TESTING OF HYDROGEN SAFETY SENSORS IN SERVICE SIMULATED CONDITIONS

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ABSTRACT

Reliable and effective sensors for the accurate detection of hydrogen concentrations in air are essential for the safe operation of fuel cells, hydrogen fuelled systems (e.g. vehicles) and hydrogen production, distribution and storage facilities. The present paper describes the activity on-going at JRC for the establishment of a facility that can be used for testing and validating the performance of hydrogen sensors under a range of conditions representative of those to be encountered in service. Potential aspects to be investigated in relation to the sensors performances are the influence of temperature, humidity and pressure (simulating variations in altitude), the sensitivity to target gas and the cross-sensitivity to other gases/vapors, the reaction and recovery time and the sensors' lifetime. The facility set up at JRC for the execution of these tests is described, including the program for its commissioning. The results of a preliminary test are presented and discussed as an example.

1.0. BACKGROUND

Alongside the economic convenience and technical feasibility, a pre-condition for a consistent penetration of hydrogen into the energy market is that at least the same levels of safety for the industry, the environment and the public can be assured for hydrogen as it is for today's fuels and energy carriers. Because hydrogen is non-toxic, its major hazard is connected with the possibility of building up potentially explosive conditions due to an unwanted release. In this respect, the key parameters for the comparing hydrogen safety, with that of conventional fuels, are flammability, detonability, ignition energy, diffusivity and buoyancy. Compatibility with materials used to contain and transport hydrogen is also an issue [1, 2]. As shown in Table 1, the flammability range of hydrogen in air covers a much wider range of concentrations than for methane, propane, or gasoline vapor. Furthermore, hydrogen can be much more readily ignited under most circumstances. Hydrogen is also detonable over a very wide range of concentrations when confined.

Table 1: Flammability and detonability characteristics of hydrogen in comparison with other fuels, after Ref. [1]. LFL: Lower Flammability Limit; UFL: Upper Flammability Limit; LDL: Lower Detonability Limit; UDL: Upper Detonability Limit

	H_2	Methane	Propane	Gasoline
LFL – UFL (% vol in air)	4 –75	5.3-15	2.1-9.5	1-7.8
Concentration at air-fuel stoichiometry (% vol)	29.5	9.5	4.1	1.8
Minimum ignition energy at stoichiometry (mJ)	0.02	0.29	0.26	0.24
LDL-UDL (% vol in air)	11/18-59	6.3-13.5	3.1-7	1.1-3.3

One consequence of the above is that the availability of rapid and reliable hydrogen detectors is important at various levels of the hydrogen and fuel cells economy. Related R&D issues have been identified as a priority both by the U.S. Department of Energy (DoE) and by the European Hydrogen and Fuel Cell Platform (HFP). Efficiency over a wide range of hydrogen (and oxygen) concentrations, low-sensitivity to gaseous contaminants and poisoning are outstanding requirements, alongside the possibility to efficiently integrate the sensing devices in future hydrogen systems, including portable ones, so that safety or emergency measures can be actuated automatically in case of necessity. Some of the envisaged goals in this field are summarized in Table 2, after Refs. [3, 4]

Table 2: R&D priorities and technical targets for hydrogen detection technologies in the context of the hydrogen economy

Hydrogen chain stage	**Area of Application**	**Ref.**	**Specific technological goal**	**Quantitative technical targets**		
				Operating Temperature (^{o}C)	**Response Time**	**Accuracy**
Production	Process plants	DOE	Large area physical sensing	-30 – 120	0.1 – 3 s for 50% response to step change	10% full scale
Distribution & Storage	Pipeline monitor	DOE	In-situ sensing of leaks	-50 – 80	3 response to changing conditions	10%
	Pipeline, refuelling and underground storage	HFP	As above	Yet to be specified (ytbs)	ytbs	ytbs
	Storage tanks	DOE	Innovative concept/materials integrated into the system to indicate permeation, leaks or critical damage	-50 – 80	3 s response for 50% of the step change	1%
	Safe operation of CGH2 systems	HFP	as above	ytbs	ytbs	ytbs
	Hydrogen supply cartridges for micro-mini fuel cells	HFP	ytbs	ytbs	ytbs	ytbs
Utilization	Vehicle passenger compartments/boots	DOE	Rapid reaction response	-30 – 80	0.1 – 1 s for 70% response to step change	1 – 10% full scale
	Stationary fuel cells	HFP	Lower cost	ytbs	Ytbs	ytbs
	Device-integrated power supply	HFP	Low-power miniature electronics	ytbs	Ytbs	ytbs
Cross-cutting issues	Permeation	DOE	See storage tanks	-50 - 80	1 s response to changing conditions	5%
	Personnel monitor	DOE	Innovative technologies	0 – 40	0.1 - 0.6 s for 75% response to step change	1 – 10% full scale
	Emissions monitoring (environmental impact)	HFP	ytbs	ytbs	ytbs	ytbs

