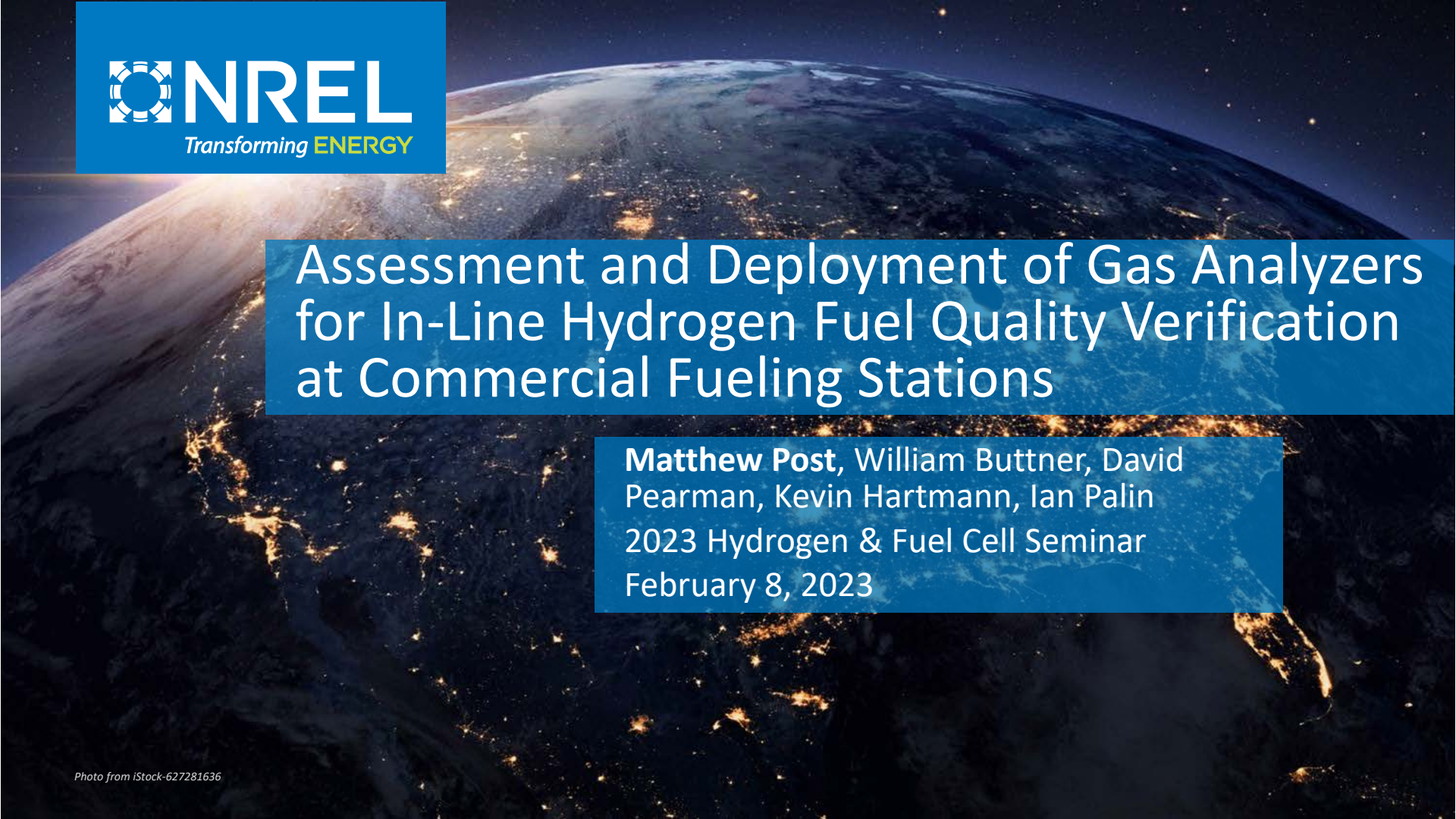


Assessment and Deployment of Gas Analyzers for In-Line Hydrogen Fuel Quality Verification at Commercial Fueling Stations

Matthew Post, William Buttner, David Pearman, Kevin Hartmann, Ian Palin

2023 Hydrogen & Fuel Cell Seminar

February 8, 2023

Photo from iStock-627281636

Why in-line real time Fuel Quality Verification?

