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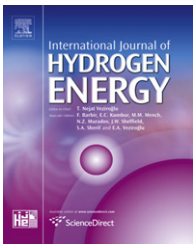

A comparison of test methods for the measurement of hydrogen sensor response and recovery times

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ABSTRACT

Response time is a critically important property of hydrogen safety sensors. Recovery times are less important from a safety perspective, but are often quoted as an indication of the speed of operation of a sensor. However, the measured values depend highly on the method used to evaluate them. The purpose of this work is to assess the suitability of different methods, both flow and diffusion-based, for the measurement of sensor response and recovery times. Four methods have been tested in terms of their repeatability and practicality of execution, as well as the accuracy of their results compared to the manufacturer's specifications. It was found that each method has its own advantages and limitations, which are discussed herein. For the measurement of response times, a diffusion-based method was found to give the shortest and most precise values and is therefore recommended. However, the flow-based method was found to be the most convenient experimentally and is the only method that is suitable for the measurement of recovery times over a wide concentration range.

1. Introduction

Unwanted release of hydrogen can, under appropriate conditions, result in the build up of potentially explosive concentrations of gas. Rapid detection of hydrogen gas is desirable to ensure a timely alert to its presence allowing sufficient time for engaging mitigative and protective actions e.g. ventilation, evacuation etc. For this reason, fast acting sensors and methods for accurately measuring the response and recovery time of these sensors are important. Since 2001 the Institute for Energy has been engaged in the testing of commercially available hydrogen safety sensors intended for the detection and measurement of hydrogen in air. A dedicated facility [1–4] has been designed and built for testing the performance of an extensive number of commercially available hydrogen sensors under a wide range of ambient conditions, testing methodologies have been developed and evaluated and the results have been published in the literature [5,6].

More recently experimental focus has shifted from testing the influence of ambient parameters on sensor performance towards the investigation and comparison of different methods for measurement of hydrogen sensor response and recovery times. Sensor end-users have indicated hydrogen sensor response and recovery time requirements of 3 s or less [7]. Such stringent requirements together with the increased market availability of progressively faster hydrogen sensors demand improved methods to assess the speed of response of these devices.

The aim of this work is to assess the suitability and reproducibility of existing methods for measuring the response and recovery time of hydrogen safety sensors. Based

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on the results and observations, modifications have been introduced where appropriate to optimise these methods. Such optimized methods should be convenient to execute, quick and inexpensive, giving repeatable results and allowing inter-laboratory comparison of measurements for validation purposes.

Measurements were made on 2 commercial sensors – one MOSFET type and one thermal conductivity sensor. The sensors were chosen so as to include a rapidly responding sensor (with a response time of <3 s and a recovery time of <10 s claimed by the manufacturer) and one somewhat slower responding sensor (claimed response and recovery times <20 s, typical: 10 s).

2. Background

In typical response time tests the hydrogen sensor is first exposed to air, after which it is subjected to a step change from air to the test gas. The transient sensor response to the increased target gas concentration is recorded until a stable final signal is observed. In typical recovery time tests, the sensor is exposed to a stepwise change from the test gas back to air while recording the signal until a stable baseline is reached. The response time, $t(90)$, is defined as the interval between the time when an instantaneous variation from clean air to the standard test gas is produced at the inlet of the hydrogen sensor and the time when the response reaches 90% of the maximum indication. The recovery time, $t(10)$, is defined as the interval between the time when an instantaneous variation from the standard test gas to clean air is produced at the inlet of the hydrogen sensor and the time when the response reaches 10% of the preceding maximum indication. For the purposes of this paper the term 'sensor reaction time' is a collective term describing both sensor response and sensor recovery times.

Conventionally sensor reaction time measurements are performed with the sensor mounted in one of two configurations:

1. A flow chamber with gas flowing over and thus transported to the sensor.
2. A diffusion chamber under static conditions where gas diffuses to the sensor.

However, in either case, the change from clean air to test gas and vice versa is not instantaneous but is time dependent. Therefore any experimental measurement of sensor reaction time will include the time taken for the concentration of the target gas to reach the desired level (either by diffusion or dynamic flow) at the sensor's sensing element. An excellent theoretical treatment of this topic is given by Ménil et al. [8,9]. According to Ménil the experimentally measured response/recovery time of a chemical sensor may be considered as the sum of two component times – the *intrinsic time* and the *extrinsic time*.

These time distinctions are also used in this paper, where the intrinsic time may be considered as the time taken for the reaction kinetics to occur at the sensor's hydrogen receptor surface. The intrinsic time represents the sensor reaction time relative to an instantaneous change of the gas mixture around the sensing element. The extrinsic time comprises the time taken for delivery of the target gas to the sensor either by gas diffusion or dynamic flow and takes into account the transient change in the gas concentration. The extrinsic time also depends on the operating principle of the sensor [8].

Unlike the intrinsic time, the extrinsic time is dependent on the gas delivery system inherent to the experimental method, conditions and equipment. The extrinsic time can be minimised by designing the reaction time measurement method and equipment to reduce as far as possible the delivery time of the gas to the sensor. There are different approaches to achieving rapid exchange of ambient gas around the sensor. Gerblinger et al. used multiple gas injection nozzles into a sensor chamber [10], while Tobias et al. and Wingbrant et al. introduced different gas flows directly to an openly mounted sensor via a moving gas outlet [11,12]. Another method described in IEC 60079-29-1 involves plunging a sensor rapidly into a chamber filled with the test gas [13]. In the present work the approach has been to minimise the dead volume of gas surrounding the sensor in all methods, to enhance diffusion in one diffusion-based method through the use of a fan and to use high test gas flow rates in the flow-based method. In doing so an instantaneous step change of the fluid concentration surrounding the hydrogen sensor can be approached.

Sawaguchi et al. [14] describe and compare three methods for measuring the response times of two different hydrogen sensors. The first method uses a flow chamber and is comparable to the Flow-through method described in this work. The second "inject-diffuse" method involves injecting a known volume of hydrogen gas into a 30 L chamber containing the uncovered sensor and a circulation fan. The third "diffuse-burst" method also uses a 30 L chamber and is comparable to the Membrane method which is described in this work. They favour the diffuse-burst method for measuring response time, stating that the flow method is "far from the practical condition", while the inject-diffuse method took "some time until the hydrogen concentration in the chamber became homogeneous". They report a decrease in $t(90)$ with increasing hydrogen concentration using the diffuse-burst method, while the opposite trend was found using the inject-diffuse method. The repeatability of their measurements is not commented upon by the authors and no method of measuring sensor recovery times is reported.

3. Experimental

3.1. Description of facility

The JRC-IE's hydrogen Sensor Testing Facility (SenTeF) is described in detail in the literature [1–5]. The facility can be used in two configurations – to test either the influence of ambient parameters on sensor performance or to measure sensor reaction time. The most important features of the latter configuration are summarised here.

The response and recovery time measurement facility comprises:

- A sensor holder (interchangeable depending on the test method used) in which the sensor is mounted
- A test gas preparation and delivery system
- A control and data acquisition system
- A gas analysis system
- Subsidiary devices for flow and pressure management and power supply

Sensor samples were tested individually and all tests were performed at room temperature (292 K ± 2 K) under dry gas conditions. The facility is controlled by National Instruments hardware and is managed through software programmed in LabVIEW. The thermal conductivity sensor analog data was acquired and stored using a 6 1/2-Digit USB digital multimeter (Keithley Model 2100) with a data collection interval of 250 ms. The MOSFET sensor data was acquired via CAN bus, giving a higher data acquisition frequency and a data collection interval of 100 ms.

