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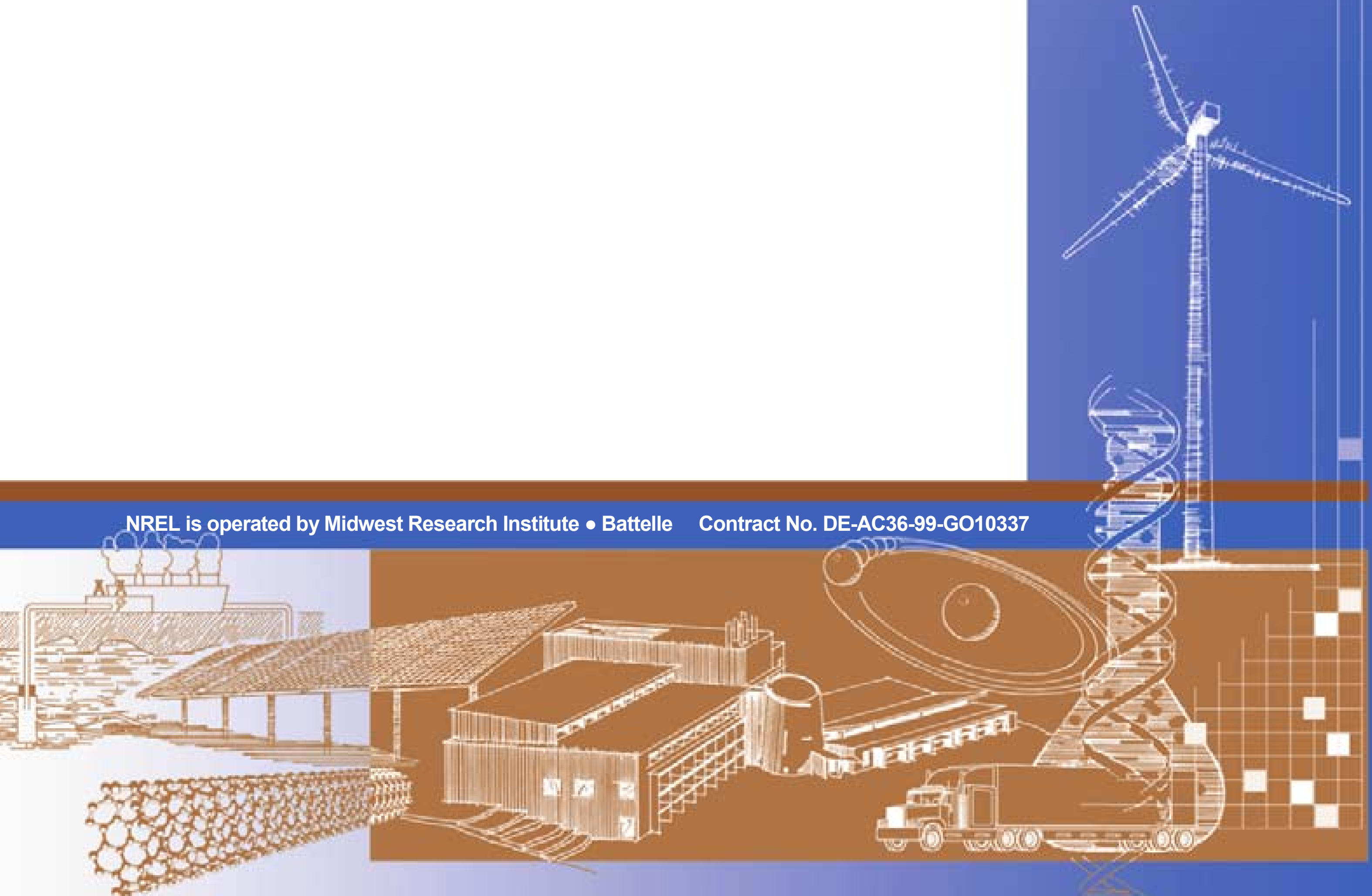
Test Protocol Document, Hydrogen Safety Sensor Testing