- 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

- Length of time between current FQ verification may be inadequate
- Out-of-Spec H_2 has been dispensed with adverse impact on FCEV performance

Contaminants in Hydrogen Fuel

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

Source: Bacquart et al, 2018, Probability of occurrence of ISO 14687-2 contaminants in hydrogen: Principles and examples from steam methane reforming and electrolysis (water and chlor-alkali) production processes model, International Journal of Hydrogen Energy, doi: https://doi.org/10.1016/j.ijhydene.2018.03.084

Regardless of the hydrogen production method, manufacturers must comply with SAE J2719

SAE J2719 Standards

Constituent	Limits [ppm]	Laboratory Test Methods to Consider and Under Development
Water (H_2O)	5	ASTM D7653, ASTM D7649, ASTM D7941, ASTM D7941M
Total hydrocarbons (C1 basis)	2	ASTM D7675, ASTM D7833
Oxygen (O_2)	5	ASTMD7649, ASTM D7607
Methane (CH_4)	100	ASTM D7653, ASTM D7675, ASTM D7833, ASTM D5466
Helium, Nitrogen, Argon (He, N_2, Ar)	300	ASTMD7649 (N_2), ASTM D7833
Carbon dioxide (CO_2)	2	ASTM D7649, ASTM D7653, ASTM D7833
Carbon monoxide (CO)	0.2	ASTM D7653
Total sulfur (S)	0.004	ASTM D7652, ASTM D6228
Formaldehyde (CH_2O)	0.2	ASTMD7653, ASTM D7941, ASTM D7892
Formic acid (CH_2O_2)	0.2	ASTM D7550 (withdrawn), ASTM D7653
Ammonia (NH_3)	0.1	ASTM D7653, ASTM D7941/D7941M
Total halogenates	0.05	ASTM D7892, ASTM D7676, ASTM D5466

Source: SAE International, 2020, Hydrogen Fuel Quality for Fuel Cell Vehicles, available at: https://www.sae.org/standards/content/j2719_202003/

Project Overview

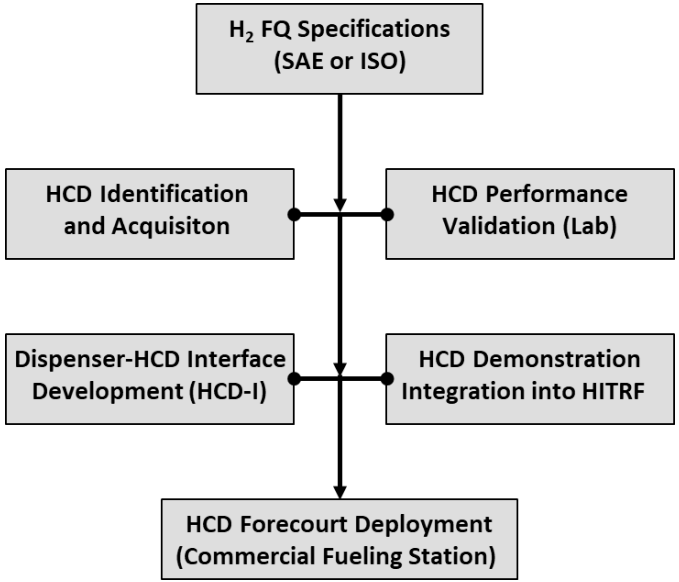
1 - HCD Hardware Selection:
- Completed Commercial FTIR (multi-components)
- LANL EC for CO

2 - Design and Build HCD-Interface:
- Completed: Basic HCD-Interface (qualify design) demonstrated on Hydrogen Infrastructure Testing and Research Facility (HITRF)
- On-going: Integration into HITRF H2 Dispenser

3 - Benchtop testing of HCD:
- Completed: Basic HCD 1 and HCD 2 performance evaluation
- On-going: Optimization testing on-going