2.0 SYSTEMS AND TECHNOLOGIES FOR HYDROGEN GAS DETECTION

The proper installation of a gas detection system poses a number of questions, which the system designer needs to answer in order to decide which sensing technology is most suitable, how many sensors are needed, where and how they should be positioned and how often they should be calibrated [5]. Points to be considered are, for instance, the properties of the gas to be detected (combustible, toxic, lighter or heavier than air), those of the possible release (slow and continuous in the case of permeation losses, jet-type in case of a pressurized element rupture), the nature of the application (are limits imposed on electronic data exchange, is there a possibility of mechanical fatigue) and that of the environment (harsh, open or closed, static or ventilated).

With reference to hydrogen, much useful practical knowledge is already laid down in national and international technical standards for flammable gas detectors [6-9]. These contain, amongst other things, synthetic descriptions of different principles and devices that can be used for the detection of hydrogen, together with a list of the main technical limitations for each sensor type. An overview of these systems is given in Table 3, summarizing Ref. [7].

Table 3. Overview of hydrogen detection apparatus with different measuring principles.

	Functioning principle	**Typical measuring ranges**	**Relative response time**	**Interferences from non combustible gases**	**Poisoning**
Catalytic sensor	Detection of the combustion heat by resistance change in an imbalance of the bridge	≤LFL	depends on species	No	Si, Alogenated compounds, H_2S, Pb
Thermal conductivity sensor	Heat loss by an electrically heated element in a gas sample stream	(0)-100%	Medium	CO_2, freons	no
Solid-state sensor	Change of electrical conductance of an oxide due to sample gas chemisorption	≤LFL	depends on species	SO_2, NO_x, H_2O	Si, Alogenated compounds SO_2
Electrochemical sensor	Change of electrical potential of electrodes due to a redox reaction with sample gas	≤LFL	Medium	SO_2, NO_x	no

Because the sound velocity in hydrogen is very high in comparison to other gases, measurement of ultrasounds attenuation can also be used as a method for hydrogen detection [10]. On the opposite, well-established detection systems based on the absorption of electromagnetic radiation (usually infrared) or upon electrical ionization of gases (Flame Ionization Detector, FID), which offer respectively good performances in terms of selectivity and sensitivity, are unfortunately not suitable for hydrogen detection [6, 7].

Over the last years, the growing interest in energy and fuel cells related applications has pushed research on hydrogen detection methods and devices forward. Several achievements have been reported recently, such as micro machined sensors based on the electrical resistance change of rare earth thin films upon hydrogenation [11], new electrolytes for electrochemical sensors [12], detectors measuring the change of the optical properties of thin films in hydrogen containing atmospheres [13, 14] and thermoelectric sensors in which a catalytic layer converts hydrogen and oxygen into vapor, emitting heat energy and resulting in temperature difference across the sensor [15]. As a result of all these activities, performance improvements have been reported by different authors, for instance in terms of response time, selectivity, sensitivity or detection range.

Against this background, it is to be envisaged that the performances and reliability of both "conventional" and "novel" sensing devices is assessed in agreement with commonly agreed methods and procedures, as this would be instrumental for sensor manufacturers and researchers in meeting future requirements, for instance in the automotive area or other applications close to the general public [16]. Furthermore, although existing standards list both minimal requirements and test procedures for combustible gas detectors in general, their applicability to innovative hydrogen sensing technologies and hydrogen applications should be verified. A few laboratories worldwide have focused their activity on sensor performance assessment [17, 18] aiming at positioning themselves as a reference in the context of the respective national hydrogen energy programs. In the case of JRC, the setup of a hydrogen sensor testing facility (SenTeF) was started in 2003, also following the results of a preliminary survey among potentially concerned parties. Since then, considerable progress has been made in refining laboratory equipment as well as in establishing relevant contacts at European level, mainly on the side of the end users and in the context of on-going R&D Projects.

