# EVALUATION OF SELECTIVITY OF COMMERCIAL HYDROGEN SENSORS

Palmisano, V.  $^1$ , Boon-Brett, L.  $^1$ , Bonato, C.  $^1$ , Harskamp, F.  $^1$ , Buttner, W.J.  $^2$ , Post, M.B.  $^2$ , Burgess, R.  $^2$ , Rivkin C.  $^2$ 

<sup>1</sup> Cleaner Energy Unit, European Commission – DG JRC Institute for Energy and Transport, Westerduinweg 3, (P.O.Box 2), 1755 ZG Petten, The Netherlands

<sup>2</sup> Hydrogen Technologies & Systems Center, National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401-3305, USA

## **ABSTRACT**

The development of reliable hydrogen sensors is crucial for the safe use of hydrogen. One of the main concerns of end-users is sensor reliability in the presence of species other than the target gas, which can lead to false alarms or undetected harmful situations. In order to assess the selectivity of commercial of the shelf (COTS) hydrogen sensors a number of sensors of different technology types were exposed to various interferent gas species. Cross-sensitivity tests were performed in accordance to the recommendations of ISO 26142:2010, using the hydrogen sensor testing facilities of NREL and JRC-IET. The results and conclusions arising from this study are presented.

# 1.0 INTRODUCTION

The European Commission and the U.S. Department of Energy (DOE) both recognize the key role hydrogen technologies will play in securing a safe, clean and secure energy supply in the future. In Europe, the 2011 Technologies Map of the Strategic Energy Technology Plan identifies hydrogen and fuel cells as promising low-carbon energy technologies [1], which can assist in Europe's transition to a low-carbon society. Similarly the Fuel Cell Technologies Program of the U.S. DOE supports the development and deployment of hydrogen as an alternative energy source [2] to ensure America's security and prosperity by addressing its energy, environmental, and nuclear challenges through transformative science and technology solutions [3]. Acknowledging the importance of safety in the future hydrogen infrastructure and the role hydrogen sensors play to help ensure this safety, sensor test facilities were independently established by the European Commission's Joint Research Centre - Institute for Energy and Transport (IET) [4] and by DOE at the National Renewable Energy Laboratory (NREL) [5]. Owing to the significant overlap of their respective missions to evaluate sensor technology and to educate the hydrogen community on the proper use of hydrogen sensors, the JRC-IET and NREL sensor laboratories have ongoing collaborative sensor research programs, formalized by a Memorandum of Agreement.

Hydrogen sensors are necessary for alerting to unwanted releases wherever hydrogen is produced, stored, transported or used. Hydrogen sensors can employ one or more sensing technologies to detect and quantify hydrogen concentration. Many of these technologies are well developed and widely implemented in industrial applications [6], however, the deployment of hydrogen safety sensors in new markets may impose new performance requirements. These include a need for increased robustness to ambient parameters changes and reduced cross-sensitivity to other gases. Stakeholders in emerging markets may be less knowledgeable about limitations associated with the various sensor platforms than their counterparts in established hydrogen industries, and thus may select a less than optimal technology for their application.

Cross-sensitivity, also called sensor selectivity and robustness against potential poisons are some of the main challenges to the developers of gas sensors. Selectivity can be defined as the relative response of a sensor to two different analytes. Ideally a gas sensor developed for a specific target analyte (e.g., hydrogen) should not respond to other gases (i.e., interferents). Selectivity reflects the ability of a sensor to respond to the target analyte, regardless of the presence of other species. When

the presence of a gas other than the target affects the sensor performance in a reversible way, it is termed an *interferent*, while species which affect sensor performance irreversibly are termed *poisons*.

Hydrogen facility designers and operators are concerned about the selectivity of their chosen hydrogen detection device. This concern was clearly evidenced during a NREL/DOE Hydrogen Sensor Workshop in 2011 when sensor selectivity was repeatedly cited by end-users as a highly important analytical parameter of hydrogen sensors [7]. The response of a sensor to an interferent can lead to false positives. Such incidents of false positive alarms and their consequences have been reported [8]. Conversely interferents may also suppress the sensor's response, leading to a false negative, which may have serious safety consequences as leaked hydrogen may go undetected.

