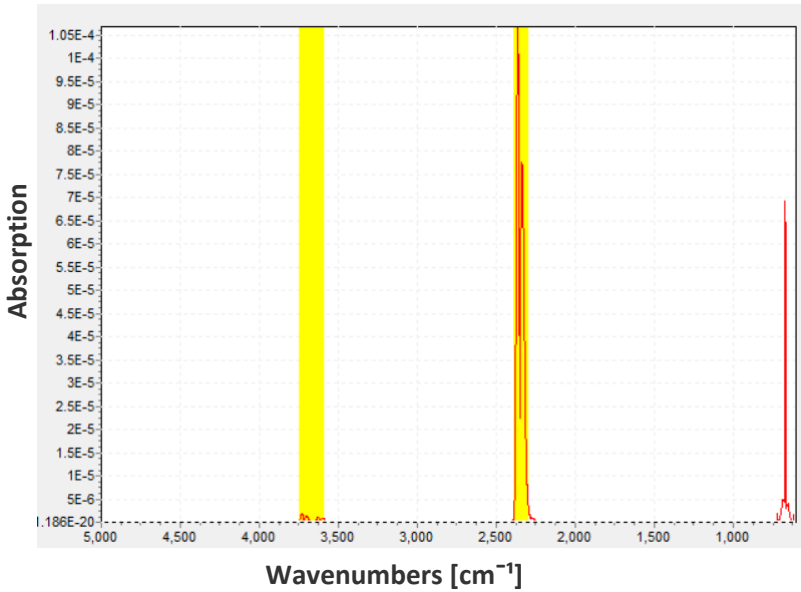
Accomplishments and Progress

Infrared Spectra Obtained by the FTIR HCD:

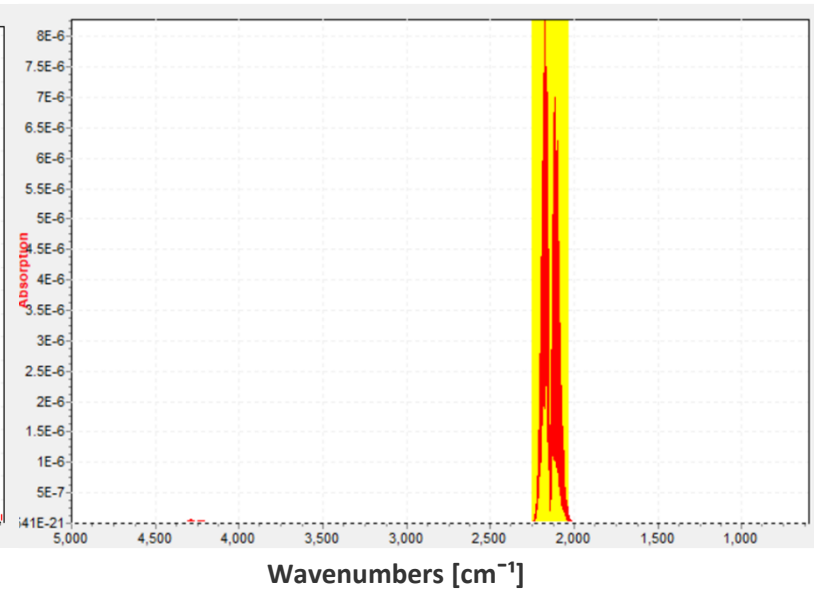
- Unique absorption spectra for each IR contaminant (for selectivity)
- The height of the peaks are defined by Beer-Lambert relationship (for quantitation):

