# 2015 U.S. DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting

## Hydrogen Safety, Codes and Standards: Sensors


P.I. & Presenter : Eric L. Brosha

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June 9, 2015

Project ID# SCS004

# Overview

- **Timeline**
  - Start: Summer FY 2008
  - Finish: 2015

- **Budget**
  - Total DOE project Value
    (Combined LANL/LLNL)
    - $4901K
  - FY14 Funding: $225K
    - $150K LANL
    - $ 75K LLNL
  - FY15 Funding $25K

- **MYRD&D Barriers**

✧ The SCS sub-program will develop hydrogen sensors with the appropriate response time, sensitivity, and accuracy for use in safety applications to reduce risk and help establish public confidence (Table 3.7.6)

(A) Safety Data and Information: Limited Access and Availability
(C) Safety is Not Always Treated as a Continuous Process
(K) No Consistent Codification Plan and Process for Synchronization of R&D and Code Development
(L) Usage and Access Restrictions

- **Partners**
  - Project lead: LANL
  - Hydrogen Frontier, Inc. - Field Trials Partner
  - Zircoa Inc. and Agile Engineering
  - Custom Sensor Solutions, Inc.
  - NREL: Codes & Standards field performance evaluation/validation team member
  - ESL ElectroScience, Inc.

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# Relevance – Objectives

- Develop a low-cost, durable, and reliable **hydrogen safety sensor** for stationary and infrastructure applications, extendable to vehicle protection, through material selection, sensor design, and electrochemical R&D investigation.

- Demonstrate working technology through performance evaluation in simulated laboratory and field tests, initiate rigorous life testing, and with NREL collaborators, evaluate sensor performance in relation to codes and standards.

- Work toward commercialization by engaging appropriate industry partners, including long-term testing and development of manufacturing methods.

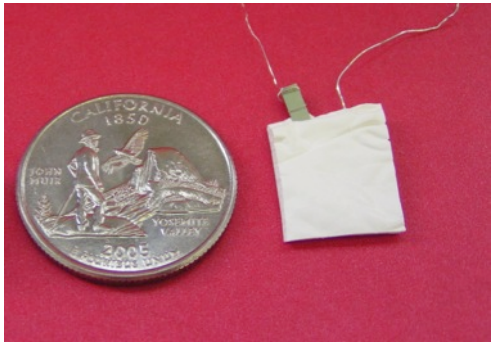
- Pursue commercialization of the new sensor technology through industry partnerships.

# Relevance – Technical performance requirements
# Why does the hydrogen community need better $H_2$ Safety Sensors?

- **Major Problem**: sensor drift leading to false positives and false negatives.
  - **Frequent calibration requirements and present technologies drive up costs substantially!**
- Lack of $H_2$ sensor technology that address accuracy and sensitivity in the concentration range where alarm points and actions are required by codes and standards.
  - **Good technology for ppm and high percent levels but there is a performance gap around the LFL.**
- An $H_2$ infrastructure will require improved $H_2$ safety sensors.
- Most recent confirmation of this view: NREL/DOE Hydrogen Sensor Workshop, June 8, 2011 (reaffirmed findings of Hydrogen Safety Sensor Workshop, Washington DC, April 3-4, 2007).
- **LANL/LLNL technology produces a high signal-to-noise with maximum sensitivity in the 1-4 vol% $H_2$ range based on a voltage generated by sensing electrochemical oxidation of hydrogen on a robust ceramic platform.**

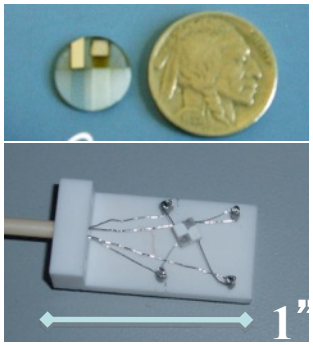
# Approach: Project timeline leading up to 2015 field trials

## 2008



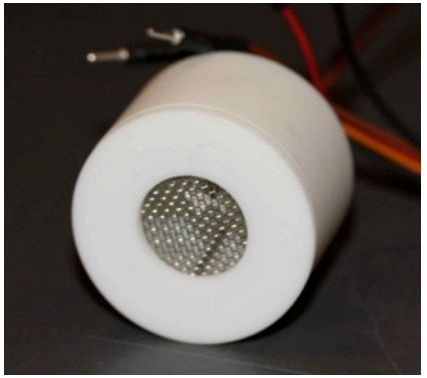
1st Generation device – tape cast using ITO electrode and controlled interface approach. **Externally-heated** with tube furnace (30lbs): **120V, 8A**.

## 2009-2010



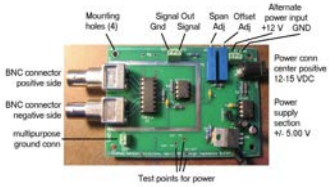
Pre-commercial mixed potential sensor in thick film version on ESL fabricated platform (LANL specs). **Power requirements**: **6.5V, 0.75A.**

## 2011



Pre-commercial ceramic packaging/sensor supported by 4 posts. **Power requirements**: **5.0V, 0.65A**. Pre- commercial prototype easily handled. 1st devices sent to NREL for **Round 1** testing.

## 2012




**Round 2** NREL testing. Begin developing sensor electronics with commercial partner.

## 2013


Round 3 NREL testing. Prototype sensor heater control board developed and tested.

## 2014

Sensor and signal / heater electronics integrated into a single unit with wireless communications. Search for commercial testing partner.

**…Field trials begin in 2015.**

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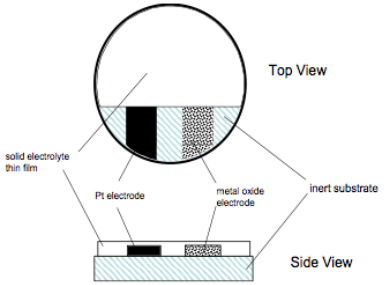
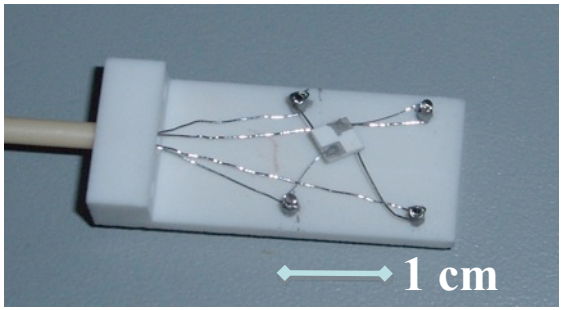
# Approach: Controlled interfaces for sensor design and development

## Sensor Technology Selection

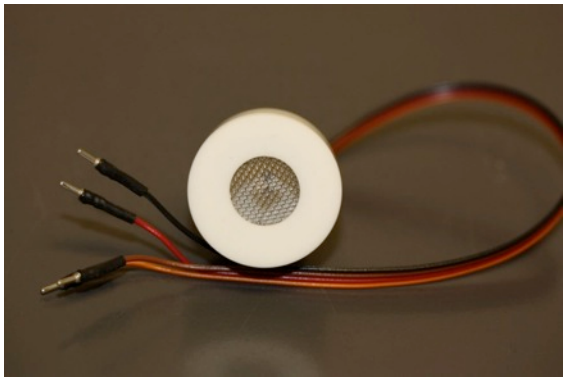
- **Derivative of the hugely successful automotive Lambda, potentiometric $O_2$ sensor.**
- Mixed-potential sensors generate a voltage in the presence of oxygen and a reducing/oxidizing gas.
- Unique class of sensors have been developed that are based on dense electrodes and porous electrolyte structures.
- Result: stable and reproducible three phase interfaces (electrode/electrolyte/gas) that contribute to their exceptional response sensitivity and stability.
- Controlled Interface Technology: Conducive to miniaturization, thin film electrodes and electrolyte greatly improve sensor response.




Schematic of a HC Sensor in planar configuration (US #, 7,264,700).




ITO/YSZ/Pt $H_2$ safety sensor built on ESL platform.



