



Review

Detection of Contaminants in Hydrogen Fuel for Fuel Cell Electrical Vehicles with Sensors—Available Technology, Testing Protocols and Implementation Challenges

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Abstract: Europe's low-carbon energy policy favors a greater use of fuel cells and technologies based on hydrogen used as a fuel. Hydrogen delivered at the hydrogen refueling station must be compliant with requirements stated in different standards. Currently, the quality control process is performed by offline analysis of the hydrogen fuel. It is, however, beneficial to continuously monitor at least some of the contaminants onsite using chemical sensors. For hydrogen quality control with regard to contaminants, high sensitivity, integration parameters, and low cost are the most important requirements. In this study, we have reviewed the existing sensor technologies to detect contaminants in hydrogen, then discussed the implementation of sensors at a hydrogen refueling stations, described the state-of-art in protocols to perform assessment of these sensor technologies, and, finally, identified the gaps and needs in these areas. It was clear that sensors are not yet commercially available for all gaseous contaminants mentioned in ISO14687:2019. The development of standardized testing protocols is required to go hand in hand with the development of chemical sensors for this application following a similar approach to the one undertaken for air sensors.

Keywords: sensors; hydrogen quality; FCEV; testing protocols



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1. Introduction

Hydrogen can be used as a feedstock, a fuel, or an energy carrier and storage, and has many applications across transport, industry, power, and buildings sectors [1]. Importantly, hydrogen does not emit carbon dioxide when used. Therefore, hydrogen can help to achieve a clean and affordable energy future. The number of countries with policies that directly support investment in hydrogen technologies is increasing, along with the number of sectors they target [2]. There are around 50 targets, mandates, and policy incentives in place today that support hydrogen directly, with the majority focused on transport [3].

Europe's low-carbon energy policy means, for example, greater use of fuel cells and technologies based around the use of hydrogen as a fuel. However, their competitiveness depends directly on their safety and the safety of the facilities where they are used. Sensing technology can ensure the safe and efficient implementation of the emerging global hydrogen market [4]. Sensors can be used to prevent hydrogen from reaching flammable levels by triggering alarms and activating ventilation or shutdown of systems [5]. Therefore, hydrogen sensors are an important enabling technology for the safe use of hydrogen. Sensors could even have other applications, such as contributing to ensure the lifetime of fuel

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cell electrical vehicles by warning if the hydrogen quality is not adequate. Here, chemical sensors that respond to a particular analyte in a selective and reversible way can be used in order to indicate the presence of impurities that may be harmful to the Fuel Cell Electrical Vehicle (FCEV). Commonly, the quality of the hydrogen dispensed at a Hydrogen Refueling Station (HRS) is controlled according to different standards such as ISO14687:2019 [6], EN17124:2020 [7], or SAE J2719:2011 [8] which include the following gaseous impurities to be monitored: water; total hydrocarbons; excluding methane; methane; oxygen; helium; nitrogen; argon; carbon dioxide; carbon monoxide; ammonia; formaldehyde; formic acid; total sulfur compounds; and halogenated compounds.

Guidance on the frequency of hydrogen fuel quality control is defined in the international standard ISO19880-8:2019 [9]. Currently, the quality control process is performed by offline analysis of hydrogen fuel. It consists of first collecting a sample at the nozzle of the HRS, the sample is then transported to a laboratory where analyses are performed. The complete process can take from a few days to several weeks, however, if this process has the advantage of allowing controlling the full compliance with the requirements in the international standards (ISO14687:2019 and ISO19880-8:2019). It is, therefore, beneficial to continuously monitor at least some of the contaminants onsite. In that sense, the implementation of sensors at the HRS is a promising solution, provided they function properly. Moreover, the cost of the sensors is also an important parameter. To be widely implemented at HRSs, it is here estimated that the cost for a sensor should not exceed 5000 euros but for the purpose of the study, we even considered sensors costing up to 10,000 euros.