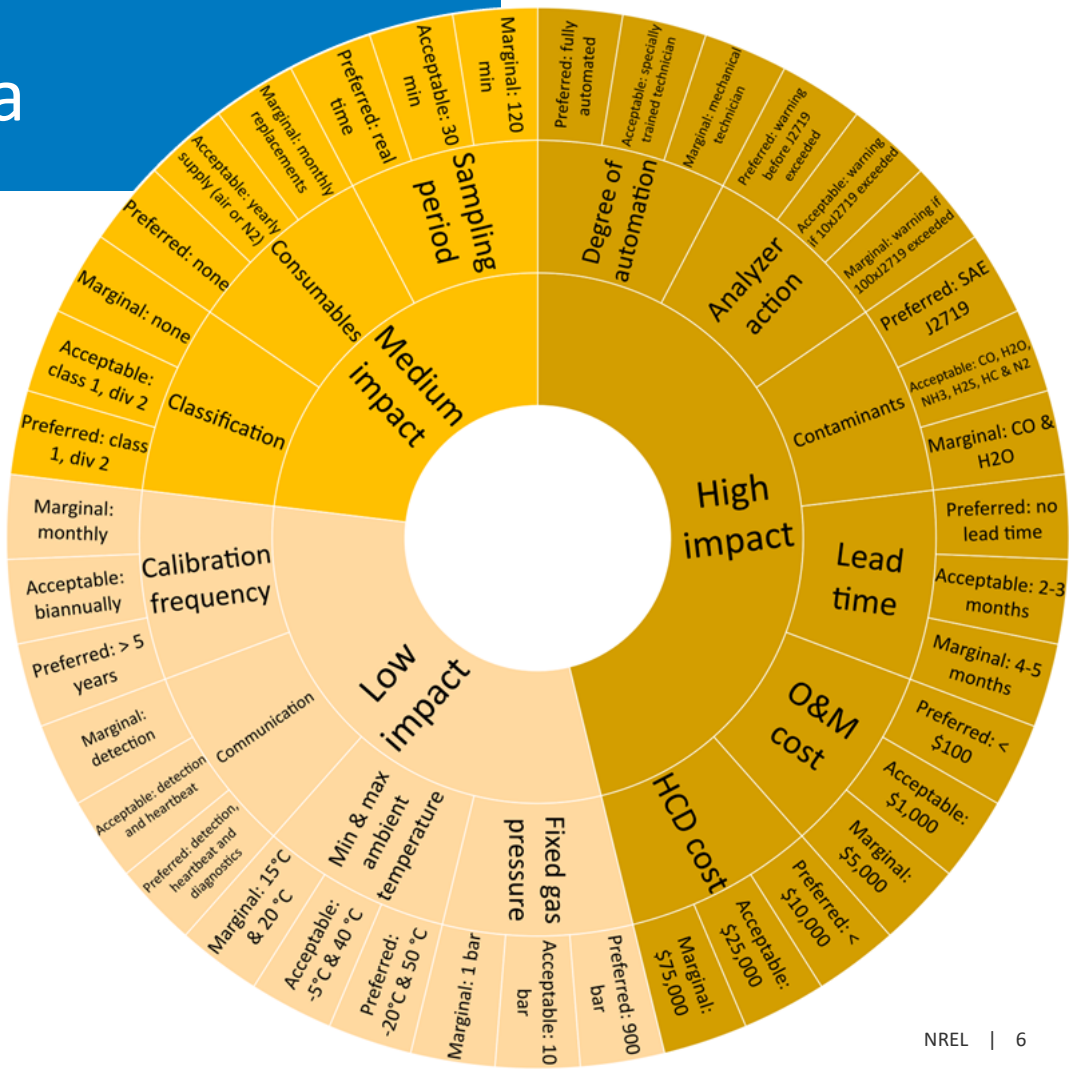
4 - Integrate into NREL's HITRF
- Engineering and Safety Documents and Process Hazard Analysis for NREL Deployment are completed
- On-going: Integration demonstration