Phase I: Non-Flammable Mixtures

R. Burgess, C. Blake, and C.E. Tracy

Technical Report
NREL/TP-560-42666
September 2008



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1 Objectives

The objective of the testing is to evaluate the performance of hydrogen safety sensors in terms of the U.S. Department of Energy (DOE) technical targets listed in the 2007 technical plan for hydrogen safety (see Table 1) and other codes and standards emerging for hydrogen sensors (e.g., UL 2075, ISO). Testing will provide quantitative assessment on a variety of critical sensor performance specifications, including linear range, lower detection limit, cross reactivity, response/recover time, and others. This test protocol document includes an overview of sensor technologies, test hardware requirements, and an outline of potential testing. A more definitive standard operating procedure (SOP) will be prepared prior to the start of test lab operation.

2 Scope

The DOE has assigned the National Renewable Energy Laboratory (NREL) to provide technical support for hydrogen codes and standards R&D. The success of the DOE's Hydrogen Program is critically dependent upon the timely development of standards to facilitate the emergence of a viable hydrogen infrastructure. In this role, NREL is supporting research and development (R&D) needed to establish the technical basis for requirements that can be incorporated into standards and model codes. One of the key areas where requirements need to be further defined is related to hydrogen sensors.

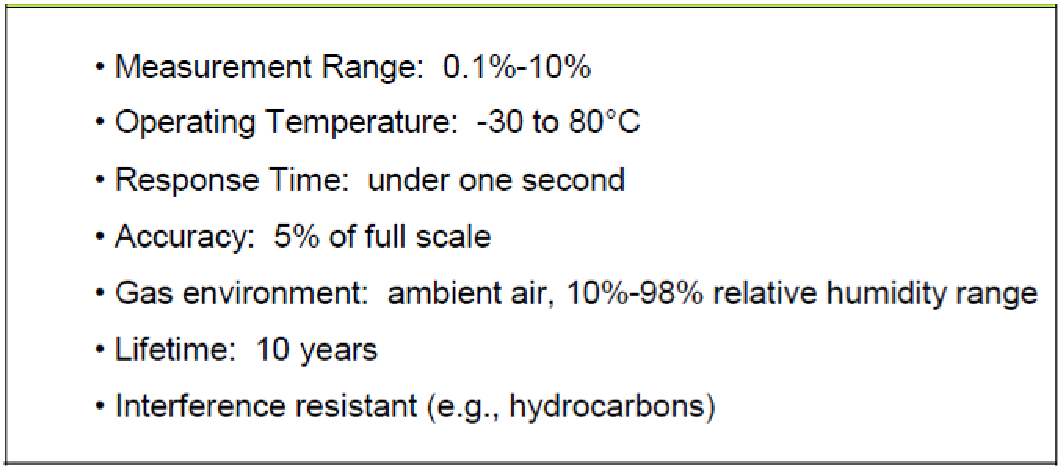
A critical area of work identified by experts in codes and standards is the refinement of existing and the development of new standardized analytical test and qualification procedures for hydrogen sensors. In anticipation of the increased use of hydrogen, and to support existing markets, members of the chemical sensor industry are developing and marketing hydrogen sensors. It is critical that hydrogen sensors meet DOE targets. Accordingly, test methods need to be established to validate hydrogen sensors performance. This requires the design and construction of a test apparatus and implementation of a specified set of standards and testing criteria. Researchers and engineers generally accept that the ubiquitous deployment of hydrogen energy technologies will not take place without an accurate, durable, and reliable hydrogen sensor.

Phase I testing will consist of test situations involving non-flammable, non-explosive mixtures of hydrogen. The lower flammable limit (LFL) of hydrogen in air is 4% by volume. All Phase I testing will be conducted with hydrogen concentrations below the LFL or with limited oxygen content. Future testing, designated as Phase II testing, will expand the test operation envelope to include mixtures above the LFL. Phase II test plans and scope will be covered in future documents.

