TEST METHODOLOGIES FOR HYDROGEN SENSOR PERFORMANCE ASSESSMENT: CHAMBER VS. FLOW THROUGH TEST APPARATUS

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ABSTRACT

Certification of hydrogen sensors to standards often prescribes using large-volume test chambers [1, 2]. However, feedback from stakeholders such as sensor manufacturers and end-users indicate that chamber test methods are often viewed as too slow and expensive for routine assessment. Flow through test methods potentially are an efficient, cost-effective alternative for sensor performance assessment. A large number of sensors can be simultaneously tested, in series or in parallel, with an appropriate flow through test fixture. The recent development of sensors with response times of less than 1s mandates improvements in equipment and methodology to properly capture the performance of this new generation of fast sensors; flow methods are a viable approach for accurate response and recovery time determinations, but there are potential drawbacks. According to ISO 26142 [1], flow through test methods may not properly simulate ambient applications. In chamber test methods, gas transport to the sensor can be dominated by diffusion which is viewed by some users as mimicking deployment in rooms and other confined spaces. Alternatively, in flow through methods, forced flow transports the gas to the sensing element. The advective flow dynamics may induce changes in the sensor behaviour relative to the quasi-quiescent condition that may prevail in chamber test methods. One goal of the current activity in the JRC and NREL sensor laboratories [3, 4] is to develop a validated flow through apparatus and methods for hydrogen sensor performance testing. In addition to minimizing the impact on sensor behaviour induced by differences in flow dynamics, challenges associated with flow through methods include the ability to control environmental parameters (humidity, pressure and temperature) during the test and changes in the test gas composition induced by chemical reactions with upstream sensors. Guidelines on flow through test apparatus design and protocols for the evaluation of hydrogen sensor performance are being developed. Various commercial sensor platforms (e.g., thermal conductivity, catalytic and metal semiconductor) were used to demonstrate the advantages and issues with the flow through methodology.

1.0 INTRODUCTION

The commitments reached during the 21st session of the Conference of the Parties (COP21) [5] highlight the concerns of the developed countries regarding the anthropogenic causes of climate change and, therefore, greenhouse gas (GHG) emissions. In order to reduce GHG emissions, the incorporation of renewable energies in the energy mix has increased in the last several years. These renewable sources include, for example, wind and solar, both of which are plagued with variable output that does not necessarily match demand. Energy storage solutions are needed to improve the efficient utilization of the renewable energy sources. Hydrogen is considered one of the energy storage solutions with higher potential, especially for seasonal storage. The fact that it can be produced from renewable energy surplus via electrolysis and transformed into power with relatively high efficiency (by means of fuel cells) and that it can also be used for energy purposes (fuel, power-to-gas), makes it an attractive solution. Hydrogen is also valuable as a chemical product (refineries, fertilizers).

However, hydrogen presents some issues regarding safety. Its broad flammability range in air, together with its small molecular size that increases the potential for leaks, requires special safety measures to avoid hazardous situations. One main approach for the assurance of safety is the use of hydrogen sensors to detect it before it reaches dangerous concentrations. It is often required that these sensors are certified to ensure safe and reliable operation. For this purpose, test protocols are described in

performance standards [1, 2] to verify various sensor parameters, such as accuracy, repeatability, lifetime, impact of environmental parameters (e.g., T, P, RH) cross-sensitivity to other gases, etc.

The introduction of hydrogen in the public sector through expanded commercial use means that potentially more sensors will be deployed. A ramification of the growing number of hydrogen applications is the emergence of large scale sensor production through advanced manufacturing methods. An efficient means of performance verification is necessary to maintain the economy-of-scale manufacturing. Although performance standards often prescribe using large-volume test chambers, this method is viewed by some as too slow and expensive for some applications such as qualification testing by an end-user for their specific application or as a QA/QC screen for sensor manufacturers. Flow through test methods have numerous advantages relative to chamber methods, including faster test times and smaller quantity of test gas.

The goal of the work presented here is to define the conditions for which flow through methods are comparable to the chamber method for hydrogen sensor evaluations, while showing its advantages in terms of shorter test duration and potential for simultaneous sensor testing. Flow through test apparatus design and operation strategies are described that allow for assessment of the impact of the gas composition and changes in environmental parameters. The discussion will include pitfalls that may be encountered if inadequate controls or improper test conditions are implemented. Sensors with different operating principles (thermal conductivity (TC), catalytic combustion (CC), and metal oxide (MOX)) were tested using both methods to compare the results and to illustrate the potential advantages that the flow through method can offer. The tests performed were: accuracy, short-term stability, pressure dependence and flow rate dependence. The flow rate dependence test was performed only with the flow through apparatus. Details on the test protocols have been described [6]. The sensor testing was performed at the Sensor Testing Facility (SenTeF, [7]), which is one of the several hydrogen technologies laboratories that belongs to the Joint Research Centre - Directorate for Energy, Transport and Climate [8]. Results and conclusions from these tests are presented below.

The work presented in this paper is the result of an on-going collaboration between the sensor laboratory at the National Renewable Energy Laboratory (NREL) in the U.S. and the Joint Research Centre (JRC) within the EC. The JRC-NREL collaboration was formalized under a Memorandum of Agreement that was signed in 2010 [9]. There have been additional collaboration agreements between NREL and the JRC, including work performed within the framework of a common call between the European Fuel Cell and Hydrogen Joint Undertaking (FCH JU) and the U.S. Department of Energy; one aspect of this agreement was the project H2Sense [10]. Presently, the NREL-JRC collaboration is under the auspices of a program-level agreement between the U.S. Department of Energy and the JRC [11]. A round-robin testing of the respective laboratories (Sensor INTerlaboratory COMparison, SINTERCOM [6]), together with numerous scientific publications [12, 13, 14, 15, 16, 17] as well as a book on hydrogen sensors[18] resulted from the NREL-JRC sensor laboratories collaboration.

2.0 EXPERIMENTAL SETUP AND PROTOCOLS

Sensors or sensing elements based upon thermal conductivity (TC), catalytic combustion sensor (CC), and semiconducting metal oxide sensor (MOX), were used to test the impact of chamber vs. flow through test methods on performance. TC sensors respond to changes in the thermal conductivity of the gas mixture. The TC sensor will respond to a change in the composition of a gas mixture, but does not change the composition. The sensor response can be correlated to the concentration of a specific gas provided the sensor has been calibrated for that specific gas relative to a reference mixture [18]. Catalytic combustion sensors detect hydrogen and other combustible gases calorimetrically, that is through the heat released from the catalytic combustion reaction of the analyte [18]. Semiconducting metal oxide are one type of conductometric sensors. The operating principle of the MOX sensor is based on the change of electrical conductance or resistance of a metal oxide material induced upon exposure to a reducing or oxidising gas that then increases or depletes the mobile charge carrier density within the conduction or valance bands of the semiconducting material [18]. Both the CC and MOX sensor will react with hydrogen, and therefore will change the test gas composition.