Chemical sensors have gained increasing attraction for applications in environmental monitoring, industrial process monitoring, gas composition analysis, medicine, national defense, and public security [10]. Chemical gas sensors are already widely developed and used to monitor air quality with regards to ozone, nitric oxides [11], and carbon monoxide [12]. The Environmental Protection Agency (EPA) has been engaged in a variety of activities to help advance the understanding of air sensors [13]. In each application, a sensor's ability to perform the measurements must meet the end-user needs which must be identified and documented. The main metrological criteria for sensors include accuracy, baseline, cross-sensitivity or selectivity, drift, environmental effects, final indication, hysteresis, limit of quantification, linear range/measuring range, noise, operation range (temperature, pressure, and relative humidity), uncertainty, response/recovery time, reversibility, resolution, saturation, and sensitivity [14].

According to EPA, there are currently no standard testing protocols or targets to evaluate the performance of air sensors uniformly [15], so it is safe to assume that this is also the case for chemical sensors for hydrogen quality control. The lack of consistent testing protocols to evaluate the performance of air sensors makes it difficult to understand how air sensor data compares to that of regulatory instruments. Without these standard procedures, it is difficult to understand the performance of any given device and select sensors that are appropriately suited for a desired application.

The objectives of this paper are first to review the sensor technologies existing for species that need to be monitored in ISO14687:2019 [6] and EN17124:2020 [7], then to describe how the performance of these sensor technologies are/can be assessed, and finally to discuss how they can be implemented and calibrated at a HRS. Sensors for detecting hydrogen have already been subject to reviews. An example of these reviews is the H2Sense database [16], which contains more than 400 different models of hydrogen sensors. The review focuses solely on sensors for ISO14687 impurities in hydrogen.

2. Chemical Sensors for Detecting Contaminants in Hydrogen

Chemical sensors respond to a particular analyte in a selective and reversible way. Sensors are defined primarily by the mechanism by which the targeted impurity interacts with the sensing element to produce an electrical signal. Another way to categorize the chemical sensors is based on the object to be detected (gas, humidity, biological samples, etc.). There are many different types of gas sensors (semiconductor gas sensor, electrochem-

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ical gas sensor, optical gas sensor, polymer gas sensor, contact combustion gas sensor, etc.) and humidity sensors (resistance sensor, capacitive sensor, etc.). As hydrogen is a relatively new sector for sensors, manufacturers mainly propose existing solutions for other matrices (i.e., nitrogen or air). It is, therefore, important to perform an in-depth review with the manufacturer into the suitability of the sensor for a hydrogen matrix. For example, H2S-B4 and CO-B4 sensors from Alphasense have been tested during the MetroHyVe project [17]. The results showed the sensors were directly overloaded in hydrogen matrix. The supplier indicated in the specifications a cross sensitivity for CO-B4 with hydrogen lower than 50 at 100 µmol/mol; this value is relatively high if compared, for example, to the indicated cross sensitivity for ethylene at 100 µmol/mol, which is below 1 [18]. Therefore, in-depth discussions with the manufacturer may have identified the likelihood of the saturation when used for hydrogen and the low potential of these sensors for hydrogen matrices. If a commercial sensor designed for another matrix gas is to be used for hydrogen application, it is important to ensure that the hydrogen itself will not give rise to a signal before further testing. Moreover, as hydrogen's flammability range is very wide, with a lower explosive limit (LEL) of about 4% and an upper explosive limit (UEL) of about 75%, it is preferable that the sensors are intrinsically safe. In the sections below, we described sensors that can be used in a hydrogen matrix and can detect a given impurity at relevant detection limits (below the thresholds in ISO14687:2019 [6] and EN17124:2020 [7]).

2.1. Electrochemical Sensors

Electrochemical sensors are based on electrochemical reactions within the sensor between the gas present and the electrolyte, which produces a current. The different compositions of the electrolyte determine the selectivity and the sensitivity to target gases [19]. Among the gaseous impurities to be monitored in hydrogen, these sensors can mostly be used for oxygen. An example of sensors that are expected to work in hydrogen matrix is the electrochemical fuel cell TO2-133 $\mu\text{MOL/MOL}$ oxygen sensor from Southland Sensing [20]. According to the manufacturer, this sensor can detect as low as 0.001 $\mu\text{mol/mol}$ oxygen with a response time (T90) of 7 s. Another sensor for oxygen is the EC91 from Systech Illinois [21]. At the cathode, oxygen is reduced to hydroxyl ions which oxidizes the metal anode where the following reaction takes place: $2\text{Pb} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{ Pb}(\text{OH})_2$. According to the manufacturer, the detection limit is 1 $\mu\text{mol/mol}$ and response time (T90) is 20 s. The OxyTrans II and Oxymaster II from DKS GmbH are other alternatives [22].