Test methods need further standardization in both the national and international areas. NREL has initiated collaborations with other organizations to facilitate the harmonization of test methods; examples include organizations such as UL (Underwriters Laboratory), IIT (Illinois Institute of Technology), and the JRC (Joint Research Centre) lab in Europe.

NREL researchers will conduct R&D of emerging sensor technologies in conjunction with testing commercially available sensors to validate and compare the various technologies. Special emphasis will be placed on identifying *Technology Gaps* in which critical needs are not met by existing or emerging hydrogen sensors.

Table 1. DOE Targets for Hydrogen Safety Sensor R&D [1]



- Measurement Range: 0.1%-10%
- Operating Temperature: -30 to 80°C
- Response Time: under one second
- Accuracy: 5% of full scale
- Gas environment: ambient air, 10%-98% relative humidity range
- Lifetime: 10 years
- Interference resistant (e.g., hydrocarbons)

3 Overview of Sensor Technology

The need for robust, affordable, and compact hydrogen safety sensors is driving the development of new sensor technology. Current production sensors can provide repeatable and accurate hydrogen sensing; however these sensors are costly and often not ideally selective to hydrogen. Preproduction sensors which show promise for meeting the DOE targets are also a focus of this effort. From an application standpoint, the placement of hydrogen sensors to detect a hydrogen leak is also a major challenge.

3.1 Sensor Placement

Sensor placement depends on many environmental factors that affect the gas cloud dispersion, and it is important to prepare for all potential failure scenarios. For this reason, it would be beneficial to have an array of hydrogen sensors to insure that a leak is detected quickly and that an effective shutdown occurs. Requiring multiple sensors to be placed in a single application further drives the need for accurate, reliable, low-cost sensors.

3.2 Sensor Reliability

There are sensors in use today that have shown a history of faulty signals (e.g., false positives or false negatives) especially over extended period of deployment. Short operational lifetime is a concern among stakeholders. The root cause of the faulty signals varies, but includes environmental factors such as dirt/dust, vibration, fluctuating temperature and humidity, and contaminant substances. Testing in a controlled laboratory environment can be used to identify causative factors that induce faulty sensor excursions and their effect. Additionally, testing conditions can be controlled to simulate sensor operation in many varied environments and applications. A sensor that works well in one application may not be ideal for another.

3.3 Hydrogen Sensor Types

Included here is a general listing of sensor types with a brief description of the technology. These sensor technologies are in various stages of development, from initial proof of concept stages to full production. Note: information in this section was presented at the 2007 Hydrogen Sensor Workshop by Dr. William Buttner [2].

Some overall conclusions are that cost reductions are needed for all the sensors. The metal oxide (MOX) sensors typically are lower cost than other sensors but have limitations in response time, selectivity, and drift. All sensor types include commercially available products; however, there are also many products that are in the process of development or not in full production.

Electrochemical

This general class of sensors includes amperometric, potentiometric, and solid/liquid electrolyte type sensors. These sensors are linear and repeatable over a broad range but have selectivity and response time limitations. They are generally commercially available.

Palladium and Palladium Alloy Film

There are several technologies that employ palladium and palladium alloys for hydrogen sensing, including electronic (resistance, capacitance), thermoelectric, evanescence wave, and mechanical (cantilever) and SAW (Surface Acoustic Wave). The palladium film is generally more expensive and not yet as readily available commercially as other types of sensors. There is potential for palladium film-based sensors due to the high number of designs being explored.

Metal Oxide (MOX)

Heated MOX sensors are a mature commercial technology that is available for use at an affordable cost. There are issues such as high power requirements, non-linear response, and poor selectivity that limit the widespread acceptability for all applications.

Pellistor

A pellistor bead sensor uses a catalyst of platinum or palladium to produce a resistivity change. There are issues relative to the selectivity, response time, and power requirements that need further improvement.