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

Absorption spectrum for carbon dioxide



Absorption spectrum for carbon monoxide

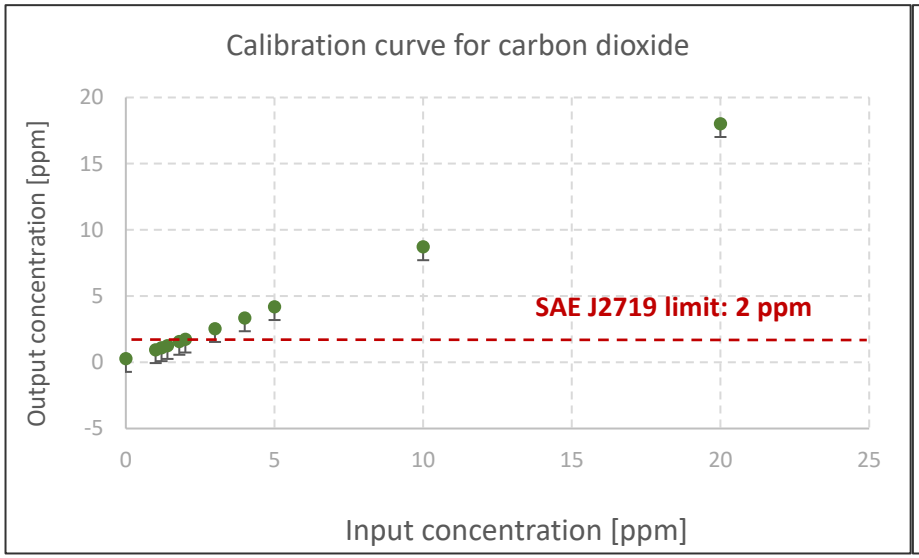


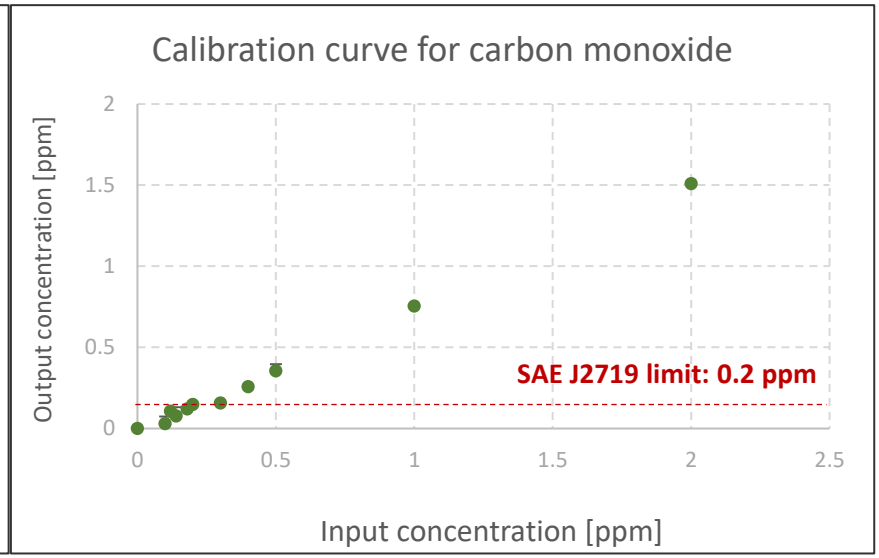
FTIR provides selective quantitation of multiple potential hydrogen contaminants