3.0 DESCRIPTION OF THE JRC INSTALLATION.

3.1 Testing needs

According to IEC 61779-1, sensors performances to be tested include for instance the determination of measurement accuracy, short and long term stability of response, sensitivity to temperature, humidity, air velocity, orientation with respect to the gas flow, resistance to vibrations and in drop tests, effects of interfering gases (with emphasis on poisons) and dust [19]. For the purpose of designing the JRC facility, testing needs were considered as divided in three classes:

- Environmental tests. They consist of assessing the response dependence on temperature, pressure, humidity, interfering species, or contaminants, in quasi-static conditions. Variability of ambient conditions include temperature variations between –40 and 130°C, relative humidity (r.h.) change between 0 and 95%, pressure excursion between 0.8 and 1.3 bar to simulate altitude changes. Contaminant species considered so far include CO, CO_2, H_2S, SO2, NO_x, C_xH_y, NH_3, ethanol, methanol and iso-propanol.

- Dynamic response tests both to gas compositional changes, i.e. to rapid switches of atmosphere composition, simulating sudden gas releases, and to environmental changes, i.e. rapid changes of temperature, humidity and pressure, simulating the sudden displacement of a detector mounted on a vehicle or on a portable device.

- Fatigue tests. They include environmental fatigue, which could cause signal drift due to poisoning and/or temperature cycling, and mechanical fatigue, typically due to vibrations and particularly important in view of mobile applications.

The facility schematically depicted in Fig. 1 was designed to respond to these needs. For its construction, Swagelock® tubing, fittings and valves (both manual and pneumatic) were used, together with Brooks® and Bronkhorst® mass flow controllers to regulate the inlet of different gases and liquids. For independent measurement of humidity, a dew point hygrometer model, 2002 Dew Prime™ made by EdgeTech was fitted into the system, whereas a Compact GC® from Interscience B.V was connected for the on-line analysis of the test gas. The resulting setup can be considered as divided into several sections, classified according to their function.

Part A (gas inlet and mixing) is a group of mass flow controllers (MFC), to control flow rates of gases and mix them together. It is connected to gas cylinders or to the central gas distribution system.

Part B (liquids management system) is for addition of vapours to the gas and is designed for humidifying the gas as well as for preparing mixtures, which simulate the environmental pollution of the atmosphere, e.g. from alcohols.

Part C (buffers) contains two reservoirs of volume 3.8 litres, which are used to stabilize gas composition. This offers a quick supply of gas mixtures of different composition for high-speed dynamic measurements and for environmental cycling tests.

Part D (pressure/evaporation control system) further prepares the atmosphere for the measurements by setting the pressure at the buffer outlets and regulating the liquid vapour content by means of two installed controlled evaporation mixers (CEM). For test atmospheres with a vapour content corresponding to a dew point above the room temperature, the tubing after the mixer outlets is equipped with a heating system, to avoid condensation.

Part E (test points) contains both an environmental test chamber (C1) and a dynamic test plate (C2). C1 enables long-term measurements to be made in controlled conditions, where temperature, humidity and gas composition changes can be gradually varied to simulate natural drifts. This chamber is double-walled, with temperature being controlled through circulation of a thermostatic fluid between the two walls. For safety when toxic gases are being used, C1 is further contained into another vessel, which is streamed with argon. The response chamber C2 enables fast dynamic changes of the gas composition, pressure and flow rate, and is intended for sensor response testing according to the "test mask" method [19], as described below in further detail.

Part F consists of the analytical equipment, and enables to measure the water vapour content and gas composition. The level of humidity created can be measured independently with a chill mirror hygrometer measuring dew/frost points from –50 to 100°C, step 0.2°C. The gas chromatograph is connected by means of multiport valve to 11 sampling points in the facility (not depicted here).

The very low concentrations of hydrogen and contaminant gases needed for testing can be obtained by diluting pre-mixed active gases and synthetic air with pure synthetic air. If necessary, the buffers can also be used to further blend the pre-mixed gases, in order to achieve more complex mixtures. The resulting effectiveness in creating test atmospheres with hydrogen and or pollutants at low concentration (ppm range) is particularly high.

3.2 Commissioning program and test examples

At the time at which the present paper is written, the effectiveness of the facility in maintaining carefully balanced conditions is being verified through a series of tests.

