Co-funded by the
Erasmus+ Programme
of the European Union

HySkills KA2 IO2 - Training Course on Hydrogen Transport and Delivery

IO2.8 – HYDROGEN SENSORS, DETECTION AND MONITORING

In this training course, students will be able to understand the theory relating to hydrogen sensors, their demands/specifications and the various types that exist in the market today. Additionally, the module will look at the location, maintenance and calibration of these sensors. Finally, the module will touch on hydrogen flame detection and thermal detectors & imaging systems.

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Hydrogen Sensors

With the aim of decarbonising our fossil fuel driven society via the means of hydrogen implementation, technical challenges are to be met. One of the main concerns with widespread adoption and conversion to hydrogen systems is safety concerns such as its explosive nature and such widespread flammability range. In order to ensure safe operation of these practices, hydrogen detection and monitoring should be implemented in all processes concerning hydrogen. Lately, there has been a focus on the research of hydrogen sensor technologies and their effectiveness given hydrogen sensors have been well studied and produced in the form of marketable, commercial products which can be purchased. Hydrogen sensors are devices that convert a chemical or physical interaction of hydrogen gas into a measurable signal. Usually, they work by adsorption of hydrogen to a solid-state sensing material , which experiences a corresponding property change and effectively provide transduction of the gas concentration to a measured value. This is further shown in Figure 1, the operational flow diagram below which outlines the functions of a hydrogen sensor.

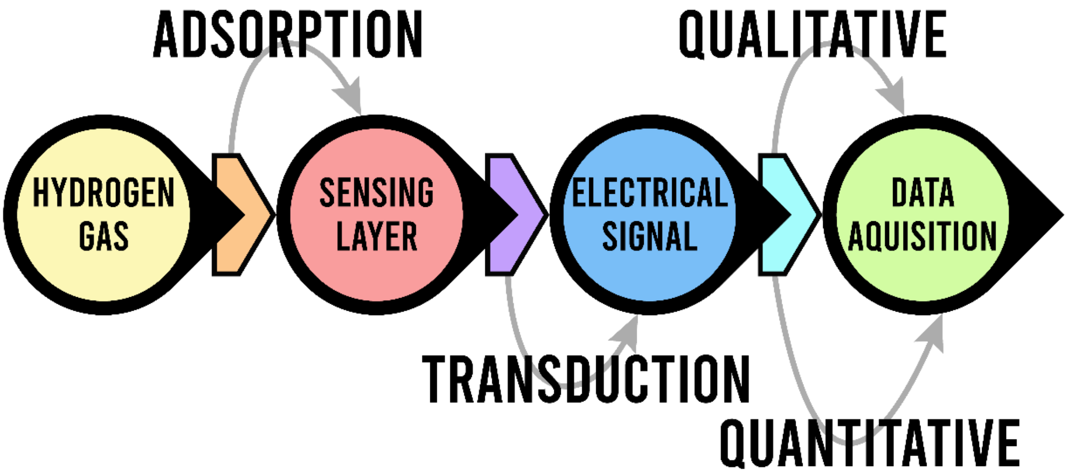

Figure 1: Operational diagram of a hydrogen sensor.

Demands and specifications for Hydrogen sensors

As outlined by Hübert et al. the demands for hydrogen sensors can be summarised as follows [1]:

- Low cost (<100€ per system)
- Low power consumption
- Small size
- Simple system integration and interface
- Simple operation and maintenance with long service interval
- Safe performance e.g. Explosion proof sensor design and protective chassis/housing
- Reliable results of sufficient accuracy and sensitivity (uncertainty <5-10% of signal)
- Fast recovery and response time (<1s)
- Long lifetime (>5 years)
- Low cross sensitivity (e.g. hydrocarbons, hydrogen sulfide, carbon monoxide)
- Stable signal with low noise
- Indication of hydrogen in the concentration range of 0.01-10% (Safety) or 1-100% (Fuel cells)
- Robustness including low sensitivity to environmental parameters such as: Temperature (1-30-80°C [safety], 70-150°C [Fuel cells]), Pressure (80-110 kPa), relative humidity (10-98%) and gas flow rate.

Table 1: *Target specifications for hydrogen sensors. Adapted from* [2].

Parameter	Value
Measurement Range	0.1-10%
Operating Temperature	-30 to 80°C
Response Time	< 1s
Accuracy	5% of full scale
Gas Environment	Ambient air, 10-98 Relative humidity %
Lifetime	10 Years
Interference	Resistance

Types of sensors

In this section we will look at five of the main types of hydrogen sensors that are commercially available on the market. Although five are included here there have been reports of other sensor types either available or emerging to market. For example, Hubert et al. has subdivided the different types of hydrogen sensors into 8 main categories:

1. Acoustic.
2. Optical.
3. Mechanical.
4. Resistance based.
5. Thermal conductivity.
6. Catalytic.
7. Electrochemical.
8. Work function based.

Whereas authors such as Pham and brown have subdivided the sensor types into ones that utilise 2D materials.