The test gas mixtures were prepared by online mixing of clean air and 2 vol% hydrogen in air up to a maximum concentration of 2 vol%. Mass flow controllers controlled the flow rates of gases or gas mixtures into the system. The gases then passed through a Bronkhorst® gas mixer where they were thoroughly mixed before passing to the sensor holder.

A calibrated compact gas chromatograph (GC) was used during diffusion-based tests to quantify and confirm the hydrogen concentration. The GC has been shown to be able to measure the hydrogen concentration within ±5% [5].

3.2. *Methods tested and developed*

One flow-based and three diffusion-based experimental methods for measuring hydrogen sensor response and recovery times are investigated and compared in this work.

Where possible, parts of the system were custom made to optimally accommodate the different sensor dimensions. In all methods the response of the sensor was recorded and the response time $t(90)$ or recovery time $t(10)$ was calculated based on the sensor output signal profile.

3.2.1. *Flow-based method – flow-through method*

The Flow-through reaction time test method measures the reaction time of sensors under dynamic conditions and relies on the transport of test gas to the sensor's sensing element. The set-up and method described here are the product of a series of tests during which improvements and optimisations were made to the flow-through method described in Annex B of ISO FDIS 26142 [15].

The sensor under test was mounted on a flange which was welded to and positioned over a hole drilled in the side of a copper pipe. The pipe was connected downstream of a 3-way valve. This valve was switched remotely to selectively flow synthetic air or test gas through the pipe. The sensor was fixed to the flange such that its sensing element was positioned directly in front of the hole. An o-ring sealed the interface between the sensor and flange. The distance between the 3-way valve and the flange was kept as short as possible (18 mm) to minimise the dead volume and hence the gas transport time to the sensor.

Variations on the ISO method involved varying the diameter of the hole and the diameter and geometry of the pipe. The tests verified that the diameter of the hole had a significant influence on the measured sensor reaction time, as did positioning of the sensor over the hole [16]. The quickest and most repeatable results were obtained when the area of the hole in the pipe coincided with that of the sensor's sensing element. Furthermore the diameter of the circular pipe was minimised to reduce the transport time of gas to the sensor and the suggested internal pipe diameter of 25 mm as proposed in ISO FDIS 26142 Annex B was not followed. While pipes with a large cross sectional area required higher gas flow rates to reduce the gas transport time it was observed that higher gas flow rates resulted in pressure and gas flow instabilities in our facility. However it was also found that pressure and flow instabilities occurred when pipes with too small a cross sectional area were used. The optimum results were obtained using a circular copper pipe with an internal diameter of 4 mm and gas flow rates between 50 and 120 sccm. A short section of the circular pipe 50 mm in length was replaced by a rectangular section with internal cross sectional dimensions 12 mm by 3 mm and the sensor support flange was attached to this section. Use of this rectangular pipe section with a larger cross sectional area than that of the circular pipe significantly reduced gas flow disturbances and pressure fluctuations in the system. Fig. 1 illustrates the mounting of the hydrogen sensor on the flange and pipe construction.

During response time measurement experiments synthetic air was allowed to flow-through the 3-way valve. A stable baseline signal was recorded from the sensor. The 3-way valve was then switched, marking the start of the experiment and resulting in test gas flowing over the sensor

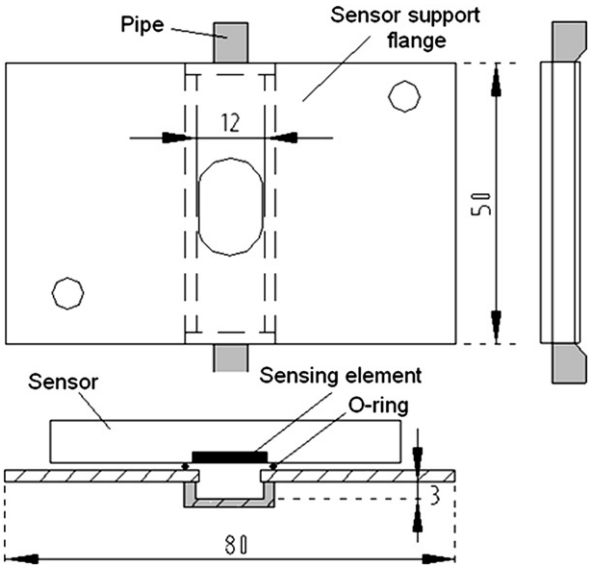

Fig. 1 – Sensor reaction time measurement set-up – Flow-through method. The upper part of this figure illustrates a top view of the sensor support flange attached to the copper pipe. The lower part shows a cross sectional view illustrating the position of the hydrogen sensor on the sensor support flange. Dimensions are shown in mm.

while the synthetic air flow was redirected. The sensor response was recorded until a final stable indication was reached. Recovery time measurements were subsequently made by switching the 3-way valve back to flow synthetic air over the sensor and redirect the test gas. The sensor response was recorded until it returned to zero.

ISO FDIS 26142 suggests the possibility of simultaneously testing more than one sensor either by arranging the sensors in series on a single pipe or by splitting the gas flow over additional pipes. However, for the purpose of assessing this method it was decided to test only one sensor at a time to eliminate any possible influence from other sensors.

3.2.2. *Diffusion-based method – membrane method*

The Membrane method measures the response time of sensors under static conditions and relies on the diffusion of test gas to the sensor's sensing element. The set-up used for these tests is based on that described in Annex A of ISO FDIS 26142 [15]. Sawaguchi et al [14] tested a variety of experimental set-ups for the measurement of response times and recommend this membrane cutting method (or the "diffuse-burst method", as they refer to it). They specify the optimum experimental set-up determined for their equipment, including the position and volume flow rate of the fan.

Fig. 2a illustrates the experimental set-up for measuring sensor reaction times using the Membrane method. An aluminium box with dimensions 310 mm × 310 mm × 310 mm (internal volume of 30 L) was used, inside of which a small aluminium holder (internal volume of 340 cm^3) housed the sensor under test.

The sensor was mounted inside the sensor holder with the sensing face directed upwards and as close to the top as possible. This was achieved by placing a piece of metal beneath the sensor so as to raise it to the required height. The holder was then sealed with a natural latex membrane, tautly stretched over a 'ridge' on the holder rim. The sensor holder was positioned in the diffusion chamber on a movable metal stand, to allow easy rupturing of the latex membrane by the cutter as shown in Fig. 2a. The cutter was a sharp scalpel fixed to the end of a lever which was manoeuvred by means of a flexible bellows from outside the diffusion chamber.

A 0.5 L gas lecture bottle was filled with 100 vol% hydrogen to a set pressure calculated to yield the desired hydrogen concentration (e.g. 1.0 vol%) following expansion into the diffusion chamber. The overpressure from this bottle was released into the diffusion chamber, leading to a negligible rise in pressure inside the chamber. The air and hydrogen were allowed to mix homogeneously inside the diffusion chamber for several minutes. Mixing was promoted by 2 electric fans located at the base of the diffusion chamber and one at the level of the hydrogen inlet. Gas samples were analysed regularly by the GC to ensure homogeneity and to measure the hydrogen concentration, which was always in strong agreement with the expected concentration calculated. Following homogenisation of the test gas mixture inside the diffusion chamber a stable base "zero" signal from the sensor was recorded.