Concerning environmental testing, the length of the piping the large volume of the chamber C1 is expected cause some delay in reaching the desired composition at the test point upon setting of the corresponding gas and liquid vapour flows. This translates into a time constant for the apparatus, which has to be measured in order to carry out experiments in which compositional changes of the test atmosphere occur as a function of time. An example of a possible evolution of test conditions as a function of time is shown in Figure 2. The hydrogen concentration is maintained constant, whereas that of a contaminant, in this case carbon monoxide, varies with time, going through a maximum during the test. This type of experiment could be fit to verify the concentration threshold at which the presence of an interfering species becomes critical for hydrogen detection and measurement.

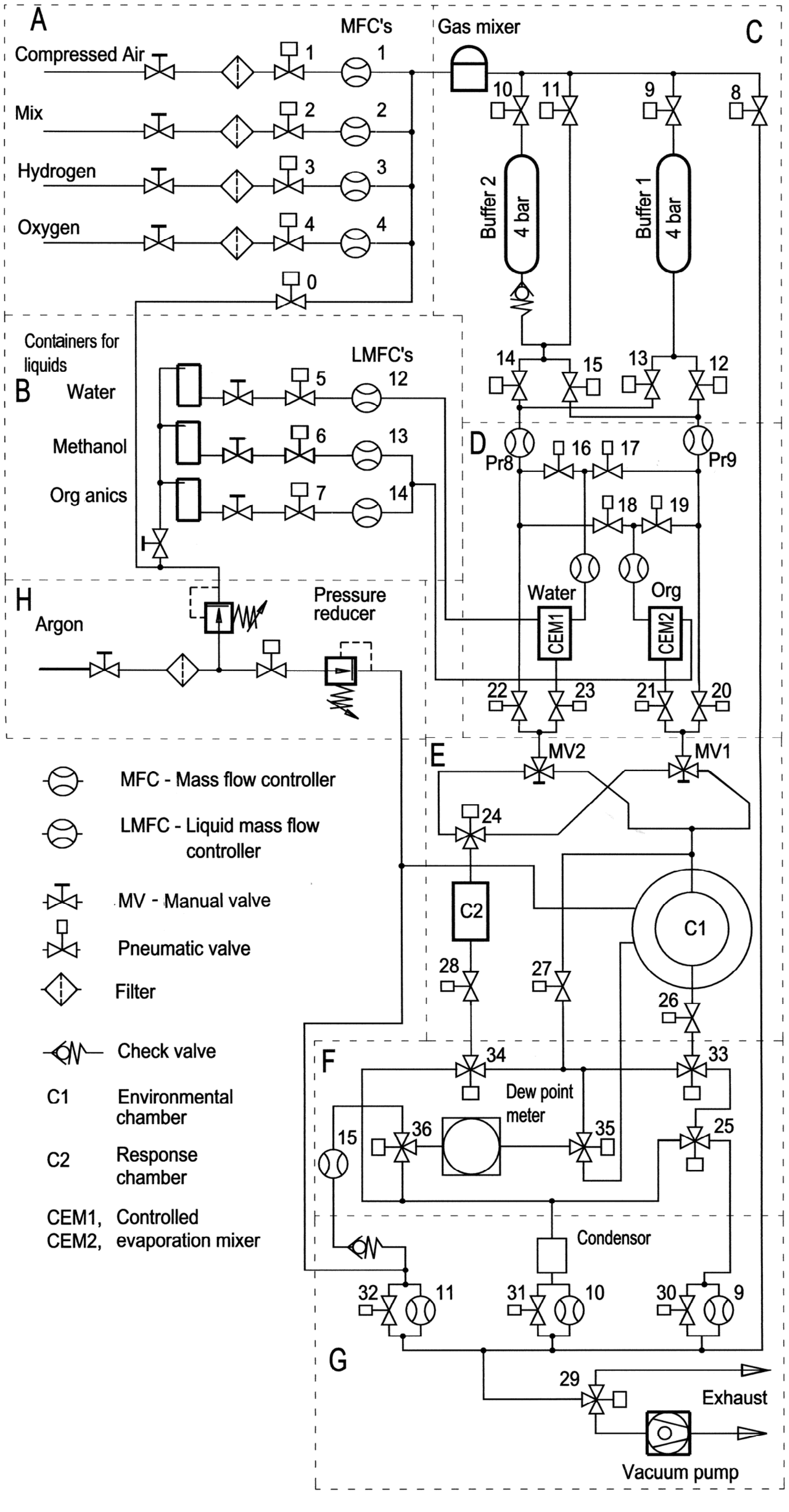

Figure 1: Schematic drawing of the sensor testing facility: A – gas inlet and mixing, B – liquid inlet and mixing, C – gas buffering system, D - vapour control system, E – test chambers, F – gas analysis, G – exhaust, H – argon purging