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



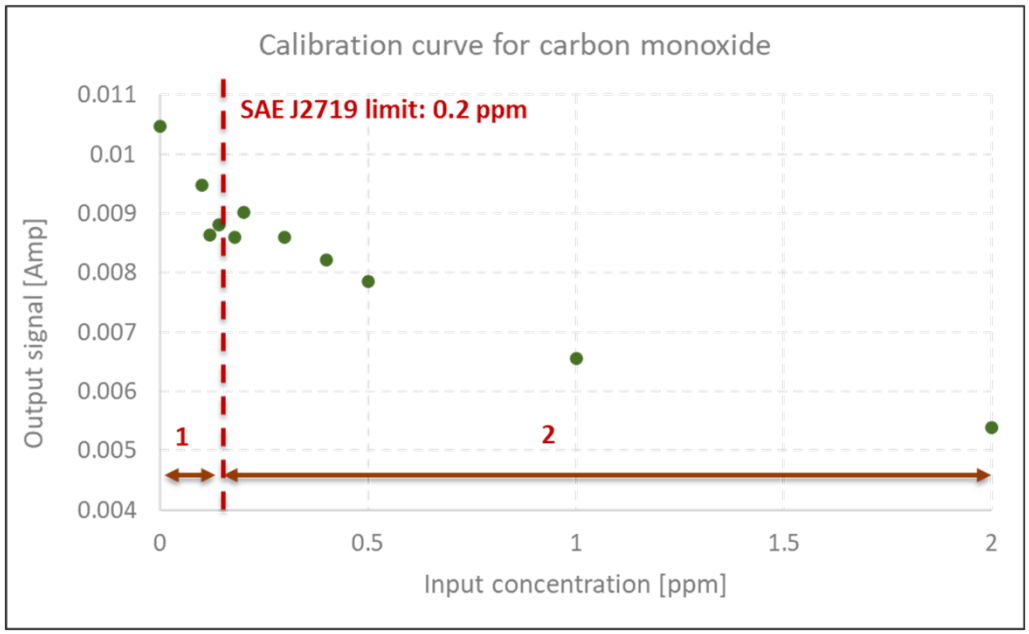


FTIR sensor performs well for the simultaneous CO_2 and CH_4 detection at SAE J2719 limits

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

- Most identified HCDs operate at near ambient pressure
- Hydrogen dispensers operate at 350 – 700 bar and temperatures down to -40˚C
- An interface is needed to serve as a pressure reducer, flow regulator, and thermal buffer
- Features of the NREL Interface (HCD-I):
  - Fully automated sample collection and analysis
  - Captures high-P hydrogen coming from the hose high pressure depressurization into a medium-P "buffer chamber". The hose high-P hydrogen would otherwise be vented
  - Delivers test gas to HCD at low-P, near-ambient T and controlled flow
  - Readily adaptable for other station/dispenser locations

The NREL Interface automatically delivers dispenser H_2 to the HCD at appropriate P, T, and flow rate

Accomplishments and Progress

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

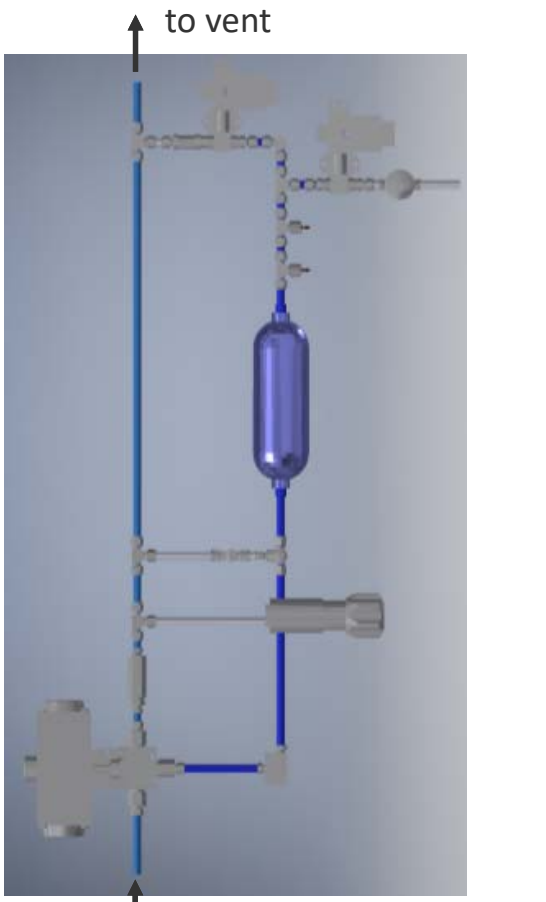
Step 1
Initial venting of high-pressure source