For hydrogen sensors, a specific species may be a significant interferent on one sensor platform (e.g., methane on a hydrogen metal-oxide gas sensor) while it may not induce a response on a second platform (e.g., methane on a hydrogen electrochemical sensor). In this paper we report the selectivity of various commercially available hydrogen sensor platforms; this work was performed under the auspices of the JRC-NREL Memorandum of Agreement. Although the number of commercially available hydrogen sensors is very large, most are based on a few sensing technologies or platforms [9], the main ones being electrochemical sensors (EC), catalytic pellistor sensors (CAT), metal-oxide sensors (MOX), thermal conductivity sensors (TCD), metal oxide semiconductor sensors (MOS) and devices based upon palladium thin films (PTF). The cross sensitivity of several of these platforms to potential interferents species, including carbon dioxide, methane and carbon monoxide, was evaluated. These interferent species were chosen because of their interest to end-users and because some have been listed as gases to which the cross sensitivity of hydrogen detection apparatus shall be evaluated in the ISO standard on hydrogen detection devices [10]. This standard also lists a number of species which can potentially act as poisons for hydrogen sensors e.g. SO<sub>2</sub>, H<sub>2</sub>S, NO<sub>2</sub>, hexamethyldisiloxne (HMDS). The effect of these species on the performance of the selected hydrogen sensors is currently being evaluated and will be reported separately.

#### 2.0 EXPERIMENTAL

## 2.1 Sensor selection

The cross sensitivity to carbon dioxide, methane and carbon monoxide was evaluated for five detection platforms. A representative commercial sensor of each platform type was selected and cross-sensitivity tests were performed on these products. The technologies tested are listed in Table 1 and a brief description of the working principle of each technology is provided in this section. More detailed descriptions of the detection principle of these and other hydrogen detection platforms are available elsewhere in the literature [11,12,13,14,15]. The sensor products were selected based on their proven robust performance, high level of development and widespread deployment.

Table 1. Sensor platforms evaluated for cross sensitivity.

Sensor technology	Acronym
Metal oxide	MOX-1
Pd-thin film	PTF-1, PTF-2
Thermal conductivity	TCD-1, TCD-2
Electrochemical	EC-1, EC-2
Metal oxide semiconductor	MOS-1, MOS-2

## 2.1.1 Metal-oxide (MOX)

Metal-oxide hydrogen sensors are widely available on the market and are popular due to their low cost and ease of use. The active sensing material is a semi-conducting metal-oxide such as tin oxide. This material is typically an insulator at room temperature but becomes conductive at elevated temperatures. The resistance of the active material changes in the presence of reducing gases such as hydrogen. Despite their advantages metal-oxide sensors exhibit poor selectivity to hydrogen, responding to other reducing gases such as carbon monoxide, methane and water vapour. Numerous design strategies have been employed to minimise sensor cross-sensitivity [16], including adjusting the MOX crystal structure and composition with dopants. Strategies can also include optimising the sensing material operating temperature for hydrogen detection and covering the metal-oxide surface with a silica layer which hinders the interaction of the metal-oxide with interferents. In this study one MOX sensor was tested: MOX-1.

# 2.1.2 Resistive Palladium Thin Film (PTF)

Resistive Palladium Thin Film (PTF) sensors are based on a change of resistance of a thin film of palladium following absorption of hydrogen. Hydrogen molecules are split at the Pd surface and atomic hydrogen is absorbed into the metal lattice forming palladium hydride which has a higher resistivity compared to palladium. While this interaction is highly selective the Pd surface can be poisoned by species such as CO, SO<sub>2</sub>, H<sub>2</sub>S and Si-based compounds. The use of protective membranes, usually polymers, enhances the lifetime and the resistance of such sensors to poisons. Two PTF sensors from the same manufacturer were tested: PTF-1 and PTF-2.