Table 1 lists the sensors and sensing elements tested in this study. According to the definition of ISO 26142 [1], a hydrogen sensing element *is the component that provides a measurable, continuously changing physical quantity in correlation to the surrounding hydrogen*, while a sensor *is an assembly, which contains one or more hydrogen sensing elements and may also contain circuit components associated with the hydrogen sensing elements, that provides a continuously changing physical quantity or signal in correlation to the physical quantity provided by the hydrogen sensing element(s)*. Multiple models of a given sensor platform were used in this study, as indicated by the numeric value added to sensor code indicated in Table 1 (e.g., TC-101 and TC-201 refers to two different thermal conductivity sensor models, while the notation TC-101 and TC-102 would indicate multiple sensor units of the same model).

Table 1: List of sensors tested

Sensor Code Name	Operating principle	Sensor/Sensing element	Output Signal Type	Hydrogen concentration range (vol%)
TC-101	Thermal conductivity	Sensor	H2 ppm	0-100
TC-201	Thermal conductivity	Sensor	H2 ppm	0-2.4
CC-101	Catalytic Combustion	Sensor	0.5-4.5 VDC	0-4
CC-201	Catalytic Combustion	Sensor	analogue V	0-4
CC-301	Catalytic Combustion	Sensor	0.5-4.5 VDC	0-4
MOX-101	Metal Oxide	Sensing element	analogue V	0-1
MOX-201	Metal Oxide	Sensing element	analogue V	0.05-1

Except for CC-201, the TC and CC sensors outputted a response that was in units of vol% H_2 or an analogue (current or voltage) response that was readily converted to vol% H_2 using a nominal manufacture-supplied calibration expression. The CC-201 sensor and MOX sensing element were integrated to an electronic circuit that outputted a voltage response that could be correlated to the hydrogen level; the circuit designs and operation were based upon standard designs for the sensor type. The electrical outputs for the MOX sensors used in this study however, were relatively insensitive to changes in hydrogen concentration (e.g., the electrical signal was nearly saturated). For this reason the MOX sensors were analysed separately from the results obtained with TC and CC sensors.

The sensors were evaluated using two different test apparatus, chamber and flow through. The chamber test apparatus is schematically illustrated in Figure 1. Each gas line was connected to a gas cylinder of known composition. Flow from each gas cylinder to the sensor test fixture was regulated by a mass flow controller (MFC) that had been calibrated for the specific gas. Regulating the relative flow rates of the gas supply MFCs ensures proper control of the test gas composition. Multiple gas lines were fed into a single pneumatic line for mixing. A back pressure regulator and vacuum pump maintained a constant pressure within the test chamber, which could be less than or greater than the ambient pressure (the actual pressure range was 80 to 120 KPa). Sensors were placed in the test chamber, which has an internal volume of around 3.1 litres. Sensor performance testing was performed at a fixed flow rate of 1000 Nml/m and consisted of a series of exposures to different gas compositions ranging from 0 to 2 vol% H_2 in air at the indicated pressure. Testing was performed at ambient laboratory temperature and a dry humidity. The duration of each exposure step was one hour to assure purging of the chamber with the proper test gas and to assure that the sensor would reach a

stable final indication. Control and data acquisition was done via Labview® software installed on a PC. The logging frequency of the sensor response was 1 point each 5 seconds. A second chamber test apparatus was used for tests to analyse temperature dependence of sensor response. The chamber of this instrument has bigger internal volume (around 3.9 litres) and also a double wall. The space between the two walls could be filled with heating/coolant fluid coming from a thermal bath, controlling in this way the temperature inside the chamber. This configuration can also be seen in Figure 1.

For the flow through method, the chamber was removed and the sensors were placed in a custom-built interface, which was directly connected in-line with the common gas supply line.

It was necessary that the interface of the sensors to the gas line be hermetically sealed to assure proper gas composition and control of sensor test parameters (especially for pressure control). In general, a specific sensor interface design was necessary for each sensor model. A different sensor interface type was required for TC-101 and the MOX sensors since their physical design rendered it unfeasible to assure a leak-tight seal between the gas line and the sensor head. These sensors were placed inside a micro-chamber (internal volume around 5 ml), where flow through conditions were simulated. Photographs of both sensor interface types (a representative sensor holder and micro-chamber) are shown in Figure 2.

Due to the reduction of the internal volume of the flow through apparatus relative to the chamber apparatus, internal pressure fluctuations induced by the pressure regulation system (e.g., the back-pressure regulator and vacuum pump) impacted the stability of the gas flow through the MFCs. In order to avoid these flow oscillations, two buffer tanks to dampen the effect of pressure fluctuations were placed between the back pressure regulator and the vacuum pump. A schematic of the flow through test apparatus is depicted in Figure 3 (without climatic chamber). As with the chamber test apparatus, control and data acquisition was done via Labview® software installed on a PC.