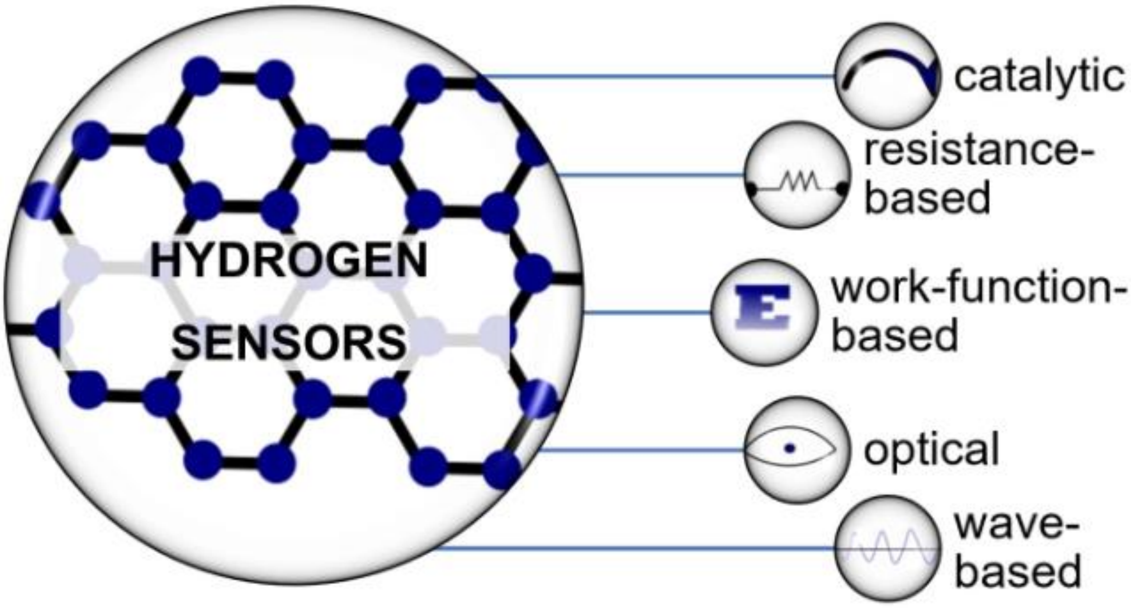

Figure 2: Different types of sensors that employ 2D materials. Adapted from (Pham and Brown, 2020).

Electrochemical sensors

Electrochemical sensors work as an electrical current passes through a sensing electrode produced by an electrochemical reaction. This takes place at the surface of the sensing electrode coated with a type of catalyst i.e. platinum. An electrochemical sensor in theory is basically a metallic anode and a metallic cathode submerged in an electrolytic solution to allow ion transportation between both the electrodes. Usually, electrochemical sensors have two or three different electrode configurations with a membrane for gas transport, the electrical current being proportional to the hydrogen concentration and this current can be measured to determine gas concentration. Sometimes the electrolyte is a solid polymer, which removes the possibility of leakage that may occur in the use of liquid electrolytes. Potentiometric and amperometric sensors are the two main configurations of electrochemical sensors.

Amperometric- Work at a constant applied voltage and the sensor signal is a current.

Pententiometric- Operate at zero current and the sensor signal is the potential difference between the sensing electrode and a reference electrode.

An advantage of electrochemical sensors is that they are well established commercially, their high sensitivity to hydrogen and they consume very little power. Additionally, they are quite cost-effective and have very good precision. One significant disadvantage to electrochemical sensors is that their high sensitivity to hydrogen decreases over time due to the degradation of the electrochemical catalyst, being easily contaminated by process gases. Additionally, they have moderate selectivity and work with a restricted temperature range.