#### 2.1.3 Thermal conductivity (TCD)

Thermal Conductivity (TCD) sensors exploit the exceptionally high thermal conductivity of hydrogen gas (0.187 W/m.K at 300 K), which is approximately 7 times higher than that of air (0.026 W/m.K at 300 K). The hydrogen concentration is inferred from the rate at which a sensing thermal element releases heat compared to a reference element. While most gases of interest have thermal conductivities close to air, other gases such as helium, argon, methane and carbon dioxide have thermal conductivities which differ significantly from air as shown by Table 2. For this reason TCD sensors can demonstrate some cross-sensitivity to these gases. On the other hand TCD sensors show a high resistance to poisons, as they do not contain catalytic metals. The cross-sensitivity of two TCD sensors from the same manufacturer was tested: TCD-1 and TCD-2.

Table 2. Thermal conductivities of gas species at 300 K and relative thermal conductivities with respect to air [17]

Gas Species	Thermal Conductivity K [mW/(m.K)]	$K/K_{Air}$
Air	26.2	1.00
Hydrogen, H <sub>2</sub>	186.9	7.13
Helium, He	156.7	5.98
Carbon Dioxide, CO <sub>2</sub>	16.8	0.64
Methane, CH <sub>4</sub>	34.1	1.30
Carbon Monoxide, CO	25.0	0.95

#### 2.1.4 Electrochemical (EC)

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. Electrochemical sensors are one of the most widely available commercial sensor platforms. Electrochemical (EC) gas sensors relate the target gas concentration to the change in some electrical parameter due to electrochemical reactions occurring at the sensing electrode: for instance,

electrochemical amperometric hydrogen sensors measure the flow of current caused by the oxidation of the hydrogen gas, while electrochemical potentiometric hydrogen sensors measure electromotive force between the sensing electrode and the reference electrode due to the presence of hydrogen. To minimise cross sensitivity, amperometric hydrogen sensors are equipped with membranes which hinder diffusion of gasses other than hydrogen into the electrode. Moreover, the electrode materials catalysing the electrochemical reactions can be chosen to be selective for hydrogen. Two EC amperometric sensors from the same manufacturer were tested: EC-1 and EC-2. The choice of amperometric sensor is due to their linearity and the higher sensitivity to hydrogen, which make them more suitable to quantify the cross sensitivity to other gases, and also for their wider availability on the market.

# 2.1.1 Metal oxide semiconductor (MOS)

Metal-oxide-semiconductor gas sensors are characterized by a three layer structure: a catalytic metal layer, an oxide layer and a semiconductor substrate. Hydrogen atoms form a dipole layer at the metal/oxide interface, which causes a change in the work function (i.e. the minimum energy required to remove an electron from a solid surface) of the metal that is proportional to the hydrogen concentration. The change in work function can be measured using Schottky diodes, capacitors or field effect transistors. The use of hydrogen specific catalytic metals, such as platinum or palladium, makes these sensors highly selective to hydrogen gas with little interference from other gases or from water vapour. Two field effect transistor MOS sensors from the same manufacturer where tested: MOS-1 and MOS-2.

## 2.2 Sensor Testing

The impact of chemical interferents on commercial hydrogen sensors was evaluated using the hydrogen sensor testing facilities at the US DOE National Renewable Energy Laboratory in Golden, Colorado and at the Joint Research Centre Institute for Energy and Transport in Petten, The Netherlands. Both facilitates have been described previously [4,18]. Test conditions were maintained at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$  and  $100 \text{ kPa} \pm 10 \text{ kPa}$ . Dry test gases obtained from gas cylinders were used in the evaluations, so that the relative humidity was typically less than 5%. The gas flow in the chambers was set to 1000 sccm.