2.2. Phosphorus Pentoxide Moisture Sensor

The principle of the measurement with a phosphorus pentoxide sensor is called coulometric hygrometry. Phosphorus pentoxide cells are used in the electrolysis of water vapor. This method is often considered to be a primary measurement method [23]. Electrodes are coated with a thin film of phosphorus pentoxide (P_2O_5). As the gas stream flows through the cell, moisture is attracted to the coating and migrates through the film to the electrodes. An electrolysis reaction (water to hydrogen and oxygen) occurs and generates, according to Faraday's law a current proportional to the concentration of the moisture [24]. Electrodes are commonly made of platinum, however, in specific conditions, platinum can act as a catalyst in a recombination reaction between the chemisorbed hydrogen and the oxygen from the electrolysis, which may lead to erroneous measurements (overestimation) in oxygen and hydrogen matrices. The use of rhodium for the electrodes eliminates this recombination reaction. One example of sensors able to function in hydrogen matrix is the Aquatrace series from DKS GmbH which can detect from 0.05 μmol/mol water according to the manufacturer [25]. Other examples are the Uber M-I sensor from Meeco, which is able to detect from 0.5 μmol/mol-vol of water and function in inert gases, oxygen, hydrogen and gas mixtures [26], and the HUMITRACE II from dr. Wernecke Feuchtemesstecknik GmbH [27].

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2.3. Aluminium Oxide Moisture Sensor

The operating principle of the aluminum oxide sensor is that its capacitance varies with the moisture concentration [28]. An aluminum layer on a ceramic support is anodized to form a thin, porous layer of aluminum oxide. The gold and the aluminum layers form the sensor electrodes. The gold layer is permeable to moisture and conductive. Water vapor in the gas stream is transported rapidly through the gold layer and equilibrates in the aluminum oxide pore walls, affecting the dielectric constant of the material and as a result, the capacitance of the unit [23]. The sensor is capable of both μ mol/mol and dew point measurements in most industrial gas streams, including hydrogen. Examples of aluminum oxide moisture sensors for hydrogen matrix are the MM300 [29] and MM400 systems from Systech Illinois [28], the AquaXact 1688 from Servomex [30], and the IQ probe [31] and HygroPro [32] from General Electric.

2.4. Chilled-Mirror Hygrometer

Chilled-mirror hygrometers operate by directly measuring the dew-point temperature (the temperature to which a volume of gas must be cooled at constant pressure to become saturated with water vapor) of a gas stream [23]. Consequently, any cooling below the dew-point temperature causes the excess water to condense, and this can then be detected optically on a mirror surface. Since the dewpoint temperature is a fundamental thermodynamic property, chilled-mirror hygrometry is considered an absolute measurement method and is also used widely as a calibration and transfer standard. However, it seems that the costs for this technology is above the target of 5000 euros. Examples of chilled-mirror hygrometers for hydrogen matrix are the Cong Prima 2M [33], the FAS-W [34], and the Hygrovision [35] from Vympel.

2.5. Surface Acoustic Wave

Ball Wave Inc. has developed a moisture analyzer based on the principle of non-diffraction propagation of surface acoustic waves (SAWs). The sensor [36] consists of a spherical single-crystal α -quartz which is a piezoelectric material that converts electrical signals to mechanical vibrations and vice versa. Electrodes are manufactured on the surface of the sensor by depositing a metal thin film called an interdigital transducer (IDT). When electrical signals are fed into the IDT, a mechanical vibration, called a Rayleigh wave, is generated and propagates along the surface. A thin layer of amorphous silica deposited on the ball SAW sensor has an ability to absorb and desorb water molecules. The amount of water molecules contained in a gas can be estimated by measuring the changes either in the velocity or in the attenuation of the Rayleigh wave propagating around the surface of the ball SAW sensor.

