INVESTIGATION INTO THE CROSS-SENSITIVITY OF DOMESTIC CARBON MONOXIDE ALARMS TO HYDROGEN

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ABSTRACT

Preliminary research suggests domestic carbon monoxide detectors with an electrochemical sensor are approximately 10 -20% sensitive to hydrogen atmospheres in their factory configuration. That is, the display on a carbon monoxide detector would give a carbon monoxide reading of approximately 10-20% of the concentration of hydrogen it is exposed to. Current British standards require detectors to sound an alarm within three minutes when subjected to a continuous concentration of ≥ 300 ppm CO. This would equate to a concentration of 1500-3000 ppm hydrogen in air, or approximately 3.75 – 7% %LEL. The current evacuation criteria for a natural gas leak in a domestic property is 20 %LEL, indicating that standard carbon monoxide detectors could be used as cheap and reliable early warning systems for hydrogen leaks. Given the wide use of carbon monoxide detectors and the affordability of the devices, the use of carbon monoxide detectors for hydrogen detection is of particular interest as the UK drives towards energy decarbonisation.

Experiments to determine the exact sensitivity of a range of the most common domestic carbon monoxide detectors have been completed by DNV Spadeadam Research & Testing. Determining the effects of repeated exposure to varying concentrations of hydrogen in air on the sensitivity of electrochemical sensors allows recommendations to be made on their adoption as hydrogen detectors.

Changing the catalysts used within the electrochemical cell would improve the sensitivity to hydrogen, however simply calibrating the sensor to report a concentration of hydrogen rather than carbon monoxide would represent no additional costs to manufacturers. Having determined the suitability of such sensors at an early stage; the technology can then be linked with other technological developments required for the change to hydrogen for domestic heating (e.g. change in metering equipment and appliances).

This report finds that from five simple, and widely available carbon monoxide detectors, the lowest sensitivity to hydrogen measured at the concentration required to sound an alarm within three minutes was approximately 10%. It was also discovered that as the hydrogen concentration was increased over the range tested, the sensitivity to hydrogen also increased.

It is proposed that coupling these devices with other elements of the domestic gas system would allow actions such as remote meter isolation or automatic warning signals sent to response services would provide a reliable and inherently safe system for protecting occupants as gas networks transition to net-zero greenhouse gas emissions. In this respect, it is noted that wireless linking of smoke and heat detectors for domestic application is already widely available in low-cost devices. This could be extended to CO detectors adapted for hydrogen use.

1.0 INTRODUCTION

The UK government has published targets to reduce greenhouse gas emissions to net-zero by 2050. One of the major issues in meeting this goal is the use of natural gas in domestic applications such as heating. The use of hydrogen as an alternative to natural gas has been widely proposed and as part of the Hy4Heat and H21 projects, DNV is working on assessing any safety concerns around transitioning the current gas infrastructure from natural gas to 100% hydrogen. With the hazards associated with hydrogen use well documented, this report suggests an early warning system that could negate the need for intrusive safety measures that would add significant costs and difficulties in transitioning to a 100% hydrogen gas infrastructure. With approximately 24 million household meter connections in the UK [1], taking advantage of existing and reliable technologies would contribute to simplifying and accelerating this transition. DNV Spadeadam Research Centre aims to prove the cross-sensitivity of the electrochemical cell in standard, domestic carbon monoxide alarms to hydrogen exposure. Knowledge of the typical cross-sensitivities is then used to assess the suitability of the sensors to provide an early warning system in the event of an unplanned hydrogen gas leak. Further work into coupling this technology with safety features such as remote gas isolation or containment is currently underway.