When performing test at different temperatures in flow through method, the sensors and part of the gas supply line are placed inside a climatic chamber that controls the temperature of the test (Figure 4).
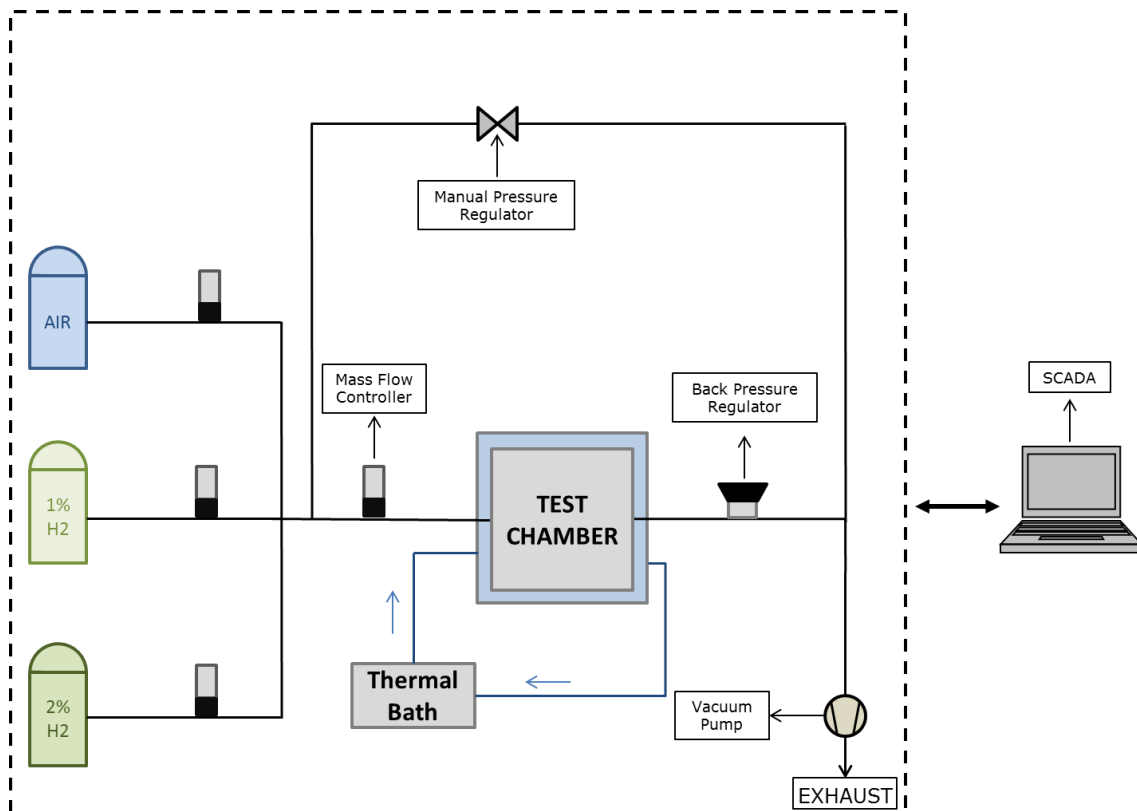
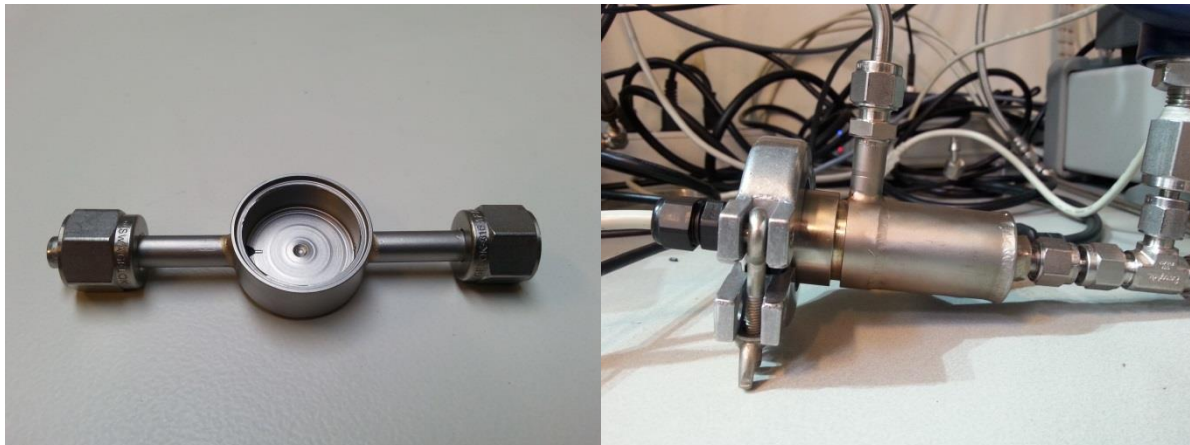Figure 1: Scheme of the experimental setting for the chamber method

Figure 2: Sensor holder (left) that fits directly over the gas interface of a hydrogen sensor and micro-chamber (right) into which the sensor/sensing element were placed. The holders were used to perform tests in the flow through apparatus.
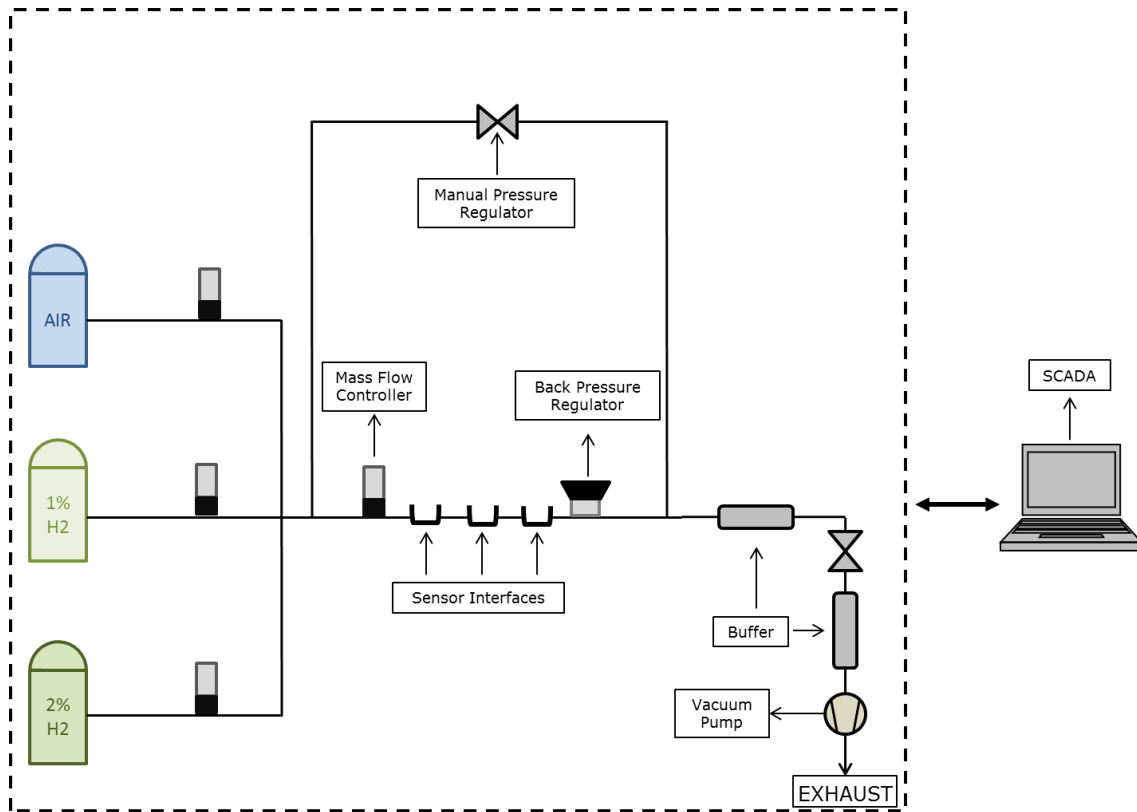
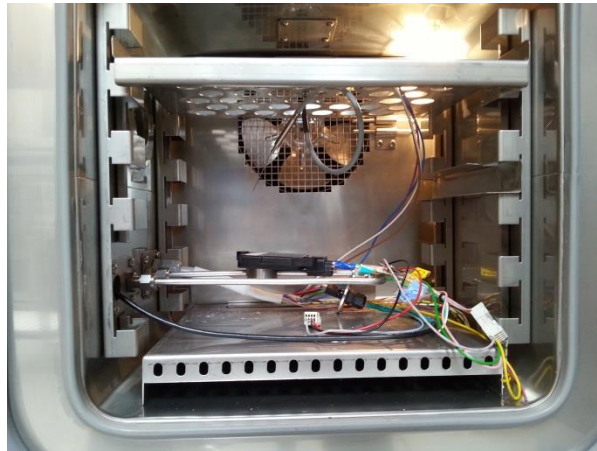Figure 3: Scheme of the experimental setting for the flow through method

Figure 4. Gas sensor and gas supply line inside climatic chamber

3.0 SENSOR TEST PROTOCOLS

The sensors were subjected to various sensor test protocols to assess sensor performance. The tests were: accuracy, short-term stability and pressure dependence [6] and were performed in the order indicated. Each of these test protocols was performed in both the chamber (Figure 1) and flow through apparatus (Figure 3). Unless noted otherwise, all testing was performed with a total fixed gas flow rate of 1000 Nml/min. For the chamber method tests, a step duration of 1 hour was used, which was a sufficient time to allow the chamber to purge and for the sensor to reach a stable final indication. Alternatively, in tests performed with flow through method, a step time of 10 minutes was sufficient. A description of these tests follows.