2.6. Chemical Optical Sensor

The principle of a chemical-optical sensor is based on the effect of dynamic luminescence quenching by molecular oxygen. Quenching refers to any process which decreases the fluorescence intensity of a given substance. The collision between the luminophore in its excited state and the quencher (oxygen) results in radiationless deactivation. After collision, energy transfer takes place from the excited indicator molecule to oxygen which consequently is transferred from its ground state (triplet state) to its excited singlet state. As a result, the indicator molecule does not emit luminescence and the measurable luminescence signal decreases. PreSens has developed oxygen sensors based on this principle which have a detection limit of $0.5~\mu mol/mol$ [37].

2.7. Proton Exchange Membrane Type Sensor

The concept of Proton Exchange Membrane (PEM) type sensors is being tested by Los Alamos National Laboratory as part of a project having as scope to develop a device using a membrane electrode assembly to measure impurities in a dry fuel stream of hydrogen at and above the SAE J2719 levels [8] with a quick response (t < 5 min). A Nafion based

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electrochemical hydrogen contaminant detector was tested at a HRS in Burbank, USA with promising results (effective detection of CO down to 1 μ mol/mol). To our knowledge, none of these sensors are yet commercially available. The sensitivity for 200 nmol/mol carbon monoxide in dry hydrogen of these types of sensors has been demonstrated [38].

2.8. Analysers

There are many other analytical principles to detect impurities, such as water, hydrocarbons, oxygen, helium, nitrogen, argon, carbon dioxide, carbon monoxide, ammonia, formaldehyde, formic acid, total sulfur compounds, and halogenated compounds in hydrogen matrix. Examples of those are spectrometry laser photoacoustic, tunable diode laser absorption spectroscopy, Fourier transformed infrared spectroscopy, cavity ring-down spectroscopy, optical feedback cavity enhanced absorption spectroscopy, broadly tunable laser technique, tunable diode laser, etc. These methods are considered here as belonging to the category of gas analyzers; however, the classification of sensors or analyzers is not always clearly defined and described in detail. Information about all these methods can be found in a report recently written as part of the European project "MetroHyVe2" [39].

2.9. Sensors Overview for Hydrogen Fuel Quality

The information about the sensors described in the previous sections is summarized in Table 1. The table just shows the sensors that have been identified so far however, other sensors (with the same technology or other technologies) are probably available as well as other sensors manufacturers.

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Table 1. Information about available sensors for impurities in hydrogen classified by technologies.

Technology	Supplier (Compound)	Model	Response Time (T90)	Selectivity	Sensitivity/Range	Stability	Temperature Range (°C)	Pressure Range (bar)	Flow Rate	Costs
Electrochemical sensor	DSK GmBH (O ₂)	OxyTransII or Oxymaster II	<45 s	n.c.	n.c.	n.c.	0 to 50	0.1 to 1	n.c.	+
	Southland Sensing Ltd. (O ₂)	TO2-133	7 s	n.c.	O ₂ : 0 to 10 µmol/mol	No info	0 to 50	n.c.	15–150 l/h	++
	Systech Illinois (O ₂)	EC91	20 s	n.c.	O ₂ : 1 to 20 μmol/mol	No info	0 to 40	0.1 to 1, up to 17 with optional sample system	1.8 to 300 l/h	0
Chemical- optical sensor	Presens (O ₂)	Oxy-1 SMA- trace-RS232	n.c.	n.c.	O ₂ : down to 0.5 μmol/mol	n.c.	n.c.	n.c.	n.c.	+
Phosphorus pentoxide moisture sensor	DKS (H ₂ O)	Aquatrace IV	Dry to wet: <5 s Wet to dry <15 min	<10 µmol/mol H2S	H ₂ O: 0.05 to 2000 μmol/mol	n.c.	5 to 65	Approx 0.2 above the measuring cell inlet	20 or 100 Nl/h	+
	DSK GmBH (H ₂ O)	Aquatrace ATT500	Dry to wet: <5 s Wet to dry <15 min	Not compatible with ammonia	H ₂ O: 0 to 500 μmol/mol	n.c.	-10 to 60	0–20	1–300 Nl/h	+
	Systech Illinois (H ₂ O)	MM50	Within 60 s	n.c.	H ₂ O: 0.1 to 1000 μmol/mol	No info	n.c.	n.c.	n.c.	n.c.
	MEECO (H ₂ O)	Uber M-I	5 min		H ₂ O: 0.5 to 5000 μmol/mol		0 to 60	0.2 to 7		+
	Systech Illinois (H ₂ O)	MM300	<5 min	Annual calibration recommended	Dewpoint: -100 to 20 °C	No compatible with HCl, NH3, Cl2	-40 to 60	450	30 to 420 N1/h	+
	Dr. Wernecke (H ₂ O)	Humitrace II			H ₂ O:0 to 2000 μmol/mol	n.c.	5 to 65	1 to 5	20 Nl/h, 100 Nl/h	
Chilled mirror	Vympel (H ₂ O)	Cong Prima 2M	5–15 min (0.3–2 Nl/min)	"No drift"	Dewpoint: -30 to 30 °C	n.c.	n.c.	160–300	0.3 to 2 Nl/min	00
	Vympel (H ₂ O)	FAS	5–15 min	n.c.	Dewpoint: -80 to 60 °C (3 different ranges)	n.c.	-20 to 80	<100	0.2 to 2 NI/min	00
	Vympel (H ₂ O)	Hygrovision	n.c.	n.c.	Dewpoint: -50 to 30 °C	n.c.	-10 to 50	<100	0.2 to 2 Nl/min	
	Baker Hughes (H ₂ O)	Optica	n.c.	n.c.	Dewpoint: -80 to 15 °C (1311-XR)	n.c.	0 to35	1 to 8	0.25 to 2.5 l/min	00