Step 2
Purging of buffer chamber

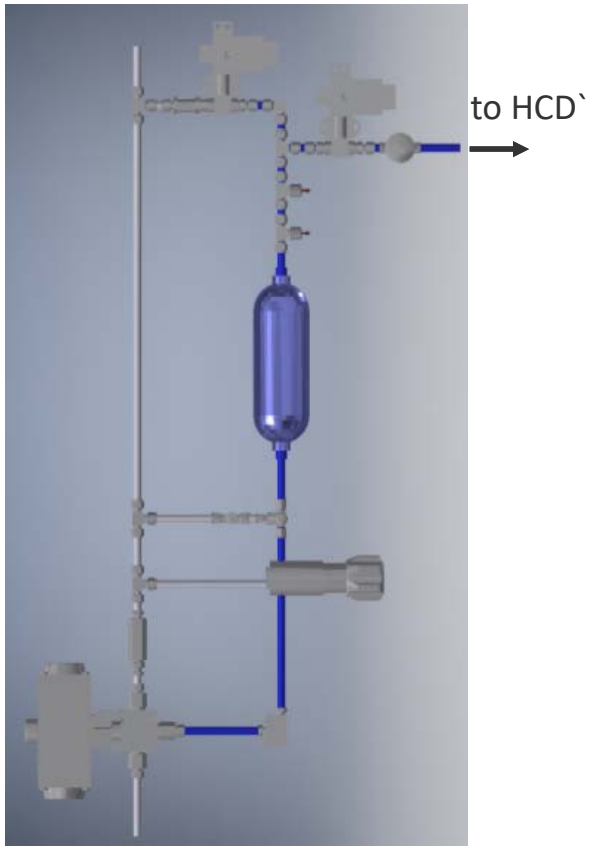
Step 3
Pressurization of buffer chamber

Accomplishments and Progress

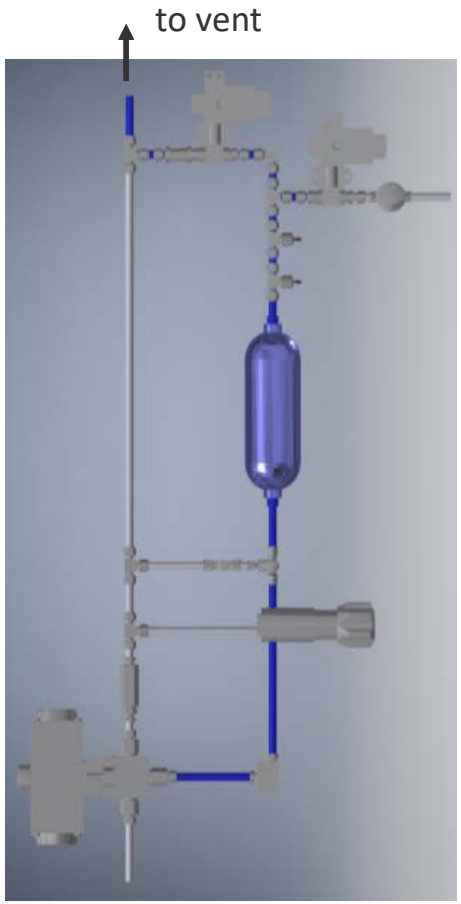
Hydrogen Contaminant Detector Interface: Method of Operation (slide 2 of 2 slides)