The latex membrane was ruptured by cutting it with the scalpel, exposing the sensor to the test gas. The corresponding start time of the experiment was signalled by manually

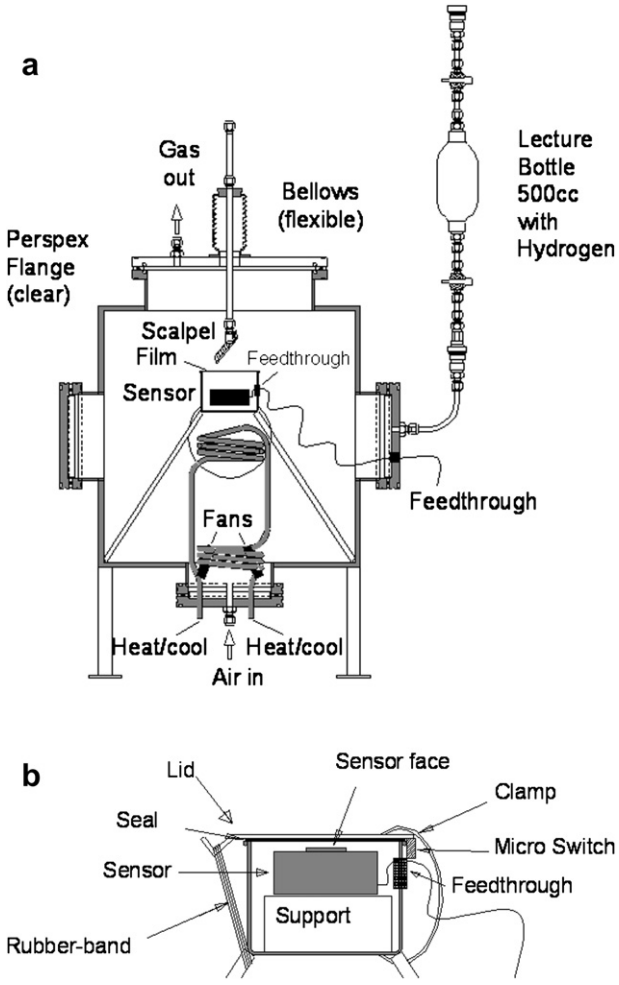

Fig. 2 – a: Sensor response time measurement set-up – Membrane method. b: Sensor holder – Lid method.

pressing a switch at the point when the membrane ruptured. The response of the sensor was recorded and the response time $t(90)$ calculated.

While the Membrane method is a known and published method for determining the response time of a sensor in the absence of gas flow, a number of practical drawbacks were encountered during the execution of measurements using this method. These will be discussed in more detail later, but included the following:

1. Inconsistent opening of the membrane because of the inevitable variation in the tautness of the film and the manner of cutting
2. Uncertainty as to the exact start time of the experiment since this is determined by a manually generated signal that may not coincide precisely with the time of cutting
3. Diffusion across the latex membrane which may result in an initial sensor response prior to cutting the membrane

Furthermore it was not possible to use this method to measure the sensor recovery time, $t(10)$. To do this it would be necessary to fill the sensor holder with a hydrogen/air mixture

and seal it before placing in the diffusion chamber. In the current experimental configuration it was not possible to do this safely or conveniently.

3.2.3. *Diffusion-based method – lid method*

To overcome some of the above difficulties experienced when measuring sensor response time using the Membrane method a number of modifications to the experimental set-up and procedure were made, resulting in the development of the Lid method.

In this method the latex membrane was replaced by a latched aluminium lid, Fig. 2b. An acrylic rubber strip, fixed to the rim of the sensor holder box, formed a seal with the lid when placed on the holder. This seal reduced diffusion of hydrogen before the start of the experiment. The lid was held firmly in place on the sensor holder by a taut elastic band on one side and by a removable clip on the opposite side. The flexible bellows was used to remove the clip holding the lid in place. Following removal of the clip the lid snapped off releasing a micro switch, which generated an electronic signal accurately defining the start time of the experiment. Apart from these modifications all other aspects remained identical to the Membrane method. As with the Membrane method, it was not possible to measure recovery times using the Lid method.

3.2.4. *Diffusion-based method – gate valve method*

The Gate valve method was developed and tested as an alternative to the Membrane and Lid methods with the advantage of being able to measure not only the sensor response time but also the recovery time. This was made possible by locating the sensor holder outside the diffusion chamber, thereby facilitating the exchange of gases within the holder itself. The experimental set-up is shown in Fig. 3. As with both previously described methods a sealed 30 L aluminium diffusion chamber was used. However a smaller chamber (0.39 L), used as the sensor holder, was attached to a flange on one face of the diffusion chamber. The two volumes were separated by a fast acting solenoid gate valve from Demaco.

The sensor was mounted inside the holder with the sensing head positioned next to the valve. In the case of response time measurement experiments, the sensor holder was filled with clean air while the diffusion chamber was filled with test gas at the desired hydrogen concentration. The desired gas concentration in both volumes was confirmed by GC. The sensor signal was recorded for a period of approximately 1 min prior to exposure to the test gas and in all cases this remained zero. The valve was then opened electronically and the sensor exposed to the test gas. This was recorded as two signals corresponding to the gate contact at the start and at the finish of the valve opening. It was found that opening of the gate valve takes 0.4–0.6 s and the starting point for measuring the response time was taken as halfway between the two contact times. The sensor signal was then recorded until it reached a steady maximum.

The procedure for carrying out recovery time measurements was identical to the procedure for response time tests, except that the diffusion chamber was filled with clean air, while the sensor holder contained the hydrogen/air mixture at the desired concentration.

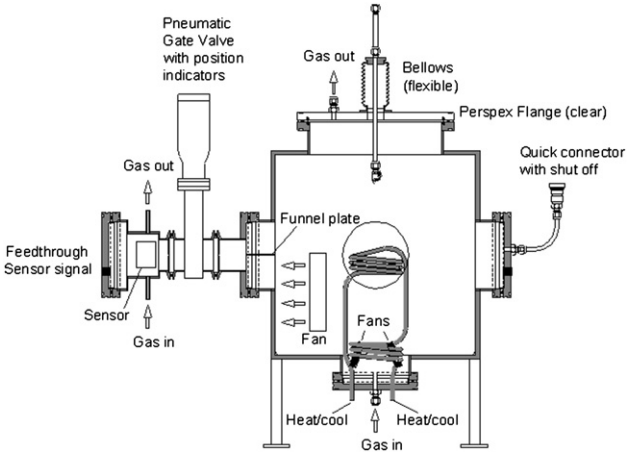

Fig. 3 – Sensor reaction time measurement set-up – Gate valve method.