5 - Forecourt Deployment (Future):
- Demonstration at California Fueling Station



Selection Criteria

- Criteria divided into **three** categories:
  - High impact, pertaining to number of contaminants from SAE J2719, cost, availability, etc.
  - Medium impact, pertaining to hazardous location classification, additional consumables, sampling period, etc.
  - Low impact, pertaining to operating conditions, calibration frequency, etc.
- Each category has a **different weight** contributing to a total score
- **Instrument readiness**, expressed as a factor by which the entire score is multiplied
- **Outcome:** we are evaluating two sensors: one commercial and one prototype analyzer



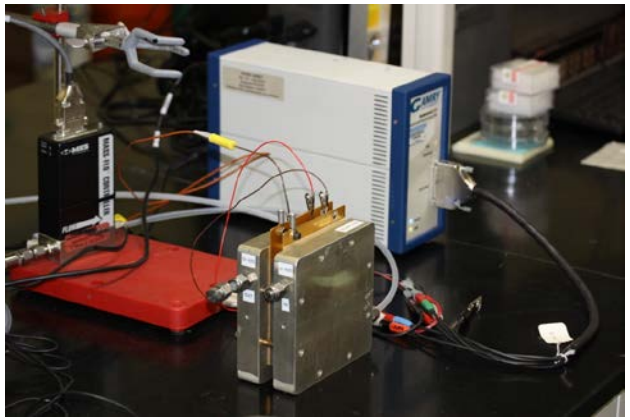
HCD Selection and Lab Evaluation

HCD 1: Fourier transform infrared spectroscopy sensor (commercial)

Targeting ***CO, CO_2, CH_4, NH_3, H_2O, CH_2O, HCOOH***
(calibration curves have been obtained)

HCD 2: Electrochemical sensor (LANL):

- Advanced prototype is at NREL
- Pre-commercial device is now available



Targeting ***CO***

HCD Selection

FTIR: A multi-analyte HCD—HCD 1
LANL Sensor for carbon monoxide—HCD 2
Phase 2: Additional HCDs (e.g., water vapor analyzer)

LANL HCD and Partnership

Partnership with LANL:

- Strengthening partnerships with other National Laboratories
- Provision of electrochemical HCD (LANL)
- Optimization of current operating conditions (NREL)
- Evaluation of sensor and testing response of different impurities

Sensor capabilities:

- CO detection

Sensor limitations:

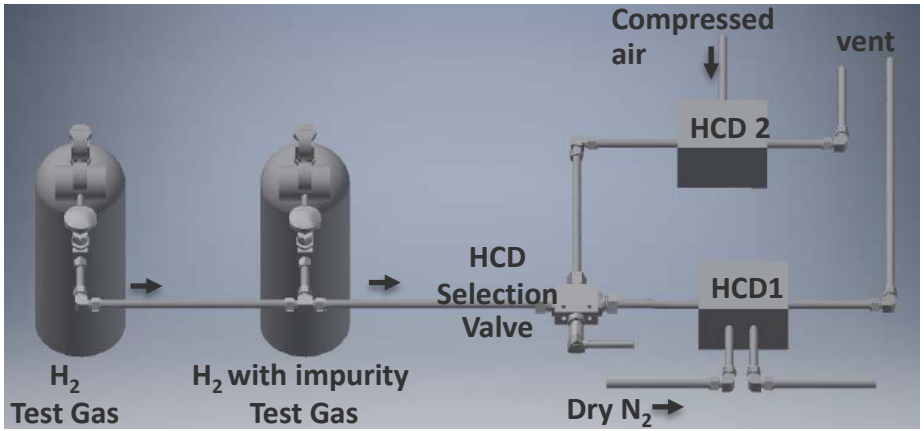
- Membrane and catalyst may be poisoned under other contaminants exposure

LANL HCD installed in the NREL Benchtop HCD Analysis enclosure.