Packaged $H_2$ safety sensor

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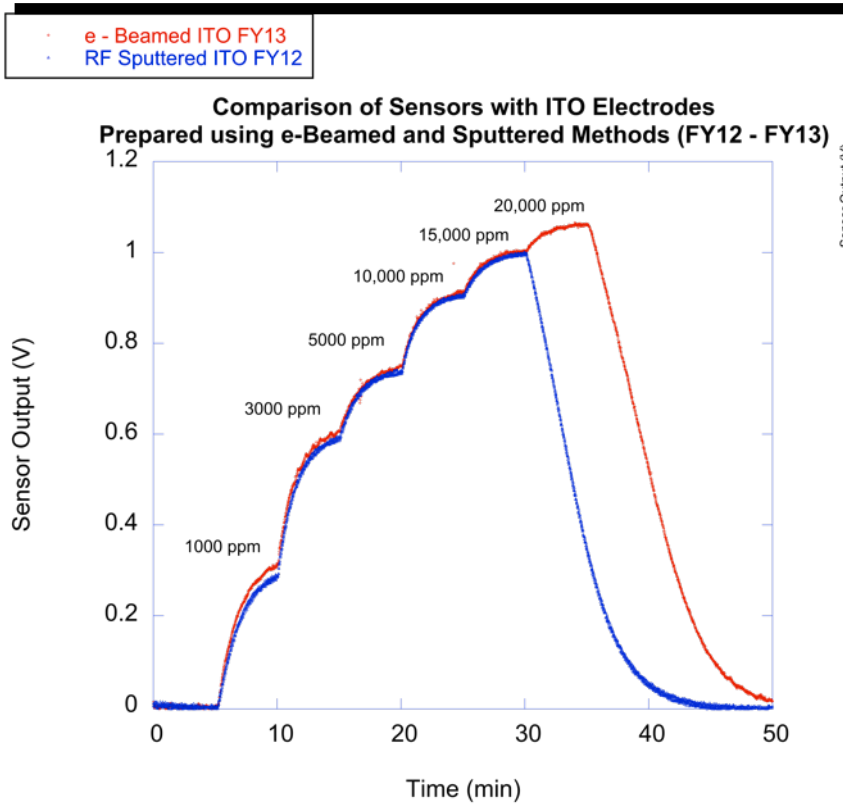
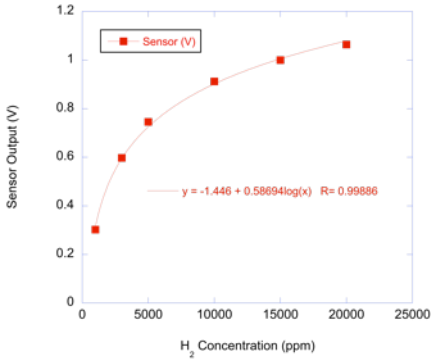
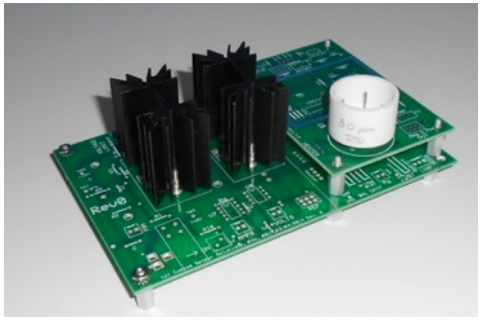
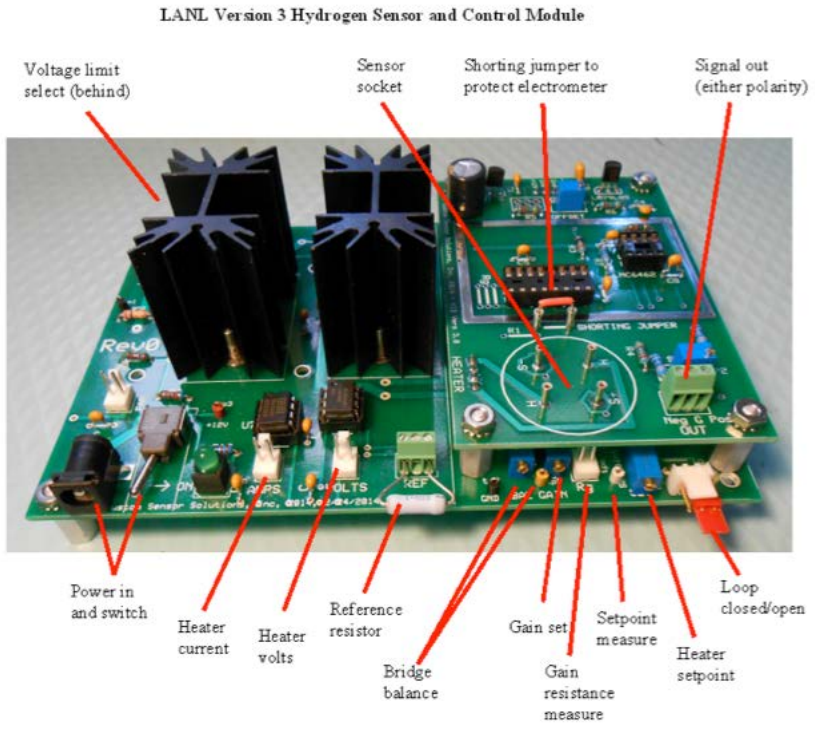
# Approach: New field trials electronics designed and built by Custom Sensor Solutions building on FY12-FY14 work






- Combines and simplifies CRPS and HIB boards previously tested.
- Designed around LANL sensor packaging. Sensor plugs into HIB.
- Easy to replace sensor element.
- Accommodations for cooling fan or convection cooling of heater circuit.

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# Technical Accomplishments FY14: Hydrogen Frontier Inc. identified and designated as the primary testing site / site visit







- Location: Burbank within a mile of the airport.
- Best location for field trials determined to be filling station island. No anticipated $H_2$ releases (baseline stability).
- Pallet locations identified, need to prioritize deployment strategy based on resources.
- Outdoor facility largely does not require sensors. Hydrogen Frontiers would like to study/monitor areas where hydrogen accumulation is believed to occur.



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# Summary of Technical Accomplishments & Milestones in FY14

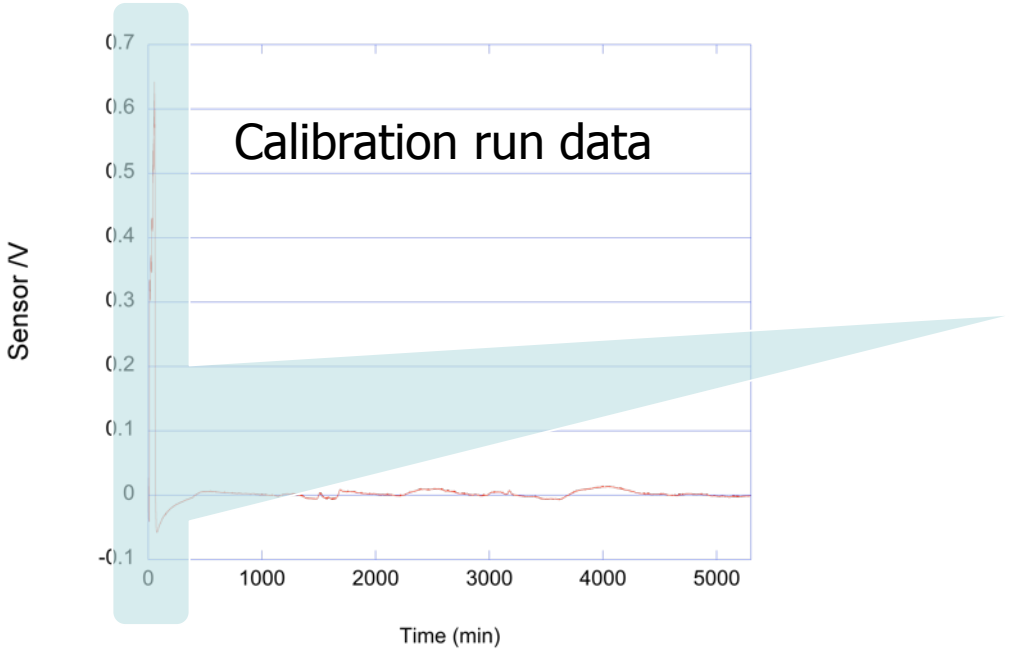
- Identified hydrogen filling station partner.
  - Hydrogen Frontier Inc., Burbank CA.
  - Visited site and scoped out areas for placement of Field Trials units.
  - Identified filling station island enclosure for known area absent of $H_2$ leaks/activity.
  - Identified area of frequent $H_2$ releases.
- Conducted ignition studies with flammable $H_2$/air mixtures and actual sensors.
  - Tested flame arrestor.
  - Verified sensor and packaging would not ignite flammable mixtures.
- Acquired and tested commercially sourced wireless system from Omega Engineering.
- Designed control / monitoring software with NI Labview® programmer.
- Designed new control electronics board with Custom Sensor Solutions, Inc. to integrate sensor heater control board and high impedance buffer circuit.
- Designed an integrated package for field trials testing around NEMA 8 enclosure and other components.

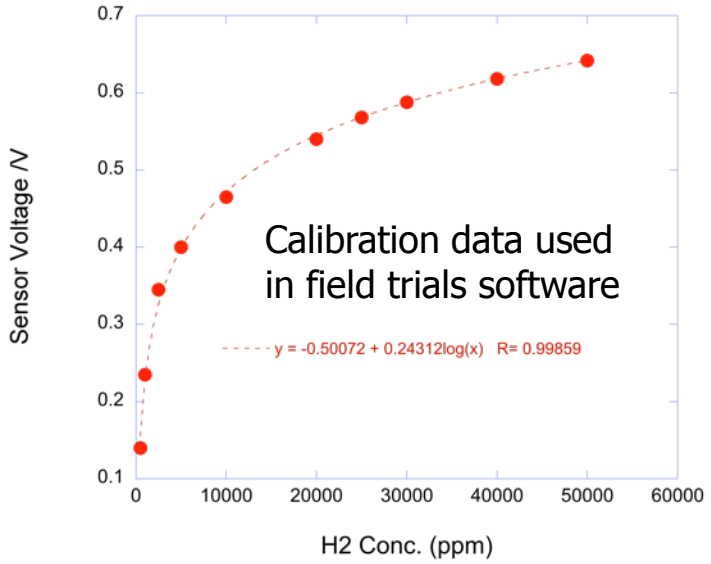
# Technical Accomplishments FY15: Construction of field trials test unit (for $H_2$ Frontier/Burbank)

- Unit designed to be placed within filling station island; **no $H_2$ anticipated based on commercial $H_2$ sensor data**.