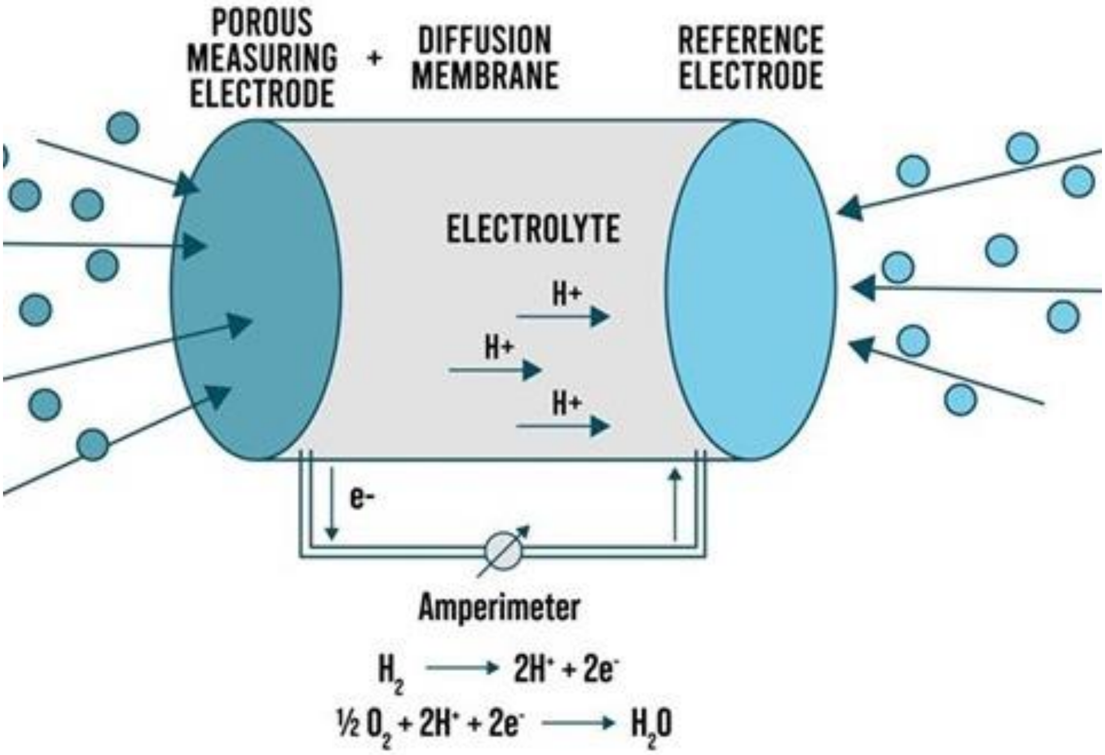

Figure 3: *Schematic of an electrochemical hydrogen sensor measuring principle.*

Thermal conductivity sensors

Thermal conductivity sensors operate on the principle of temperature induced change of an electrically heated sensing element. Thermal conductivity is a property for each gas. Readings are positive for hydrogen, using air as the reference gas. The reason for this is because the thermal conductivity coefficient for hydrogen at normal conditions (273K and 101325 Pa) is the greatest of all known gases. As shown in figure 5 below, a thermal conductivity sensor measures a concentration os a gas in a binary mixture by measuring the thermal conductivity to the reference gas. Thermistors are used to form the sensing element, one in contact with the sample gas and the other one in contact with the reference gas. The sensing element temperature, that determines the electrical resistance, is conditioned by the heat loss through the surrounding gas, the sensor signal being a change in resistance. This change is proportional to the hydrogen concentration in the gas mixture.

An advantage of thermal conductivity sensors is that they are very stable devices as there is no chemical interaction. This ultimately means that they are much less susceptible to contamination. Additionally, they are highly accurate, reliable, have a long operational life (>5 years) and have a wide hydrogen detection range (<1-100% H_2).

However, there are some disadvantages to using this type of sensor. For example, thermal conductivity sensors have difficulty in detecting low concentrations of hydrogen gas. Due to this, they are usually coupled with other types of hydrogen sensors. As they also have a low gas selectivity, this creates a problem in process applications but not when only a combustible gas is present.

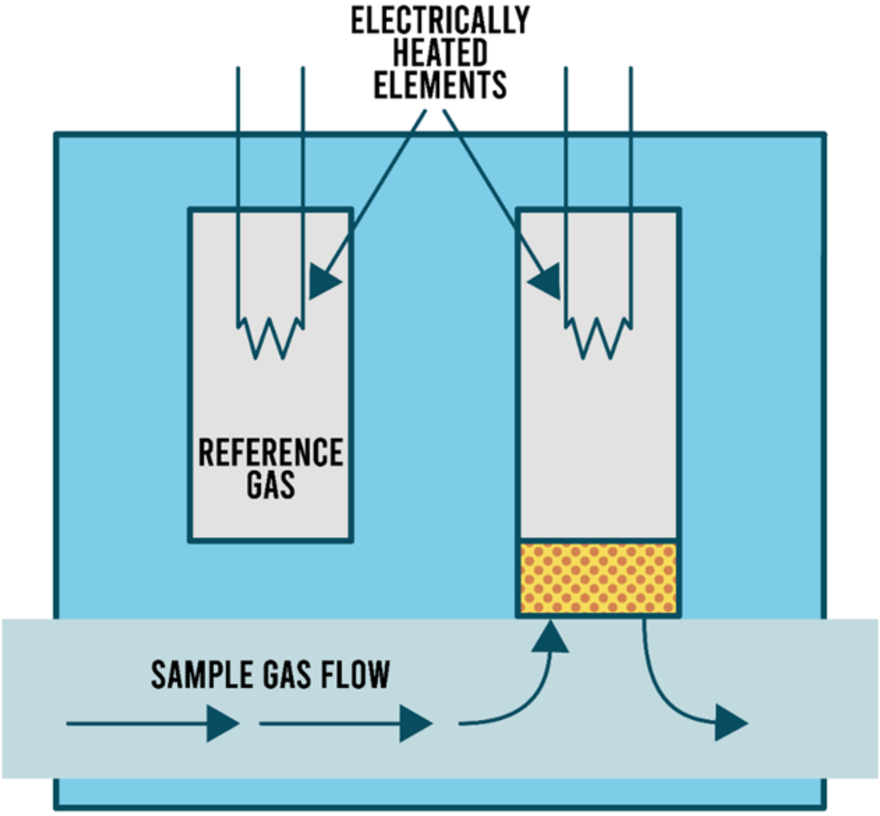

Figure 4: *Schematic of a thermal conductivity sensor.*

Catalytic sensors

Catalytic hydrogen sensors are based on gas oxidation on the surface of a catalytic elemtn electrically heated. This oxidation uses the oxygen of the air and causes a temperature increase on the sensing element, which depends on the gas concentration. He most common type of detector is the pellistor type, formed by two ceramic beads with platinum wires embedded, one of them being coated with a catalyst material in which hydrogen oxidate occurs. The gas oxidation produced a temperature increase on the catalyst bead, causing a change in electrical resistance of the platinum wire, also acting as the heater, which is a measure of gas concentration.