The desired test gas mixtures were generated by dynamic mixing of synthetic air, 2 vol% hydrogen in air and certified mixtures of the interferent gas in air. The exposure profile used for the cross-sensitivity test is illustrated in Figure 1 and consists of the following stages:

- (a) Sensor operation in clean air, followed by exposure to 1 vol% hydrogen in air and subsequent recovery in clean air (the control measurement stage).
- (b) Exposure to the interferent at the concentration specified in Table 3 followed by simultaneous exposure to 1 vol% hydrogen in air and subsequent recovery in the interferent gas mixture (the cross-sensitivity measurement stage).
- (c) The exposure sequence in stage (a) was repeated to highlight any short term influence on the sensor's response to hydrogen following exposure to the interferent (the cross-sensitivity recovery stage).

Each step in the exposure profile had a typical duration of one hour.

During tests the hydrogen concentration was measured by a gas chromatograph, which was calibrated for this purpose. Conversely the concentration of the interferant was calculated from the ratio of gas flows as measured by the mass controllers. It was observed that the calculated interferant concentration changed by 2-4% when a flow of hydrogen in air was introduced into the system in stage (b). This change does not affect the results as it gives a contribution far below the experimental error.

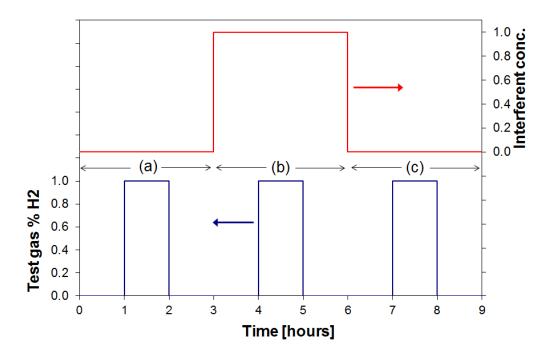


Figure 1. Exposure profile for the cross sensitivity test showing hydrogen concentration (vol% in air) and interferent concentration (arbitrary units). The letters a – c correspond to the different stages of the test.

Table 3 indicates the concentrations of the interferent gas mixtures used in this study. Interferant gas concentrations were selected to approximate regulated levels; beyond this range the interferent itself becomes hazardous and supplemental safety systems should be installed for its detection. This is a valid approach for general safety applications, but some scenarios may exist which could encounter higher levels of the specific interferent (e.g., carbon dioxide levels at fermentation facilities; such unique situations were not investigated here). For carbon monoxide, the American Conference of Governmental Industrial Hygienists (ACGIH) recommended time weighted average (TWA) is 35 ppm, while the short term exposure limit is 200 ppm; for carbon dioxide, the ACGIH has a recommended TWA of 5000 ppm; while the LFL of methane is 5 vol%. Hydrogen concentrations were 1 vol%, which is 25% of the LFL and a common alarm set point.

Table 3. Interferent species and their concentrations used in the cross-sensitivity tests

Interferent	Concentration [ppm]
Carbon Dioxide, CO <sub>2</sub>	5000
Methane, CH <sub>4</sub>	10000
Carbon Monoxide, CO	50

# 2.3 Cross-sensitivity performance evaluation

The effect of the interferent on the sensor response was evaluated by comparing both the sensor response to air and to 1 vol% hydrogen in air in the presence and absence of the interferent. In order to compare the cross-sensitivity of the different sensors tested to the various interferent species two cross-sensitivity factors,  $X_0$  and  $X_H$  were evaluated. The former factor may be defined as the ratio of net sensor response to each interferent and the net sensor response to 1 vol% hydrogen in air and is given by formula (1); the latter factor may be defined as the ratio of the difference in sensor response

to 1 vol% hydrogen in air in the presence and absence of the interferent to the net sensor response to hydrogen in air and is given by the formula (2).