HCD Benchtop Setup

Simplified Test Gas Generation System Block Diagram:

- Two gas lines with flows regulated by mass flow controllers (not shown) 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
- Dry nitrogen purge is supplied to HCD 1 to remove background moisture
- HCDs run remotely and personnel communicate through ethernet from the adjacent control room

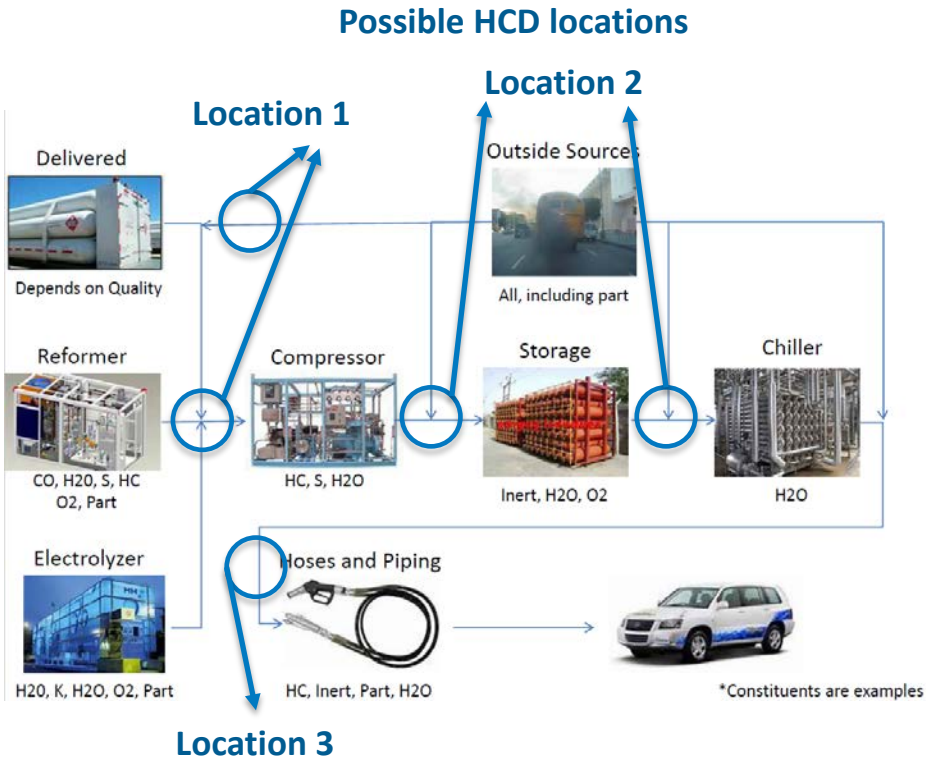


The Test Gas Generation System produces a range of contamination levels for HCD validation and calibration

Sampling Hydrogen Fuel at Stations

Where should an in-line analyzer be placed?

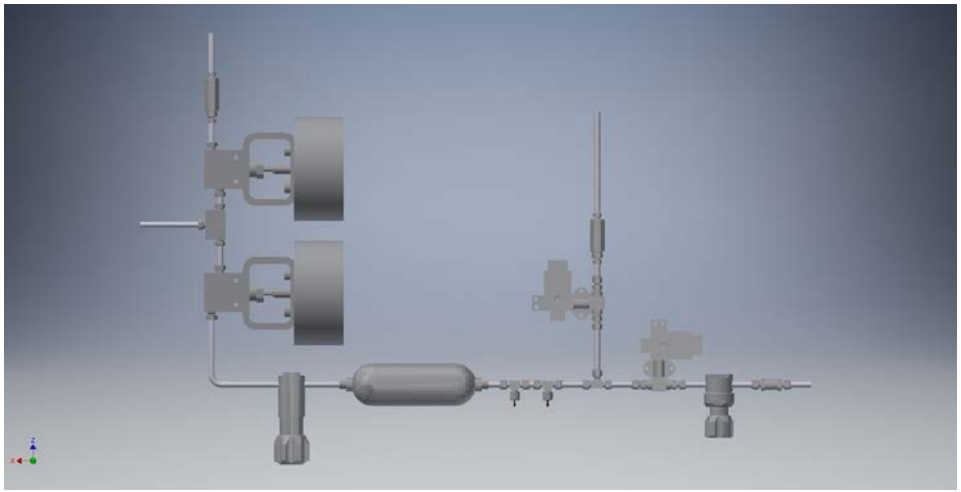
- Location 1 (After Production):
  - Will detect contaminants from the production process
  - Won't detect contaminants from operation (compression, dispensing)
  - Lower pressure
- Location 2 (Storage System):
  - Will detect additional contaminants from compression process
  - Won't detect possible contaminants from the dispenser
  - High pressure
- Location 3 (At the Dispenser):
  - Closest to the vehicle and where the regulatory samples are taken for lab analysis
  - Hose volume is vented as part of the process
    - Vented gas can be collected and analyzed
    - Vented gas pressure can be regulated