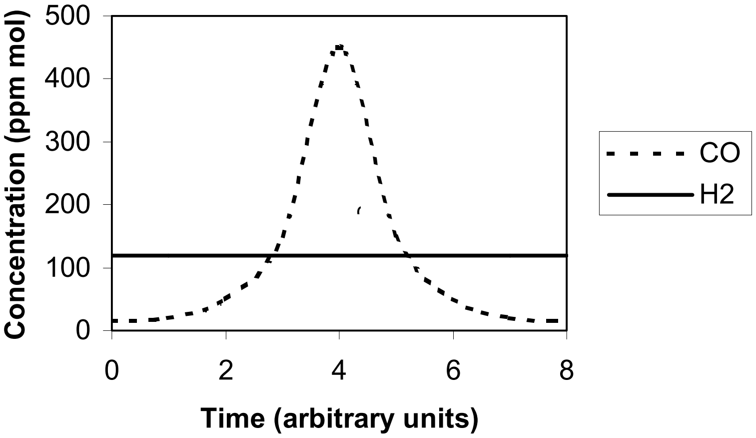

Figure 2: Possible variation of test atmosphere composition during an environmental test

As for dynamic response testing, preliminary tests were carried out on a commercial sensor of the electrochemical type. A hydrogen/argon mixture 1% volume in hydrogen was prepared by blending the pure gases, and stored in the gas buffer 1. By further diluting this with pure synthetic air (22% oxygen, 78% nitrogen), a mixture containing 5% argon and 500 (±25) ppm H_2 in air was made ready for the test in the second buffer. The gas sensor was mounted on the test plate and pressed against the gas outlet as shown in Figure 3, so that a three-way valve positioned below the plate (number 24 in Fig. 1) could be used to switch the gas flow directed towards the sensor between pure synthetic air and synthetic air containing 500 ppm of hydrogen.

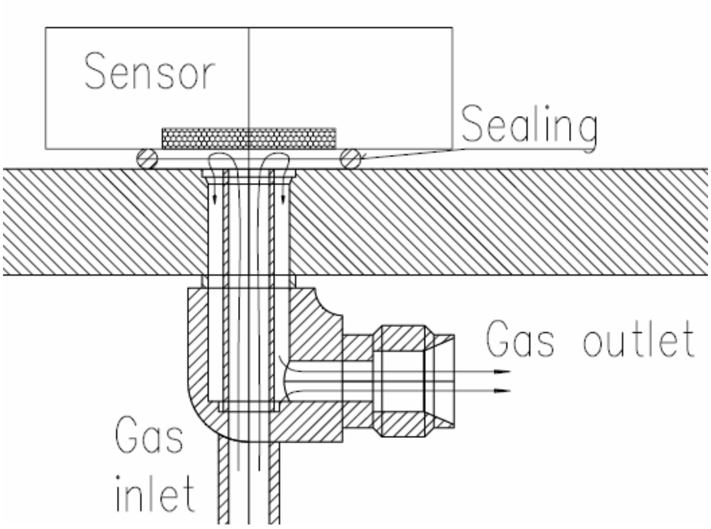

Figure 3: Sensor mounting for the response time test. Appropriate test masks can be fitted on top of the gas inlet/outlet orifice.

This mounting reduced the dead volume to less than 1 ml, which implied a complete renewal of the test atmosphere in less than one second at every flow switch for flow rates higher than 60 ml/min at 100 kPa pressure. Over an entire test time of 3000 s, air and air/H_2 flows were alternated every 300 s, using different flow rates, while the response of the sensor was recorded.

The results shown in Fig. 4 a) to c) illustrate the good functionality of the system. Overall, the dynamic response of the sensor was in the order of some tens of seconds (Fig. 4a), which is coherent with the information available on this type of sensor (See table 3).