Typical carbon monoxide sensors work through redox reactions in an electrochemical cell [2]. Carbon monoxide oxididises at the working electrode of the cell in the presence of water from the electrolyte to produce carbon dioxide, electrons, and protons. Protons are transported through the electrolyte towards the counter electrode with electrons flowing through an external circuit from the working electrode to the counter electrode. A third reference electrode is used to control the working electrode potential, to ensure accurate and reliable measurement of any current arising from the presence of test gas. The current produced in clean air is used to zero the system, and the change in current under exposure to known concentrations of carbon monoxide is used for test gas calibration. DNV propose that calibrating the sensors using hydrogen, rather than carbon monoxide, would allow manufacturers to give accurate display readings with little, if any, extra cost.

To combat this cross sensitivity to hydrogen, some manufacturers choose catalysts which selectively limit the hydrogen oxidation process. These sensors are marketed as CO/H2 LOW sensors and are often more expensive. In industries where there is a likely source of hydrogen, for example around battery charging facilities, CO/H2 NULL sensors are often found however being more expensive than the CO/H2 LOW sensors these are seldom found in domestic settings. These sensors employ a four-electrode system with one system measuring carbon monoxide (and hydrogen interference) and the other measuring only hydrogen concentration. The hydrogen only reading is used in the calibration of the carbon monoxide measurement to null the effect of hydrogen interference on this reading [3].

Carbon monoxide alarms are generally triggered when a concentration of carbon monoxide of ca. 50ppm is consistently detected over a given period of time (typically 60-90 mins). This time-to-alarm is reduced as higher concentrations are measured. It is reported that standard carbon monoxide detectors have a cross-sensitivity to hydrogen of around 20% [4,5], meaning that the display of a standard carbon monoxide alarm would read approximately 20% of the actual hydrogen concentration it is exposed to. Accurate determination of the cross-sensitivity and analysis of the effects of varying hydrogen concentrations on carbon monoxide detectors both on their sensitivity and under repeated exposure will indicate whether these devices could be used as a safe and reliable early hydrogen detection and warning system as the UK moves towards it's net-zero targets .

2.0 EXPERIMENTAL ARRANGEMENT

2.1 Equipment

To fairly represent the range of domestic carbon dioxide detectors available, five devices from common brands were chosen, priced from £10 to £40. These included leading manufacturers, such as AICO, Kidde, FireAngel and Honeywell, some with a digital display and some without.

An electrical equipment housing, IP65, was used to enclose the alarms during testing; maintaining a small internal positive pressure. The internal volume (without CO detectors) was approximately 0.001 m^3. To minimise the pressure in the enclosure, the enclosure was vented directly to atmosphere. A range of hydrogen concentrations were achieved using a Signal 821S gas divider, shown in Figure 1.

Figure 1. Sigma 821S Gas divider used to control hydrogen concentration at test environment inlet

With a certified hydrogen/air mix used as the span gas (S), and compressed air used as the zero gas (Z), the divider mixes both streams accurately by closing one of eleven valves, indicated by a red LED as in Figure 1. The setting of 70% indicates that the zero gas is able to flow through three capillary tubes, and the span gas through seven. By balancing the pressures in each capillary, the ratio of open tubes is directly proportional to the concentration of span gas that exits the divider. The balancing of pressures does not take into account the viscosity of the zero and span gases, and so the true concentration is achieved through the correction calculation detailed in the gas divider manual.

2.2 Physical arrangement

The experimental equipment was arranged according to Figure 2. In this arrangement, the hydrogen span concentration could be changed to allow testing over a larger concentration range by changing the span cylinder. Span and Zero gas bottle regulators were set to 1.7 and 2.4 bar respectively, in accordance to the gas divider manual. The flow through the gas divider into the enclosure was approximately 3-4 SLPM as indicated on the rotameter on the front of the divider.