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Table 1. Cont.

Supplier (Compound)	Model	Response Time (T90)	Selectivity	Sensitivity/Range	Stability	Temperature Range (°C)	Pressure Range (bar)	Flow Rate	Costs
Vympel (H ₂ O)	FAS-SW	n.c.	n.c.	Dewpoint: -100 to 20 °C (2 different ranges)	n.c.	-40 to 60	<300	0.5 to 5 Nl/min	
Baker Hughes (H ₂ O)	HygroPro	15 s	n.c.	Dewpoint: -110 to 20 °C	n.c.	-20 to 60	to 345	n.c.	+
Baker Hughes (H ₂ O) (aluminum oxide)	M Series Probe	n.c.	n.c.	Dewpoint: -110 to 60 °C overall in 3 ranges (ex: -110 to -50 °C)	n.c.	0 to 60	<0.01 to 345	n.c.	n.c.
Servomex (H ₂ O)	Aquaxact 1688	n.c.	n.c.	Dewpoint: −100 to 20 °C	n.c.	n.c.	n.c.	n.c.	n.c.
Ball Wave (H ₂ O)	FT-300WT	<1 s	n.c.	H ₂ O: 1–4000 μmol/mol	n.c.	10–40	Atmospheric pressure	0–1 l/min	0
	(Compound) Vympel (H ₂ O) Baker Hughes (H ₂ O) Baker Hughes (H ₂ O) (aluminum oxide) Servomex (H ₂ O)	(Compound) Vympel (H ₂ O) FAS-SW Baker Hughes (H ₂ O) HygroPro Baker Hughes (H ₂ O) M Series Probe (aluminum oxide) Servomex (H ₂ O) Aquaxact 1688	(Compound)Model(T90)Vympel (H_2O)FAS-SWn.c.Baker Hughes (H_2O)HygroPro15 sBaker Hughes (H_2O) (aluminum oxide)M Series Proben.c.Servomex (H_2O)Aquaxact 1688n.c.	(Compound)Model(T90)SelectivityVympel (H_2O)FAS-SWn.c.n.c.Baker Hughes (H_2O)HygroPro15 sn.c.Baker Hughes (H_2O) (aluminum oxide)M Series Proben.c.n.c.Servomex (H_2O)Aquaxact 1688n.c.n.c.	(Compound)Model(T90)SelectivitySelectivitySelectivityVympel (H2O)FAS-SWn.c.n.c.Dewpoint: -100 to $20 ^{\circ}$ C (2 different ranges)Baker Hughes (H2O)HygroPro 15s n.c.Dewpoint: -110 to $20 ^{\circ}$ CBaker Hughes (H2O) (aluminum oxide)M Series Proben.c.n.c.Dewpoint: -110 to $60 ^{\circ}$ C overall in $3 ^{\circ}$ ranges (ex: -110 to $-50 ^{\circ}$ C)Servomex (H2O)Aquaxact 1688 n.c.n.c.Dewpoint: -100 to $20 ^{\circ}$ CBall Wave (H2O)FT-300WT -18 n.c.n.c.H2O: $1-4000$	(Compound)Model(T90)SelectivitySelectivitySelectivitySelectivityVympel (H2O)FAS-SWn.c. $n.c.$ <td< td=""><td>Compound)Model(T90)SelectivitySelectivitySelectivity/RangeStabilityRange (°C)Vympel (H2O)FAS-SWn.c.n.c.Dewpoint: -100 to 20 °C n.c.-40 to 60Baker Hughes (H2O)HygroPro15 sn.c.Dewpoint: -110 to 20 °C n.c.