3.3. *Sensors*

Two commercial sensors were chosen to evaluate the four test methods considered. The first, a MOSFET sensor, is described by the manufacturer as suitable for detecting hydrogen gas in automotive and refuelling station safety applications. The sensor has a catalytic metal gate stack which interacts with hydrogen molecules resulting in a change in the characteristics of the associated field-effect transistor. A constant current source feeds the sensor whose voltage output is proportional to the logarithm of the hydrogen concentration in the ambient. The sensor has a CAN bus electrical interface with standard MQS six-pin connector. It is capable of measuring hydrogen concentration in the range 0–4.4 vol% hydrogen in air with a stated accuracy of ±3000 ppm. The response and recovery times specified by the manufacturer are <3 s and <10 s respectively and were measured at a hydrogen concentration of 2 vol% using a flow-through type method.

The second sensor tested was a thermal conductivity detector (TCD). According to the manufacturer the measuring range of this sensor is 0–100 vol% and the accuracy is ±1 vol%. It is capable of working in the absence of oxygen. Both response and recovery times are quoted as <20 s, with a typical value of 10 s. No details are available on the test method used to determine these reaction times.

These sensors were chosen because they had previously been found to perform with reasonable accuracy and consistency [7]. For most methods the reaction times of the sensors were measured at different hydrogen concentrations to highlight any influence this may have on the measurement.

4. Results

4.1. *Flow-through method*

The two sensors have very different geometries and so two different chambers (consisting of a pipe and flange) were designed for the Flow-through method, keeping the volume to a minimum in both cases.

4.1.1. MOSFET

Measurements were made using hydrogen concentrations in the range 0.5–2.0 vol% in air to investigate the influence of test gas concentration on the measured reaction times. Test gas flow rates of 90 and 120 sccm were chosen because gas flow and pressure instabilities were shown to be minimised for this set-up at these flow rates [16]. However, it must be stressed that the optimum conditions of flow are dependent on the experimental set-up and that those used here are specific to this particular flow-through chamber's dimensions.

Measured response times are given in Table 1 and are shown in Fig. 4 as a function of concentration. It is clear from Fig. 4 that the scatter of the results is greater at lower concentrations. This observation can partially be explained by the occurrence of a plateau in the sensor output signal before the maximum. This plateau is due to a feature of the sensor electronics. For measurements made at higher concentrations the plateau tended to occur after the sensor output reached 90% of the maximum indication. Conversely, for measurements made at lower concentrations the plateau regularly occurred before this point. An example of each case is illustrated in Fig. 5. This resulted in an increase in the measured t(90) at 0.5 and 0.75 vol% hydrogen in air. This greater scatter at lower concentrations lends support to the practice of measuring reaction times at hydrogen concentrations in the middle of the sensor's measuring range, as proposed in ISO FDIS 26142. According to the sensor manufacturer this is also their practice for measuring sensor reaction times [17].

The response time tends to decrease with increasing concentration. This is due partly to the influence of the plateau on the lower concentration measurements, but may also be related to faster hydrogen adsorption processes, which at higher concentrations dominate over competing surface adsorption reactions.

During MOSFET recovery time measurements no plateau was observed at any concentration and there is less scatter in the recovery time results, Fig. 6. Contrary to response time measurements there is a slight tendency for the MOSFET recovery time to decrease with decreasing test gas concentration as fewer hydrogen molecules are required to desorb from the sensor surface. Results are given in Table 1.

No details were given in the technical specifications about the gas flow conditions under which the MOSFET sensor can operate. Measurement of both t(90) and t(10) made at gas flow rates of 90 and 120 sccm showed no significant influence of these gas flow rates on the measurements, as determined previously for this specific flow-through set-up [16].

4.1.2. TCD

The TCD was tested using a slightly larger chamber required to accommodate its larger sensing head. The maximum flow rate specified for this sensor is 1 m/s, which corresponds to a volume flow rate of 424 sccm for this set-up. The flow rates used here, in the range 90–175 sccm, were well below this value. Response and recovery times were measured in the concentration range 0.5–2 vol% hydrogen.

It was found that the flow rate had an influence on the response of this sensor. As the flow rate increased both the "zero" reading and the reading in hydrogen increased. This may be explained in terms of its mode of operation – the faster the flow the greater the effective thermal conductance of the gas as it cools the heating element. This did not affect the measured reaction times however as the flow affected the "zero" reading and the reading in hydrogen equally.

Results of t(90) and t(10) measurements are given in Table 1 and shown as a function of flow rate in Figs. 7 and 8 respectively. The output signal resolution from this sensor is lower than that from the MOSFET, 0.1 vol% versus 0.02 vol%, and as

Table 1 – Response times, t(90) and recovery times, t(10)/s. Flow-through results are for a flow rate of 90 and 150 sccm for the MOSFET and TCD respectively.

$[H_2]$/vol%	Membrane	Lid	Gate valve		Flow-through	
	t(90)	t(90)	t(90)	t(10)	t(90)	t(10)
			MOSFET			
0.5	11.1	2.9	5.4	7.1	4.2	9.3
	12.0	2.6	2.7	5.1	4.2	9.2
	6.1	2.3	4.9	8.2	6.9	9.2
	6.9		5.9		7.3	9.3
	1.9					
0.75	–	2.0	3.1	8.9	4.0	10.0
		2.1	2.4	10.8	4.3	10.0
		2.4	2.5	11.6	7.2	10.0
					4.0	10.0
1.0	1.9	2.4	2.2	9.8	4.0	10.2
	2.4	2.1	2.3	7.5	3.9	10.1
	45.2	2.3	2.3	13.5	3.8	10.1
	28.3	1.8			3.8	10.3
	16.8					
	16.0					
	8.7					
	2.5					
	8.9					
1.5	–	2.5	2.1	–	3.8	10.8
		2.6	2.5		3.7	10.9
		2.0	2.9		3.9	10.8
			3.0		3.8	10.9
2.0	–	2.4	2.4	–	3.5	11.1
		2.2	2.6		3.8	11.3
		2.0	2.2		3.8	10.9
					4.0	11.1
			TCD			
0.5	–	2.8	5.5	5.4	5.2	9.1
		3.4	5.8	4.0	5.0	8.2
		3.9	4.6	4.6	4.7	8.3
			6.7	8.0	5.6	8.0
0.75	–	–	4.6	4.6	4.9	8.4
			3.9	7.6	5.0	8.3
			4.5	4.0	5.0	8.6
			6.4	4.5	4.1	8.8
1.0	–	2.2	4.7	5.7	4.9	9.6
		3.4	3.2	4.1	4.5	9.3
		3.9	5.5	4.2	6.5	9.8
			5.9	4.3	5.1	9.2
1.5	–	–	8.5	5.1	4.5	7.7
			4.7	4.4	6.3	7.6
			4.3	5.9	5.0	7.8
			4.4	6.5	5.0	7.6
2.0	–	3.9	4.3	5.5	5.5	8.3
		4.0	6.0	6.5	5.5	8.0
		4.8	4.9	4.2	5.1	8.1
			5.3	5.9	5.4	8.0
					5.6	7.8

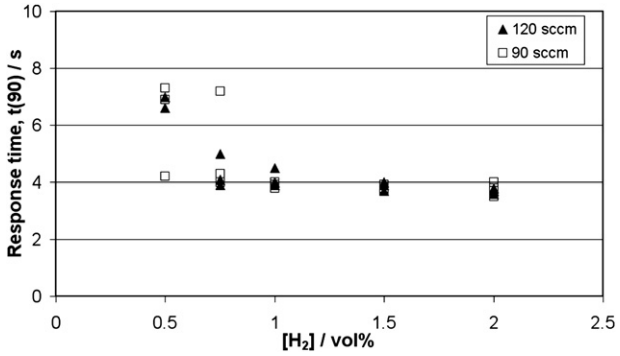

Fig. 4 – Response times of MOSFET sensor using Flow-through method.