$$X_0^i = \frac{R_i - R_0}{R_H - R_0} \tag{1}$$

$$X_{H}^{i} = \frac{R_{H,i} - R_{i}}{R_{H} - R_{0}} - 1 \tag{2}$$

 $R_0$  represents the sensor response in clean air;  $R_H$  is the sensor response to 1 vol% hydrogen in air;  $R_i$  is the sensor response in the presence of the interferent "i" (at concentrations listed in Table 3);  $R_{H,i}$  is the sensor response to 1 vol% hydrogen in air in the presence of the interferent "i" (at concentrations listed in Table 3). Notice that according to the definitions above, when the a gas species has no influence on the sensor response the cross sensitivity factor is equal to zero; when the sensor shows a response to the interferent of the same (opposite) sign compared to the response to hydrogen, the cross sensitivity factor is positive (negative). The error on the values of the cross sensitivity are given by the sensor resolution, which is determined experimentally.

## 3.0 RESULTS AND DISCUSSION

The cross-sensitivity to carbon dioxide, methane and carbon monoxide has been evaluated for five sensor models each employing a different detection platform. The cross-sensitivity factors,  $X_0$  and  $X_H$ , are calculated from the response profiles recorded for each sensor during the cross-sensitivity tests and these factors are reported for each sensor below.

#### 3.1 Metal oxide (MOX) sensor

The MOX tested had a measuring range of 0 - 2 vol% hydrogen in air. The sensor output signal was in Volts. The sensor is marketed as a general combustion sensor, including hydrogen. Accordingly, it is expected to show cross-sensitivity to hydrocarbons and other flammable gases. During the crosssensitivity tests this sensor showed no response to carbon dioxide either in the presence or absence of hydrogen. There was a modest response to 50 ppm carbon monoxide in air (no hydrogen present), corresponding to a response equivalent to approximately 0.03 vol% hydrogen. The sensor response to 50 ppm carbon monoxide and 1 vol% hydrogen in air invoked a response nearly identical as that measured in 1vol% hydrogen in air alone, indicating that the carbon monoxide and H<sub>2</sub> responses are not additive on the MOX sensor. When exposed to 1 vol% methane in air (no hydrogen present) the sensor showed a significant response, equivalent to 0.5 to 0.7 vol\% hydrogen, as can be seen in Figure 2. The response drifted somewhat decreasing in magnitude. The evaluation of the error takes into account such a drift. Notice that the sensor drift is negligible compared to the requirements to the final response by the ISO standard. Subsequent exposure to hydrogen yielded a final indication significantly less than would be expected for both the individual responses to hydrogen and methane implying that the net response of the metal-oxide sensor to 1 vol% hydrogen was significantly different in the presence of methane compared to the response in the absence of methane. Similar cross-sensitivity behaviour of metal-oxide sensors has been observed by others using propane as the interferent [19]. Following exposure to clean air the sensor response returned to its normal baseline and during the cross-sensitivity recovery stage the sensor response to hydrogen was similar to that before exposure to methane. Values for the cross-sensitivity factors are shown for each interferent in Table 4.

Table 4. Cross-sensitivity factors calculated from the MOX sensor response to interferents

Species	$\mathbf{X_0}$	$\mathbf{X}_{\mathbf{H}}$
0.5% CO <sub>2</sub>	$-0.00 \pm 0.02$	$0.00 \pm 0.02$
1% CH <sub>4</sub>	$0.65 \pm 0.05$	-0.6 ± 0.1
50 ppm CO	$0.03 \pm 0.02$	$-0.03 \pm 0.02$

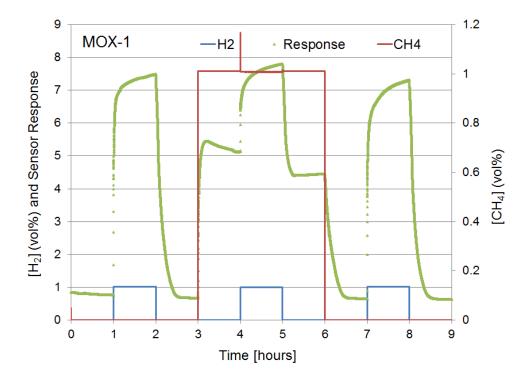


Figure 2. MOX response during the exposure profile with 1 vol% hydrogen in air and 1.0 vol% methane in air