Thermal Conductivity

The thermal conductivity of hydrogen gas is almost seven times higher than the thermal conductivity of air. Thermal conductivity sensors measure the thermal conductivity of the ambient gas, which is proportional to the hydrogen content. Most other gases of interest also have thermal conductivities much closer to air. See table 2 below for a summary of thermal conductivities for several gases of interest. Note that helium gas has a thermal conductivity closest to hydrogen.

Table 2. Thermal Conductivity of Gases

Gas	Thermal Conductivity K (mW/m)	K/K_{AIR}
Air	33.3	1.00
Helium, He	190.6	5.72
Hydrogen, H_2	230.4	6.92
Methane CH_4	49.1	1.47
Propane C_3H_8	30.6	0.92
Water Vapor H_2O	27.1	0.81
Nitrogen, N_2	32.3	0.97
Oxygen, O_2	33.7	1.01

Thermal conductivity sensors are commercially available. They have good response time but tend to be sensitive to environmental drift and have selectivity issues.

Optical/Acoustic Devices

This general category contains devices such as colorimetric and indicator dyes, evanescent wave, fiber optic hydrogen absorption, fiber optic with thin palladium film, speed of sound, and tuning fork technologies. Several of these technologies are in the early stages of development, but commercial prototypes may soon be available. One advantage is that they are intrinsically safe with no electrically powered device in contact with the hydrogen. The relative merits of several technology types need to be measured and analyzed.

4 Test Hardware and Data Acquisition

4.1 Test Station Definition

In order to perform the desired tests, we will equip the sensor test laboratory with test apparatus capable of exposing sensors to controlled environmental conditions. The test station schematic is presented in Figure 1. Gases are provided in pressurized cylinders, and certified for purity and composition. These gases are metered using mass flow controllers. Bypass lines around the mass flow controllers are provided for dilution and purging purposes. Additionally, water vapor can be added to the gas mix. Potentially, other vapors can be added to this configuration. Gases can either be premixed as supplied from the gas vendor or can be mixed in-situ to the required concentration in the mixing chamber. From here gas/vapor mixtures can flow to the test chamber where sensors are mounted.

The test hardware's response time is minimized by minimizing the gas volume between the mixing chamber downstream valve and the test chamber. The test chamber design includes the capability for controlling the temperature and pressure environment. Pressure is to be regulated by using a combination of a compressed gas supply, vacuum pump venting, and pressure regulators. Gas sampling from various test points and analysis by GC is planned to validate mixtures in the test chamber. We expect that the accuracy of data obtained by gas analysis will provide more precise test conditions and increase sensor measurement accuracy. All valves are controlled by the lab-based computer and automated test operation will allow for extended unattended life testing. Additional interlock shutdowns will be used to insure proper isolation of hydrogen gas in the event of an upset condition.