Accuracy Test: In the accuracy test, the sensor final indication was compared to the various concentrations of a hydrogen test gas. The hydrogen concentration was controlled by in-line mixing

of certified calibration gas standards of $1.0 \pm 0.02\%$ hydrogen in air (for concentrations up to 1 vol% H2) and $2.0 \pm 0.02\%$ hydrogen in air (for concentrations between 1-2 vol % H2) with synthetic air. The hydrogen concentration was increased and then decreased in discrete steps. The hydrogen concentration was set according to the following sequence: 0, 0.2, 0.5, 0.8, 1.0, 1.2, 1.5, 2.0, 1.5, 1.2, 1.0, 0.8, 0.5, 0.2, and 0 vol% in air. The sequence of this test is depicted in Figure 5. Each concentration step was maintained for 1 hour in the chamber test versus 10 minutes for the flow through testing. Environmental conditions were maintained at ambient laboratory temperature, 100 KPa pressure and dry humidity (e.g., the test gas as obtained directly from the gas cylinder without humidification or drying, and was typically < 5% RH).

Short-term Stability Test: In the short-term stability test, the sensors were exposed to the hydrogen profile depicted in Figure 6 (0, 1.0, and 2.0 vol% hydrogen in air). This exposure sequence was performed 9 times in order to assess the sensor short-term signal stability. Test conditions were maintained at ambient laboratory temperature, 100 KPa pressure and dry humidity.
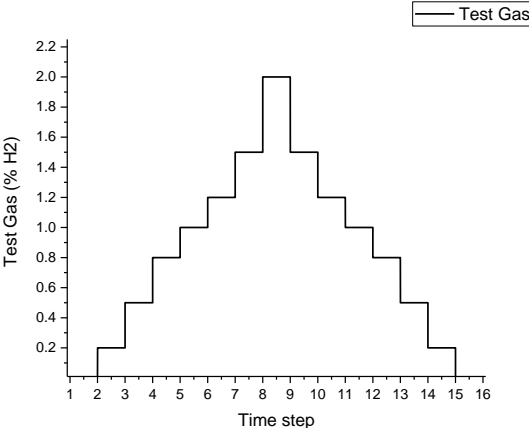

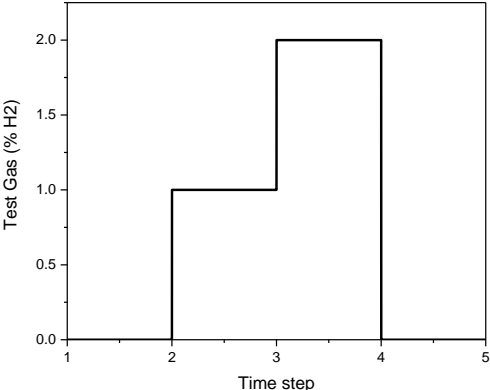Figure 5: Hydrogen concentrations used during accuracy test

Figure 6. Hydrogen concentrations for each step in Short-term Stability test
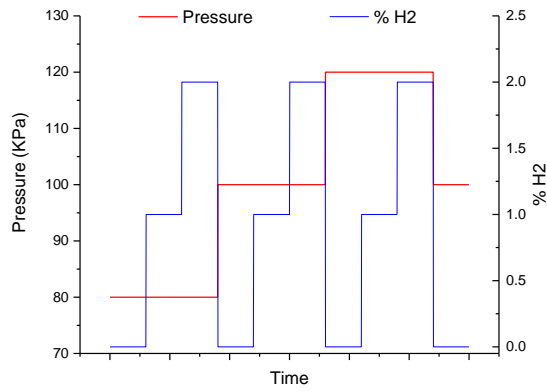
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Figure 7. Pressure and hydrogen concentration evolution during pressure dependence test
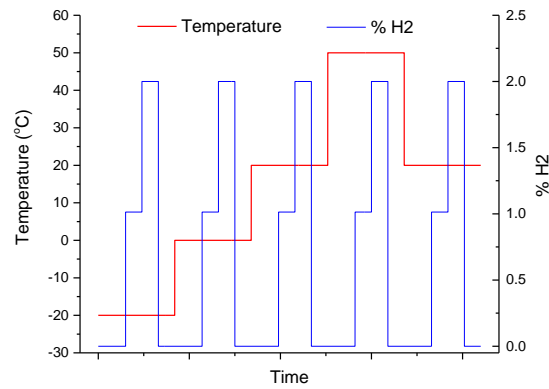

Figure 8. Temperature and hydrogen concentration evolution during temperature dependence test
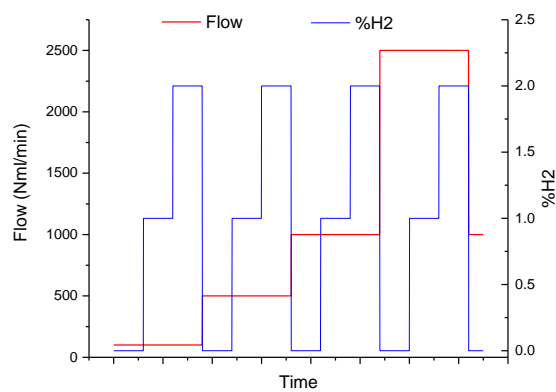

Figure 9. Flow and hydrogen concentration evolution during flow dependence test

Pressure Dependence Test: The pressure dependence test was performed in order to determine the influence of pressure on sensor response in the absence and presence of hydrogen. It was also

performed to develop the design requirements for a flow through sensor test fixture that can accommodate the pressure dependence test. Gas exposures were performed at pressure set points of 80, 100 and 120 kPa. For each pressure set point, the sensors were subjected to the following exposures, 0, 1.0, and 2.0 vol% hydrogen in air. FIGURE 7 shows the evolution of pressure and hydrogen concentration during the test.

Temperature Dependence Test: The temperature dependence test was performed in order to determine the influence of temperature on sensor response in the absence and presence of hydrogen. It was also performed to develop the design requirements for a flow through sensor test fixture that can accommodate the temperature dependence test. Gas exposures were performed at temperature set points of -20°C, 0°C, 20°C , 50°C and again at 20°C. For each temperature set point, the sensors were exposed to 0, 1.0, and 2.0 vol% hydrogen in air. The evolution of temperature and hydrogen concentration during the test is shown in FIGURE 8.

Flow Dependence Test (Performed only for flow through testing): Sensors were exposed to total gas flow rates of 100, 500, 1000 and 2500 Nml/min. For each flow set point, the sensors were subjected to the exposure profile 0, 1.0, and 2.0 vol% hydrogen in air. The evolution of gas flow and hydrogen concentration during the test is shown in FIGURE 9.

