

## Testing the Performance of Hydrogen Sensors

Nathan D. Marsh

*National Institute of Standards and Technology, Gaithersburg, MD USA*

Thomas G. Cleary

*National Institute of Standards and Technology, Gaithersburg, MD USA*

### Abstract

The acceptance of hydrogen as a widely-available energy source will depend to some extent on the perceived and actual safe dispensing and storage of hydrogen by the general public. Reliable detection of an accidental hydrogen gas release and mitigation of the hazard through designed safety systems is a key component of hydrogen powered systems in commercial, residential, and transportation uses. In anticipation of this emerging market, inexpensive hydrogen gas sensors based on a range of sensing technologies are becoming increasingly available.

We have developed a new bench-scale test apparatus for hydrogen sensor performance, the Hydrogen Detector Environment Evaluator (HyDEE), based on our previous experience with hydrogen sensors in a small flow cell and in the Fire Emulator / Detector Evaluator. In particular, we have found that dynamic changes are relevant to hydrogen sensor performance, as they affect both response rate of the sensor and are also necessary to return the sensor environment to its baseline state. The ability to induce dynamic changes is most easily accomplished with a flow system similar to a small wind tunnel. In this system, we can expose sensors to hydrogen and other gases (particularly hydrocarbons, which many hydrogen sensors are also sensitive to) as well as humidity and changes in temperature. Improvements over the previous exploratory tests include substantially reduced volume allowing higher gas concentrations, and the ability to cool the system as well as heat it, in order to achieve a wider dynamic range in temperature and to more accurately simulate the environments to which sensors may be exposed in the real world.

## Introduction

The hydrogen economy envisions wide application of energy delivery solutions based on hydrogen fuel cells or combustion systems. The public's acceptance of these new energy delivery systems will rely to some extent on the perceived and actual safe application of the technologies. To this end, reliable detection of an accidental hydrogen gas release and mitigation of the hazard through designed safety systems is a key component of hydrogen powered systems in commercial, residential, and transportation uses. In anticipation of this emerging market, inexpensive hydrogen gas sensors based on a range of sensing technologies are becoming increasingly available. There is a need to characterize sensors in conditions relevant to their end-use application.

Currently acceptance standards applied to hydrogen sensors follow the existing UL 2075 "Standard for Safety Gas and Vapour Detectors and Sensors" and in the United States the relevant flammable gas standards such as National Fire Protection Association (NFPA) 52 "Vehicular Fuel Systems Code" and NFPA 55 "Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks". Developing standards include ISO/DIS 26142 "Hydrogen detector" (by the International Organization for Standardization (ISO) Technical Committee 197) and NFPA 2 "Hydrogen Technologies Code".

In this work, we tested sensor performance under conditions representative of real-world challenges, taking into consideration where hydrogen sensors might ultimately be deployed. As automotive applications appear to be an early adopter of hydrogen technology, current and near future use of hydrogen sensors might take place in hydrogen filling stations, which often are part of or adjacent to traditional gasoline filling stations, and residential or commercial garages. All of these spaces may be outdoors, although sheltered, neither heated nor air conditioned, and experiencing relatively high concentrations of vehicle exhaust including CO, CO<sub>2</sub>, NO<sub>x</sub>, and unburned hydrocarbons.

To this end, we acquired a representative sample of eight sensors, from five manufacturers, employing four different sensing technologies. They were tested in our Fire Emulator / Detector Evaluator (FE / DE) [1] an apparatus previously used for extensive studies of fire detectors [2-4]. The FE / DE is easily modified for the evaluation of hydrogen sensors, with the primary difference that we use only the gas exposure part system, and do not use any of the smoke generation options. The sensors were tested for hydrogen exposure, as well as CO, CO<sub>2</sub>, propene (propylene, C<sub>3</sub>H<sub>6</sub>), condensing water vapour, and temperature variation.

These environmental changes and gas compositions were also tested in conjunction with hydrogen exposure to determine whether any synergistic or obfuscating effects were significant.