Step 4
Isolation of buffer chamber; upstream depressurization



Step 5
Sample delivery to HCD at controlled P & Flow

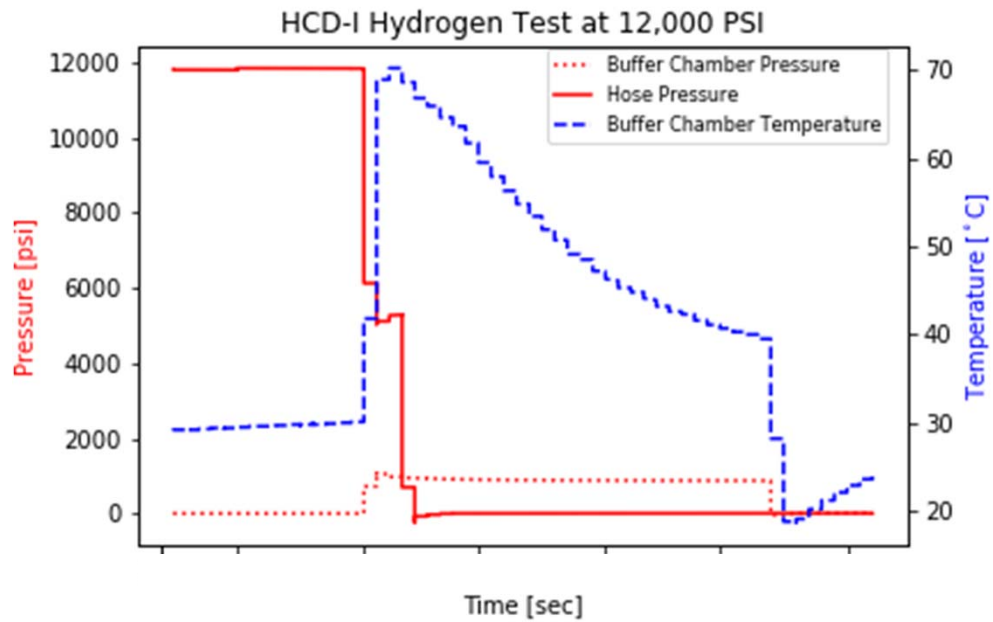


Step 6
Depressurization of buffer chamber

Accomplishments and Progress

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

Hydrogen Contaminant Detector Integration at Fueling Station: Concept

STEP 1:
A typical FCEV refueling includes a P check of the hose where H_2 is normally vented but 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 P-Check H_2 into a P-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.

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

Remaining Challenges and Barriers

- Adaptation of the gas generation system to more accurately generate test gas generation at low concentrations
- Sample corruption associated with the FTIR sensor with contaminants such as water vapor and ammonia
  - Ammonia tends to stick to surfaces (e.g., pneumatic 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
- None of the sensors can detect all SAE J2719 contaminants
- Integration of HCD for automatic analysis within the dispenser

Proposed Future Work

- Statistical analysis of accuracy, precision, and detection limit of HCDs measurement
- Integrating HCD and HCD-interface into a dispenser at NREL Hydrogen Infrastructure and Testing and Integration Facility (HITRF) and commercial hydrogen fueling stations
- Keeping abreast with latest detection technologies
- Provide HCD manufacturers with a test platform to demonstrate their analyzers' performance

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

Summary

- Detection of hydrogen contamination will prevent damage to fuel cells 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 analysis of the 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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Publication Number