These test protocols were slightly modified for the characterisation of the MOX sensors (MOX-101 and MOX-201), since the manufacturer specified range was only up to 1 vol% H_2 in air. For the short-term stability test, pressure dependence test, and flow dependence test, the hydrogen concentration steps were changed to 0, 0.1 and 1 vol% in air. Temperature dependence tests were not performed with this sensor technology. Certified calibration gas standards of 0.1 and 1 vol% hydrogen in air were used. The accuracy test was performed using 0, 0.2, 0.5, 0.8, 1, 0.8, 0.5, 0.2, 0 vol% H2 in air. To generate these hydrogen concentrations, a certified calibration gas standard of 1 vol% hydrogen in air was dynamically mixed with synthetic air.

Due to the different range of the sensors, the chamber method tests were performed sequentially with two different sets of measurements. In the first set, the thermal conductivity and catalytic combustion sensors were mounted within the test chamber. In the second set, the metal oxide sensors were installed in the test chamber. Once the chamber method tests were completed, the sensors were transferred to the flow through apparatus and retested. As mentioned above, the tests performed in the flow through apparatus were identical to the ones performed in the chamber apparatus. The test protocol was, however, modified with a change in the time step (1 hour for chamber method, 10 minutes for flow through method).

One of the advantages of the flow through is the possibility of testing a large number of sensors simultaneously, however, and in order to analyse the results obtained disregarding any influence of their particular location within the test setting, most of the experiments described were on sensors that were tested individually. The TC-101 and CC-201 sensors were, however, tested simultaneously in order to assess the influence of a series configuration on the test results. The transduction mechanism of the TC does not change the chemical composition of the test gas, unlike the CC sensor, which chemically reacts with hydrogen. Therefore, the order in which the sensors are placed in the test fixture in a series configuration may have an effect on the sensor response. Testing was conducted to quantify the effect of sensor position in a series configuration as well as the effect of the flow rate.

Data Analysis and Workup: The sensor signal was logged into an electronic data file at a measurement frequency of 1 point each 5 seconds. The sensor final indication to a test gas was taken as the average of the last 100 sec (20 data points) taken at the end of step. The final indication for the sensor response was either in units of vol% H2 or converted to vol% H2 using a manufacturer supplied calibration expression. The final indication of the MOX sensing element is volts, which was not converted into vol% H2. Sensor responses were compared to the tolerances specified in ISO 26143 [1] for the comparable test protocol. The results obtained with the two configurations were compared to determine the impact of test method on sensor behaviour.

4.0 RESULTS

The sensor responses obtained in the various tests were in general within the tolerances defined in [1] for both the chamber and flow through test method. This indicates that flow through method can provide comparable performance data as that obtained with the chamber method, but with the advantages of shorter testing time and less gas consumption. However, the sensor responses for the flow through method were not identical to the chamber method. Specific details on the comparison of the test methods on sensor performance assessments are presented in the following sections.

TC and CC Sensors: The initial comparison between sensor test methods was performed using data from the accuracy test. The data points in the following graphs show the sensor final indication in response to the test gas. Results from accuracy test in chamber and flow through method for TC and CC sensors are shown in Figure 10 and Figure 11, respectively. The sensor response for both the ascending and descending hydrogen concentration steps is depicted, but the symbols overlap, which means there is no hysteresis. For comparison, the accuracy tolerance, as specified in ISO 26142 [1], is presented as well. In general, the results for the sensors tested in the chamber method showed a good accuracy, within the limits established by ISO 26142 [1], where the allowable sensor response in vol% has to be ± 20% of the hydrogen test gas concentration (grey area in Figure 10 and Figure 11). The only deviations from the ISO specifications were for the TC sensors at low hydrogen concentrations.

In order to better highlight the differences induced by the test method, a sensor-specific calibration expression was obtained using the accuracy data from the chamber method. The sensor readings were then transformed using the resulting calibration expression. The result of this transformation for the chamber method test data is shown in the right plot of Figure 10. With recalibration, all sensor responses fall directly on the calibration line. Recalibration of each sensor response removes variability in sensor to sensor behaviour, and also allows easier visualization of the impact of the test method on sensor performance. In the right side of Figure 10 and Figure 11 we can see the values from the sensor specific calibration. It can be observed in Figure 10 that the calibrated values fall, logically, in the black line that represent the actual hydrogen concentration of the test gas. For the flow through method (in Figure 11, right side) it can be seen that catalytic sensors deviate slightly from the values obtained in chamber method, meanwhile the responses of TC sensors were nearly identical in both methods.
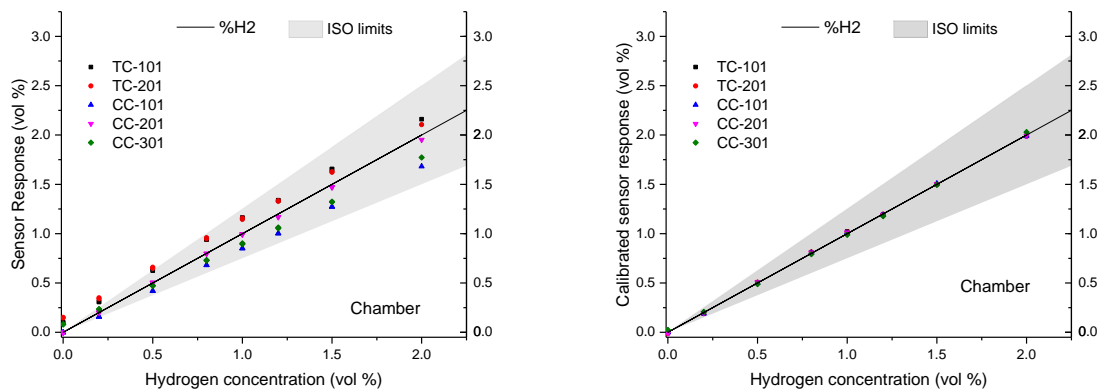

Figure 10: Accuracy test results for TC and CC sensors with chamber method. Left: Sensor response (vol% H2) using the factory supplied calibration. Right: Transformation of the sensor response using an empirical sensor specific calibration expression.
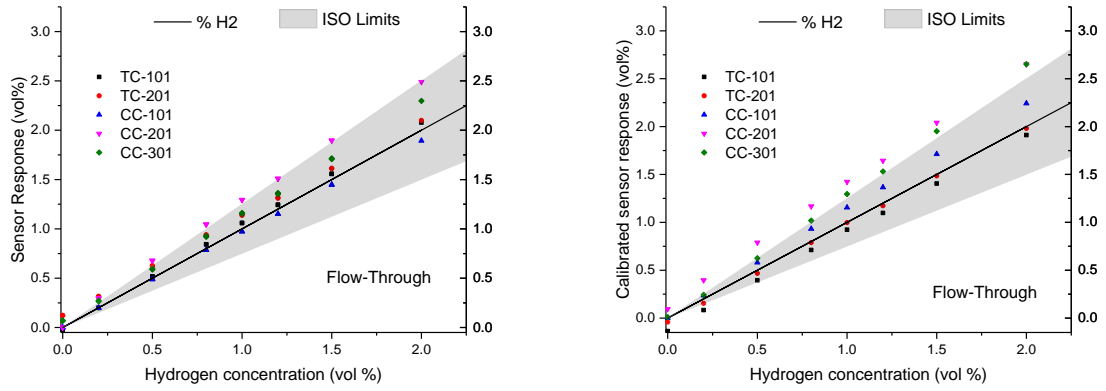
Figure 11. Accuracy test results for TC and CC sensors with flow through method. Left: Sensor response (vol% H2) using the factory supplied calibration. Right: Transformation of the sensor response using the empirical sensor specific calibration expression as obtained from the chamber accuracy test