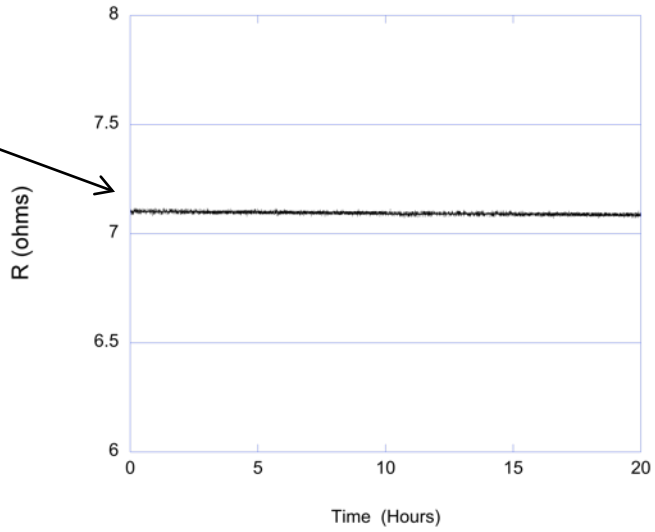


# Technical Accomplishments FY15: Unit calibration and off-site testing. Final logging of heater circuit functions.




Heater resistance during calibration




Resistance of sensor Pt heater loop and hence temperature of the sensor element.

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# Technical Accomplishments FY15: Burbank installation (November 4, 2014)


New enclosure added


- Assembled unit once on site / drilled mounting holes into enclosure of filling station island.
  - Attached carbon filter and replaced wireless Li battery for Omega transmitter (LANL shipping requirement).
- Installed computer and Omega receiver inside new enclosure provided by $H_2$ Frontiers.
- All equipment is outdoors and exposed to elements.
  - Cooling of electronics bays to be added in the future.

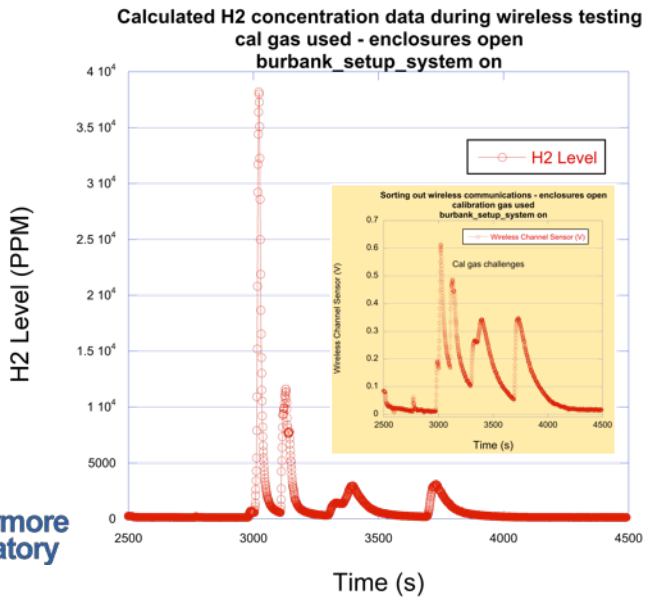
24VDC power run through explosion proof conduit / new lines to main bus and dedicated fuse.

# Technical Accomplishments FY15: November 4, 2014 Burbank installation and testing and final check-out

Commercial $H_2$ sensor

Filling station island


Conduit for 24V DC power


LANL/LLNL unit #2 installed on 11-5-14. Cal gas exposure testing before leaving site.

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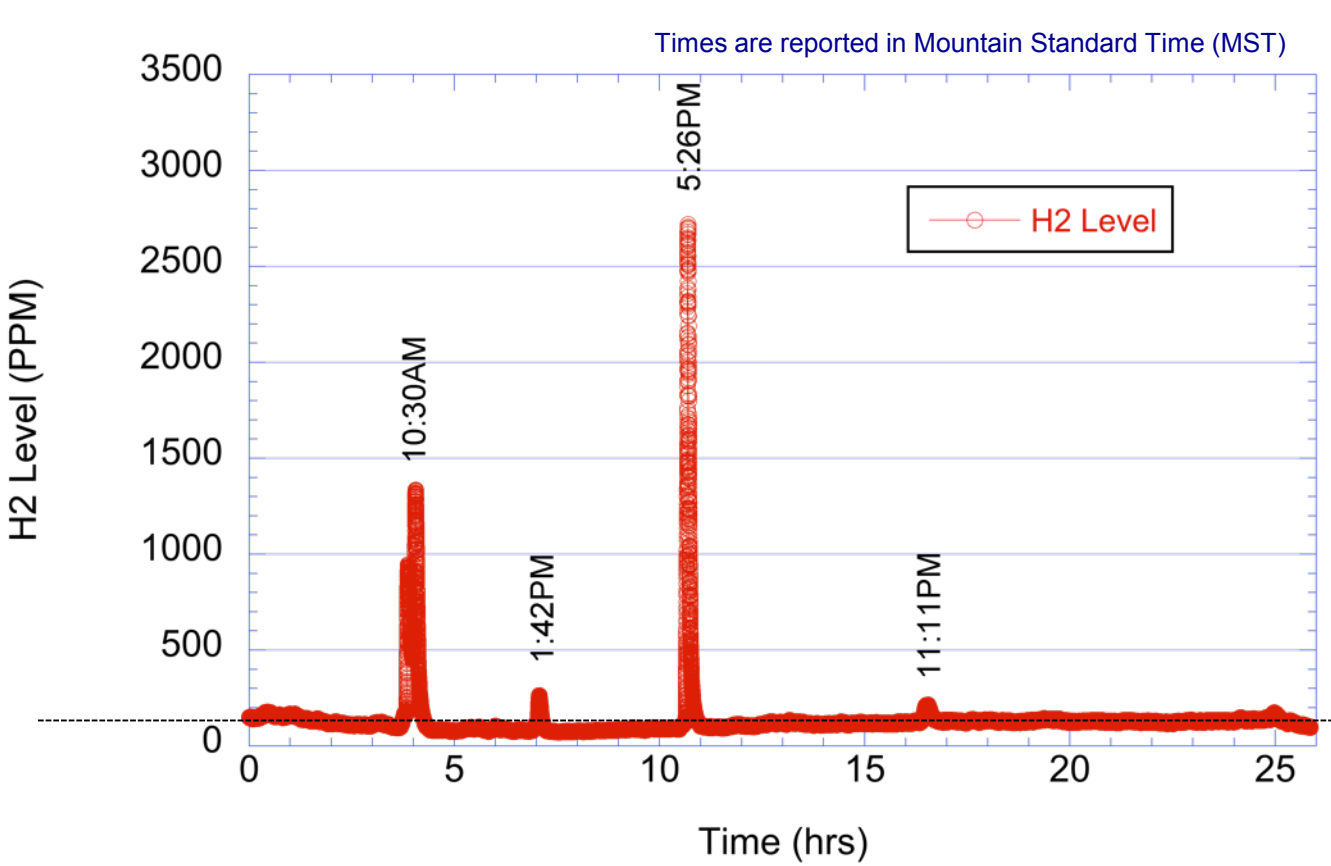
# Technical Accomplishments FY15: Burbank testing – Results for Thursday 11-6-14





There does not appear to be significant drift in sensor baseline over this first full day.

- Filling station dispensing island chosen as first site to place LANL/LLNL field trials unit because known to be **leak free and "confirmed" by commercial sensor**.
- Time of sensor activity *not periodic* and *vary in magnitude*.
- Stable baseline behavior.

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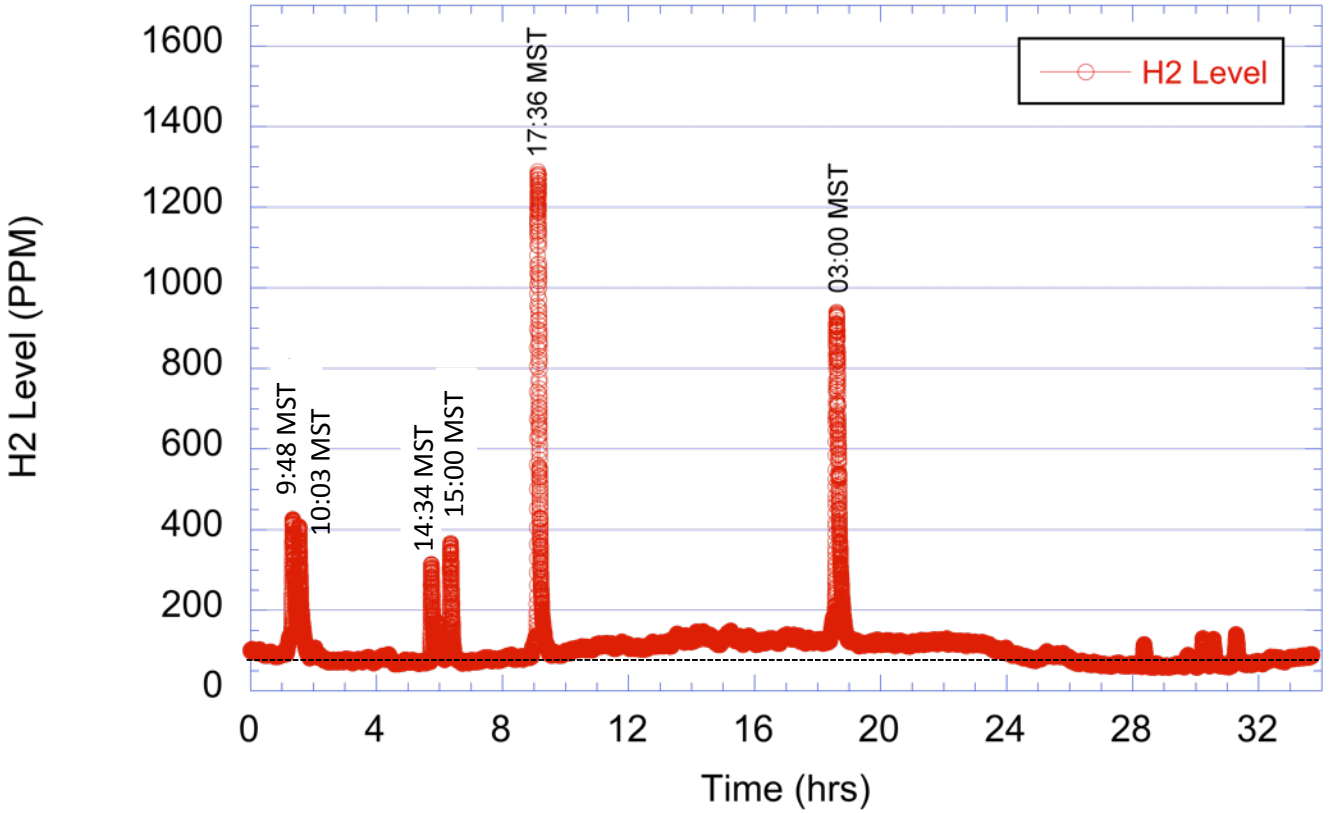
# Technical Accomplishments FY15: Data log for Thursday 11-7-14