# 3.2 Resistive Palladium Thin Film (PTF) sensor

The PTF sensor selected for this study has a specified range of 0.4 to 5 vol% hydrogen with an accuracy of around 0.25%. The sensor output voltage was converted to hydrogen concentration (vol%) based on the calibration data from the certificate of conformance provided for each unit by the manufacturer. According to the specification datasheet the sensor has no cross-sensitivity to other combustible gasses. Table 5 shows the cross-sensitivity factors calculated during the cross-sensitivity tests and they confirm the lack of response of the PTF sensor to all interferents tested.

Table 5. Cross-sensitivity factors calculated from the PTF sensor response to interferents

Species	$\mathbf{X}_0$	$X_{\mathrm{H}}$
0.5% CO <sub>2</sub>	$0.00 \pm 0.02$	$0.00 \pm 0.02$
1% CH <sub>4</sub>	$0.00 \pm 0.01$	-0.02 ± 0.02

Species	$\mathbf{X}_0$	$\mathbf{X}_{\mathbf{H}}$
СО	$0.00 \pm 0.01$	$0.00 \pm 0.02$

Figure 3 shows the sensor response to the interferent exposure profile using carbon monoxide as the interferent species and is typical of the PTF-1 sensor response to the other interferents whereby a high selectivity for hydrogen was demonstrated. The same results were found for both sensors tested. Ongoing tests will assess the robustness of the PTF sensor to potential poisons.

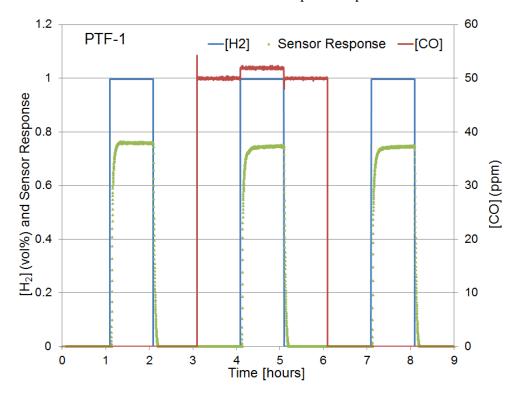


Figure 3. PTF response during the exposure profile with 1 vol% hydrogen in air and 50 ppm CO in air

# 3.3 Thermal conductivity (TCD) sensor

The thermal conductivity sensor tested had a specified measuring range of 0-10 vol% hydrogen in air and an accuracy of  $\pm 0.2\%$ . The sensor output voltage was converted to hydrogen concentration based on the manufacturer's specifications. No claims regarding selectivity were made by the manufacturer in the specification sheet.

The cross-sensitivity factors calculated from the sensor response to the three interferent gases are shown in Table 6. The values illustrate non-negligible effects on the sensor baseline in presence of carbon dioxide and methane. In the former case, the slight negative value of the cross sensitivity factor  $X_0$  is in agreement with the lower thermal conductivity of carbon dioxide compared to the one of air (see table 2). In the latter case, the positive value of the cross sensitivity factor  $X_0$  is in agreement with the higher thermal conductivity of methane compared to the one of air, but the value is higher than expected.

Table 6. Cross-sensitivity factors calculated from the TCD-1 sensor response to interferents

Species	$X_0$	$X_{H}$
0.5% CO <sub>2</sub>	$-0.03 \pm 0.02$	$-0.00 \pm 0.05$
1% CH <sub>4</sub>	$0.14 \pm 0.02$	-0.01 ± 0.02
СО	$0.00 \pm 0.02$	$0.01 \pm 0.02$

Figure 4 illustrates the sensor response during the methane exposure profile where the increase (equivalent to 0.14 vol% hydrogen in air) in the sensor's zero reading following introduction of 1 vol% methane in air into the sensor's ambient environment is shown. The net response of both TCD sensors tested to hydrogen remains unchanged by any of the interferent gas species.