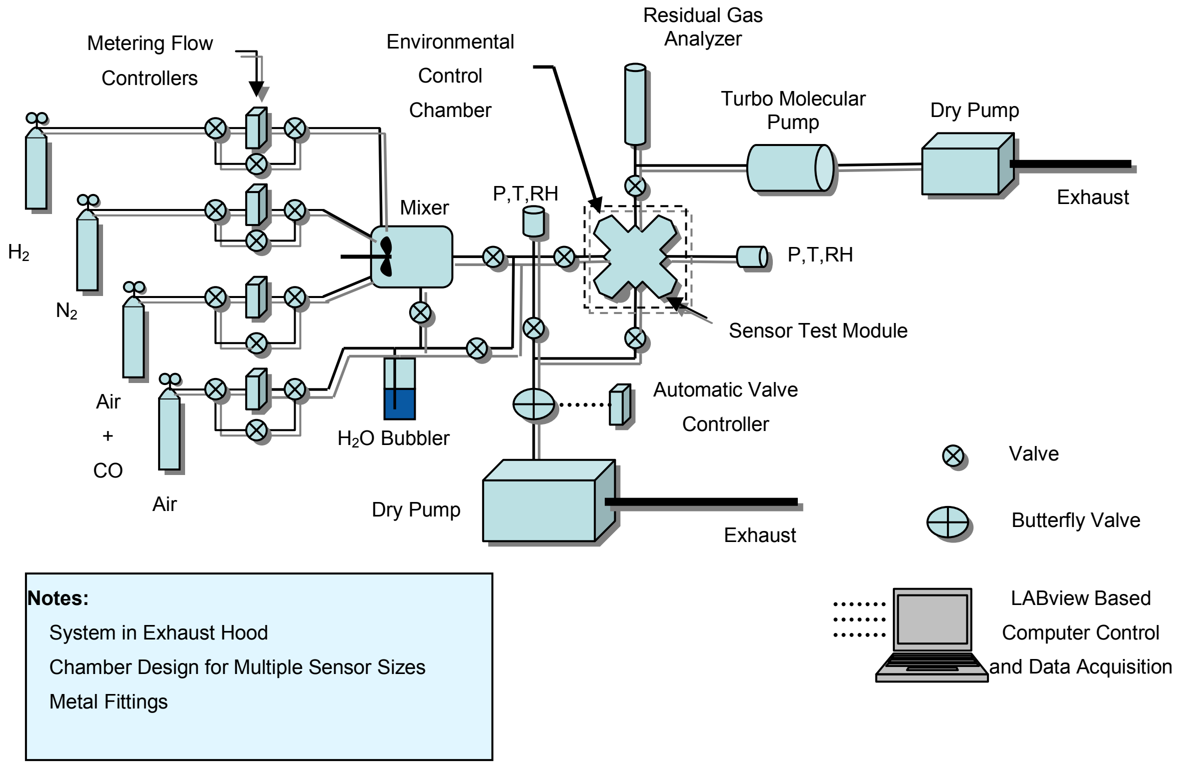


Figure 1. Hydrogen Safety Sensor Test Schematic

4.2 Data Acquisition

A LabView based computer data acquisition system will provide automated controls, actuation for all test functions, and data logging into an electronic file of all sensor responses. Controls will include appropriate interlocks for safe shutdown of the apparatus in the event of a system upset or failure. Data sampling rates will be sufficient to verify response times of less than one second, but will be adjustable so as to allow lifetime testing. A response time of less than one second is targeted for hydrogen safety sensors based on published DOE safety plans specifications [1]. Data acquisition and controls will be capable of autonomous operation of test parameters. This will allow for extended life testing. Sensitive data will be stored in a secured location to protect against unintended disclosure to non-essential personnel and to protect proprietary information.

5 Standard Conditions

Input parameters that may have an effect on the output of the sensor are listed in the following outline.

Hydrogen Safety Sensor Performance Matrix

1 Analytical
  1.1. Environmental
    1.1.1. Temperature -30°C to 80°C
    1.1.2. Pressure 0.8 atm to 1.2 atm
    1.1.3. UV exposure
    1.1.4. RF Exposure
    1.1.5. Velocity Effects
    1.1.6. Non-homogeneous Effects
    1.1.7. Hydrogen Consumption
    1.1.8. Permeation/Soak Back
    1.1.9. Strain
    1.1.10. Dust
    1.1.11. Static Discharge
    1.1.12. Vibration
    1.1.13. Orientation
    1.1.14. Selectivity/ Contamination
      1.1.14.1. Gas Contamination
      1.1.14.2. Vapor Contamination
      1.1.14.3. Multiple Contaminant Effects
      1.1.14.4. Reversibility/Irreversibility
      1.1.14.5. Poisoning Effects
  1.2. Accuracy/Capability
    1.2.1. Signal Drift
    1.2.2. Baseline Drift (Zero Drift)
    1.2.3. Analytical Resolution
    1.2.4. Linear Range
    1.2.5. Dynamic Range
    1.2.6. Lower Detection Limit

        - 1.2.7. Gauge R&R
            - 1.2.7.1. Reproducibility
            - 1.2.7.2. Repeatability
    - 1.3. Sampling Size /Time Scale
        - 1.3.1. Response Time
        - 1.3.2. Recovery Time
        - 1.3.3. Saturation (flooding)
        - 1.3.4. Statistical Sampling
            - 1.3.4.1. Test to Test Variation
            - 1.3.4.2. Part to Part Variation
            - 1.3.4.3. Design of Experiment