Our experience with the sensor behaviour in the FE / DE led to our design and construction of a new bench scale apparatus (Hydrogen Detector Environment Evaluator or HyDEE) with an increased range of conditions and smaller supplies of compressed gas and electricity, which is described here.

### Procedure

A schematic of the FE/DE is shown in Fig. 1. A variable-speed fan draws room air and passes it through a series of 9 annular finned heating elements (5 kW each for a total maximum heat input of 45 kW) resulting in air velocity at the test section between 0.02 m/s to over 2 m/s and an available rate of temperature rise of 0.5 °C/s, up to maximum of about 80 °C. The flow is conditioned before it reaches the 0.5 m × 0.3 m test section by passing through a 10 cm long aluminium honeycomb with 5 mm rectangular openings. CO, CO<sub>2</sub>, or other gas blends may be be metered into the flow just downstream of the heater via electronic mass flow controllers. A laboratory steam generator can inject low-pressure steam, also just downstream of the heater, to humidify the air from ambient room to saturated conditions at elevated temperature. Water, CO, CO<sub>2</sub>, and hydrocarbon gas concentrations at the test section are monitored by non-dispersive infrared (NDIR) analyzers. Temperature and gas analysis are recorded in the same data acquisition system as the sensors.

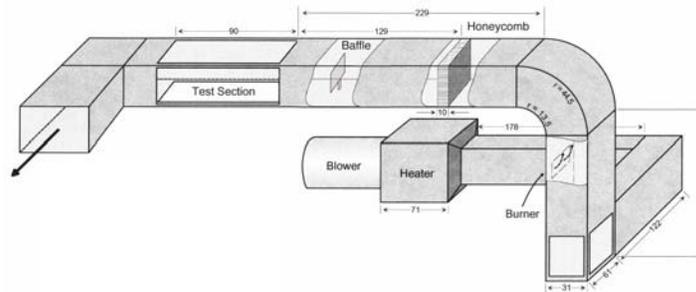


Fig. 1: Schematic of the FE / DE

Sensors, summarized in Table 1, were installed three or four at a time in the test section of the FE/DE, powered and monitored. Sensors were exposed to the following challenges:

- Temperature rise from 25 °C to 50 °C followed by a return to 25 °C
- 100 % relative humidity with condensing water vapor
- Carbon monoxide (120 µL/L to 250 µL/L) and carbon dioxide (2000 µL/L)
- Propene (3000 µL/L)
- Hydrogen (300 µL/L)
- Hydrogen (300 µL/L) with temperature rise from 25 °C to 50 °C followed by a return to 25 °C
- Hydrogen (300 µL/L) with 100 % relative humidity and condensing water vapour
- Hydrogen (100 µL/L) with carbon monoxide (50 µL/L) and/or carbon dioxide (600 µL/L)
- Hydrogen (300 µL/L) with propene (3000 µL/L)

These tests were carried out with an air flow rate of 12 cm/sec to 25 cm/sec, with the lower velocity used for chemical exposures and the higher velocity used for temperature and moisture exposure.

Table 1: Summary of Tested H<sub>2</sub> Sensors

Sensor	Tech <sup>a</sup>	Range (vol fraction)	
A	TCD	0.0 % to 100 %	
B	MOS	0.0 % to 2.0 %	
C	MOS	0.0 % to 2.0 %	
D	CAT	0.0 % to 2.5 %	
E	Multi	0.4 % to 5.0 %	Film resistor and MOS capacitor, Pd/Ni film
F	MOS	0.0 % to 0.20 %	Includes molecular sieve
G	CAT	0.1 % to 4.0 %	Includes molecular sieve
H	EC	0.0 % to 4.0 %	

<sup>a</sup>TCD: Thermal Conductivity Detector; MOS: Metal Oxide Semiconductor; CAT: Catalytic Bead Pellistor; Multi: Multiple integrated technologies; EC: Electrochemical sensor.