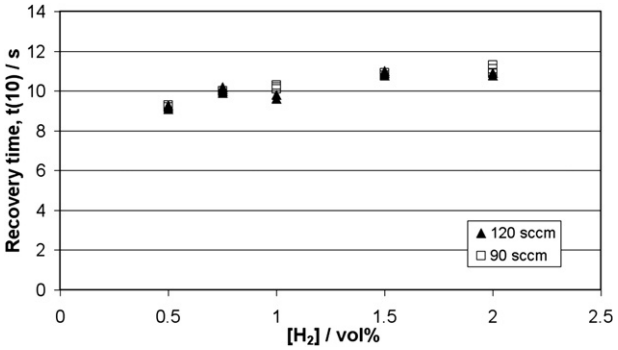

Fig. 6 – Recovery times of MOSFET sensor using Flow-through method.

a consequence there is more scatter in the experimental data. The response time results, Fig. 7, suggest that at flow rates higher than 90 sccm, the influence of the flow rate is negligible. The TCD recovery time results, see Fig. 8, indicate that above 150 sccm in this case, an increase in the flow rate does not cause a consistent decrease in the measured values. A flow rate of 150 sccm is recommended for this set-up as the optimum in terms of minimising reaction times and maximising the repeatability of the measurements.

It is also clear from Figs. 7 and 8 that there is no apparent systematic influence of hydrogen concentration on either the response or recovery time of this sensor. However such a trend may be obscured by the limited hydrogen concentration range over which measurements were made. For safety reasons, these experiments were carried out at a maximum hydrogen concentration of 2 vol% and as the measuring range of this sensor is 0–100 vol%, it is likely that any influence of concentration would not be detectable as a result of the relatively small variations. To properly investigate the influence of concentration on the reaction times of this sensor, measurements would need to be made over a wider concentration range. This is also in keeping with the practice of testing in the middle of the measuring range as referred to above, but was not possible here due to the safety restriction on the maximum hydrogen concentration used.

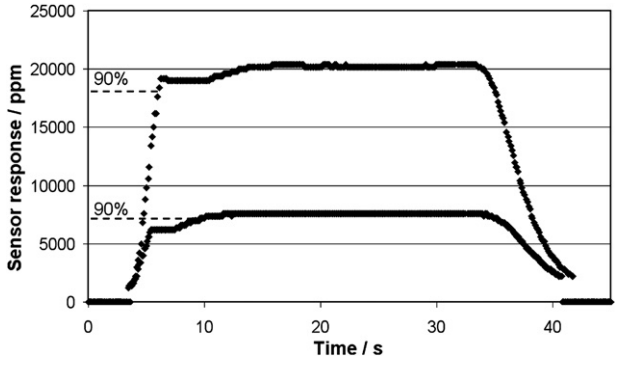

Fig. 5 – Response curves of MOSFET sensor at final indications 0.75 vol% and 2 vol% using Flow-through method, with plateau before and after 90% of maximum respectively.

4.2. *Diffusion-based method – membrane method*

4.2.1. *MOSFET*

Response times were measured only for the MOSFET sensor using the Membrane method at concentrations of 0.5 and 1 vol %. Results are shown in Table 1. The lack of repeatability in these measurements is immediately evident and for this reason measurements were not performed at several hydrogen concentrations or for the TCD sensor.

This lack of consistency in the data can be attributed to two factors in particular. Firstly, the manner in which the membrane opens plays a large role in determining the sensor response and it is extremely difficult to ensure that this opening is consistent from one experiment to the next. Secondly, the start time of the experiment, from which the sensor response time is measured, is indicated by a manual switch which is pressed at the same moment the membrane is cut. Errors inevitably arise in measurements if the switch is not pressed at precisely the correct time.

4.3. *Diffusion-based method – lid method*

4.3.1. *MOSFET*

Response times were measured for the MOSFET sensor using the Lid method in the concentration range 0.5–2 vol% hydrogen. Results are given in Table 1. These values are in good agreement with each other and with the specification of the manufacturer of <3 s. There is no evident influence of

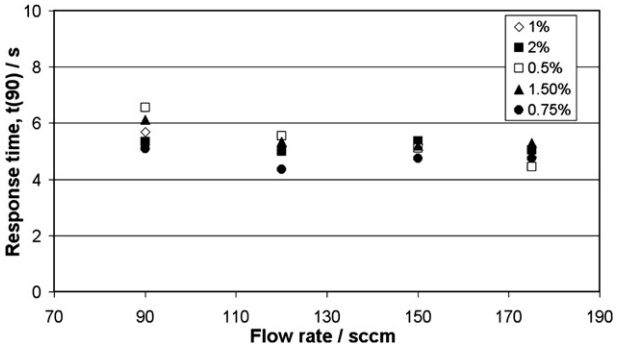

Fig. 7 – Response times of TCD sensor using Flow-through method as a function of flow rate; each point is the average of 3–5 experiments.

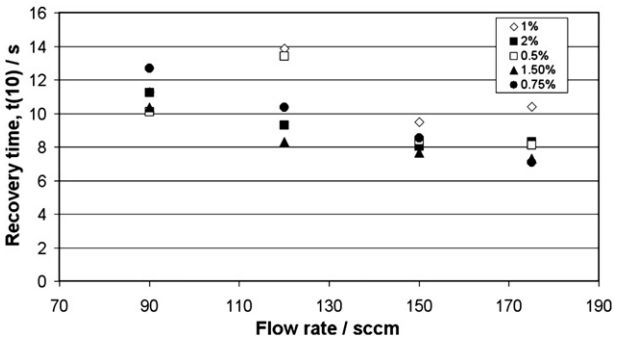

Fig. 8 – Recovery times of TCD sensor using Flow-through method as a function of flow rate; each point is the average of 3–5 experiments.

concentration, although the longest measured response time occurs at the lowest concentration tested, as in the case of the Flow-through method. This is also in keeping with the results of the Gate valve method described later.

4.3.2. *TCD*

Response times were also measured for the TCD at hydrogen concentrations of 0.5, 1 and 2 vol%. Results are shown in Table 1. As found previously, there is greater scatter in the TCD results than the MOSFET ones, due to the greater output signal resolution of the latter. Interestingly, these response times are significantly shorter than the typical value quoted by the manufacturer of 10 s. As mentioned in relation to the Flow-through results, any concentration dependence of the response time of this sensor is likely to be hidden as measurements were only carried out at restricted hydrogen concentrations at the lower end of the sensor's measuring range. For this reason measurements were not performed at the intermediate concentrations of 0.75 and 1.5 vol%.

4.4. *Diffusion-based method – gate valve method*

Significant modifications were made to the experimental set-up to realise the Gate valve method. It is more technically complex than the previous methods but allows the measurement of both response and recovery times.

