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PRELIMINARY PERFORMANCE ASSESSMENT OF COMMERCIALLY-AVAILABLE HYDROGEN SENSORS

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As part of an effort to develop standard test methods for the performance of commercial hydrogen sensors, we employed the Fire Emulator / Detector Evaluator, an instrumented flow system designed to study the response of fire detectors (smoke, heat, gas), in a preliminary study to evaluate the performance of a representative selection of commercially-available hydrogen sensors. These sensors depend on a variety of sensing technologies including metal-oxide semiconductors, electrochemical cells, catalytic bead pellistors, thermal conductivity sensors, and sensors employing a combination of technologies. They were evaluated both for their response to hydrogen concentrations up to half the lower flammability limit, and their response to nuisance gases (CO, CO₂, NO_x, hydrocarbon gas and vapor—all potentially present in hydrogen dispensing and storage areas), as well as dynamic changes in environmental conditions by varying temperature, humidity, and flow velocity. These performance evaluations provide guidance for the development of a test method designed to assess real-world performance of hydrogen gas sensors. The ultimate goal is to develop standard test methods to be employed by product certification agencies.

1. 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 Vapor Detectors and Sensors"

and the relevant flammable gas standards in the US such as NFPA 52 and 55. The International Organization for Standardization (ISO) Technical Committee 197 has formed a working group (WG 13: Hydrogen Detectors) to focus on an international standard, ISO/CD 26142 “Hydrogen detection apparatus”. In the ISO standard there is a recognized need to test sensor performance in terms of sensitivity, response time, recovery time, environmental changes (temperature, humidity, pressure) and nuisance sources, i.e. substances which may trigger a false alarm. However, the standard recommends a static test chamber, which is limited in its ability to expose sensors to dynamic and repeated changes in the environment and gas composition; in particular, it is unclear how one would test sensor recovery time in such a system.

In this work, we are interested in testing performance under conditions representative of real-world challenges. We therefore considered 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 automobile exhaust including CO, CO₂, and unburned hydrocarbons.

To this end, we acquired a representative sample of seven sensors, from four manufacturers, employing four different sensing technologies. These sensors were first calibrated and tested for exposure to hydrogen in a benchtop calibration flowcell. They were then 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 again tested for hydrogen exposure, as well as CO, CO₂, propene (propylene, C₃H₆), condensing water vapor, 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.

2. Procedure

2.1. Calibration Flow Cell

The calibration cell consists of a chamber 0.1 m cross-section and 0.6 m long. Mixed gas from two mass flow controllers is introduced into one end of the

chamber, where it must pass through a 0.1 m long section of honeycomb flow straightener, past the sensor, and out of the chamber.

Sensors were exposed to between 500 $\mu\text{L/L}$ and 6500 $\mu\text{L/L}$ hydrogen in air, as determined by the mixing of a calibrated bottle of 2 % hydrogen in air with additional air via the mass flow controllers. The dimensions and flowrates used resulted in gas velocities from 15 cm/sec to 25 cm/sec.

A schematic of the FE/DE is shown in Figure 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 aluminum honeycomb with 5 mm rectangular openings. CO, CO₂, or other gas blends may 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, CO₂, and hydrocarbon gas concentrations at the test section are monitored by non-

Figure 1. Schematic of the FE/DE

dispersive infrared (NDR) analyzers. Temperature and gas analysis are recorded in the same data acquisition system as the sensors.

Sensors, summarized in Table 1, were installed three or four at a time in the test section of the FE/DE, powered and monitored in the same way as in the calibration cell. 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 (130 µL/L)
- Hydrogen (250 µL/L)
- Hydrogen (250 µL/L) with temperature rise from 25 °C to 50 °C followed by a return to 25 °C
- Hydrogen (250 µL/L) with 100 % relative humidity and condensing water vapor
- Hydrogen (250 µL/L) with carbon monoxide (50 µL/L) and/or carbon dioxide (600 µL/L)
- Hydrogen (250 µL/L) with propene (120 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 H2 Sensors

Sensor	Tech	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

TCD: Thermal Conductivity Detector; MOS: Metal Oxide Semiconductor; CAT: Catalytic Bead Pellistor; Multi: Multiple integrated technologies

3. Results

Figure 2 shows typical results to a sensor test, in this case exposure to 1) 50 µL/L CO; 2) 50 µL/L CO and 250 µL/L H₂; and 3) exposure to H₂ alone. Most notable from this test is that while Sensor B does respond with a limited false positive to CO exposure, this response is not added to that for hydrogen

when both gases are present. None of the other sensors in this test had any response to CO exposure.