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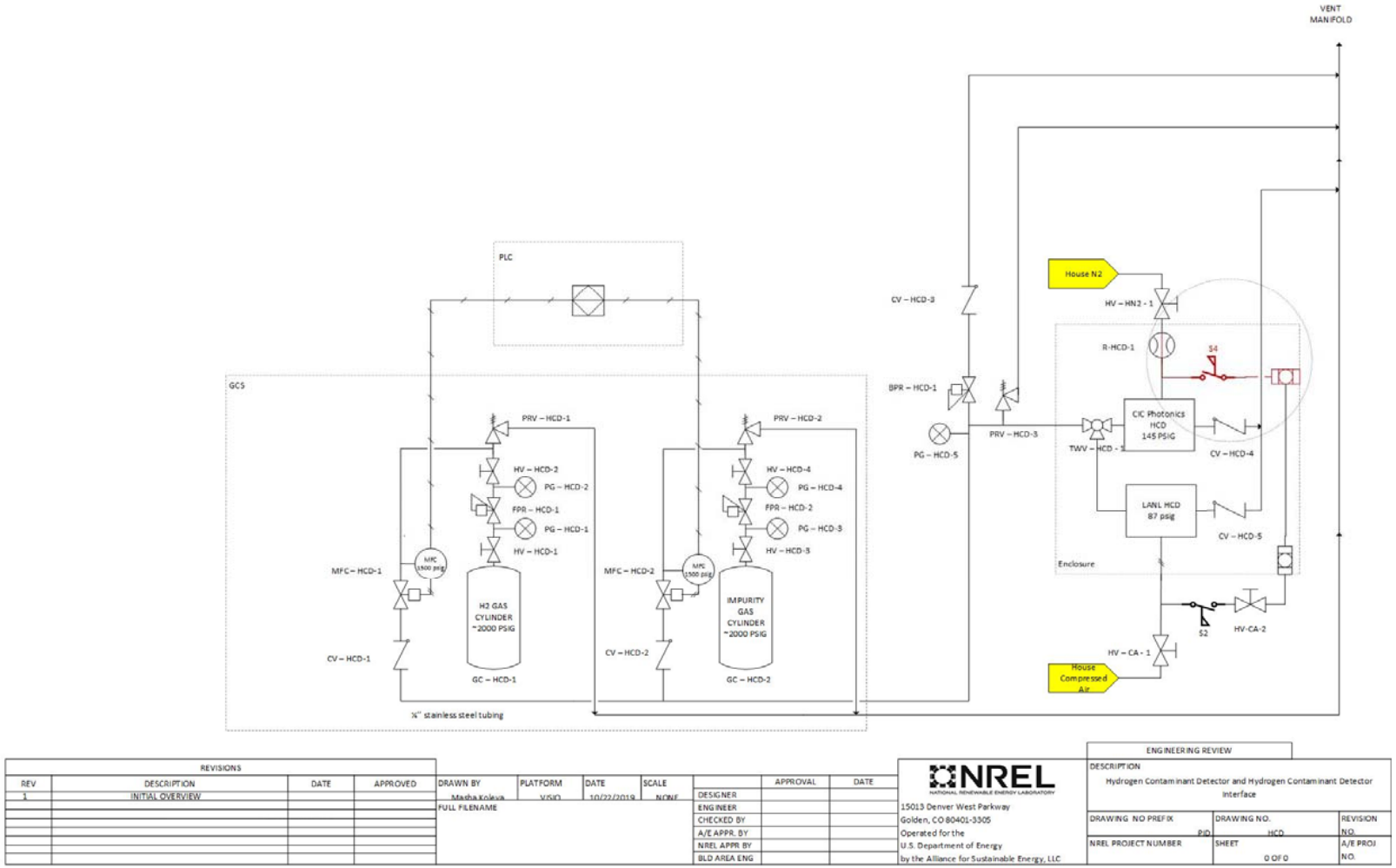
Technical Back-Up Slides

(Include this “divider” slide if you are including back-up technical slides [maximum of five]. These back-up technical slides will be available for your presentation and will be included in Web PDF files released to the public.)