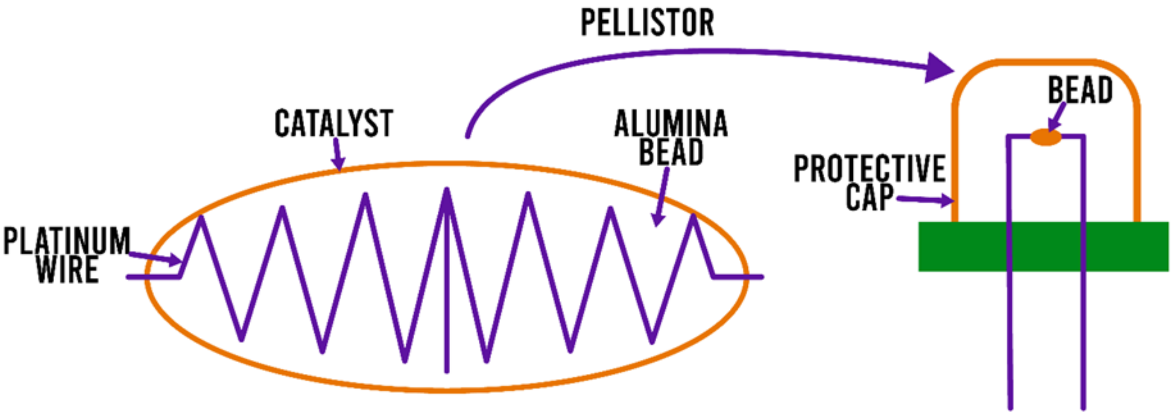

Figure 5: *Pellistor Schematic.*

The heated wire is contained within an ex-certified enclosure with a porous sintered metal inserted that allows the gas to enter. To measure these changes, both pellistors are connected to each other in what is known as a wheatstone bridge as seen in Figure 7 below. Another type os catalyst sensor, the thermos electric sensor, is based on the same principle of generating an electrical signal by a catalysed exothermic oxidation reaction of hydrogen but, in this case, it uses the thermoelectric effect, which basically consists of a direct conversion of temperature difference to electrical voltage , to generate the electrical signal.

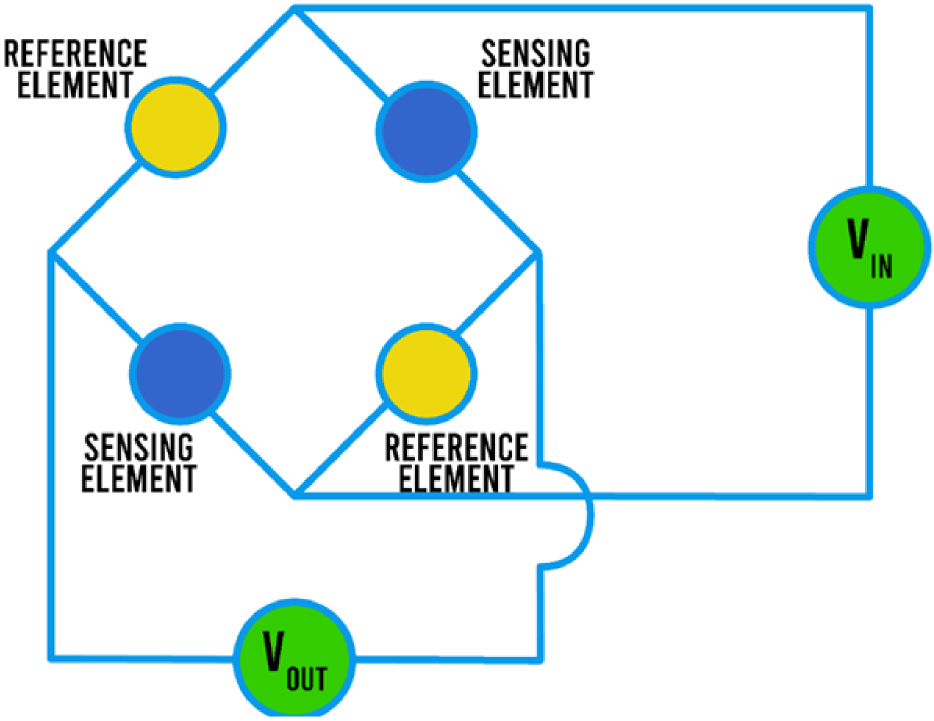

Figure 6: *Catalytic sensor measure principle.*

A big advantage to using Catalytic sensors is that they have a well-developed technology and it can be used to detect any combustible gas. These detectors are small and are used for detecting flammable gases from 0% to 100% lower explosion limit (LEL).