4.4.1. *MOSFET*

It was clear from initial tests on the MOSFET sensor that the use of a fan to direct the gas flow towards the sensor significantly reduced the response times measured using this method. During these initial tests the fan was positioned remote from the gate valve opening and used only to ensure homogeneity of the gas mixture in the large chamber. However, the resulting measured response times were excessively long in comparison to those obtained using the other test methods and those given in the technical specifications, sometimes exceeding 30 s. When the fan was repositioned directly in front of the opening to the sensor holder, directing the gas flow towards the sensor, the response time was significantly reduced and the response curve showed a steeper rise in signal. The sensor response curves are illustrated for both fan positions in Fig. 9.

The influence of the diffusion time on the measured response time and sensor response profile is immediately obvious from this figure. When the fan served only a mixing function, the measured response time was 30.4 s whereas when it was used to direct gas flow to the sensor the response time was 3.4 s. This implies that a large part (approximately 27 s in this case) of the first measured response time (remote position) is due to the time taken for the mixture to diffuse to the sensor face and mix homogenously.

However positioning the fan directly in front of the opening to the sensor holder changes the nature of the test method in that it no longer relies solely on diffusion for movement of gas to the sensor surface. The fan is in fact used to enhance diffusion, rather than simply to ensure homogeneity of the mixture.

In order to allow for a precise definition of the position of the fan, a metal frame was constructed that allowed for 3D adjustment. It was also found necessary to place a thin sheet of aluminium in the short passage between the chamber and the gate valve in order to direct and separate gas flows into and out of the chamber. Use of such a sheet is thought to reduce turbulence around the sensor and allow for more efficient displacement of the dead volume of gas, and resulted in shorter measured response times.

The fan was positioned at the opening of the passage to the gate valve, 17 cm from the sensor face. The measured wind speed at the sensor, generated by the fan in this position, was 2.2 m/s. There are no details given in the manufacturer's specifications as regards the maximum wind speed at which this sensor should be used and this wind speed was deemed permissible as no adverse influence on the sensor performance was observed.

Response times were measured using this method at hydrogen concentrations of 0.5–2 vol% and results are given in Table 1.

As can be seen, there is significant scatter in the response times measured at 0.5 vol%. As in the case of the Flow-through method, this is due to the occurrence of a plateau which was often observed in the response curve at this concentration before *t*(90) was reached.

Recovery times were also measured using this method under the same conditions as the response time. For 0.5, 0.75 and 1.0 vol% mixtures, the signal decreased to zero, but for concentrations of 1.5 vol% and higher, it did not, because the

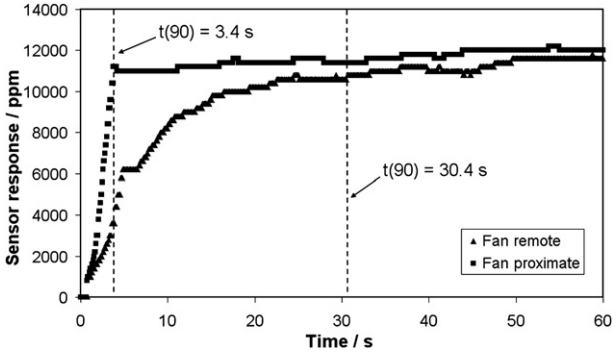

Fig. 9 – Response curves of the MOSFET sensor for 2 different fan positions using the Gate valve method.

hydrogen concentration remained above the lower detection limit of the sensor. In fact, for tests performed at 1.5 and 2 vol % the sensor response did not even decay to below 10% of the maximum indication, making measurement of $t(10)$ impossible despite the fact that the homogenised hydrogen concentration had fallen well below this value, to approximately 2% of the maximum indication. Previous experiments have shown that sensor response at such low concentrations will not necessarily be accurate and is often in fact much higher than expected [7].

The results of the MOSFET recovery time measurements carried out at 0.5, 0.75 and 1.0 vol% are given in Table 1. In general the recovery times measured at 0.5 vol% are lower than those measured at higher concentrations. At higher concentrations it was evident from the recovery curves that it took longer for the gas mixture to homogenise and for the concentration to fall below the lower detection limit of the sensor. This accounts for the longer measured recovery times at these concentrations.

For this sensor, a slight upward creep was evident in the response curves recorded using the Gate valve method, which was less pronounced or not observed in recordings from other methods. This creep may be related to the influence of gas impacting directly on the sensor face. This perpendicular gas flow due to the fan differs from that in the Flow-through method in which the gas passes parallel to the sensor.

4.4.2. *TCD*

Response times were measured using this method for the TCD in the concentration range 0.5–2 vol%. However, in order to respect the specifications of the manufacturer as regards wind speed (<1 ms^{-1}) it was necessary to position the fan at a greater distance, 22 cm, from this sensor than from the MOSFET.

Results are given in Table 1. As found with the Flow-through and Lid methods, there is no evident trend in terms of the influence of concentration.

Recovery times were also measured over the concentration range 0.5–2 vol%. Unlike the MOSFET, the TCD signal fell to zero during each test, allowing for measurement of $t(10)$ at all concentrations. This difference can be explained by the fact that the measured lower detection limit of the TCD (0.15 vol%) is higher than that of the MOSFET (<0.03 vol%) [7].

The measured TCD recovery times are given in Table 1. No influence of concentration is apparent, although as noted above, this may not be evident within such a limited span at the extreme of the measuring range.

5. Discussion

5.1. *Flow-through method*

The use of flow in the measurement of sensor response and recovery times allows the complete displacement of one gas mixture by another. This is an advantage of flow-based methods over those based on diffusion.

However, the influence of flow on the sensor response cannot be discounted. This was observed in this study for the TCD sensor, whose response shifted as a function of the gas flow rate. In addition, there can be difficulties with this method due to pressure and flow instabilities. The procedure must be optimized for the geometry of a particular experimental set-up in order to ensure controlled gas flow and pressure.

Once optimized however, this is a very efficient method experimentally, requiring much less time and smaller volumes of gas than the diffusion-based methods.

The response times measured for the MOSFET using this method varied between 3.5 and 7.3 s, while the recovery times ranged from 9.3 to 11.1 s. Response times measured for the TCD were 4.1–6.5 s, with recovery times in the range 7.6–9.8 s.

5.2. *Membrane method*

One of the principal difficulties encountered with the Membrane method related to opening of the membrane. It was impossible to ensure the exact same tautness of the film from experiment to experiment and the manual cutting movement varied inevitably. As a consequence, the membrane did not open in a repeatable fashion – at times it burst open immediately on contact with the cutter, whereas at other times, it merely tore at the point of contact obstructing gas diffusion to the sensor. This problem was somewhat overcome by increasing the tautness of the film. Nonetheless the repeatability of measurements remained poor.

This lack of repeatability can also be attributed to uncertainty over the exact start time of the experiment, which was signalled by manually pressing a switch. It was not possible to ensure that this coincided exactly with opening of the membrane.

The resulting MOSFET response time measurements were not only imprecise but they were also inaccurate when compared with the sensor's specifications. The measured response time varied from 1.9 to 45.2 s, with an average value of 12.8 s, while the response time reported in the specifications is 3 s.

Another drawback of this method is the potential for diffusion of hydrogen across the membrane before cutting. This can result in a non-zero reading from the sensor before the start of the measurement. A simple experiment was performed where hydrogen was injected into the diffusion chamber and the membrane was left intact. The sensor response was recorded and after 315 s the response rose above zero due to hydrogen diffusion through the membrane.