- 2 Logistical
    - 2.1. Deployment
        - 2.1.1. Capital Cost
        - 2.1.2. Installation Cost
        - 2.1.3. Physical Size
        - 2.1.4. Control Circuitry
        - 2.1.5. Power Requirement
        - 2.1.6. Electronic Interface
        - 2.1.7. Pneumatic Connections
        - 2.1.8. Shelf Life
        - 2.1.9. Maturity/Availability
        - 2.1.10. Manufacturability
        - 2.1.11. Grounding
        - 2.1.12. Alarm/Audibility
        - 2.1.13. Government Regulation
        - 2.1.14. Certification (UL, IEC…)
    - 2.2. Operational
        - 2.2.1. Operational Lifetime
        - 2.2.2. Consumables
        - 2.2.3. Calibration & Maintenance (frequency and complexity)
        - 2.2.4. Sample Size
        - 2.2.5. Matrix Requirements
        - 2.2.6. Signal Management
            - 2.2.6.1. Data acquisition
            - 2.2.6.2. Control Protocol
            - 2.2.6.3. Fail Safe
            - 2.2.6.4. Redundancy

Sensor output can be defined as the device's ability to accurately measure the hydrogen concentration. The overall purpose of the testing is to determine the input parameters that have the maximum effect on the output and to quantify those effects. Use of "design of experiment" methods can be used to help identify the primary input parameters and determine effects on output. An added advantage of the design of experiment technique is that is can be used to define confounding effects, where multiple input parameters have a combined effect on the output.

6 Standard Protocol

Prior to performing tests on hydrogen safety sensors, a number of standard tests will be performed on the test apparatus to determine the capabilities of the system and insure the accuracy of the test methodologies.

6.1 Leak Integrity Test

The test apparatus will be checked for leakage prior to testing. The leak check will be repeated after hardware changes, on a regularly scheduled timetable, and anytime there is question about the integrity of the system. Leak check will consist of pressurizing the system to a known pressure above atmosphere and verifying that the system is able to maintain pressure over time. To isolate and repair faulty fittings or components, the system can be pressurized with a known service gas such as helium. Helium leak detectors can be employed to search for the location of the leak.

6.2 Contamination/Cleanliness Test

All test apparatus components will be cleaned and inspected prior to any required assembly or reassembly. Care will be taken to cover openings to prevent contaminants from entering. The assembled system will be purged of impurities by inert gas. Gas samples will be analyzed to insure that impurity levels are below detectable limits. If needed, a bake-out process can be used to accelerate the purging process. A steady state hold, with regular gas sampling, will be used to determine that impurities are not permeating into the test gas.

6.3 System Response Time Test

One of the key parameters for hydrogen safety sensor testing is response time. The DOE target of less than one second response time will be a difficult target to reach for many of the sensor technologies in current use. It will help if the test apparatus response time is much faster than the sensor response time being measured. In order to determine the test apparatus system response time, a heated gas test can be used. The heated gas at equilibrium conditions in the mixing chamber can be introduced to the test chamber. A fast-acting thermocouple can be used to determine the time between opening the valve and measuring the elevated temperature. Fast acting thermocouples with small wire diameter can have response times on the order of 0.003 seconds.

6.4 Sensor Calibration

Sensor calibration procedures will vary with each sensor. Sensors that are to be tested will be calibrated per the manufacturer’s recommendations. Calibration data will be recorded at regular intervals or as required by the test sequence.

7 Baseline Testing

All test data and product specific information will be maintained in secure storage. Test data of existing commercial products will be reviewed with the manufacturer prior to publishing the data for general use. Test data of prototype sensors will be confidential. Testing defined in this section represents typical tests. Specific testing to recognized codes and standards and /or SOPs will be defined in a later document.