The Hydrogen Contaminant Detector Interface (HCD-I)

Features of the HCD-I

- Most identified HCDs operate at near ambient P & T
- 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



Operation of the NREL Interface (HCD-I):

- Fully automated multi-step sample collection and analysis
- Captures high-P hydrogen from the hose de-pressurization into a medium-P “buffer chamber”.
- Delivers test gas to HCD at low-P, near-ambient T and controlled flow
- Readily adaptable for other station/dispenser locations

Laboratory Demonstration of Sampling Concept

- A full pressure test was performed using a demonstration system and a hose vent simulator
- 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
- A sample was successfully captured in less than 4 seconds in the demonstration

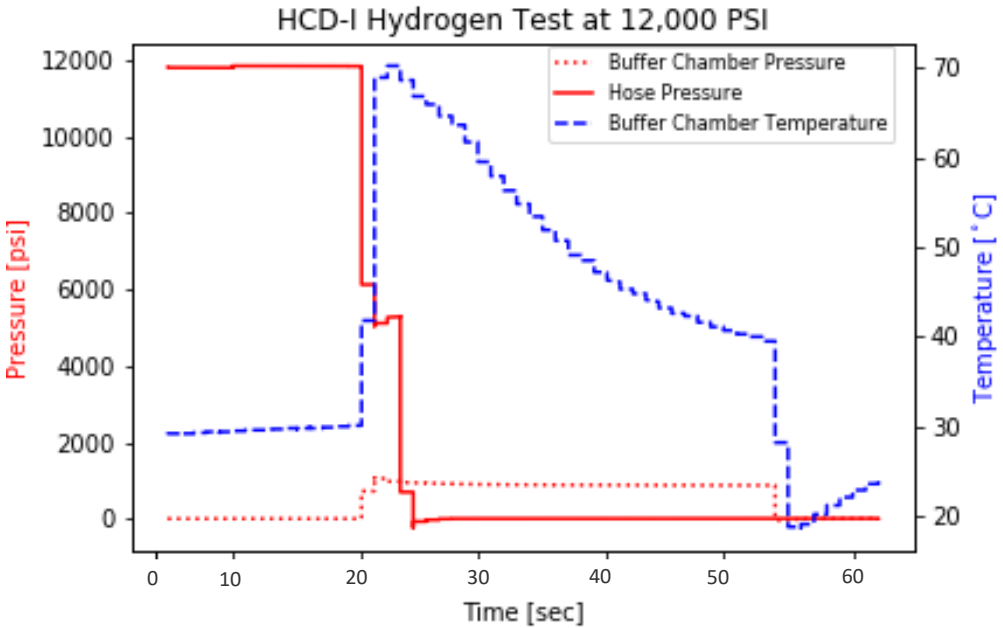
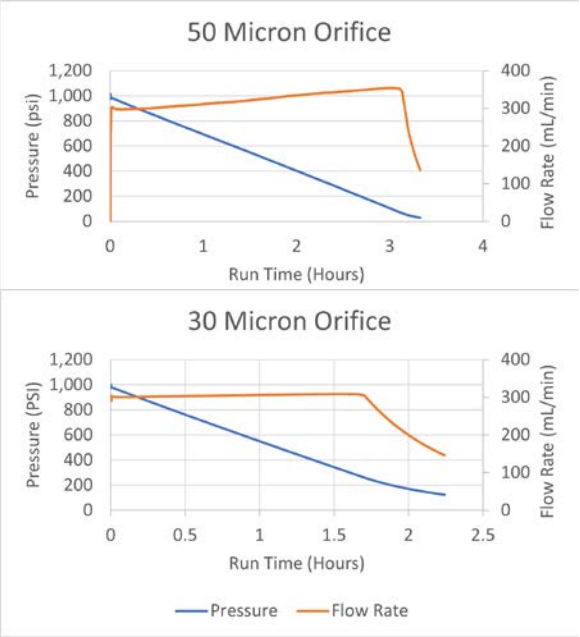