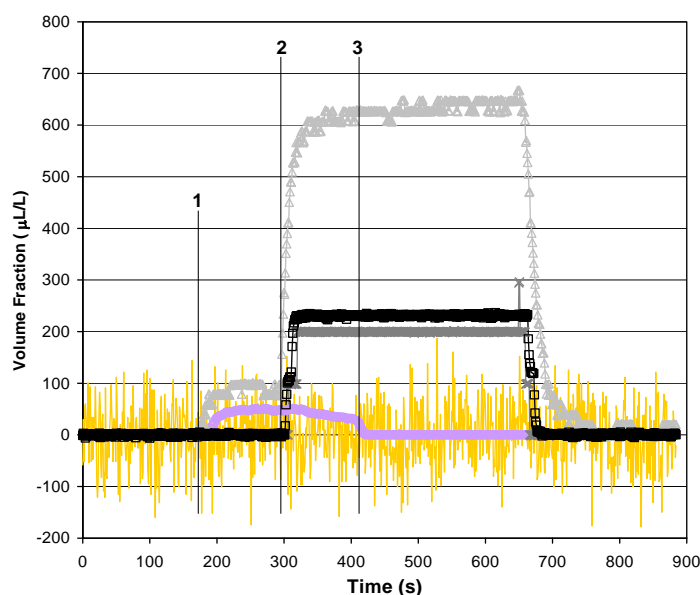


Figure 2. Typical result of an exposure test. Circles: CO; no symbol: Sensor A (TCD); light triangles: Sensor B (MOS); medium Xs: Sensor C (MOS); dark squares: Sensor D (CAT). 1) 50 $\mu\text{L/L}$ CO; 2) 50 $\mu\text{L/L}$ CO and 250 $\mu\text{L/L}$ H_2 ; and 3) 250 $\mu\text{L/L}$ H_2

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

- Sensor A (TCD) was not sensitive enough to detect H_2 anywhere, even up to 7000 $\mu\text{L/L}$ in the calibration cell. It was however sensitive to condensing water vapor, reading the equivalent of 3000 $\mu\text{L/L}$ H_2 at 25 $^\circ\text{C}$ and 100 % relative humidity.
- Sensor B (MOS) experienced the most cross-sensitivity, responding to temperature, humidity, CO/ CO_2 and propene. It also read consistently high in the presence of H_2 . 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_2 : it appears to be sensitive to humidity **only** in the presence of H_2 .
- Sensor D (CAT) is cross-sensitive to everything except CO/ CO_2 . It is extremely sensitive to hydrocarbons. It is also inversely temperature sensitive: increasing the temperature by 25 $^\circ\text{C}$ reduces the baseline by a

voltage equivalent to 200 $\mu\text{L/L}$. (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 $\mu\text{L/L}$ of H_2 in the FE / DE.

Table 2 summarizes the response of the different sensors to hydrogen and the various challenges, all expressed in equivalent volume fraction of hydrogen. Reported actual values are from the independent monitoring instruments, so for example the 130 $\mu\text{L/L}$ reported as the actual fraction of propene is the value recorded from the NDIR hydrocarbon analyzer.

Table 2. Responses of Hydrogen Sensors (all values in $\mu\text{L/L}$)

	A	B	C	D	F	Actual
H_2	0	590	200	200	350	250
+ 25 °C	0	20	0	-200	0	+ 25 °C
H_2O	3000	120	0	300	0	condensing
CO / CO_2	0	190	0	0	10	120, 2000
C_3H_6	0	930	600	2500	70	130
H_2 + 25 °C	0	640	300	-200	320	250, + 25 °C
		510 ^a	100 ^a			
H_2 + H_2O	3000	740	300	300	390	250, condensing
H_2 + CO/CO_2	0	610	200	220	310	250, 50, 600
H_2 + C_3H_6	0	1210	900	2800	390	250, 120
Uncertainty ^b	1000	10	100	100	10	