Thursday 11-7-14




- Discussion with Hydrogen Frontier and was informed that 2 FCV fills occurred that seemed to coincide with sensor readings.

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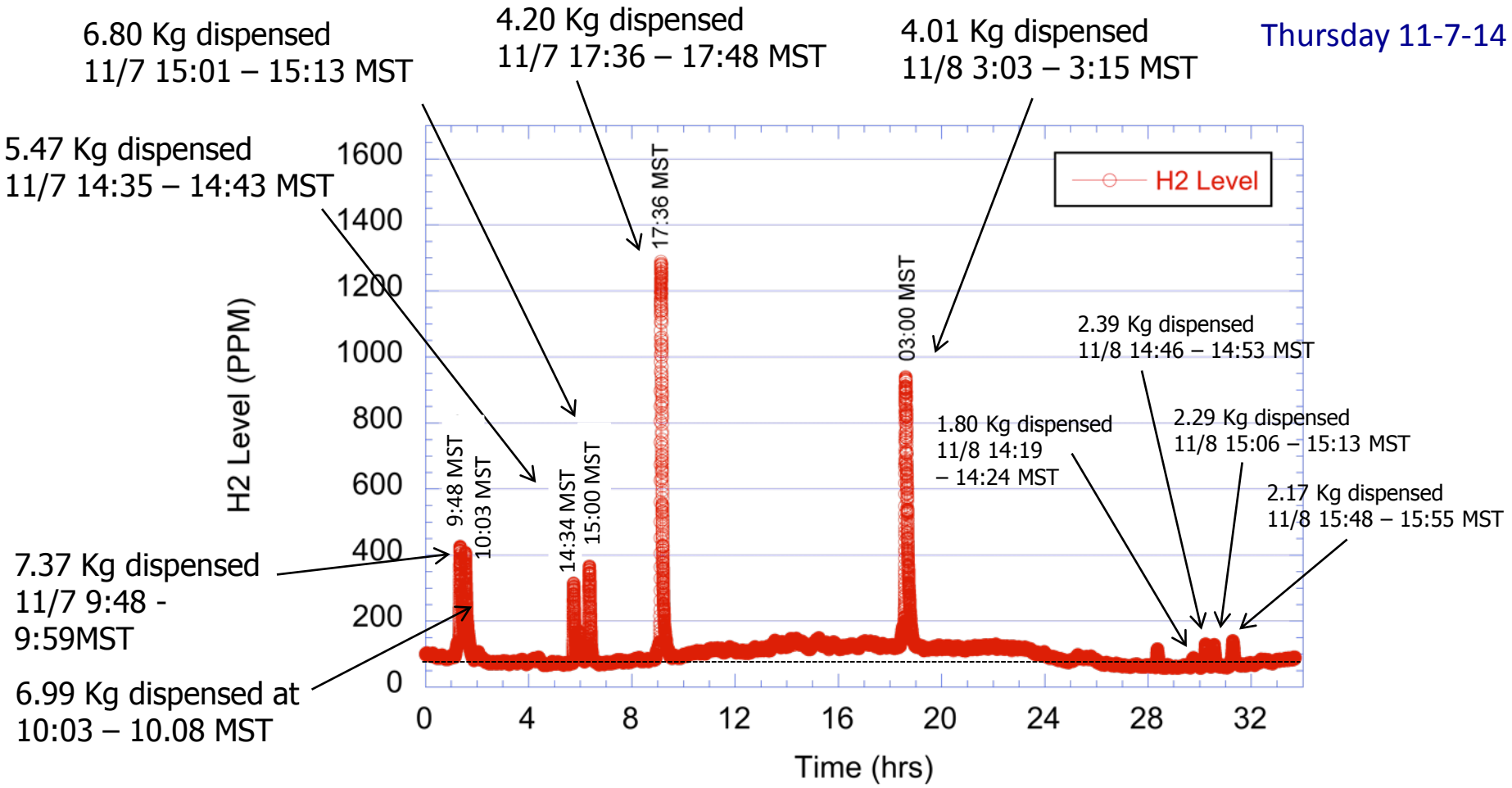
# Technical Accomplishments FY15: Inspection of Burbank Station Filling Logs show FCV filling occur at the same time of $H_2$ events!




- Log data provided starting with 11/7/14, 14:39 MST
- Sensor activity correlates to station event activity. Very little baseline drift.

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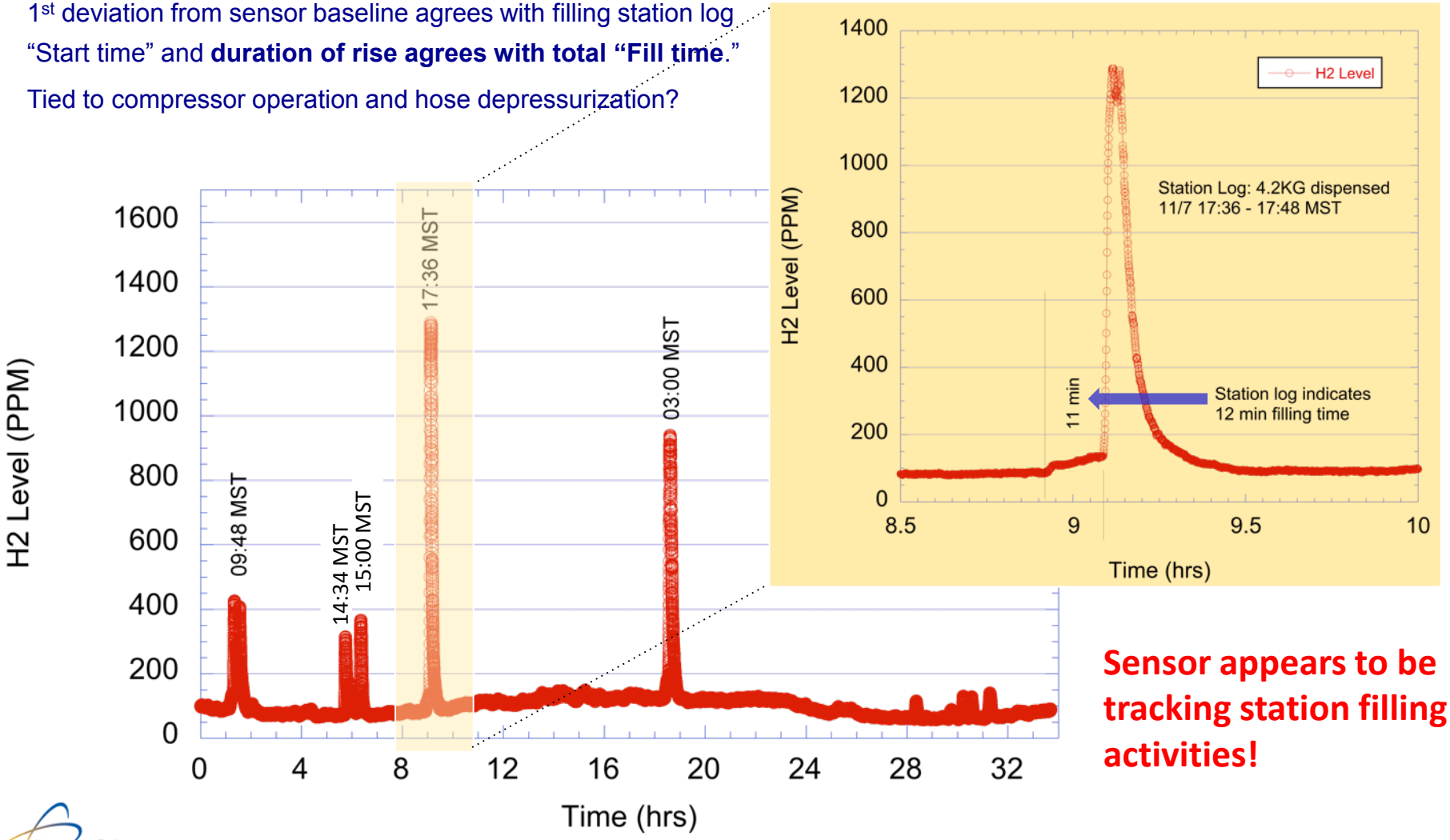
# Technical Accomplishments FY15: Closer inspection of data for 11-7-14 reveal more details of FCV fueling

- Inspection of sensor data shows two distinguishable segments to the overall event.
- 1st deviation from sensor baseline agrees with filling station log "Start time" and **duration of rise agrees with total "Fill time."**
- Tied to compressor operation and hose depressurization?