One thing to note is that catalytic sensors are not exclusive to hydrogen. This means that often they cannot differentiate between combustible gases. Oxygen presence is required for their operation, and it is not recommended above the lower explosion limit. Additionally, they can give false readings in gas-rich atmospheres, e.g. above the upper explosion limit (UEL). The catalyst can also be poisoned by trace gases such as hydrogen sulfide and silicones and subsequently, requires regular calibration and replacement.

Semiconductive metal-oxide sensors

The operating principle of metal-xoide sensors (MOX) is that a surface interaction between a reducing gas and a gas-senitive semiconductor modifies the conductivity of the latter. Basically, a metal oxiden film is applied on a substrate material between two electrodes, which shows sensitivity toward hydrogen gas (as shown in Figure 8 below). The change in electrical conductivity of the semiconductor is a measure of concentration of hydrogen gas.

An advantage of using a MOX detector is that they can have a fast response time and acceptable lifetime. Additionally, it is a low cost, small senor type and has tolerable power consumption.

One significant disadvantage is that MOX sensors are very sensitive to water vapour and many other gases that may produce a false reading and they are not considered selective devices. Additionally, they have a long and nonlinear response time, being susceptible to contamination as well.

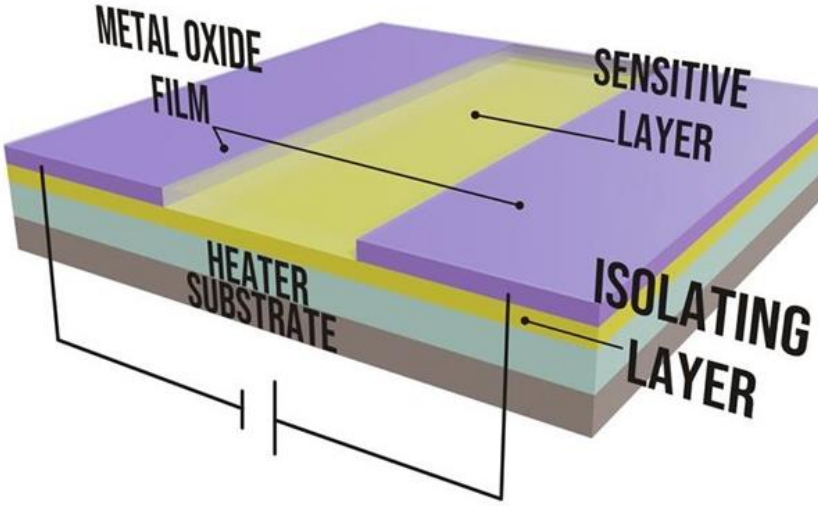

Figure 7: *Schematic of a metal-oxide hydrogen sensor.*

Optical Hydrogen sensors

Optical sensors are based on an optically active material that transforms the hydrogen concentration to an optical signal. They are adequate to operate in explosive atmospheres because they are electrically isolated. There are many types of optical sensors, the most referenced being the devices based on optical properties of palladium films. The exposure to hydrogen produces a dimensional change in this metal, causing a modification in its effective optical path, which is proportional to the hydrogen concentration. Thus, variation techniques employed to measure this dimensional change, for example interferometric or reflectivity measurement.

An advantage of using the optical sensor is that it eliminates the risk of providing a source of ignition in the place of the leak because it is an optical signal rather than electrical and due to its configuration in the field it could cover a wide monitoring area using only one device. Besides, it is less sensitive to electromagnetic noise than other and may operate in the absence of oxygen.

On the other hand, a disadvantage is that optical sensors may be sensitive to interference from ambient light and to temperature changes.

Ultimate comparison of Hydrogen sensor technologies

When considering what type of hydrogen sensor should be employed, one should consider using a comparison table. The typical characteristics and information relating to the five main types of hydrogen sensors are summarised in Table 2 below. Additionally, this table provides technical data of the different sensors that are commercially available.

***Table 2:** Overview of Hydrogen sensor type technologies.*

	Operating Principle	**Sensor Type**				
		Electrochemical	**Thermal Conductivity**	**Catalytic**	**MOX**	**Optical**
		Electrical Current	**Temperature Change**	**Temperature Resistance**	**Conductivity Change**	**Optically active material**
Performance	**Lifetime (years)**	2	>5	>5	2-4	<2
	Selectivity	Acceptable	Low	Low	Low	--
	T_{90} (seg)	<30	<15	<20	<30	<60
	Measuring Range (vol%)	<4%	<1-100%	<4%	<2%	0.1-100%
	Humidity Influenced	Yes	Yes	No	Yes	No
	Temperature Influenced	Yes	Yes	No	Yes	Yes
	Power Consumption	Low	Low	Tolerable	Tolerable	Tolerable
	Cost	Good	Low	Low	Low	High
Characteristics	**Advantages**	1.Well-established commercially 2. Good level of precision 3. Small in size	1. Stable devices 2. Small in size	1. Well Developed technology 2. Small in size	1. High sensitivity 2. Small in size	1. Wide area of operation 2. Not electromagnetically influenced 3. No source of ignition
	Disadvantages	Easily contaminated	1. Difficulty in detecting very low concentrations of Hydrogen	1. Regular calibration needed 2. Can be poisoned by trace gases 3. Can Give False readings	1. Non-linear response time 2. Susceptible to contamination 3. Can give false readings	Sensitive to ambient light interference
	Common applications	Leak detection + Process monitoring	Process monitoring	Leak detection	Leak detection	Leak detection