All sensors tested in this study exhibited very good stability for both the chamber and flow through test method as indicated by the results obtained from the short-term stability test (see TABLE 2). The values shown in this table are the maximum deviation in percentage observed within the 9 cycles performed in the short-term stability test, for every sensor and hydrogen concentration. This maximum deviation is calculated following equation (1).

$$Deviation = MAX\left(100 * \frac{SR_i - Av}{Av}\right), \qquad Av = \frac{\sum_{i=1}^{9} SR_i}{9} \qquad (1)$$

where SR_i is the sensor response in cycle i (i from 1 to 9).

Their responses stayed within the limits specified in ISO 26142 [1] for a comparable test (±10% deviation in sensor response). As observed in the accuracy test, the CC sensors showed a slight increase in their response in the flow through method compared with the chamber method.

Table 2-Maximum percentage deviation from the average sensor response observed in short-term stability test for TC and CC sensors in chamber and flow through methods.

	Chamber method					Flow through method				
	TC-101	TC-201	CC-101	CC-201	CC-301	TC-101	TC-201	CC-101	CC-201	CC-301
0%H2	4.9	2.0	0.0	0.3	1.1	6.3	3.9	0.0	0.0	0.5
1%H2	0.5	0.6	0.3	0.3	0.8	0.1	0.8	0.1	0.0	0.4
2%H2	0.2	0.4	0.2	0.7	0.5	0.1	0.5	0.2	0.0	0.3

Figure 12 depicts the results from the pressure dependence tests. It can be observed that the sensor response generally increases with increasing pressure (except for TC-201), for the same hydrogen concentration in the test gas. This effect is stronger in the case of CC-101and CC-301 sensors. When comparing results between chamber and flow through method, it can be seen that the influence of the pressure on the sensor response is smaller for the flow through method. According to ISO 26142 [1] for the equivalent test, the values obtained for 80 kPa and 120 kPa should not deviate more than 30%

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from the value obtained at 100 kPa. The sensors tested fulfil this requirement for both testing methods. Only CC-301, for 1 vol% hydrogen, 80 kPa, when tested in the chamber method has fallen outside this limit.
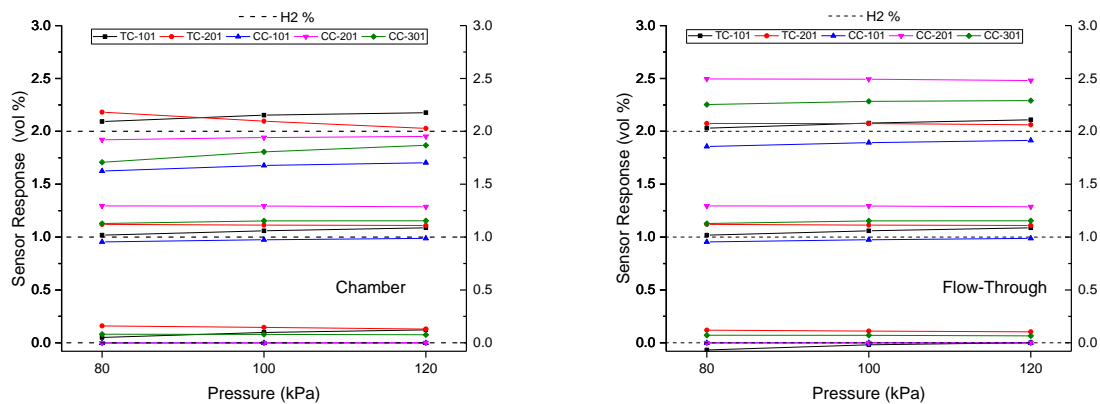

Figure 12. Pressure dependence test results for TC and CC sensors with chamber method (left) and flow through method (right).

In Figure 13 the results from the test on temperature dependence are presented. According to ISO 26142 [1] for the equivalent test, the values obtained for -20°C, 0°C and 50°C should not deviate more than 20% from the value obtained at 20°C. For the test performed with chamber method, all sensors perform within the requirements of ISO 26142. For sensor CC-101 the results at -20°C revealed an erratic response which may have to do with the placement of the sensor on the chamber and need to be investigated further. These results are therefore not shown. There is no clear trend in the response of the sensors when changing the environmental temperature. For some sensors the response decreases with the temperature (CC-201 and CC-301), others increase their response up to 20°C and then decrease it when tested at 50°C (TC-201 and CC-101). In the case of TC-101, its highest response is obtained at 0°C. Also the baseline is affected by the temperature.

Tests performed with flow-through method (Figure 13, right) gave a similar qualitative result, sensors did not deviate more than 20% from the value obtained at 20°C, as stated in [1]. As with the test performed with chamber method, CC-201 and CC-301 responses decrease when increasing the temperature. In the case of CC-301, the response is significantly higher when tested in flow-through compare to the results obtained with the chamber method, as also observed in accuracy and pressure dependence tests. TC-101 showed a similar behaviour than CC-201 and CC-301, the sensor response was decreasing with higher temperatures. This dependence was also observed in chamber method, but in the range from 0°C to 50°C, since from -20°C to 0°C the response was slightly increasing.

In general the two methods lead to very similar results for the sensors. For CC-101 it was observed that sensor response was barely affected by the temperature when tested in flow through and more strongly in chamber method. TC-201 results in flow-through method are similar to the ones obtained in chamber method. It can also be observed that the sensor response decreased considerably when tested at 50°C, as when tested with chamber method. All the sensors have been operated within their temperature operational range.
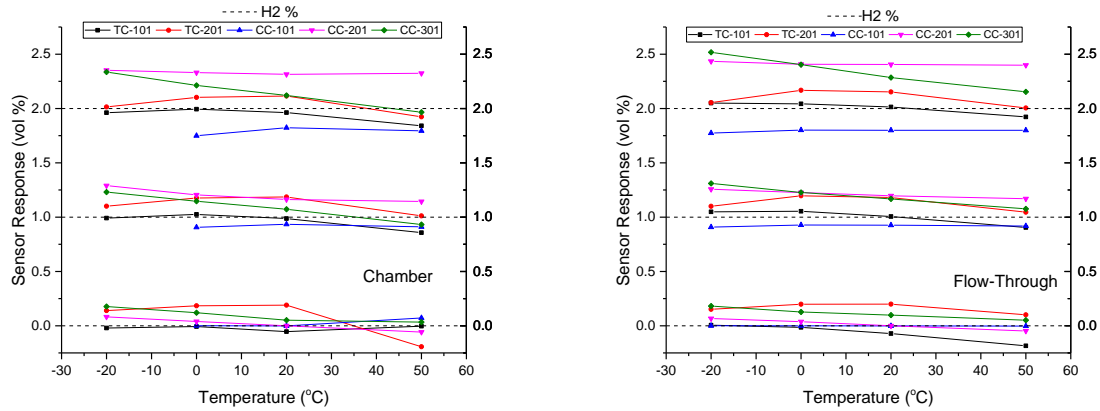
Figure 13. Temperature dependence test results for TC and CC sensors with chamber method (left)
and flow through method (right).