**Select 11-7-14, 17:36 fill to examine more closely.**




**Sensor appears to be tracking station filling activities!**

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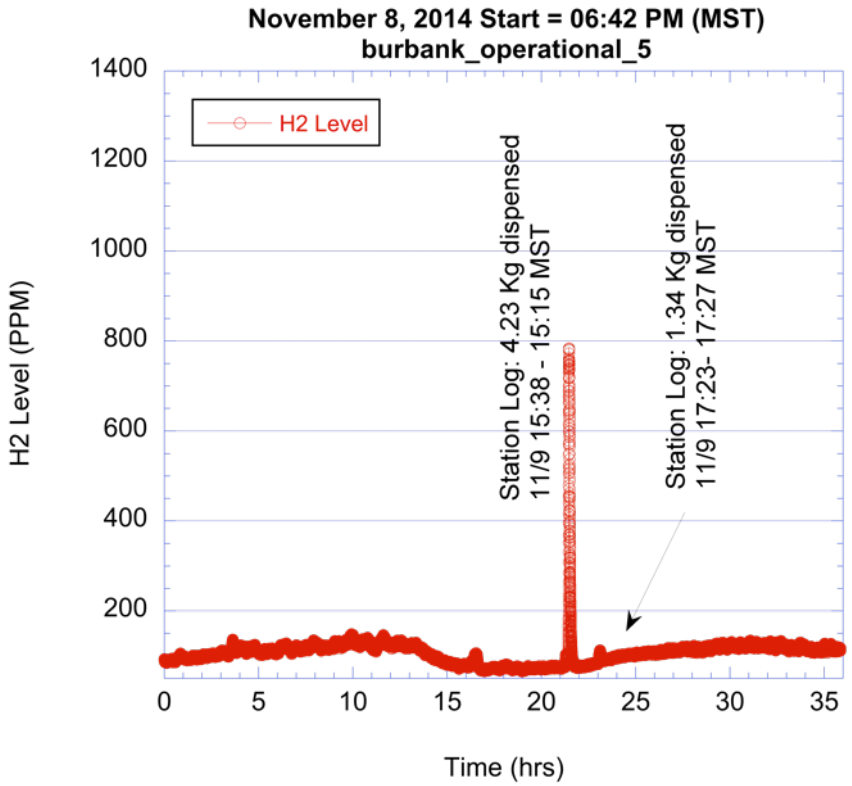
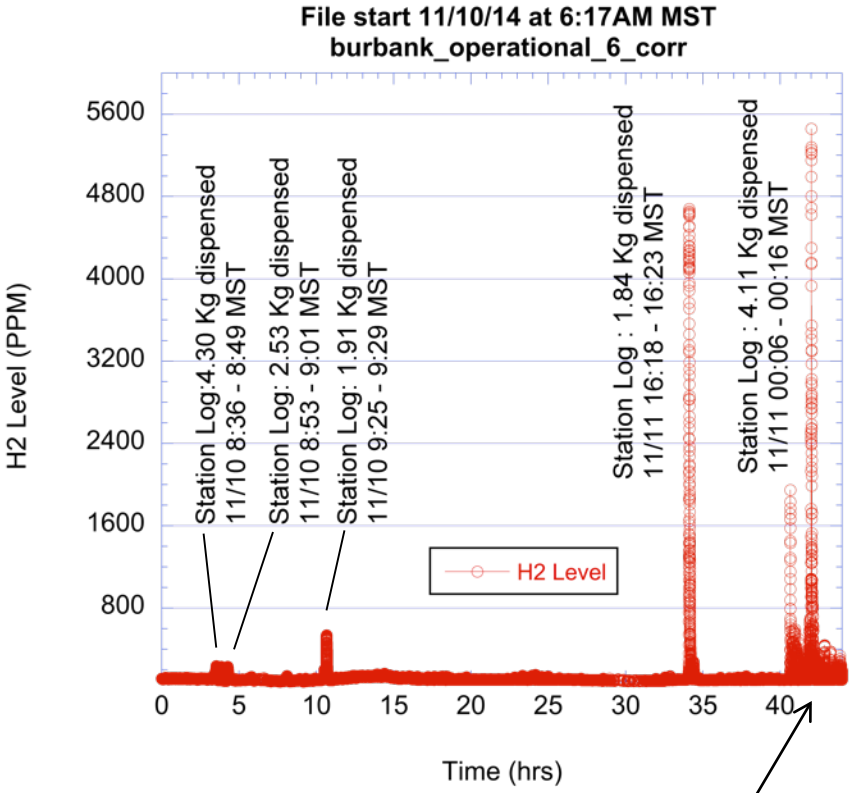
# Technical Accomplishments FY15: Burbank testing – Results for First Week / Data reduction 11-8-14 through 11-12-14




- Continue to see sensor activity / station activity correlations for remainder of critical milestone week.
- In general: ***sensor activity correlates well to station activity.***
- Towards end of 11/12/14, wireless noise began to rise and signal drop outs began to occur.

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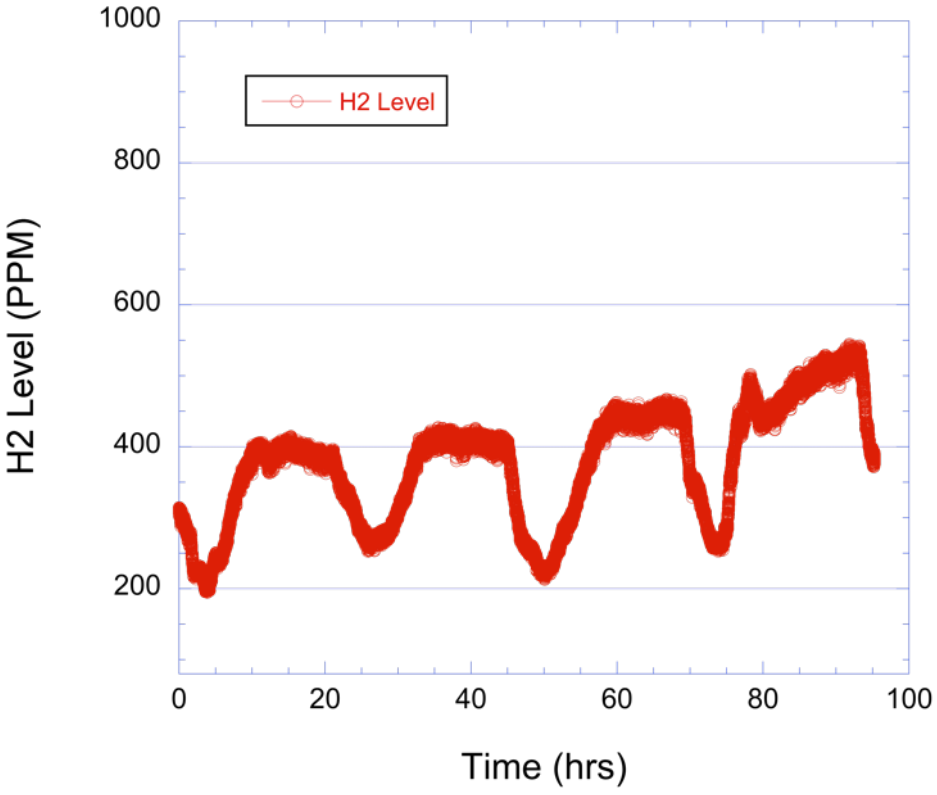
# Technical Accomplishments FY15: December 2014 testing show regular intervals of larger amounts of hydrogen

- Sensor continuously showed elevated $H_2$ concentration levels.
- First 100 hrs. in December showed unusual cyclic behavior.
- West Coast began to received much higher levels of precipitation than earlier in November during this time period weather does not explain periodicity.
- Sensor experienced downpours, high winds and blowing water and standing water inside dispensing island enclosure.
- No evidence that large changes in levels of humidity affected sensor performance confirming NREL test results in FY12-14.

- **There were no abrupt / discontinuous changes seen commensurate with weather reports of rain, wind, etc.**

Unlike November data, sensor response appears **elevated with periodicity**.