Chart showing pressures and temperature in a full pressure demonstration of the sampling concept

Automated test gas collection by the NREL HCD-interface for impurity analysis was successfully demonstrated at full pressure operation (700 bar)

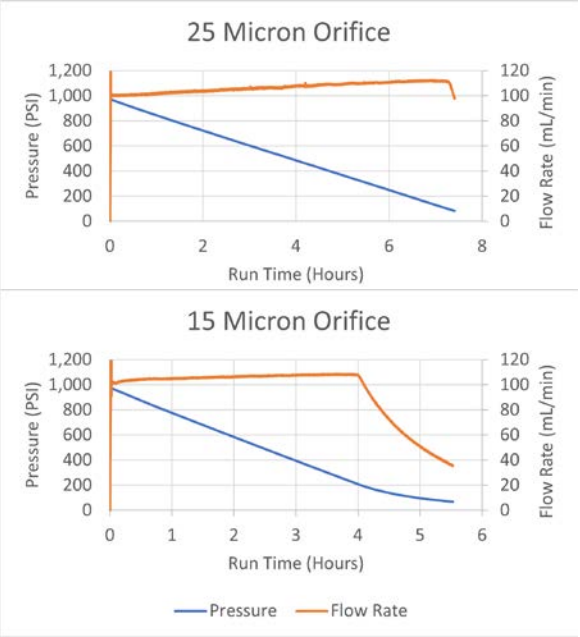
Control of Gas Delivery by HCD-I

300 mL/min Target (HCD-1)



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

100 mL/min Target (HCD-2)



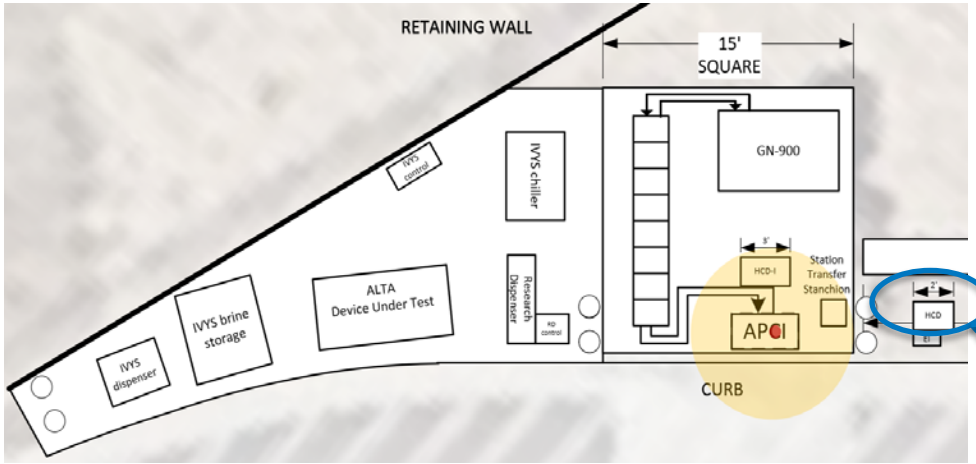
Upper: 25-micron orifice sample run
Lower: 15-micron orifice sample run