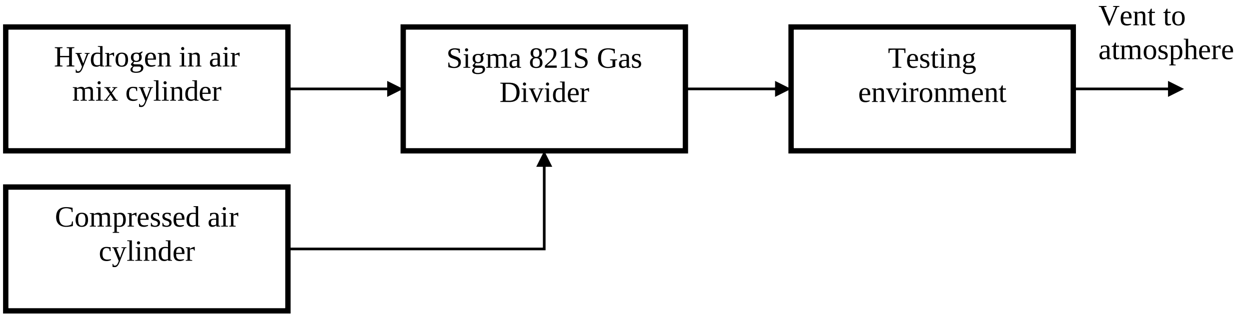

Figure 2. Block diagram showing experimental arrangement

3.0 EXPERIMENTAL PROCEDURE

3.1 Procedure

Two sets of experiments were conducted on the three devices with digital displays. First a calibration, where the detector display was read at known hydrogen concentrations, and secondly the time taken to reach a maximum alarm and display reading. Prior to testing, each detector alarm was tested using the on-board test button to ensure the device worked as expected and was reset once each test had finished. When not in use, the devices were kept away from the enclosure and outlet vent.

3.2 Calibration

The calibration data is used to determine the apparent sensitivity of the electrochemical cells inside the carbon monoxide detectors to hydrogen, and to predict what concentrations of hydrogen will trigger each alarmed state. The concentration of hydrogen passed into the enclosure was controlled by a Sigma 821S gas divider and ramped from 10% span up to 100% span. This gives a range 100 to 20,000 ppm hydrogen in air, which was sufficient to trigger each alarm state in all the detectors tested. By increasing the span concentration in this way, any errors associated with the detectors not having time to reach their maximum reading were rendered conservative. To explain: by taking a reading lower than the alarm may have eventually measured, a ‘worst case’ scenario is created whereby the carbon monoxide detectors appear less sensitive to hydrogen than they might be. If this worst-case reading still falls within a tolerable limit, it is implicit that the exact sensitivity the detector finishes at will be greater than the tolerable value measured.

3.3 Time-to-alarm

The calibration data was then used to make a prediction on the concentration of hydrogen required to give the maximum detector readings. Using this concentration, each of the alarms were tested to determine the response of the detectors to a high concentration gas hydrogen leak. The time for these alarms to sound, and reach their maximum reading provides information on parameters such as any delay built into the devices by manufacturers, and also the time taken for the testing enclosure to purge with the hydrogen mix span. The time to stop alarming and for the displays to reach zero is also measured both when the detectors were removed from the testing atmosphere to clean air and when left in the enclosure with a pure air purge. For these experiments, two of the alarms (Honeywell and FireAngel, or Kidde with and without display) were together placed in the container and subjected to a constant hydrogen concentration of 2000 ppm and 6000 ppm hydrogen respectively. Readings were taken every 30 seconds for five minutes, and then once per minute thereafter.

For the detectors without digital displays, the concentration of hydrogen to initiate the highest alarm was determined by measuring the time to alarm at various concentrations of hydrogen. The standard for gas detectors, EN50291-1, specifies an alarm must sound within three minutes when exposed to concentrations above 300 ppm carbon monoxide. The maximum alarm for the detectors without displays is therefore is based on this time, with allowances made for the purge time calculated following these experiments.