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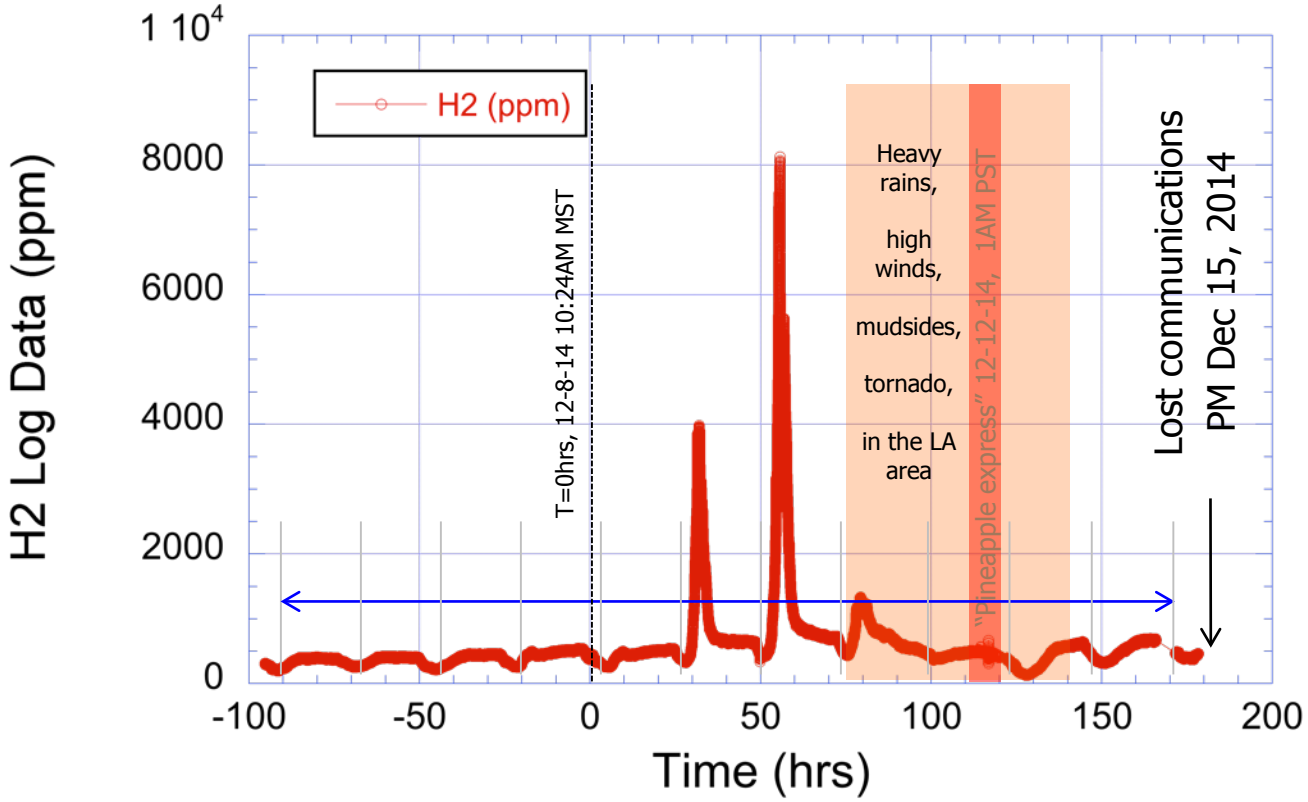
# Technical Accomplishments FY15: Burbank testing – Sensor tracks increased station hydrogen production activities!

- **Station Log:** Reformer was **Online** and **Operational** in December! Speculation: On-site Hydrogen production and compression to FCV filling pressure would naturally lead to greater opportunity to detect hydrogen releases at the station.
- Again, sensor data correlates well with station activities!
- Are large release events caused by reformer/compressor activity? Future work!



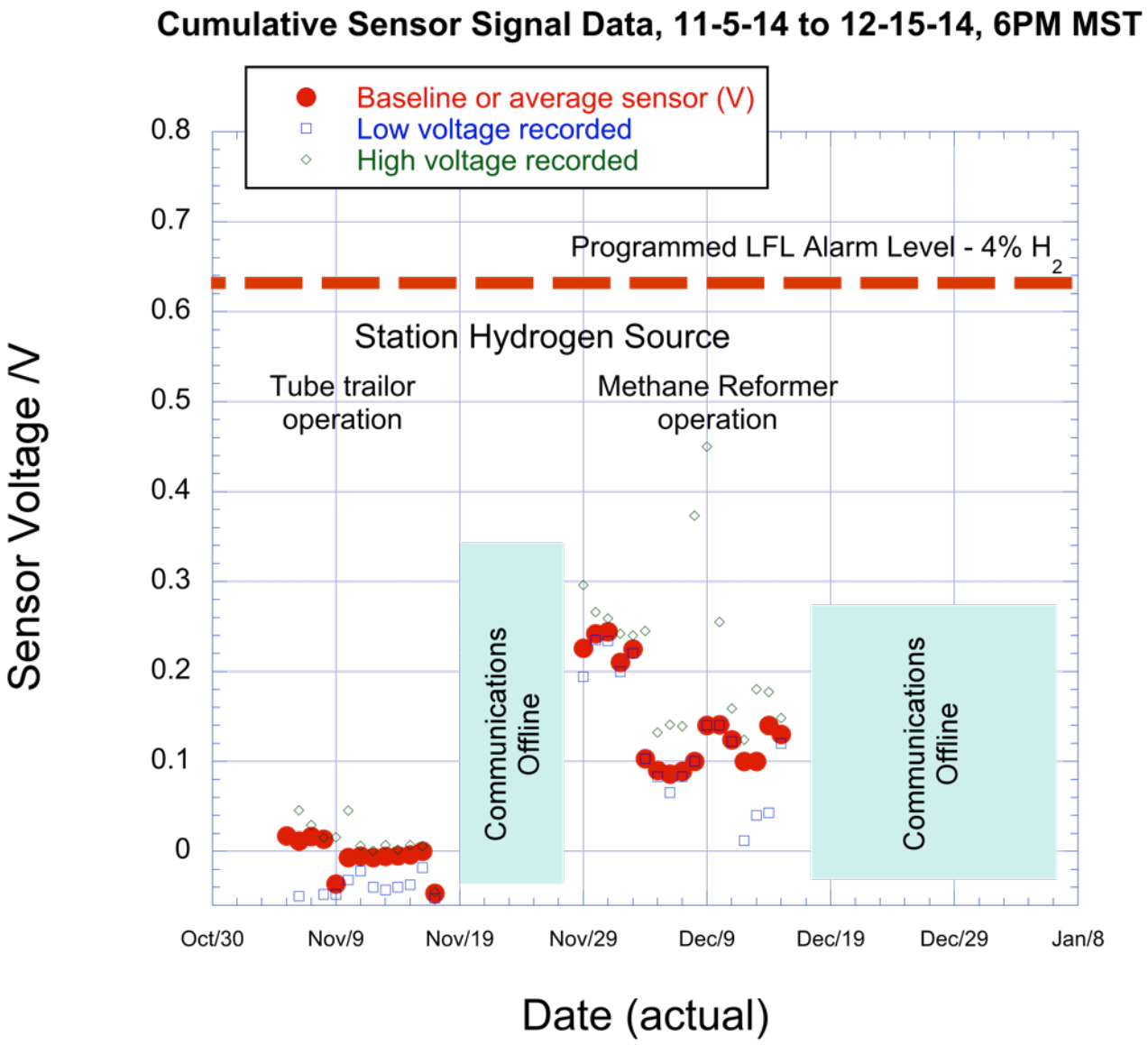

**Severe weather events did not cause a sensor response.**

**No apparent sensor drift.**

12 separate files were combined that cover the first 12 days of the month of December 2014.

# Technical Accomplishments FY15: Burbank testing – Results of all sensor data during field trials testing show activity but no drift.

- Initial field trials testing presented opportunity to see two aspects of Burbank station operations:
  1) Tube trailer.
  2) Reformer/compressor.
- Greater activity of hydrogen release associated with on-site production very plausible since…
- There are known leaks in system related to compressor operations / venting.
- **Over the Field Test experiment, no apparent sensor drift.**

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# Reviewer Comments

- **Tailoring the already very successful automotive $O_2$ sensors for hydrogen is very good. Success should lead to a cost-effective sensor. Running the ignition study at the minimum ignition energy (MIE) (22% to 26% hydrogen) would have been better than 20%—ignition energy varies by a couple of orders of magnitude (this is really an issue in execution). The presenter agreed to address this in the future.**
  - This was very valuable guidance/feedback received during the 2014 AMR presentation. Several reviewers and audience members participated in a discussion on better testing conditions to establish safety boundaries in the event of an upset condition. These types of testing will be crucial in follow-on work as the technology matures and moves closer to commercialization. Unfortunately, resources were not available in FY15 to modify the testing apparatus to compensate for the reduced ambient pressure (LANL at 7200ft would require a "pressurized system" to simulate sea-level conditions involving flammable mixtures per LANL pressure safety policy) and the experiments could not be performed without the proper authorizations and engineering controls.
- **Sensor testing is conducted in enclosed spaces only. The NREL sensor laboratory seems to be looking at using sensors at refueling stations (outdoors). There may be a disconnect here.**
  - Small, confined testing chambers permit exposure of the sensor to precise concentrations of H2 for periods of time to establish stability, reproducibility, reversibility, etc. without exposing large room volumes to H2 release – research cannot be an excuse to produce a safety hazard. While outdoor facilities like the one selected for FY15 testing do not even require point sensors in the State of California, as our testing has shown, there are enclosures that can capture H2 and could potentially reach an LFL condition. The FY15 field trials work clearly show that the technology is well suited and valuable to outdoor operation.
- **The "real world" testing is good, but it is in a very benign climate. Consideration of extremes of heat, cold, and humidity would be important. The project should take place in Chicago, not Los Angeles.**
  - During Burbank testing, we were fortunate to experience not just hot dry conditions, but torrential downpours, flooding, high winds, large swings in RH, and even tornado activity over the course of testing. The weather pattern known as the "Pineapple Express" resulted in mudslides and widespread disruptions in the LA area. The extended low temperatures that one would expect in Chicago would easily be compensated by the control electronics; we had "excellent" weather for field trials testing and have shown that the sensor did not track weather events.