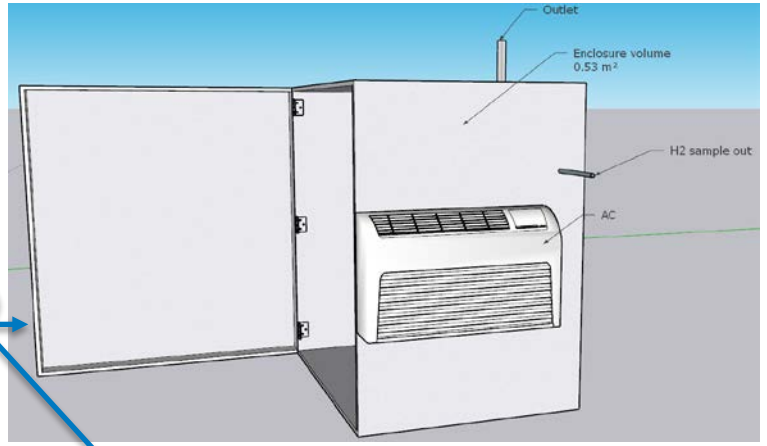
Sample Delivery Characterization Results

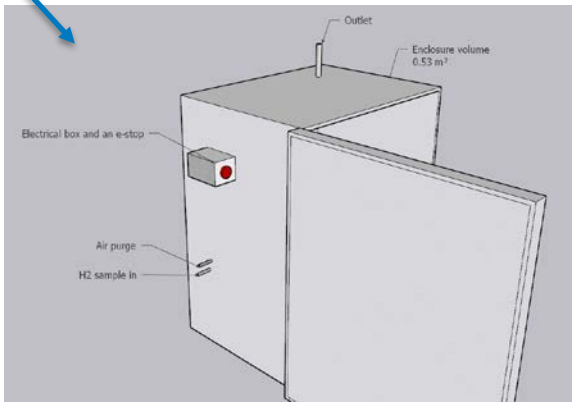
- Larger orifice sizes:
  - Lower pressure required
  - Buffer chamber able to be depleted further
  - Longer sample times
- Smaller orifice sizes:
  - Increased pressure required
  - More stable flow with pressure variations
  - Sample time decreased
- Flow stability influences orifice size more than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

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

HCD Integration Layout at NREL







- Layout of the HCD and HCD-Interface at the dispenser
- NEMA air-conditioned enclosure for HCD
- Design Review and the Process Hazard Analysis for the integrated system are completed
- HCD-I installation currently underway
- Class I Division 2 Group B area inside the yellow bubble
- HCD can be located outside the C1D2 area

Dispenser Tie-In Points

Hose Vent Tie-In Point

Vent Continuation Tie-In Point (behind dispenser)

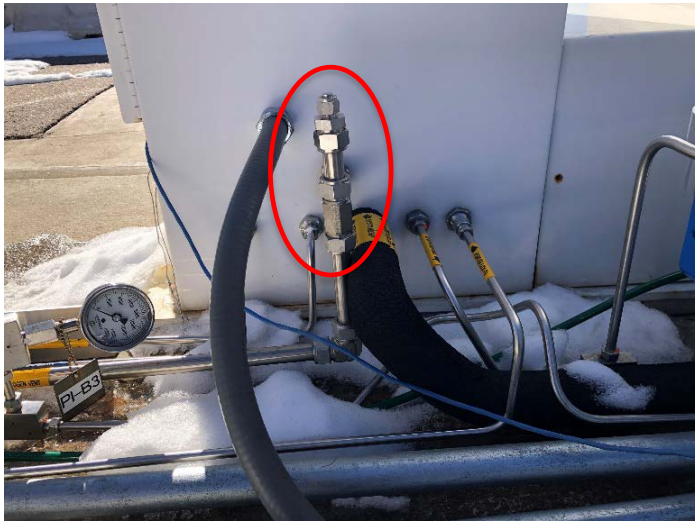
Photo by Dennis Schroeder, NREL 34586

Dispenser Tie-In Points Before Installation

Hose Vent 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



- 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.

Beginning of Installation

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

Hardware Installation Progress

- Installation of HCD-I is complete
  - Shakedown nearly complete
- Next Steps
  - Readiness Verification (Safety)
    - Formal authorization to work
  - Sample collection demonstration
  - Integration of HCDs into HCD-I

Photos by Werner Slocum, NREL 74360 and 74358

Thank You

www.nrel.gov

NREL/PR-5700-85143

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Hydrogen and Fuel Cell Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

Photo from iStock-627281636

NREL
Transforming ENERGY