Execution of individual measurements was cumbersome, time consuming and required relatively large volumes of gas. Following each test the 30 L diffusion chamber needed to be flushed with air, the membrane removed and replaced and the sensor holder repositioned. The chamber then needed to be refilled with the test gas, which had to be left to homogenise and the gas composition analysed by GC before a subsequent measurement could be performed. Furthermore recovery time measurements were not possible with this method.

For these reasons only a limited number of measurements were made for the MOSFET sensor using the Membrane method and preference was given to developing an improved method for sensor response time measurement. However an important advantage of this method is its ability to simulate more closely the expected working conditions of many hydrogen safety

sensors compared to flow-based methods. For this reason it was of interest to develop other diffusion-based methods.

5.3. *Lid method*

The Lid method incorporates a number of improvements on the Membrane method. These include increased repeatability in the manner of exposing the sensor to the test gas and the use of an automatic signal for precise indication of the experiment start time. The response times measured for the MOSFET sensor varied between 1.8 and 2.9 s. Measurements for the TCD sensor varied between 2.2 and 4.8 s. No significant dependence of the measured response time on the test gas concentration was observed for either sensor in the range 0.5–2.0 vol% hydrogen in air. These results highlight the improvements on the Membrane method and indicate that it is possible to measure the response time with increased precision and accuracy using the Lid method.

As with the Membrane method, the possibility of diffusion before the start of the experiment was investigated and the sensor response was found to rise above zero 1200 s after injection of hydrogen into the diffusion chamber when the sensor holder remained sealed. This suggested that the rate of diffusion of hydrogen into the sealed sensor holder was much lower compared with the Membrane method. In addition inconsistencies related to membrane cutting were eliminated, as was the possibility of damage to the sensor from the cutter. The micro switch provided a clear measurement start time.

Furthermore execution of the test was technically simple and low in cost as no expensive solenoid valve was required, as is the case for the Gate valve method. However, similar to the Membrane method, significant time and gas were required to evacuate and flush the 30 L chamber between tests and to reseal the sensor holder. Recovery time measurements were not possible with this method.

5.4. *Gate valve method*

Unlike the Membrane and Lid methods, the Gate valve method allows for flushing of the sensor holder with either air or test gas, and so this method can also be used to measure sensor recovery times. In addition, similar to the Lid method it represents a number of improvements on the Membrane method in that opening of the valve is repeatable and provides a precise experimental start time.

However, an inherent problem was encountered whilst measuring sensor recovery times by this method. This arose due to the fact that the test gas mixture to which the sensor was initially exposed was not flushed out, but instead highly diluted. The hydrogen concentration therefore decreased greatly during the experiment, but did not drop to zero. In the MOSFET recovery time measurements performed at 1.5 and 2 vol%, the residual hydrogen concentration remained above the detection limit of the sensor. Due to inaccuracy at such low concentrations the sensor response did not fall below 10% of the maximum indication, making measurement of $t(10)$ impossible even though the calculated homogenised hydrogen concentration had fallen well below this value.

In general therefore, recovery time measurement using the Gate valve method may be problematic in cases where, at very low concentrations, the sensor under test gives a higher reading than the actual value due to inaccuracy or to a "memory effect".

Table 2 – Average response and recovery times of MOSFET sensor compared to <3 s and <10 s respectively as quoted by the manufacturer.

Method	Response time		Recovery time	
	$\overline{X}$	σ	$\overline{X}$	σ
Flow-through	4.4	1.2	10.2	0.7
Membrane	12.8	12.1	–	–
Lid	2.3	0.3	–	–
Gate valve	3.0	1.2	9.2	2.6

It was also found that diffusion of gas through the short passage from the diffusion chamber to the sensor face took a considerable amount of time compared to the response time of the sensor. It was therefore necessary to use a fan to direct the gas flow towards the sensor face. As a result, this method is not strictly speaking a diffusion-based method. In addition, the influence of gas flow perpendicular to the sensor may be a concern for some sensor types.

Furthermore, this method shares the common disadvantages of all the diffusion-based methods tested in terms of the time and gas volume required to flush out the diffusion chamber between measurements.

The response times of the MOSFET sensor measured using this method varied between 2.1 and 5.9 s, while the recovery times ranged from 5.1 to 13.5 s. Response time measurements for the TCD sensor varied between 3.2 and 8.5 s, and recovery times ranged from 4 to 8 s.

5.5. *Comparison of results of the 4 test methods*

The response time of the MOSFET sensor according to the technical specifications is <3 s. This can be compared with the results of the four measurement methods tested as presented in Table 2. It is evident that the Lid method is the only one to give consistent agreement with the specifications of the manufacturer.

These results are compared graphically in Fig. 10 which shows that the Lid and Gate valve methods consistently give faster measured response times than the Flow-through method, with the Lid method the fastest overall. The

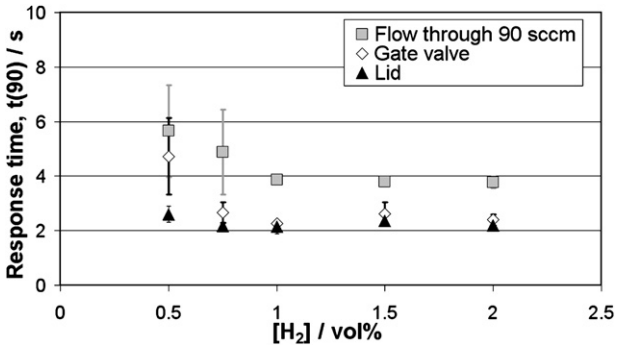

Fig. 10 – Average response time of MOSFET sensor using three test methods; error bars represent standard deviation. Membrane results omitted for clarity.

Table 3 – Average response and recovery times of TCD sensor compared to < 20 s, 10 s typical for both, as quoted by the manufacturer.

Method	Response time		Recovery time	
	$\overline{X}$	σ	$\overline{X}$	σ
Flow-through	5.2	0.6	9.7	2.0
Lid	3.6	0.8	–	–
Gate valve	5.2	1.2	5.3	1.2

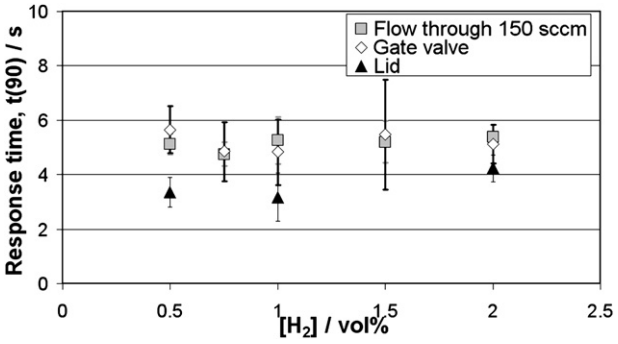

Fig. 11 – Average response time of TCD sensor using three test methods; error bars represent standard deviation.

difference between the average results of the Lid method and the Flow-through method is 2.1 s for the MOSFET (1.6 s for the TCD). The minimum time required to flush out the dead volume at a flow rate of 90 sccm, assuming simple displacement and no mixing, is approximately 1.4 s. These two values are in reasonable agreement, indicating that the difference between the results of the two test methods is due to the gas delivery time in the Flow-through method and that this time is close to a minimum in the Lid method.