3.4 Procedural adjustments

Slight adjustments were made to the experimental procedure as testing progressed. Several arrangements of the detectors within the enclosure were trialled, before settling on the arrangement shown in Figure 3. By testing two alarms at once, not only was the operator time requirement reduced, but consistency between separate device tests improved. Experimental variations in enclosure concentrations would therefore be indicated by both detectors providing unexpected readings. Should only one detector give inconsistent data, the factor of concentration variations within the enclosure can be dismissed.

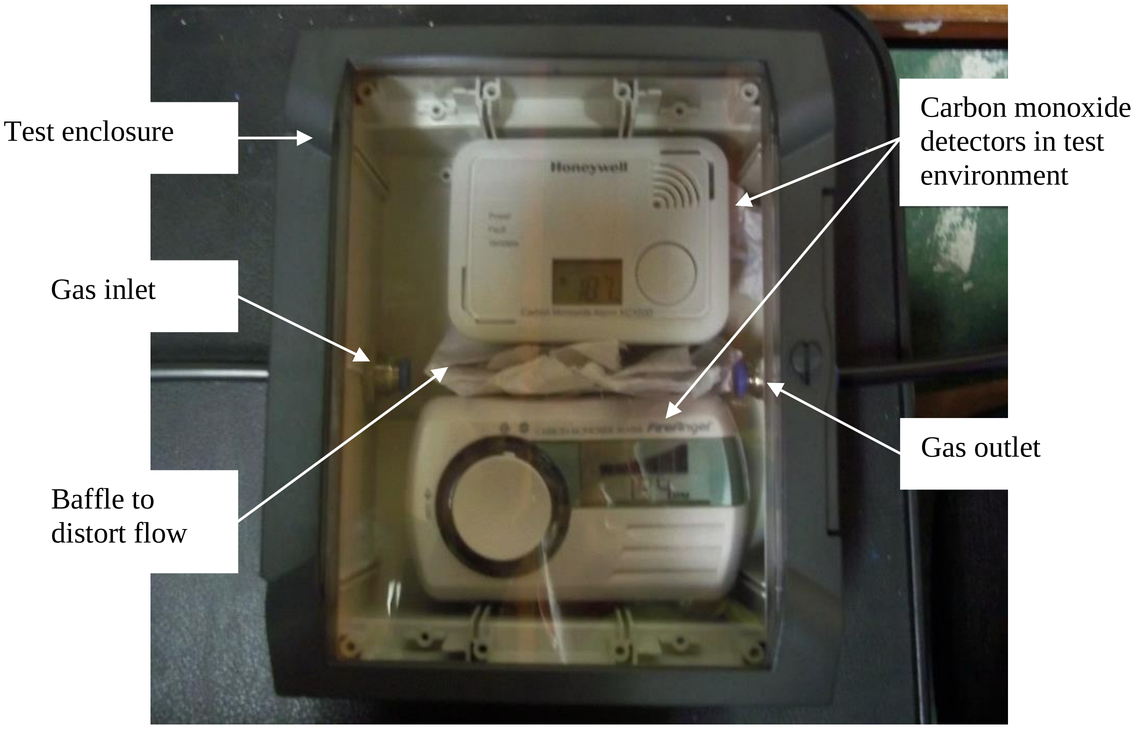

Figure 3. Photograph of test enclosure containing Honeywell and FireAngel carbon monoxide detectors

Testing two alarms at once created an unobstructed channel directly from gas inlet to outlet. It was decided to disrupt the flow of hydrogen within the channel by adding a paper baffle. This would ensure the enclosure was fully purged and that detector readings accurately represented the concentration within the chamber.

4.0 ANALYSIS AND DISCUSSIONS

The results of the experiments are displayed graphically in Appendix A: Graphs. For simplicity, where concentrations of hydrogen are referenced, they are approximate values and do not include the viscosity correction factors discussed above. For example, 2000 ppm hydrogen refers to a test carried out using this approximate concentration. The exact hydrogen concentration, 2081.8 ppm, is in analysis. The percentage error for the concentration of hydrogen inside the chamber is +/-2.2%, with the span gas being accurate to +/-2% and the gas divider being accurate to +/-0.2%. These are displayed as horizontal error bars on all graphs involving fits to the data.