START OF BLOCK 2

Maintenance of Hydrogen sensors

In hydrogen sensors, the sensing element is the sensitive element responsible for converting a physical measure such as hydrogen concentration into a useful output signal. On the other hand, a transducer turns the output signal into meaningful information displayed by the user interface. The performance of most hydrogen detectors deteriorates with time, the rate of deterioration depending on the type of hydrogen sensor and the operating conditions. Sensing element aging may cause drift in time. Subsequently, maintenance is therefore essential for keeping hydrogen detectors at a high-performance level and is required for safe use. In regard to the information stated, detectors should be:

- Calibrated (zero and sensitivity adjusting) with a standard gas in accordance with the procedure outlined in the instruction handbook.
- Regularly cleaned, especially the head of the detector, to allow gas to reach the sensitive element.
- Regularly inspected for possible malfunctions, visible damages or other types of deterioration.

Hydrogen sensor Calibration

With regards to hydrogen sensors, calibration needs to be a function relating to the concentration of hydrogen and the sensor’s signal. Additionally, it should allow the obtaining of a reference to determine the accuracy of the sensor. In an ideal scenario, a linear response is expected but each type of sensor technology has its own unique response. This fact is clear when electrochemical, semiconductor and catalytic sensors are compared [1]. This can be seen in Figure 10 below, whilst also comparing with the linear and non-linear response in Figure 9. In Figure 10, the first one has a linear response while a nonlinear response appears for electrochemical and semiconductor sensors. When high hydrogen concentrations occur, a nonlinear response of a sensor causes its sensitivity to decrease. This fact has to be studied when a sensor technology is to be chosen for a given application.

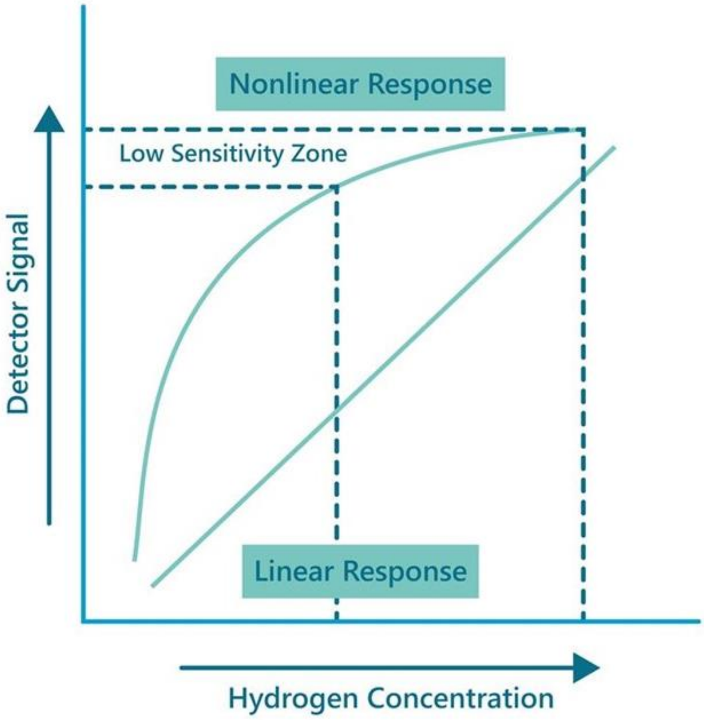

Figure 8: *Comparison of a nonlinear and linear response for a hydrogen sensor related with calibration operation.*