## Results

Fig. 2 shows typical results to a sensor test in the FE / DE, in this case exposure to 1) 3000 µL/L propene; 2) 3000 µL/L propene and 300 µL/L H<sub>2</sub>; and 3) exposure to 300 µL/L H<sub>2</sub> alone. In this way, we tested the sensors' responses to individual gases as well as their response to multiple gases, i.e. hydrogen and a nuisance gas. We also ran these tests in both directions to determine whether the presence of one gas

influenced the sensor's response to the second gas. The concentration of nuisance gas was independently measured, as shown by the response represented by circles in the figure. The volume fraction measurements reported for the hydrogen sensors are the recorded output voltage or current of the sensor applied to a calibration relation for that sensor.

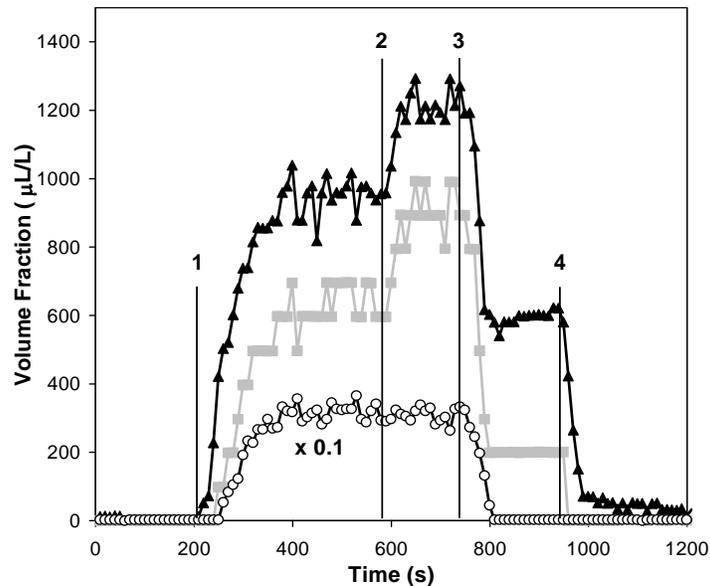


Fig. 2: Typical data from an exposure test. Circles: propene \* 0.1; Triangles: Sensor B (MOS); Squares: Sensor C (MOS). 1) 3000  $\mu\text{L/L}$  propene; 2) 3000  $\mu\text{L/L}$  propene and 250  $\mu\text{L/L}$   $\text{H}_2$ ; and 3) 250  $\mu\text{L/L}$   $\text{H}_2$  only.

Fig. 3 shows the response of 6 sensors to various gas and environmental exposures. (The remaining two sensors, E and G, are designed to sense higher concentrations of hydrogen and did not respond to any of our gas or environmental exposures.)

The performance of the sensors tested here can be summarized as follows:

- Sensor A (TCD) was not sensitive enough to detect  $\text{H}_2$  anywhere, even up to 7000  $\mu\text{L/L}$ . It was however sensitive to condensing water vapor, reading the equivalent of 3000  $\mu\text{L/L}$   $\text{H}_2$  at 25 °C and 100 % relative humidity.

- Sensor B (MOS) experienced the most cross-sensitivity, responding to temperature, humidity, and propene. It also read consistently high in the presence of H<sub>2</sub>. In general, cross sensitivities appear to be linear combinations, i.e. no synergistic effects.
- Sensors C and F (both MOS) experienced some cross-sensitivity. In Sensor C there appears to be a synergistic effect with humidity and H<sub>2</sub>: it appears to be sensitive to humidity only in the presence of H<sub>2</sub>.
- Sensor D (CAT) is cross-sensitive to everything except CO/CO<sub>2</sub>. It is extremely sensitive to hydrocarbons. It is also inversely temperature sensitive: increasing the temperature by 25 °C reduces the baseline by a voltage equivalent to 200 μL/L. (Reducing the temperature by the same amount raises the baseline—essentially producing a false positive.)
- Sensors E (Multi) and G (CAT) were not sensitive to any challenge gases or conditions. However they were also not sensitive enough to detect 250 μL/L of H<sub>2</sub> in the FE / DE.