4.1 Calibration trials

Through comparison of the three devices with digital displays it becomes clear that the Honeywell and FireAngel detectors are both highly sensitive to hydrogen. The Kidde detectors on the other hand were far less sensitive, achieving a maximum sensitivity lower than the minimum sensitivity measured for both Honeywell and FireAngel sensors across the tested hydrogen concentration range. The most probable reason for this, given the similarities in price, being the electrocatalysts used within the sensor itself. It is likely that the materials used to coat the electrodes in the Kidde sensor simply have a lower affinity to catalysing the oxidation of hydrogen.

From a safety perspective, the least sensitive alarm is of the highest importance. If this sensor still meets the required safety parameters, then it can be assumed that most domestic carbon monoxide alarms will also meet these specifications. Figure 4 shows the calibration data, with fitted 2nd order polynomial trendlines.

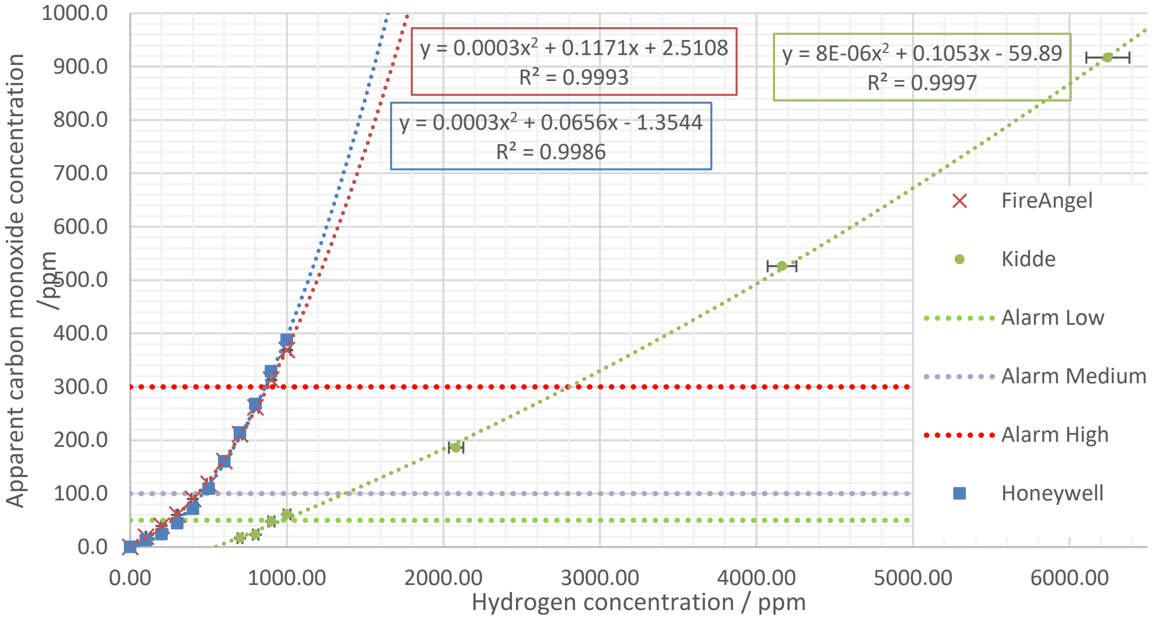

Figure 4. Calibration data for average response across repeated runs for the three detectors with digital displays

Figure 4 shows the Kidde alarm intercepts the threshold for a rapid alarm response at approximately 2800 ppm H2. This represents a sensitivity of 10% and indicates the carbon monoxide detector will sound an alarm within three minutes when exposed to hydrogen at a concentration of 7 %LEL. This result is significant as an alarm will sound, alerting the occupants of a potential leak at relatively low hydrogen concentrations. Currently the evacuation criteria for natural gas leaks is at a concentration of 20 %LEL, implying that these carbon monoxide detectors would be useful in identifying similar evacuation situations in hydrogen applications.