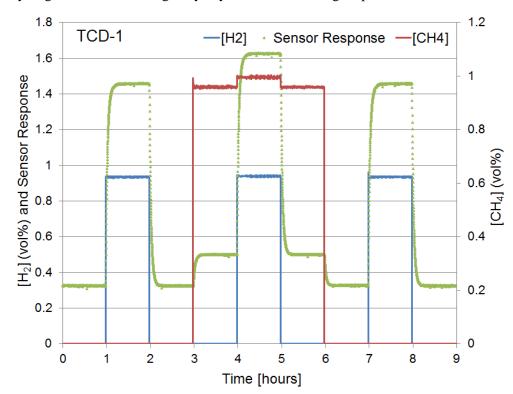


Figure 4. Response of the TCD-2 sensor during the exposure profile using 1 vol% hydrogen in air and  $1 \text{ vol}\% \text{ CH}_4$  in air

The shift in TCD sensor baseline response has been observed previously [20] and can be explained by the significantly higher thermal conductivity of methane relative to air which is displaced by methane during the exposure profile.

# 3.4 Electrochemical (EC) sensor

The EC sensor selected for this study had a specified measuring range of 0-4 vol% hydrogen. The output was converted to hydrogen concentration in accordance with the manufacturer's specifications. According to the manufacturer's specifications the sensor response should not be affected by low concentrations of the most common interferent species (including those investigated in this study) however the manufacturer warns of cross-sensitivity to silane, etylene and nitric oxide.

This sensor did not show a significant response to any of the interferent species used in this study and a typical sensor response trace obtained during the carbon monoxide cross-sensitivity profile is shown in Figure 5. This sensor was used as delivered from the manufacturer and slightly overestimated the hydrogen concentration by around 10 - 20%, but this could have been corrected by recalibration. The final indication of the sensor response to 1 vol% hydrogen in air showed a positive drift which had not stabilised at the end of the one hour exposure. Because of this drift, the sensor signal was taken as the final indication obtained at the end of the 1-hour exposure. Notice that in this region the actual drift is negligible compared to the requirements to the final response by the ISO standard. Similar results were found for both EC sensors tested.

Table 7. Cross-sensitivity factors calculated from the EC sensor response to interferents

Species	$\mathbf{X}_0$	X <sub>H</sub>
0.5% CO <sub>2</sub>	$0.00 \pm 0.05$	$0.01 \pm 0.04$
1% CH <sub>4</sub>	$0.00 \pm 0.05$	-0.01 ± 0.04
СО	$0.00 \pm 0.05$	$0.03 \pm 0.04$

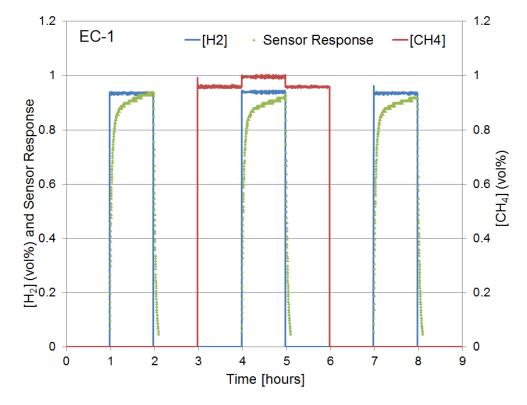


Figure 5. Response of the EC sensor during the exposure profile using 1 vol% hydrogen in air and 50 ppm CH<sub>4</sub> in air

# 3.5 Metal oxide semiconductor (MOS) field effect transistor sensor

The MOS sensor has a specified range of 0 to 4.4% hydrogen and an accuracy of  $\pm$  3000 ppm. The logged signal from these sensors was converted to hydrogen concentration in accordance to the instructions of the manufacturer. According to the sensor specifications the sensor shows no cross-sensitivity to other gas species.