MOX Sensors: As stated above, the MOX sensing elements were subjected to a different testing
protocol than TC and CC sensors, with a maximum hydrogen concentration in air of 1 % vol. The
values plotted in the following graphs are the sensor final indications, which were obtained as the
average output signal (in volts) of the sensor within the last 100 seconds of each time step.

The results of the accuracy tests on the MOX sensors are shown in Figure 14 for both the chamber and
flow through methods. The MOX Final Indication showed a low sensitivity within the hydrogen
concentration range tested, meaning that the change of the resistance of the sensing element with
changes in hydrogen concentration was small, even though this test was performed within the range as
specified by the manufacturer. The extremely small change in electrical response with a change in
hydrogen concentration made it difficult to generate a useful calibration expression for these specific
MOX sensors. Accordingly, in the following analysis, the analogue voltage was used for the sensor
response. When comparing results with both methods, it can be observed that MOX-101 response had
a slight increase in the flow through method compare to chamber method, meanwhile MOX-201
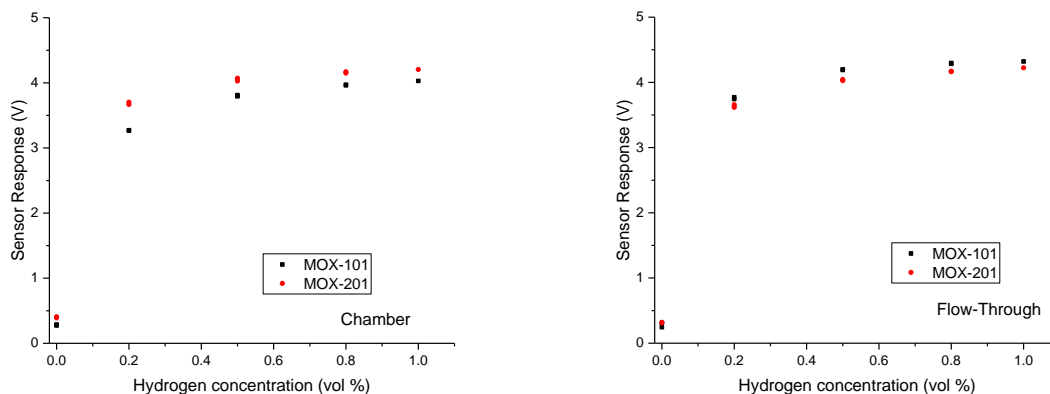obtained similar results in both methods. Both sensors showed negligible hysteresis.

Figure 14. Accuracy test results for MOX sensors with chamber method (left) and flow through
method (right).

In the short-term stability test MOX sensors responses to hydrogen were quite repeatable. The
pressure dependence tests showed that MOX sensors response is barely affected by changes in the
pressure, in the range 80-120 kPa. Tests performed with chamber and flow through methods gave
similar results.

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Impact of flow rate on sensor response in the Flow through method: A characterisation of flow dependence is depicted in Figure 15 for TC and CC sensors. It can be seen that, in the case of CC sensors, the response of the sensors increases with increasing flow, especially at small flows. This effect is not observed for TC sensors, for which the flow rate has a negligible effect on the sensor response. Comparing the sensor responses for the two methods, it can be observed that for CC sensors, the values obtained at low flows (100 Nml/min) in the flow through method are similar to the ones of the chamber method with a flow of 1000 Nml/min. In the case of TC 101 sensor, the chamber method generally produced higher responses than flow through for any flow considered, but the difference is not deemed significant. The MOX sensors response in general did not show a strong dependence of the flow.

A nominal flow rate set for the chamber method does not mean that this flow rate is actually reaching the sensing element, which may help to explain these findings in case of the CC sensors. Depending on the configuration inside the chamber, an area of local hydrogen depletion may form around the CC sensor, even for the flow rate of 1000 Nml/min. Further experiments are planned to verify this effect.
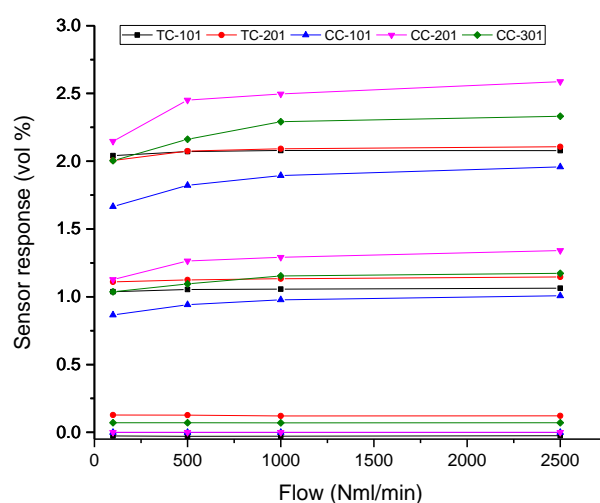

Figure 15. Flow dependence test results in flow through method for TC and CC sensors

Flow dependence tests were also performed with two sensors configured in series in the flow through apparatus. As previously mentioned, some sensor platforms consume hydrogen through the specific detection mechanism. This means that the hydrogen level in the test gas is depleted through the operation of those sensors. Therefore the placement of sensors consuming hydrogen in a series configuration has to be considered carefully, as the sensors downstream may not be exposed to the same hydrogen concentration as the sensors upstream. In order to assess the magnitude of this effect, TC-101 and CC-201 were installed in two different configurations. To reiterate, the TC sensor will not change the test gas composition. In the first configuration (config. 1 in Figure 16), TC-101 was placed upstream relative to CC-201. In the second configuration (config. 2 in Figure 16) the sensors positions were reversed. If the CC sensor is measurably depleting hydrogen in the test gas, the TC sensor should give a lower reading in the second configuration compared to the first. In Figure 16, the sensor responses obtained for different flows of 0 vol% H2 and 1 vol% H2 in air are shown for the two configurations. It can be observed that TC-101 had a significantly lower response when placed downstream from CC-201 (configuration 2, open black square symbols), demonstrating that the CC sensor changed the composition of the gas. This effect is, as expected, more pronounced at lower flows. The results suggest that this influence can be reduced by increasing the flow. In the current set-up the effect of hydrogen depletion is minimal at 2500 Nml/min, but this will depend on the test apparatus used and the sensors used.
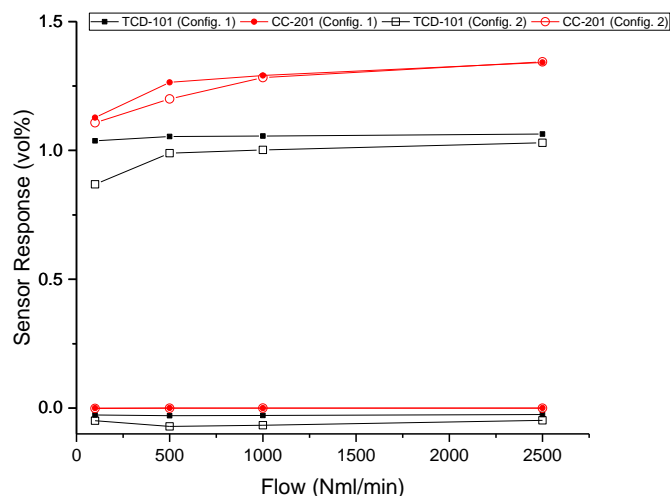
Figure 16. Influence of sensor location in flow through apparatus for sensors arranged in series