# Collaborations

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Fundamental electrochemical sensor R&D, establish prototype designs, packaging, field testing, off-site safety protocols development

*Federal Laboratories within DOE Hydrogen and Fuel Cells Programs*

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Materials selection, field testing, partner and off-site protocols development

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Codes & Standards field performance evaluation/validation team member

## ***Commercial Partners:***

HYDROGEN FRONTIER INC

Field trials partner. Commercial Hydrogen production partner

Zircoa

Agile Engineering through Zircoa: field trials software development and testing

Custom Sensor Solutions, Inc. ...since 1997

Hardware for sensor control electronics

ESL ElectroScience

Manufacturing, scale-up, engineering processes

# Remaining Barriers and Challenges / Technology Transfer

- Address Reviewer's concerns regarding the need for expanded minimum ignition energy envelope testing of the sensor package.
- Conduct more field trials at other filling station locations / geographic regions. Collect more field trials data to build performance database.
- Meet all applicable safety codes and standards for the system.
- Convince a commercial partner to invest resources in final development and commercialization without a market big enough at present to recoup development and certifications costs.

## Technology Transfer

- Working with CA AQMD to obtain follow-on funding to expand field trials testing at more CA $H_2$ filling station locations starting at end of FY15.
- Responded to Nine Sigma call for $H_2$ sensing technology for Fuel Cell Infrastructure.
- LANL conducted first sensor commercialization Webinar to advertise/attract licensing interest.
- LANL negotiating exclusive licensing of electrochemical, mixed potential sensor IP to an automotive Tier-1 suppler and subsumes this project's background IP.

# Proposed Future Work

- Return to Burbank site (aligned with filling station operation status) and add a second sensor unit in an area around reformer and high pressure compressor to help identify source of $H_2$ releases.
- Install electronic weather station to mast atop electronics bay at Burbank facility.
  - Continuous logging of wind speed and direction, R.H. and rainfall will be extremely valuable. Easy to correlate releases with station activity / environment conditions.
  - Direction of prevailing wind in relation to station layout could add significant explanation to sensor data collected by LANL.
- Re-orient/re-position antenna of wireless units to reduce signal drop outs.
- Begin work with California AQMD to expand field testing at other CA $H_2$ locations.


## Acknowledgements

- Dr. Leta Woo, EmiSense Inc.
- Charles (Will) James Jr. Ph.D., U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy
- Dr. William J. Buttner, National Renewable Energy Laboratory
- Dr. Boris Farber, Zircoa Inc.

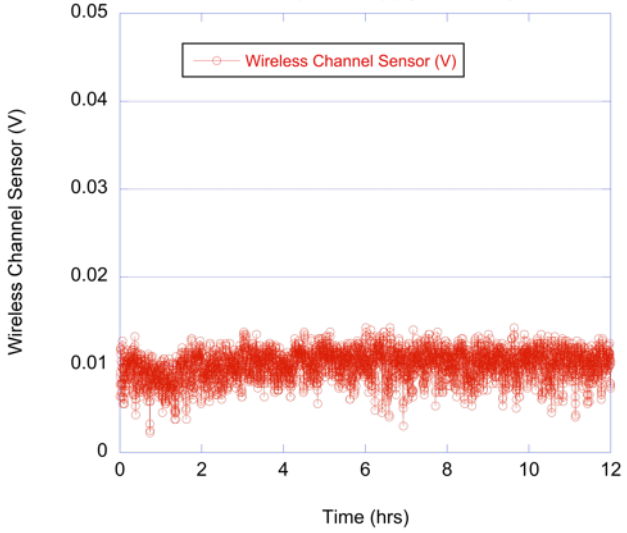
# Summary

- ✓ Field trials testing at Burbank $H_2$ Frontier successful with results nicely correlated to station activities – both FCV filling and production could be tracked at LANL by examination of sensor response (**FY 15 Milestone**). **$H_2$ release activity was seen in areas identified with low probability for detection**.
- ✓ No obvious drift in sensor voltage over course of testing and known severe weather events did not affect sensor.
- ✓ Recorded hydrogen exposures were not reported by the commercial sensor and have initiated discussion for relocation and design of station hydrogen vents with station owner.
- ✓ H2F dispensing island enclosure selected because of anticipated quiescent conditions but hydrogen was present during station operations.
- ✓ Station Log data support conclusions that $H_2$ releases appear to be related to filling of FCV's and production/compression activities.

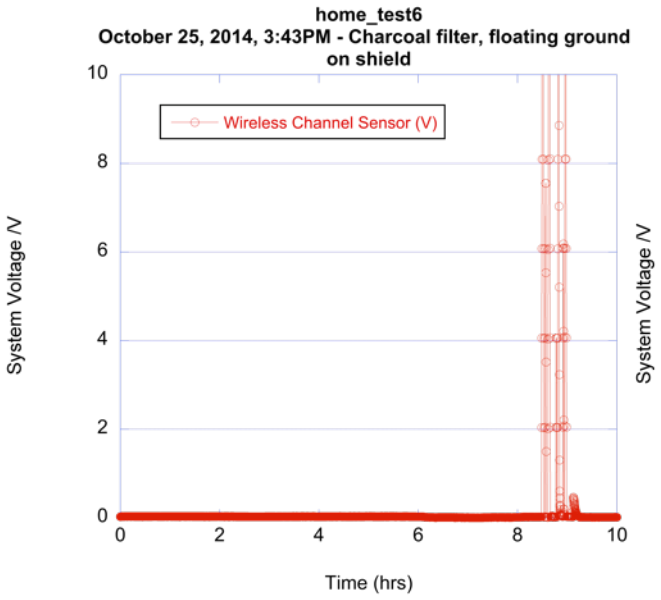
# Technical back-up slides

# Technical Accomplishments FY15: Off-site testing of Advantech PC, wireless, and effectiveness of activated charcoal canister

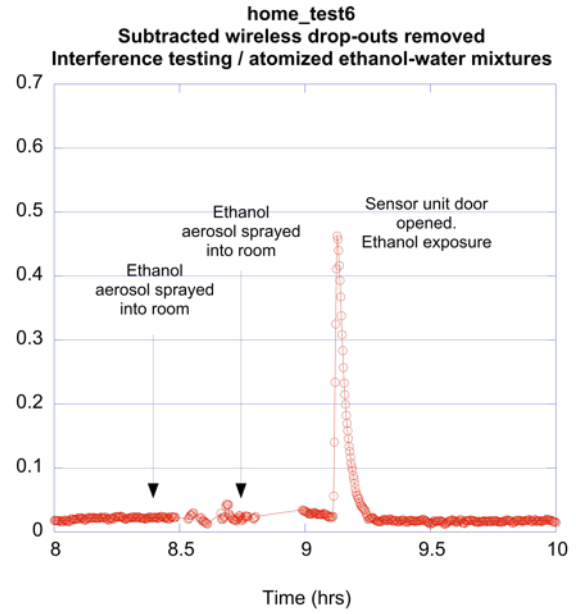
Baseline run




Example of wireless signal drop-out.
Default – Omega receiver unit outputs +10V when signal is lost.
Easy to identify!



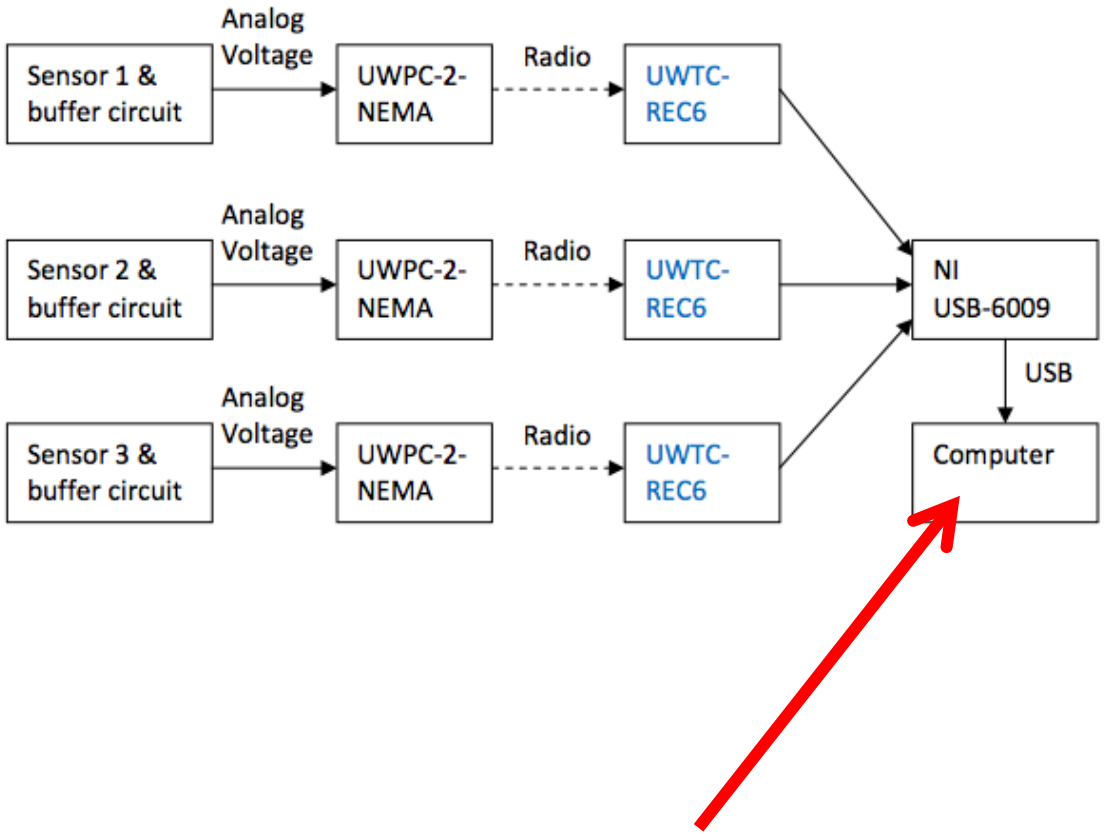

Testing of charcoal filter to minimize interference from VOCs




- Wireless distance tested well exceeded transmission distances at Burbank.
- Understand what to expect if wireless dropouts occur after installation at Burbank.
- Sensor could never generate voltages above 1V output from HIB board.