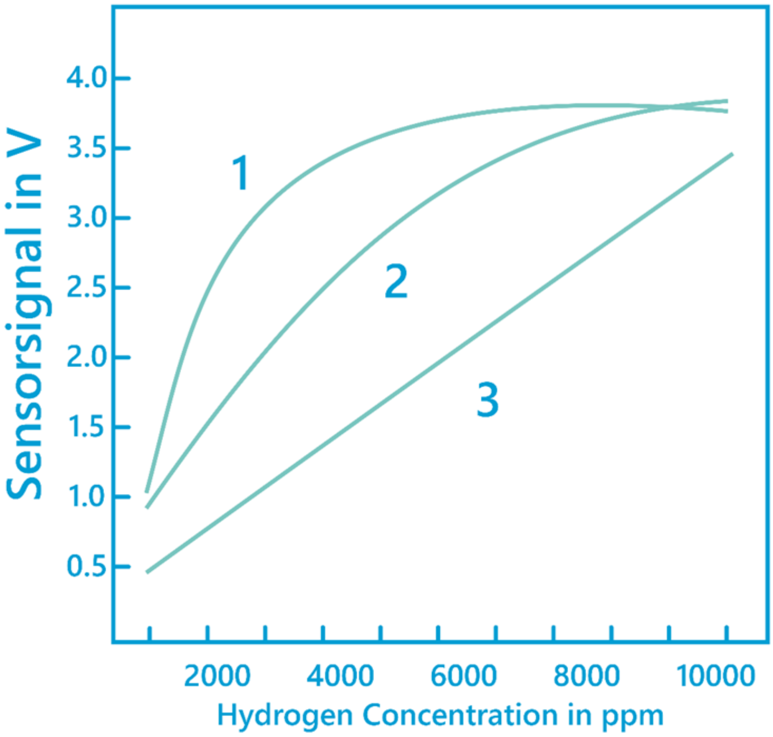

Figure 9: *Calibration curve of three different hydrogen sensors over the concentration range of 0.1-1%; 1) Semiconductor sensor, 2) Electrochemical sensor, 3) Catalytic combustion sensor.*

START OF BLOCK 3

Importance of Hydrogen detection

Knowledge and awareness of the properties of Hydrogen is essential for detection, as most of the hazards of hydrogen are related back to its properties. This block covers the importance of hydrogen detection with regards to gas and flame detection, how this relates to the properties and the need for appropriate choice of sensor type and sensor location. Block 1 lists the types of hydrogen gas detection sensors.

Hydrogen Properties

The key parameters are summarised below:

- Hydrogen has a flammability limit in air of 4% to 75% by volume.
- Hydrogen is 14 times lighter than air and rises at 20 m/s under ambient conditions.
- Hydrogen is a small molecule and diffuses rapidly in air – four times faster than methane.
- Hydrogen is a small molecule and leakage rates are four times higher than methane.
- Hydrogen has a low ignition energy and may be triggered by spark, heat, or sunlight.
- Hydrogen burns with a pale blue flame, which is almost invisible in daylight.
- Hydrogen flames have low radiant heat and so are not felt at a distance.
- Hydrogen is colourless.
- Hydrogen is odourless.

Gaseous hydrogen

At standard temperature and pressure (STP1) hydrogen is a colourless, odourless, tasteless gas. For this reason, human senses cannot easily detect hydrogen leaks. As a method to aid leak detection of other gases – e.g., natural gas, odorants such as Mercaptans are used; however, these cannot be added to hydrogen systems as they will contaminate/poison hydrogen technologies such as fuel cells. Additionally, hydrogen molecules are smaller in size when compared to those of known odorants and this means that hydrogen can leak through openings that the odorant molecules are not able to pass through, meaning that this technique would be ineffective. Hydrogen gas moves away from the source of leak faster than any odorants due to its buoyancy/high dispersion coefficient. Although hydrogen is non-toxic and non-corrosive it can cause danger to human life by diluting oxygen in the air below the concentration levels necessary to support life – this is known as asphyxiation. Hydrogen is also the lightest of all known gases and it has a relatively high flow rate if it leaks through seals, fittings or porous material. Hydrogen is a flammable compound, therefore a build-up hydrogen gas, as well as leading to asphyxiation risk can lead to a high risk due to the flammable atmosphere. For these reasons hydrogen detection is essential wherever hydrogen is being employed.

Types of hydrogen fire/flames

Hydrogen produces only water vapour during its combustion, but no smoke, with the exception when other flammable materials are also involved in the fire. The adiabatic flame temperature of hydrogen is 2403K. An obvious hazard resulting from this property is severe burns of people directly exposed to hydrogen flames. Compared to hydrocarbon combustion, hydrogen flames radiate significantly less heat. Thus, a human physical feel of this heat does not occur until direct contact is made with the flame. A hydrogen fire may remain undetected and will propagate in spite of any direct monitoring by people in the areas where hydrogen can leak, spill or accumulate and form potentially combustible mixtures. The hazards associated with thermal radiation are smaller compared to hydrocarbon based fuels. The danger, which may lead to severe burns, is in the poor visibility of hydrogen flame in daylight, when hydrogen flames are detectable through a direct contact.

Hydrogen Flame Detection

A fire detection system is typically configured to provide a visual or audible alarm and activate a fire suppression system. There are numerous methods to detecting a fire based on the following:

Heat detection	Frangible bulbs
Rate compensated heat detectors	Fusible plugs
Linear heat detection (cables routed through fire risk areas)	Ionisation smoke detection
Optical Smoke (line of sight/obscuration) detection	High speed and high sensitivity smoke detection
Optical flame detection (IR and UV and combined IR-UV)	Gaseous products of combustion detection; e.g. Volatile organic compounds (VOC), Carbon monoxide

CCTV based systems	

Due to the nature of hydrogen flames radiating significantly less heat compared to their hydrogen counterparts when combusted, human physical perception of this heat does not occur until direct contact is made with the flame. Thus, hydrogen fires may remain undetected and propagate in spite of any human direct monitoring in the areas where hydrogen can leak, spill or accumulate, forming potentially combustible mixtures. Hydrogen fire detectors can help to take the immediate actions in these situations. Hydrogen fire detectors can be either fixed for continuous monitoring of remote operations or portable for field operations. The most common types of hydrogen detectors are summarised in the table below.