All alarms showed an increase in sensitivity to hydrogen as concentration was increased. The rate of increase in the sensitivity of the Kidde alarm appears to decrease under testing with 20,000 ppm hydrogen span, however the display reads a maximum value of 999 ppm CO before this effect becomes significant.

All results in this section were gathered with 10-minute intervals between the changes in applied concentration. Performing the same activity again but with an extended duration between the applied concentration steps might yield better performance but the results presented here are considered conservative in terms of the application.

4.2 Time-to-alarm trials

Using the calibration data for the Honeywell and FireAngel devices, it became apparent that a hydrogen concentration of 2000 ppm would result in the display reaching its maximum value. With the Kidde alarm being much less sensitive than the others, a concentration of 6000 ppm hydrogen was chosen. All three of the detectors with digital displays were tested further using these concentrations (FireAngel & Honeywell – 2000 ppm, Kidde – 6000 ppm) with the Kidde detector chosen for further analysis.

From a safety perspective, large unexpected leaks provide a greater hazard both in terms of risk and severity, than those of a much lower flow rate and subsequently lower accumulation levels. For this reason, the response over time was measured under immediate exposure to these higher concentrations, and the device's behaviour monitored. Figure 5 shows the response of the Kidde detector following exposure to 6000 ppm hydrogen in air.

In addition to being the least sensitive, the Kidde device was the least consistent in terms of time-to-alarm, ranging from 3.5 – 9 minutes following test initiation. Despite this, the tests showed that under exposure to this concentration of hydrogen (15 %LEL) a warning would be issued in under 10 minutes of hydrogen concentration reaching the detector. Repeats 4, and 6-8 included a purge with pure air following the test.