-20 to 60Baker Hughes (H2O) (aluminum oxide)M Series Proben.c.n.c.0 to 60 °C overall in 3 ranges (ex: -110 to -50 °C)n.c.0 to 60 °C overall in 0 ranges (ex: -110 to 0 over 0 considered and 0 ranges (ex: 0 to 0 °C)Servomex (H2O)Aquaxact 0 ranges (0 ranges)0 to 0 ranges (0 ranges)0 to 0 ranges (0 ranges)0 to 0 ranges (0 ranges)Ball Wave (H2O)FT-300WT0 ranges0 ranges0 ranges0 ranges0 ranges</td><td>Compound)Model(T90)SelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivityDewpoint: -100 to 20°Cn.c.$-40 \text{ to } 60$$<300$Baker Hughes (H2O) (aluminum oxide)HygroPro15 sn.c.Dewpoint: -110 to 60°C overall in 3 ranges (ex: -110 to -50°C)n.c.$0 \text{ to } 60$$<0.01 \text{ to } 345$Servomex (H2O)Aquaxact 1688n.c.n.c.Dewpoint: -100 to 20°Cn.c.n.c.n.c.n.c.Ball Wave (H2O)FT-300WT<18 n.c.n.c.<10.00 n.c.n.c.<10.00 n.c.Atmospheric pressure</td><td> Vympel (H2O) FAS-SW n.c. n.c. Dewpoint: -100 to 20 °C n.c. -40 to 60 <300 0.5 to 5 Nl/min </td></td<>	Compound)Model(T90)SelectivitySelectivitySelectivity/RangeStabilityRange (°C)Vympel (H2O)FAS-SWn.c.n.c.Dewpoint: -100 to 20 °C n.c. -40 to 60 Baker Hughes (H2O)HygroPro 15 sn.c.Dewpoint: -110 to 20 °C n.c. -20 to 60 Baker Hughes (H2O) (aluminum oxide)M Series Proben.c.n.c. 0 to 60 °C overall in 3 ranges (ex: -110 to -50 °C)n.c. 0 to 60 °C overall in 0 ranges (ex: -110 to 0 over 0 considered and 0 ranges (ex: 0 to 0 °C)Servomex (H2O)Aquaxact 0 ranges (0 ranges) 0 to 0 ranges (0 ranges) 0 to 0 ranges (0 ranges) 0 to 0 ranges (0 ranges)Ball Wave (H2O)FT-300WT 0 ranges 0 ranges 0 ranges 0 ranges 0 ranges	Compound)Model(T90)SelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivitySelectivityDewpoint: -100 to 20° Cn.c. $-40 \text{ to } 60$ <300 Baker Hughes (H2O) (aluminum oxide)HygroPro15 sn.c.Dewpoint: -110 to 60° C overall in 3 ranges (ex: -110 to -50° C)n.c. $0 \text{ to } 60$ $<0.01 \text{ to } 345$ Servomex (H2O)Aquaxact 1688 n.c.n.c.Dewpoint: -100 to 20° Cn.c.n.c.n.c.n.c.Ball Wave (H2O)FT-300WT <18 n.c.n.c. <10.00 n.c.n.c. <10.00 n.c.Atmospheric pressure	Vympel (H2O) FAS-SW n.c. n.c. Dewpoint: -100 to 20 °C n.c. -40 to 60 <300 0.5 to 5 Nl/min

n.c.: information not available or not communicated; The prices are indicated by ranges; ++: $<1000\cite{c}$; +: $1000-5000\cite{c}$; 0: $5001-10,000\cite{c}$; 0: $>10,000\cite{c}$.