In summary, the performance of the different sensors, from a qualitative point of view, were similar with both methods, thus demonstrating that changing the test methodology will not fundamentally yield different results. Sensors performances fall within the limits stated in in the ISO standards [1] (in the case of TC and CC sensors) for the equivalent tests regarding accuracy, short-term stability and pressure dependence. Comparable conclusions can be reached from the results obtained with MOX sensors.

From a quantitative aspect, the TC sensors results obtained in the chamber method were better replicated in flow through method. However CC sensors showed a higher response when exposed to the same hydrogen concentration in flow through relative to that obtained in chamber method. Perhaps this was due to the reaction of hydrogen on the CC surface, which lowered the local concentration of hydrogen at the sensor, an effect that is offset by higher flow rates.   In the case of MOX sensors, MOX-201 comparable results were obtained in both methods, within the experimental error.

The main advantage of the flow through testing is that the experiments can be performed much faster (a factor of 10 seems feasible) than the chamber method. This also means that the volume of test gas will be lower. For both methods, multiple sensors can be tested simultaneously. For the chamber method, there is a limitation to the number of sensors based on the space in the chamber and the gas purge rate into the chamber. For the flow through fixture, in principle a large number of sensors can be placed in series or parallel. Therefore flow through testing instruments can be recommended for the performance testing of sensors, as long as some general guidelines are adhered to, which are discussed below.

5.0 CONCLUSIONS

The aim of this work was to validate the flow through method as a faster and more economical alternative of the traditional chamber method to assess hydrogen sensors performance. Accuracy, short-term stability and pressure dependence tests were performed on several sensor platforms (Thermal Conductivity, Catalytic Combustion and Metal Oxide) in experimental apparatus based on chamber and flow through methods [1].

A new flow through apparatus was designed and built to perform the tests mentioned above. During the implementation of this system several potential pitfalls were encountered. In order to enable the accurate characterisation of sensors on flow through test apparatus, guidelines are presented on the design and testing protocols.

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Of the issues encountered for the test apparatus, the most challenging was working out a well-functioning flow/pressure control of the system and the ability to maintain a leak proof interface between the sensor and gas supply line. A leak proof interface was particularly troublesome for some sensor designs. Solutions to these problems were implemented in the design features of the flow through apparatus. For example, some sensors required a micro-chamber (Figure 2).

For a series configuration for the testing of sensors, there is a potential influence on a sensor response due to the presence upstream of sensors that have an operating principle based on hydrogen consumption (Catalytic, MOX). This effect has been demonstrated. The response of the TC sensor was lower when placed downstream the CC sensor that the one obtained when the TC sensor was placed upstream the CC sensor. This effect can be minimized with higher flow rates or avoided when sensors are placed in parallel.

Regarding the testing methodology itself, the flow rate dependence needs careful consideration. The response of the CC sensors tested shows marked flow rate dependence and, correspondingly, a higher response in the flow through method than for the chamber method, for all flow rates above 100 Nml/min. The TC sensors did not exhibit significant flow rate dependence.

Some guidelines for the design and operation of a flow through method test apparatus have been developed and include:

General:

• Pressure control (above and below ambient) is feasible with a vacuum pump and pressure controller as shown in Figure 3. The apparatus should be fitted with a back-pressure controller plus a buffer tank, as otherwise pressure control may cause flow fluctuations through the MFCs. The effect is most pronounced if there is a small internal volume of the experimental system.

• Temperature control (above and below ambient) can be reached by different ways. In our experimental set-up a thermal bath in the case of chamber method (Figure 1) and a climatic chamber for the flow-through (Figure 4) have been used. In the case of the flow-through it was also considered the possibility of wrapping the supply lines with electrical heaters, however this solution would only work for testing at temperatures above room temperature. In addition, the climatic chamber provides a better control of the cooling/heating process.

• The interface of the sensor (or sensing element) to the gas manifold needs to be leak tight, which is not always easy to achieve. For some types of sensors, the construction of a micro-chamber containing the entire sensor may be the only option to ensure a tight seal. In particular pressure dependency tests require a good level of leak tightness.

Testing methodology:

• The same testing protocols as for the chamber method can be performed. However, for the pressure dependence testing, the results should be checked carefully as abnormally low responses of the sensors may indicate leaks at lower than ambient pressures (i.e. dilution of hydrogen by air leaking into the testing apparatus).

• Temperature dependence in big chambers would require the use of internal fans in order to avoid temperature stratification inside the chamber.

• Flow rate dependence of sensor response should be taken into account when choosing the flow rate. Not all sensor platforms are affected by flow rate changes. For CC sensors, the sensor response shows the highest variation at flow rates below 1000 Nml/min and seems to reach a maximum at flow rates above 2500 Nml/min.

Placement of sensors:

• Series configuration may cause problems if the sensors operation is influencing the test gas composition. The detection mechanism of some platforms is based on the consumption of hydrogen (e.g. combustible gas sensors, MOX sensors), therefore sensors downstream may be exposed to less hydrogen than those upstream. Setting an appropriately high flow rate may circumvent this issue. The relationship between flow rate and hydrogen consumption must be quantified. It may be necessary to implement an independent verification of the hydrogen concentration in the incoming and exhaust gas lines to verify that hydrogen consumption was not significant.

• Parallel configuration calls for the placement of multiple MFCs in order to ensure that all the sensors will be exposed to same flows and hydrogen concentrations. Although this may lead to additional complexity of the testing apparatus, in case of testing CC and MOX sensors, this configuration is recommended.

Evaluation of sensor performance:

• The experiments have shown that the flow rate can have an influence on the response of the sensors. In particular the CC sensors show a significantly higher response with higher flow rates, which can be explained by their mode of operation. The response for these sensors may even be outside the ISO 26142 limits if the sensors were calibrated at a lower flow rate. The deployment conditions should be considered and the flow rate chosen accordingly, but this may not be feasible experimentally in case this would result in very low flow rates. Therefore the flow rate at which the sensor calibration is performed should at least be taken into account when evaluating the results.

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