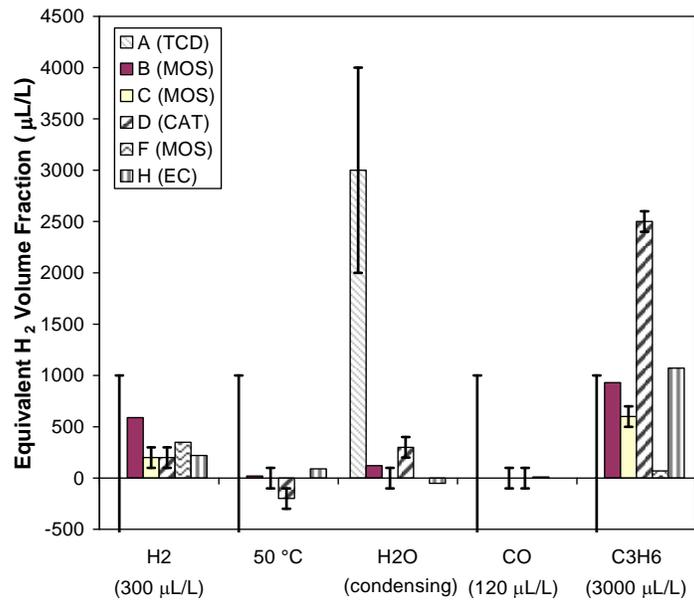


Fig. 3. Response of sensors to environmental exposures

### Future Work

Based on these results, that a collection of commercially-available hydrogen sensors would produce false positive detection upon exposure to other gases and environmental changes, we have designed a facility with an expanded range for further sensor testing. The Hydrogen Detector Environment Evaluator (HyDEE) is a wind tunnel designed to perform exposure tests similar to those conducted in the preliminary hydrogen sensor evaluation in the FE/DE. It is shown schematically in Figure 4.

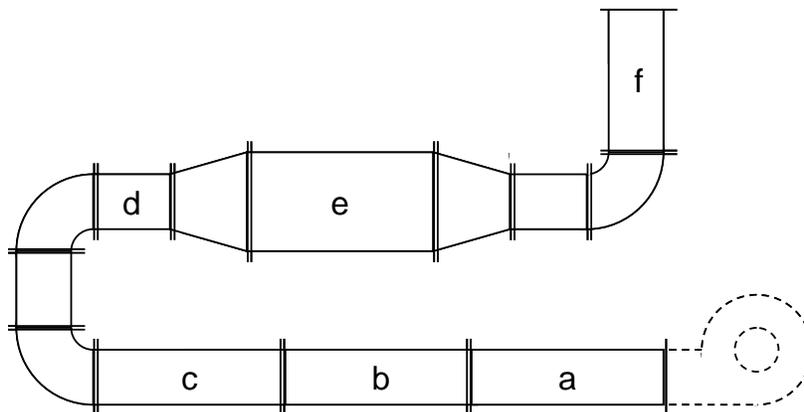


Fig 4. Hydrogen Detector Environment Evaluator (HyDEE); a) air conditioning; b) heaters; c) steam injection; d) flow straighteners; e) test section; f) exhaust

The air flow is provided from a air conditioning blower. The air conditioner lowers the tunnel air flow temperature to a fixed dew-point temperature. Temperature controlled air heaters re-heat the air flow to a set temperature. Steam from an atmospheric steam generator can humidify the air. Section c is where gases (hydrogen mixtures or other gases) are injected. Mass flow controllers are used to meter the gases into the tunnel. It was designed to use forming gas, a mixture of nominally 5% hydrogen and the balance nitrogen to provide hydrogen concentrations below the flammability limit in the detection range of hydrogen safety equipment. Forming gas does not produce a flammable mixture when released into air. There is a honeycomb flow straightener in section d just prior to the tunnel expansion. It features a test section (e) cross section of 20 cm by 20 cm to accommodate most hydrogen sensors or

detectors. Tests are being conducted to determine the operating ranges of the tunnel.

### References

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