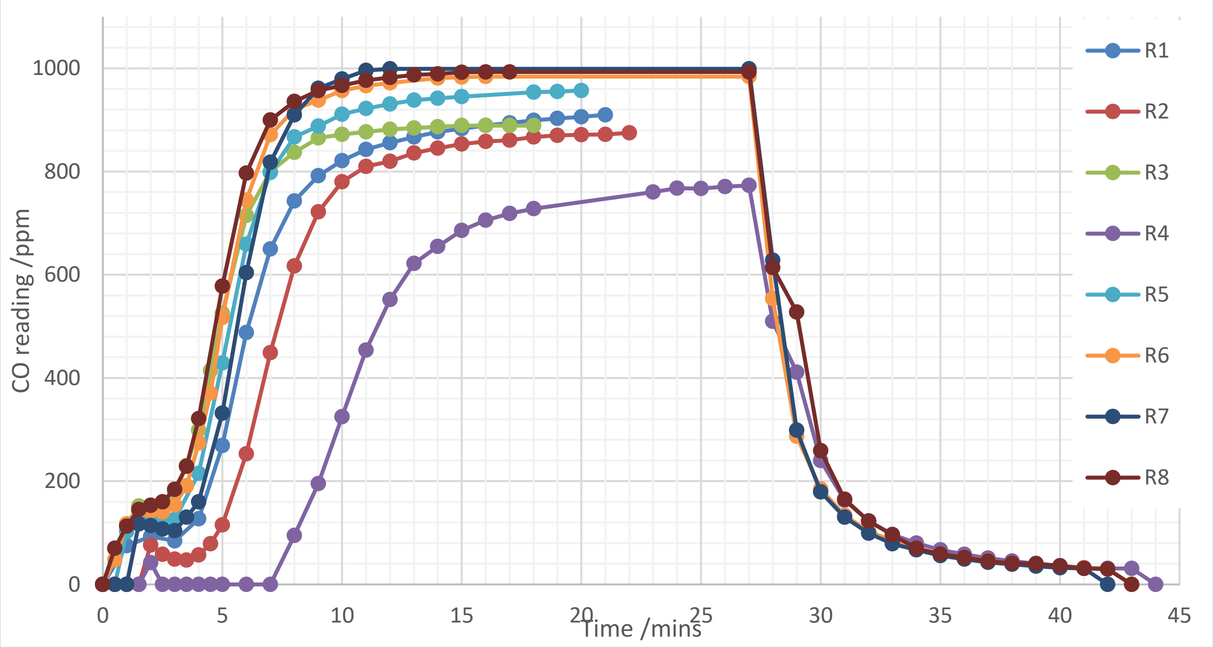

Figure 5. Response of Kidde detector to 6000 ppm hydrogen

Figure 5 shows the general trend of the carbon monoxide detector displays when exposed to a constant hydrogen concentration. Repeats 1,2,3 and 5 show only the response to the introduction of hydrogen to the test enclosure, with the detector being removed to a hydrogen-free atmosphere for time-to-zero measurement. The remaining repeats show how the detector reacted to purging the enclosure with pure air for comparison and to calculate the time to purge the test enclosure.

4.3 Alarm delay factors

Throughout the above testing, several factors influenced the time taken to initiate an alarm. These include the time taken to purge the enclosure with the desired hydrogen mix, any delay built into the device by the manufactures so as to prevent ‘nuisance alarms’ and any effects on the sensor arising due to repeated and prolonged exposure to high hydrogen concentrations. The testing also revealed that a delay exists between the sensor emitting a signal and the display reading the corresponding value, and that the temperature of the sensor, despite being within operational recommendations, may affect readings. This is evidenced by the Honeywell and FireAngel devices sounding within three minutes despite reading a concentration lower than 300 ppm CO.

It is important to consider the time taken to purge the enclosure after each change in gas inlet concentration. This purge time was assessed by comparing the difference between the time taken for the sensors to display 0 ppm and stop alarming when moved to fresh air and the time taken when the detectors remained in the enclosure and the enclosure was flushed with pure air at inlet through the gas divider (so consequently at the same flow rate as when flowing hydrogen mixtures into the enclosure).

Using this estimate of the purge time; based on the known flow of 3 SLPM and the known volume of the enclosure of 1 L, the flow from the gas divider can be described as providing enough flow for 3 changes of atmosphere per minute within the enclosure and that this rate is sufficient to purge the enclosure in nominally 30 seconds.

Using this purge time, any delay built into the devices could be estimated by subtracting 30 seconds from the time taken to start displaying readings. For the Honeywell and the FireAngel devices, this would indicate a response to hydrogen exposure within 30 seconds. This is consistent across all of the exposure concentrations tested. Under exposure to 6000 ppm hydrogen and excluding R4, the Kidde sensor alarmed consistently within 5.5 minutes after purge and began displaying a reading within 1.5 minutes. Factoring in Repeat 4, the slowest time-to-alarm was found to be 8.5 minutes. Considering this experiment did not result in hydrogen detection until the 7.5 minutes after purge, this result may not indicate a loss of sensitivity but more likely an issue in purging the container correctly.

To that end, no evidence was found to suggest that repeated exposure to hydrogen causes a decay of the catalytic materials used within the electrochemical sensors. Both the Honeywell and Kidde sensors were tested in 1000 ppm hydrogen following all 20,000 ppm hydrogen tests, and showed no significant decrease in CO measurement. A further, long term experimental programme would be required to assess this to the fullest extent. However, it should be noted that repeated exposure to hydrogen would be highly unlikely in any practical application. The potential for failure of the sensor as a result of long duration exposure (e.g. overnight) may be important to understand.