7.1 Linear Range (dynamic range)/Accuracy/Zero Drift

Basic sensor capability will be measured by this series of tests. The linear range will define the lower detection limit and the point where saturation is reached. Hold points at zero concentration will be used to determine zero drift. Output readings will be compared with gas analysis to determine the accuracy of the readings.

7.2 Response/Recovery Time

The sensors will be exposed to a cyclical test, varying the concentration of hydrogen from zero to a fixed fraction of the LFL (LFL = 4%). Response time and recovery time will be measured for each cycle and compared over multiple cycles.

7.3 Environmental Testing (Temperature, Pressure, Relative Humidity)

Effects of pressure, temperature, and relative humidity will be measured under controlled conditions in accordance with the DOE target specifications (Table 1). Temperature will be varied from -30°C to 80°C; pressure will be varied from 0.8 to 1.2 atm. Relative humidity will be varied from 10% to 98%.

7.4 Contamination Testing

Contaminants that have been identified for potential testing are hydrogen sulfide, carbon monoxide, carbon dioxide, nitrogen oxides, specific hydrocarbons, ammonia, and select alcohols. Testing for interference effects of these contaminants will require an extensive testing program. Priorities will be based on selecting contaminants with known effects on specific sensor technologies. As an example, thermal conductivity sensors will respond to helium due to its high thermal conductivity. Helium would not be expected to contaminate other sensor types.

8 Life Testing

Extended life testing will be conducted to determine the ability of sensors to meet the DOE goal of 10 years of operational life. The lifetime of a sensor is a critical parameter that needs to be addressed by further R&D testing. Environmental factors that need to be considered when conducting life testing are repeated exposure, temperature cycling, pressure cycling, humidity cycling, dust exposure, and UV exposure. The automated test apparatus will be capable of running continuous testing with variable conditions, including accelerated life type tests.

9 Plans for Future Work

Future plans are to expand the testing capability to include flammable and explosive operating regimes, denoted as Phase II testing. Most of the interest in safety sensor performance is to detect hydrogen before reaching flammable concentrations. For this reason, we have limited the Phase I testing to non-flammable (below 4%) conditions. The driving force for testing in flammable/explosive atmospheres is to verify that sensors are capable of operation under higher concentrations and to examine whether the sensors themselves (many electrically-based) are potentially capable of being an ignition source.

Test hardware requirements for Phase II testing will require designing the test housing for explosion containment. This is intended to provide an added safety measure in the remote chance of an uncontrolled thermal excursion induced by unintended hydrogen combustion. Hydrogen forms a flammable mixture over a wide range of concentrations in air and requires a minimum ignition source; only one-tenth of the energy required for gasoline vapors. When using flammable mixtures, it is possible that an unintended ignition could occur. Additionally, the high flame speed of a hydrogen deflagration will create a pressure peak within a few milliseconds. Burst disk technology would not be capable of relieving the pressure peak due to the inherently slow burst disk response time of 5 to 10 milliseconds. National Fire Protection Association (NFPA) 69 provides design requirements for explosive containment pressure vessels [3].

In addition, we plan to test sensors under simulated/controlled leak scenarios. This testing would be used to anchor computational fluid dynamics (CFD) model codes. CFD codes are currently being used to predict hydrogen cloud dispersion under various leak scenarios. Modeling results are then used to determine the most effective placement locations for safety sensors. We envision that testing would place sensors in a simulated garage space environment while providing a known hydrogen gas leak.

10 References

1. DOE Office of Energy Efficiency and Renewable Energy, Hydrogen Safety Plan, http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/safety.pdf

2. “Today’s Commercial Hydrogen Sensors” Presentation at the Hydrogen Sensor Workshop, 04 Apr 2007, by Dr. William Buttner. http://www.lanl.gov/orgs/mpa/mpa11/TechBriefing-Buttner-Sensors.pdf

3. NFPA 69 “Standard on Explosions Prevention Systems”

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This test protocol document includes an overview of hydrogen sensor technologies, test hardware requrements, and an outline of potential testing.

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