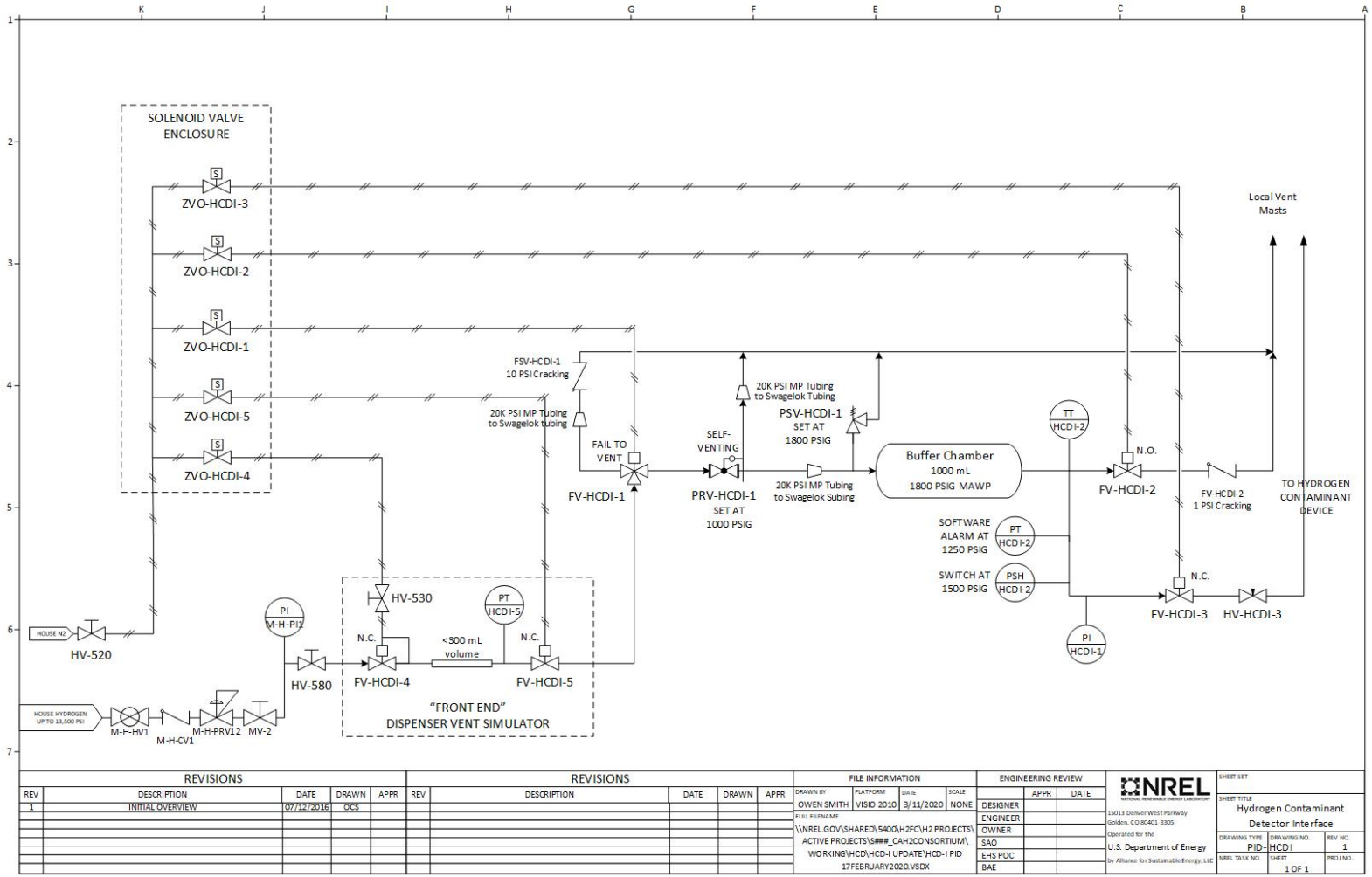
Technical Back-Up Slides

- P&ID diagram for the HCD system



Technical Back-Up Slides

- P&ID Diagram for HCD-I system



Publications and Presentations

Talks and Presentations

- "On-Site, Near Real-Time Analysis of Critical Impurities in Hydrogen" Mariya Koleva, William Buttner, Matthew Post, Jennifer Kurtz, Fuel Cell Seminar, Long Beach CA (November 5 -7, 2019)

- "Ongoing Component Validation R&D at the National Renewable Energy Lab", Cory Kreutzer, Mike Peters, Josh Martin, Matt Ruple, Kevin Hartmann, Erin Winkler, Dan Leighton, Bill Buttner, Mariya Koleva, Matt Post, Jake Thorson, FC Expo: International Hydrogen & Fuel Cell Expo, Tokyo, Japan (February 26 to 28, 2020)

- "California-DOE Hydrogen Research Consortium--The NREL In-Line Hydrogen Contaminant Detector Project" William Buttner Mariya Koleva, Matthew Post, Kevin Hartman, Presented to the H2@Scale Working Group Webinar (May 19, 2020).