^a High value only on T rise with hydrogen present; low value for hydrogen added at high T

^b Type B uncertainty based on sensor manufacturer's documentation

It is worth noting the relatively disparate responses of the sensors to an ostensibly uniform flow of hydrogen. We attribute this discrepancy to four possible sources. First, although the flow in the FE/DE has been observed to be relatively uniform [1-4], the profile of hydrogen itself has not been measured in the FE/DE, and is in fact the subject of ongoing work. Hydrogen's buoyancy and high diffusivity may in fact lead to its non-uniform accumulation in unexpected ways. Second, the volume fraction of hydrogen in the FE/DE was at the low end of the sensor calibration range; thus any non-linear response in one or more sensors to low concentration of hydrogen could account for disagreements between the sensors. Third, the effect of flow conditions on the sensors is unknown; differences in velocities both during the calibration procedure and between the calibration cell and the FE/DE could have an affect

on the sensors' detection efficiency. Finally, the sensors were calibrated using dry compressed air and a calibration-grade hydrogen-air mixture, while the FE/DE uses room air, which in addition to having a relative humidity of 40% to 60% may contain other trace gases or vapors to which some sensors are more sensitive than others.

Sensors were also evaluated for response time in the calibration cell. Response times were characterized as being the time from the initiation of hydrogen flow to reach 95 % of the maximum reading (activation), and the time from the cessation of the hydrogen flow to reach 5 % of the maximum reading (relaxation). We make three general observations for the sensors tested here. First, activation times were generally on the scale of 1 min to 3 min, with the inherent response time of the calibration cell (i.e. the response time of the system for a sensor with instantaneous response) being less than 10 s. Second, relaxation times were generally much faster than activation times. Third, the effect of concentration on activation times was not consistent between different sensors: in some sensors, increasing concentration increases activation time, while in others it decreases activation time. Figure 3 shows the uncorrected response times for Sensors E and F.

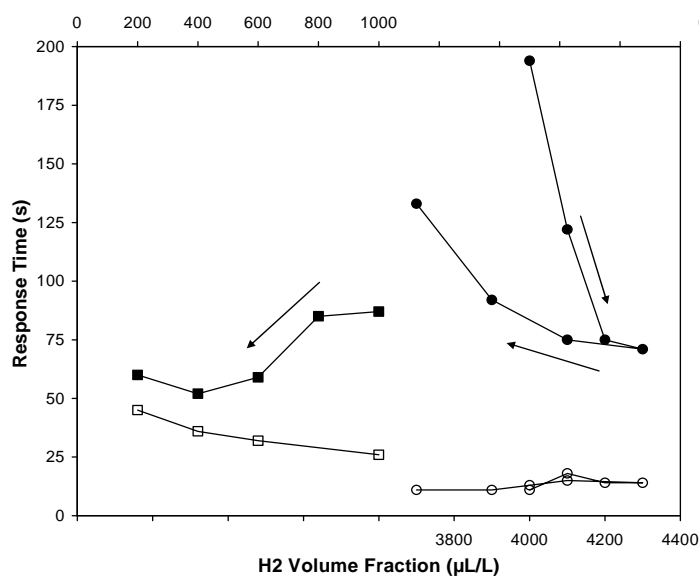


Figure 3. Response times of sensors. Squares: Sensor F (MOS); Circles: Sensor E (Multi); Filled symbols: response to hydrogen flow initiation; open symbols: response to hydrogen flow cessation. Arrows indicate order of tests. Times are not corrected for the response time of the calibration cell.

4. Conclusions

The FE/DE was modified to test an array of commercially-available hydrogen sensors that may be used for leak detection in hydrogen dispensing and storage facilities. Sensor cross-sensitivities to heat, moisture, and various gases in low concentrations were measured. In the presence of hydrogen, cross-sensitivities appeared to be additive in some cases and synergistic in other cases. The extent to which the observed cross-sensitivities would lead to nuisance alarms or missed alarms is unknown. Further testing at the desired hydrogen alarm concentrations needs to be performed. Sensor response times were on the order of one to three minutes, with relaxation times observed to be faster. Ultimately, performance evaluations need to consider dynamic environmental and concentration changes to assess temporal sensor performance.

References

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