# Approach: New field trials electronics will use commercial wireless communications; software coded in FY14

- Simplifies field trials.
- No need for running long sensor leads through explosion proof conduits at testing site.
- Cheap – COTS technology from Omega Engineering.
- Accommodations for operating up to 3 independent sensors at 3 different placement points at a test facility.




**Laptop with executable Labview™ code written by Agile Engineering and integrated with wireless components and validated at Zircoa Inc.**
**Logs up to 3 sensors at once.**
**Accepts calibration curve to convert raw voltages to % $H_2$.**
**User selectable alarm points.**
**User selectable logging rates / averaging / file write rates.**

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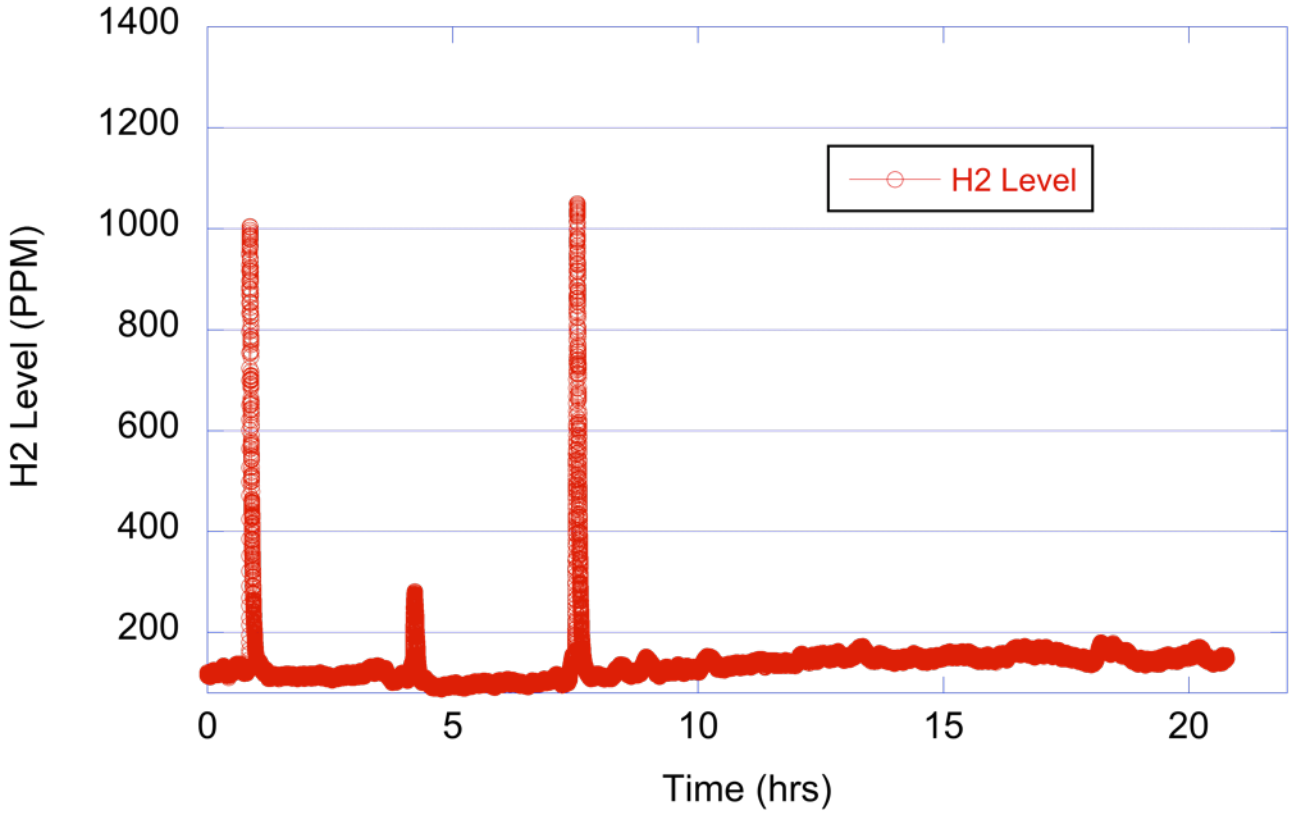
# Technical Accomplishments FY15: Results for Wednesday 11-5-14 Burbank testing





- First full day of data collection is shown.
- Filling station dispensing island chosen as first site to place LANL/LLNL field trials unit because known to be **leak free and "confirmed" by commercial sensor**.
- Open top unit, with four side walls / metal enclosure.

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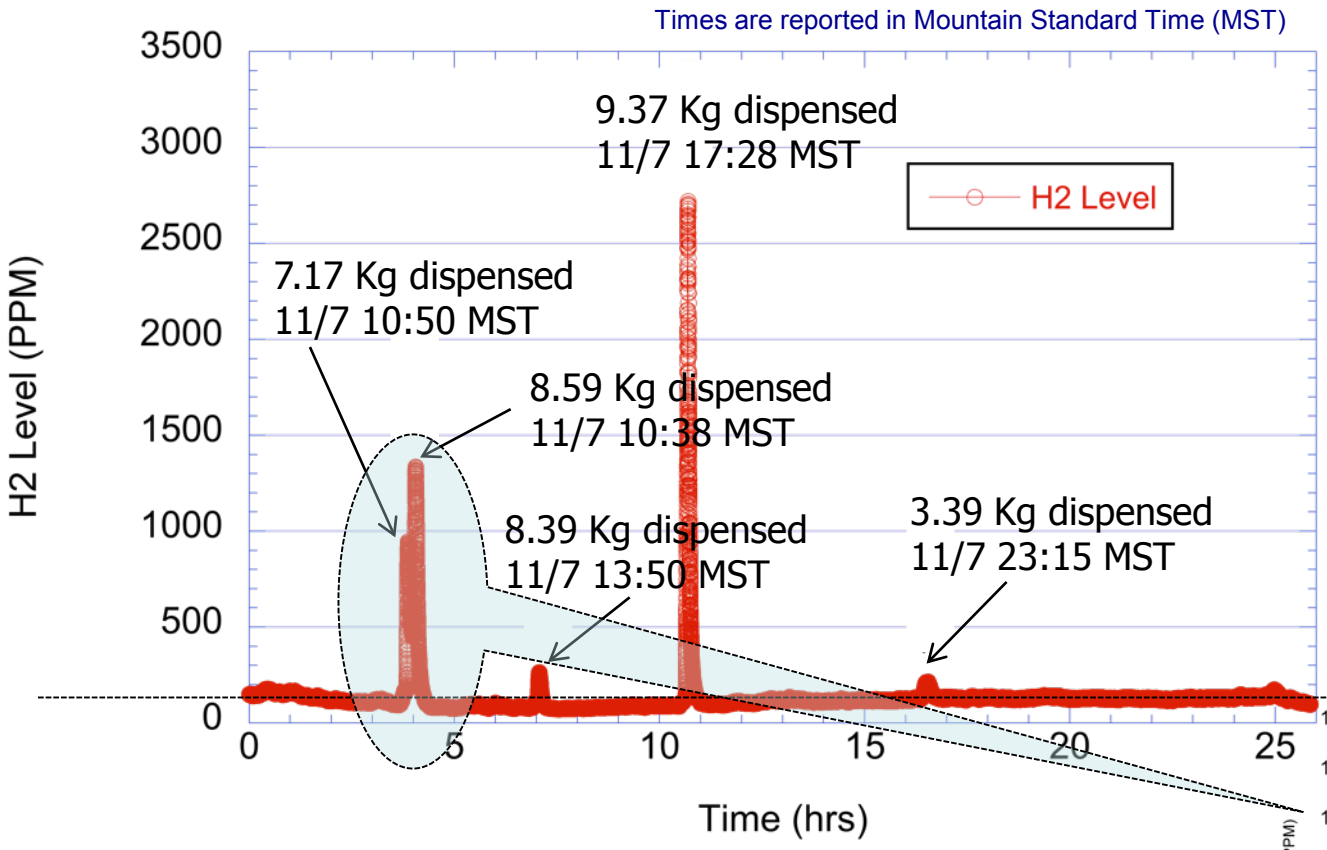
# Technical Accomplishments FY15: Burbank testing – Results for Thursday 11-6-14 against station log data obtained 4-20-15

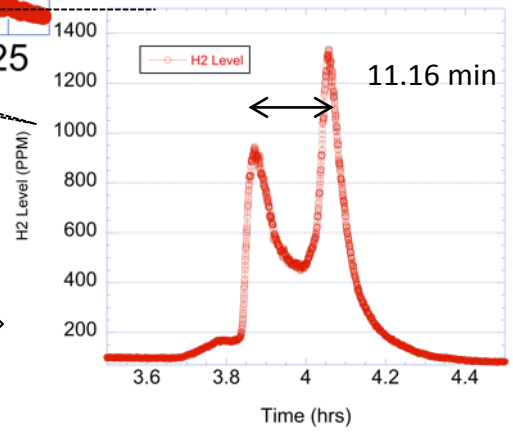



Log Data provided for this time period on 4-2-15.

5 FCV's filled on 11-6-14.

**No other events** are measured outside of recorded FCV fills.

Here, time between peak $H_2$ events agrees very well with the difference in time from fill log….12 min between FCV fills.

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