As discussed above, the refresh rates of the Honeywell, FireAngel and Kidde devices were approximately 10, 30 and 10 seconds respectively. Throughout the testing, alarms began sounding within three minutes despite reading concentrations far below 300 ppm CO. In some cases, an alarm sounded before any reading was displayed on the digital interface. This would imply a delay between the sensor responding to the presence of hydrogen and updating the display. This is reflected by the shape of the response found during time-to-alarm testing. It would be expected that once the concentration of hydrogen within the test enclosure had stabilised that the sensor begins providing its maximum output current to the detector’s circuitry. This might explain the initial peak found within the first few minutes of each time-to-alarm test, with the remainder of the response curve corresponding to the circuitry and display following the sharp increase in current output from the sensor. Sounding of the alarm ahead of the display being updated would support the assertion that the alarms levels may be hard-wired to the sensor output signal rather than the digital display circuitry.

4.4 Non-digital detectors

Accounting for the above factors, the detectors without digital displays were assessed in terms of the hydrogen concentration required to sound an alarm within a certain timeframe. An allowance of two minutes was made before classifying the times into the high or medium category, to allow for both the purge and nuisance exposure time.

As expected, the Kidde alarm without display alarmed at the same time as the device with the display, indicating the presence of the same sensor and circuitry in both. Further tests for the Honeywell and FireAngel without displays would provide information on whether this is common practice. The AICO EI device appears to have a similar sensitivity to the Honeywell and FireAngel devices, however more extensive testing is required to confirm this with confidence.

5.0 SUMMARY

This report provides the results and commentary from experiments involving the exposure of the most common and affordable domestic carbon monoxide alarms to hydrogen. This work is important in determining viable solutions for safety as the UK drives towards decarbonising their energy infrastructure. As a potential fuel, hydrogen presents the risk of ignition or explosion in confined spaces. Being able to reliably detect and warn occupants of any significant presence of hydrogen is important.

DNV Spadeadam found that the tested carbon monoxide detectors worked effectively as early hydrogen detection devices. By taking advantage of the electrochemical sensor technology used in cheap, and reliable carbon monoxide detectors, this experimental programme was conducted to determine the minimum concentration of hydrogen that would trigger an audio and visual alarm. Through this work, DNV found that the maximum concentration required to sound an alarm within three minutes of exposure was approximately 2800 ppm hydrogen. This corresponds to 7 %LEL, and with appropriate protocols would provide an early warning for occupants to evacuate to safety. These results are encouraging when considering that a concentration of 20 %LEL natural gas is the current level for occupant evacuation.

The apparent sensitivity of each of the devices tested was found to increase with hydrogen concentration, ranging from approximately 15 – 40% for both the Honeywell and FireAngel sensors, and from 10 – 15% for the Kidde device. A good level of consistency was found between devices of the same brand, however further research is required to validate this.

Coupling these findings with other existing technologies, such as remote meter isolation or an automatic warning sent to the gas safety bodies, the use of carbon monoxide detectors could present a novel hydrogen detection system for early leak identification. As mentioned, this would be of use as the UK pushes towards a carbon neutral future. The findings in this report indicate little expense to manufacturers in calibrating detectors to hydrogen rather than carbon monoxide, with the sensitivity to hydrogen already being commonly considered during sensor manufacture. By adjusting the alarm parameters to future standards, and with only little additional research for manufacturers, these findings represent a viable means of early hydrogen leak detection and warning.

As with their use at present, the devices must be placed in areas where hydrogen gas is likely to accumulate. The length of time to alarm, and allowable hydrogen build up concentrations are yet to be defined, but DNV propose that standard carbon monoxide alarms, with slight adjustments to their internal circuitry could be affordably and readily supplied for early hydrogen detection and warning.

Whilst the odorant in piped gas is an effective means of alerting domestic occupants, it is known that long duration exposure (such as overnight) can desensitise occupants. The gas release may also occur in an unoccupied room. The adaptation of CO detectors to hydrogen detectors offers a lower cost of conversion option that will result in hydrogen installations being safer than those with natural gas, particularly as the detectors will warn of both internal leaks and external releases entering the property

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