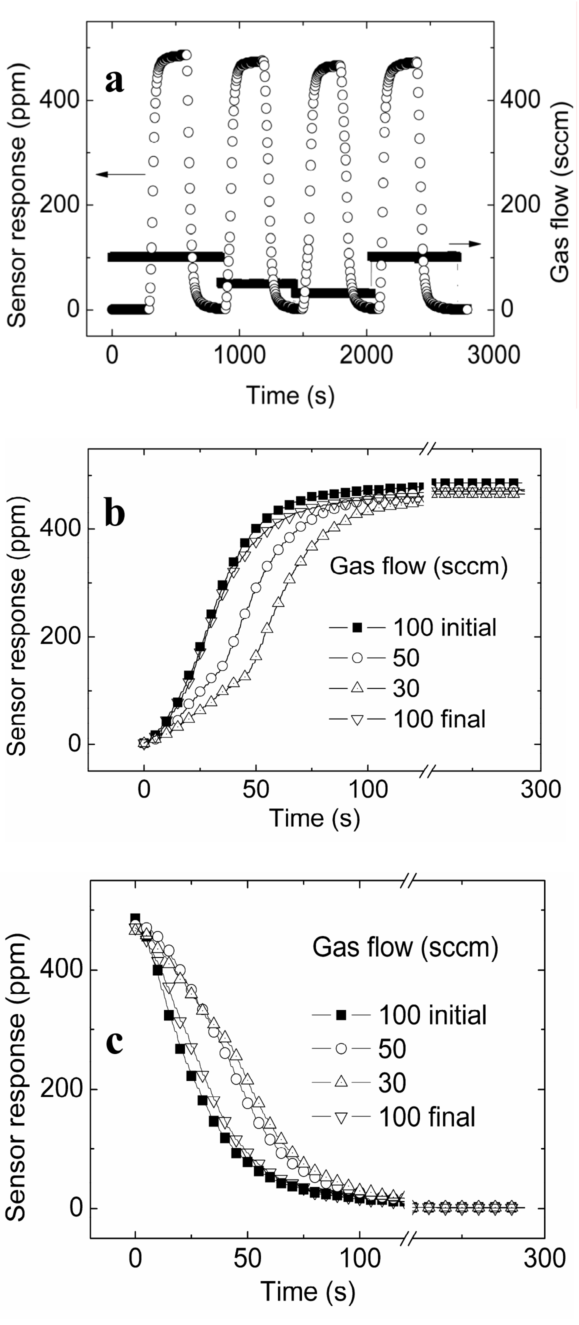

Figure 4: Example of dynamic response test data for an electrochemical sensor. **a)** response and recovery on rapid change of hydrogen concentration in air at various flow rates; **b)** comparison of ascending ramp of sensor response at various flow rates; **c)** comparison of descending ramp of sensor response at various flow rates

Both the response and recovery time showed a significant lengthening with decreasing flow rates [Figs. 4b) and c)]. This confirmed the information, available in the literature [19], that the dynamic response of a sensor can be strongly influenced by both gas velocity and pressure, especially when the sensor is mounted very close to the gas inlet orifice, which corresponds to the so-called "test mask" method. Although this method gives the great advantage of minimizing dead volumes, it requires in principle that the mounting of the sensor on the test plate reproduces the conditions used by the manufacturer for the sensor calibration. It is also for this reason that “test and calibration masks” are often available on request from the manufacturers for clients willing to verify the efficiency of their devices on a periodic basis. Because of its simplicity, the systems depicted in Fig. 3 allows to modify the mounting of the sensor under test on top of the orifice quite easily on a case-by-case base, for instance by fitting appropriate test masks or by inserting a gas diffuser to prevent the direct impact of the gas against the sensor inlet.

4.0 SUMMARY AND CONCLUSIONS

The paper describes the activity on-going at JRC for the setup and commissioning of an experimental facility for hydrogen safety sensor environmental and dynamic response testing. The facility has been designed in such a manner as to simulate service life environmental and climatic conditions with a high level of accuracy, through independent control of the test atmosphere composition and humidity, as well as of temperature and pressure. For dynamic response testing, the present setup consists of a quick-response test plate immediately adjacent to a gas flow switch, which enables to reduce the time requested for a complete test atmosphere change to less than one second simply by reducing the dead volume of the experimental apparatus to a minimum. The layout of the present system has a high level of flexibility, which allows to adapt the mounting of the sensor under test in order to ensure coherence with the conditions used by the manufacturer for the initial calibration of the device. Further development of the facility and sensor performance characterization is planned, which will cover investigations on long term drift, hysteresis and dependence on environmental conditions.

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