For all methods, the scatter is greatest at lower concentrations, with much greater precision evident above 1 vol% hydrogen. These findings lend support to the recommended procedure in ISO FDIS 26142 of testing at the midpoint of the measuring range, which for this sensor is 2.2 vol%. If the lower concentration measurements are taken into consideration, there does seem to be an influence of concentration on the measured $t(90)$. However, the trend for $t(90)$ to decrease with increasing concentration disappears above 0.75%, suggesting that it is related to the greater scatter at lower concentrations.

The recovery time of the MOSFET sensor according to the technical specifications is <10 s. This can be compared with the results of the two measurement methods tested as presented in Table 2. The two methods give reasonably good agreement with the technical specifications and both indicate asymmetry between the response and recovery time, as accounted for by Ménil et al. [8] for sensors with a logarithmic dependence on hydrogen concentration. Both methods also suggest a slight increase in recovery time with increasing hydrogen concentration.

Table 4 – Advantages and disadvantages of sensor reaction time measurement methods.

Method	Advantages	Disadvantages
Flow-through	Reasonable repeatability Technically simple Experimentally convenient $t(10)$ measurement possible Short experimental times Low gas volumes required Well defined start time	Relatively low accuracy Influence of flow on some sensors
Lid	Good accuracy Good repeatability Technically simple No flow Diffusion before start relatively slow Well defined start time	$t(10)$ measurement not easily possible Time consuming High gas volumes required
Gate valve	Reasonable accuracy Reasonable repeatability Limited $t(10)$ measurement possible No diffusion before start Well defined start time	Technically more complex Influence of flow on some sensors $t(10)$ measurement at high concentration not always possible Results dependent on position of fan
Membrane	Technically simple No flow	Low accuracy Poor repeatability Cumbersome to perform $t(10)$ measurement not possible Diffusion before start Time consuming High gas volumes required Uncertain start time

The quoted response time of the TCD sensor is <20 s, with a typical value of 10 s. This can be compared with the values given in Table 3. The response time measured by all methods is in fact lower than that specified by the manufacturer, with the Lid method once more giving the lowest values.

Results are shown graphically in Fig. 11, from which it is evident that the error is greater in measurements on this sensor. This is due to the lower resolution of the TCD output compared to the MOSFET (0.1 versus 0.02 vol%). As with the MOSFET, the Lid method consistently gives the fastest response times. However, the Gate valve method is in agreement with the Flow-through method for this sensor, whereas it gave faster results for the MOSFET. This is a result of the fan position. For tests on the TCD, the fan was placed farther from the sensor to respect the specifications of the manufacturer regarding the sensor's maximum tolerable wind speed. As a result the gas transport time increased, as did the measured response time.

According to the technical specifications, the recovery time of the TCD sensor is <20 s, with a typical value of 10 s. The measured values are shown in Table 3 and are in reasonable agreement with the specifications of the manufacturer.

As detailed above, no influence of concentration was discernible over this range. In order to investigate this properly, the sensor would need to be tested over a wider range, ideally covering the midpoint of its measuring range.

6. Conclusions

The advantages and disadvantages of the four methods are summarised in Table 4. They are derived from the results of measurements made on two commercially available hydrogen safety sensors, a MOSFET sensor and a thermal conductivity sensor.

The method that results in the shortest response times is the Lid method, which also demonstrates good repeatability and is therefore recommended for response time measurement. However, there are two principal disadvantages of this method. Firstly, it is relatively time consuming due to the need to flush the large diffusion chamber and to reseal the sensor holder between experiments. Secondly, it is not possible to perform recovery time measurements using this method without significant modifications to the experimental set-up.

For recovery time measurement, the Flow-through method is recommended as it is the only method in which the test gas is really switched to clean air rather than being highly diluted. This method is also the simplest and quickest to perform, which may be a consideration in response time measurement too, depending on the relative importance of accuracy and efficiency.

In relation to the influence of concentration on sensor reaction times, the following observations were made:

- There is a slight tendency for the response time of the MOSFET to decrease with increasing concentration, which is not evident above 0.75 vol% hydrogen and may be partially attributable to high scatter at lower concentrations due to early plateaus in the response curves.
- Recovery times of the MOSFET show a slight steady increase with increasing concentration.
- No concentration dependence of the TCD sensor, if any, could be ascertained as measurements were only carried out at the extreme of its measuring range due to safety restrictions on the maximum allowable hydrogen concentration.

Acknowledgements

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REFERENCES

[1] Salyk O, Castello P, Harskamp F. A facility for characterization and testing of hydrogen sensors. Meas Sci Technol 2006;17:3033–41.
[2] Castello P, Salyk O. Characterization and application of a facility for independent customer testing of hydrogen sensors. Int Sci J Alternative Energy Ecology 2006;5(37):61–2.
[3] Castello P, Salyk O. Testing of hydrogen safety sensors in service simulated conditions. International conference on hydrogen. Pisa, Italy; September 8–10; 2005.
[4] Salyk O, Castello P. Hydrogen sensors in systems for alternative fuels. Chem Listy 2005;99:116–9.
[5] Boon-Brett L, Bousek J, Castello P, Salyk O, Harskamp F, Aldea L, et al. Reliability of commercially available hydrogen sensors for detection of hydrogen at critical concentrations: part I – testing facility and methodologies. Int J Hydrogen Energy 2008;33(24):7648–57.
[6] Boon-Brett L, Bousek J, Moretto P. Reliability of commercially available hydrogen sensors for detection of hydrogen at critical concentrations: part II – selected sensor test results. Int J Hydrogen Energy 2009;34(1):562–71.
[7] StorHy – Hydrogen storage systems for automotive application: Integrated Project Number 502667, Final report on sensor testing, Deliverable DSA10, http://www.storhy.net/
[8] Ménil F, Susbielles M, Debéda H, Lucat C, Tardy P. Evidence of a correlation between the non-linearity of chemical sensors and the asymmetry of their response and recovery curves. Sensors Actuators B: Chem 2005;106:407–23.
[9] Ménil F. Modélisation des temps de réponse des capteurs chimiques. CR Acad Sci Paris Chimie 2001;4:899–905.
[10] Gerblinger J, Meixner H. Fast oxygen sensors based on sputtered strontium titanate. Sensors Actuators B: Chem 1991;4:99–102.
[11] Tobias P, Mårtensson P, Göras A, Lundström I, Lloyd Spetz A. Moving gas outlets for the evaluation of fast gas sensors. Sensors Actuators B: Chem; 1999:58389–93.
[12] Wingbrant H, Lundström I, Lloyd Spetz A. The speed of response of MISiCFET devices. Sensors and Actuators B: Chem 2003;93:286–94.
[13] IEC 60079-29-1 Electrical apparatus for the detection and measurement of flammable gases – part 1: general requirements and test methods; 1998.
[14] Sawaguchi N, Nishibori M, Tajima K, Shin W, Izu N, Murayama N, et al. Practical test methods for hydrogen gas sensor response characterization. Electrochemistry 2006;74:315–20.
[15] ISO FDIS 26142 Hydrogen detection apparatus; 2009.
[16] Boon-Brett L, Bousek J, Black G, Frischauf N, Harskamp F, Moretto P. Hydrogen sensor response and recovery time measurement methods. Private EC-JRC report to members of ISO TC197 WG 13; 6 March 2009.
[17] Private communication (email) from MOSFET manufacturer dated 06/05/2009.