Advantages and disadvantages of H_2 flame detection technologies

Type	Advantages	Disadvantages
UV/IR	• Low false alarm rate • Moderate Sensitivity • Moderate Speed • Automatic self-test • Not blinded by CO_2 fire protections discharges	• High-cost • False alarms possible in case combination of IR and UV sources • Blinded by thick smoke and vapours
Triple IR	• Very high sensitivity • Very high speed	• High-cost
IR/vis Imaging	• Images the flame • Used by the likes of NASA	• High-cost

UV Detectors

UV systems are favoured to IR because they are extremely sensitive. Additionally, the probability of encountering an interfering signal is lower as long as UV detectors are shaded from sun light. Their disadvantages are the cost and their reduced efficiency with liquid hydrogen flames as it fogs and blocks UV rays. False alarms can be released by random UV sources such as lightening or arc welding. The ability of the detector to distinguish between sunlight induced UV radiation from hydrogen flames to avoid false alarms is the main challenge.

Subsequently, various techniques can be applied:

- Use of a filter to cut any wavelength >0.29µm to keep wavelengths attributable only to a hydrogen fire accident. As a drawback, this solution also cuts down nearly 66% of the UV band and therefore decreases the detector accuracy.

- The use of two concomitant cells that watch the same zone. One of the cells mostly analyses the visible spectrum where the sunlight signal is predominant in comparison with hydrogen flame emitted signal whereas the other one focuses on the UV band. The UV signal from the UV cell is only taken into account if it diverges from the signal from the concomitant cell.

- The flickering behaviour of a flame can also be taken into account. In that case, the modulated part of the UV signal would be looked at. This technique may not be compatible with a fast response needed.

- Finally, if parasitic signals are known to be minor, a positive signal may be assumed whenever a given threshold is reached.

IR Detectors

Fog may hinder UV transmission to the sensor cell. However, IR detectors are not sensitive to these issues. Besides, hydrogen flames emit significant IR to use them for hydrogen flame detection. The main challenge remains the same as before that is to say to discriminate IR related to hydrogen fire from those of the sun, any light sources or any hot materials. IR sources powered with alternative electric currents can be filtered due to their own 100Hz modulated signal. However, neither hot bodies nor sunlight display a modulated signal that can be picked up and filtered. The solution consists in focussing on the 1.7 µm wavelength that corresponds to a peak emission of steam.

Thermal detectors & Imaging Systems

Thermal Detectors

Thermal detectors; for example, temperature sensors detect the heat of the flame. Thermal detectors work as rate of temperature rise or overheat devices to pick up radiative, convective or conductive heat. These reliable and tested detectors of various types are suitable for hydrogen fire detection means, as long as they are located close to where the fire breaks out. Such detectors need to be located very close to or at the site of a fire.

Imaging Systems

Imaging systems mainly are available in the thermal IR region and do not provide continuous monitoring with alarm capability. A trained operator is required to interpret whether the image being viewed is a flame. UV imaging systems require special optics and are very expensive. Other common fire detector types like those with ionising cells are not appropriate to detect hydrogen fires.

Location of Sensors

Location of a hydrogen sensor is one of the most crucial issues to consider when a sensor is to be utilised. The location of the sensor is directly related to the time of response.

The standard ISO/TR 15916:2015 “Basic considerations for the safety of hydrogen systems” [3] includes some suggested locations for hydrogen sensors:

1. Locations where hydrogen could accumulate
2. At hydrogen connections that are routinely separated (e.g. Hydrogen refuelling ports)
3. In building exhaust ducts, if hydrogen could be released inside the building
4. In building air intake ducts, if hydrogen could be carried into the building
5. Locations where hydrogen leaks or spills are possible

Aside from these five points that are outlined and the fact of knowing in depth the hydrogen system where a system of detection needs to be installed (pipe connections, forward/return pipes of ventilation systems), it is necessary to have other tools to be able to locate detectors in a proper way.

Figure 10: *Honeywell BW Solo Hydrogen (H2) Single Gas Detector.*

References

[1] T. Hübert, L. Boon-Brett, G. Black, and U. Banach, “Hydrogen sensors - A review,” *Sensors and Actuators, B: Chemical*, vol. 157, no. 2, pp. 329–352, 2011, doi: 10.1016/j.snb.2011.04.070.

[2] G. Manjavacas and B. Nieto, *Hydrogen sensors and detectors*. Elsevier Ltd., 2016. doi: 10.1016/b978-1-78242-364-5.00010-5.

[3] “ISO - ISO/TR 15916:2015 - Basic considerations for the safety of hydrogen systems.” https://www.iso.org/standard/56546.html (accessed Aug. 30, 2022).