This sensor's selectivity was confirmed in the cross sensitivity tests as the sensor did not respond significantly to any species investigated as can be seen from the  $X_i$  and  $X_H$  values calculated and shown in Table 8. Figure 6 shows the response curve of the MOSFET sensor during the gas exposure profile with 0.5 vol% carbon dioxide in air as the interferent. The lack of impact of carbon dioxide on the sensor zero response and the response in 1 vol% hydrogen in air can be clearly seen and this hydrogen selective behaviour was similar for tests using methane and carbon monoxide as interferents. The same results were obtained for each of the MOS sensors tested.

Table 8. Cross-sensitivity factors calculated from the MOSFET sensor response to interferents

Species	$X_0$	$X_{\mathrm{H}}$
0.5% CO <sub>2</sub>	$0.00 \pm 0.06$	-0.01 ± 0.02
1% CH <sub>4</sub>	$0.00 \pm 0.06$	$0.01 \pm 0.02$
50 ppm CO	$0.00 \pm 0.06$	$0.01 \pm 0.02$

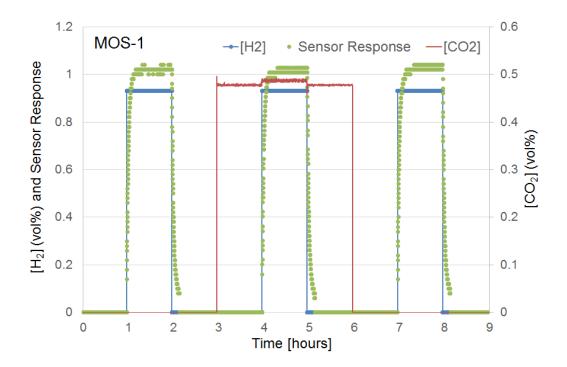


Figure 6. MOSFET response during the exposure profile with 1 vol% hydrogen in air and 0.5 vol%  $CO_2$  in air

#### 4.0 CONCLUSION

Considering the potential implications on the safety and operation of hydrogen applications, selectivity of hydrogen sensors is a valid concern of the sensor user. The inconvenience and cost associated with system shutdown, not to mention the potential risk to system integrity, should not arise due to shortcomings of hydrogen sensor performance, particularly shortcomings which can arguably be minimised through sensor design improvements.

This study has illustrated the cross-sensitivity resistance of some commercial hydrogen detection technologies towards carbon monoxide, carbon dioxide and methane. The palladium thin film,

MOSFET and electrochemical sensors tested showed little or no influence of the interferent species on the sensor response both in the absence and presence of hydrogen. Some interferents, particularly those at higher concentrations i.e. methane, shifted the baseline of the thermal conductivity sensor. This shift in baseline was equivalent to 0.14 vol% hydrogen for a methane concentration of 1 vol% in air. This change in baseline could result in a false alarm (e.g. for an alarm level set to 10% LFL equivalent to 0.4 vol%) at sufficiently high methane concentrations. Despite this the net thermal conductivity sensor response to hydrogen was unaffected indicating no change in the sensitivity towards hydrogen. The metal-oxide sensor showed a significant response to methane in air however it is important to recall that this sensor was not optimised for hydrogen detection and so cross-sensitivity to other combustible gases was to be expected. It is likely that, through the use of dopants or a protective silica layer over the metal oxide material, cross-sensitivity of this type of sensor to interferents could be mitigated significantly.

In all cases where cross-sensitivity was observed, the effects were temporary and following removal of the interferent the response of the sensor to hydrogen returned to its pre-exposure value. While the investigation of other species, which can permanently alter the response of hydrogen sensors (i.e. poisons such as SO<sub>2</sub>, H<sub>2</sub>S, NO<sub>2</sub> and hexamethyldisiloxne) was not in the scope of this study the effect of such species on hydrogen sensor performance is currently being evaluated and will be reported separately.

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