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3. Implementation of Sensors at Hydrogen Refueling Stations

Challenges Related to the Location of Sensors at HRS

While continuous measurements have benefits for the quality control, it may prove difficult to find a location for the sensor offering a constant flow, as hydrogen flow at each point in the HRS system is coupled to events (i.e., refueling, maintenance, purge, and compression). This becomes even more obvious by looking at a sampling point near the nozzle. Here, a flow occurs only during the refueling process (in addition with a very high mass flow) while, most of the time, the hydrogen is static or even vented. Most HRS systems are designed to not continuously operate the production or the compression stage over longer time periods. A sensor requiring a continuous (low) flow rate is, therefore, dependent on alterations of the HRS system with a bleed line originating in the storage to ensure a stationary flow. This could be avoided by timing the measurements with the hydrogen flow. In this case, depending on the measurement point, the sensor response time has to be low to achieve more than one measurement during the operation period. Especially, warm-up procedures of sensors need to be short or planned accordingly.

Hydrogen refueling stations can have various designs depending on how the hydrogen is provided to the station (i.e., onsite production by electrolysis, tube-trailer, or pipeline delivery) and how the hydrogen is stored onsite (i.e., low-pressure bank, high-pressure bank, or compressors). These different designs will, in turn, provide a variety of scenarios (i.e., different critical components needed to be detected, different operational conditions such as pressure, or temperature or mass flow). Even if the measurement at the nozzle is the international standard requirement for quality control, it may prove difficult to implement sensors for evident safety reasons, as well as for technical reasons, as most sensors operate at low pressure.

Therefore, sensors need to be implemented in more suitable locations (see Figure 1) and the selection of sensors must be based on the probability of presence of the contaminants at these locations [40] as well as the actual operational conditions.

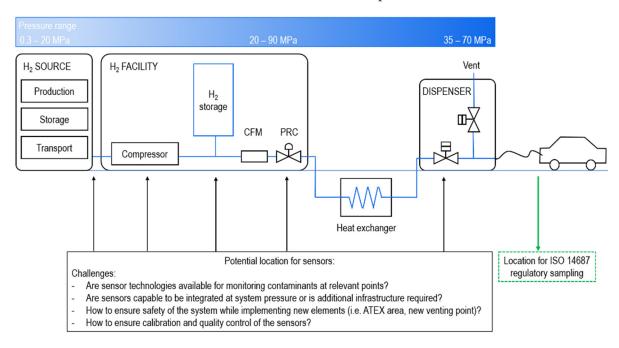


Figure 1. Scheme of a HRS station with potential locations for sensors and associated challenges.

A few specific locations/zones can be mentioned: at the onsite production or at the delivery by tube-trailer, at the storage bank, at the compression stage, or close to the nozzle. Each zone will have specific requirements in terms of contaminants and operational conditions (flow, pressure, or temperature). The choice of the sensors and their location should be made after developing a quality control plan as detailed in ISO 19880-8 [9].

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The onsite production or hydrogen delivery is challenging due to the variety of production methods (i.e., steam methane reforming, or electrolysis) that require a different set of sensors. For example, when hydrogen is produced onsite with a proton exchange membrane water electrolyzer, sensors for water and oxygen should be implemented after the production [40]. Production by electrolysis does not operate at high pressure (7–30 bar) and several sensors may be able to operate in these conditions (see Table 1). If hydrogen from steam methane reforming is delivered by tube trailer, it would require sensors to monitor carbon monoxide, methane, and nitrogen [40]. The tube-trailer pressure is around 200–250 bar, which is above what most of the sensors are rated for (except for some sensors for water). To implement sensors in this location, it will require a specific line with pressure reduction. Moreover, it will require handling the hydrogen released by the sensor which is at lower pressure and determine if it requires safe venting (i.e., explosive atmosphere or ATEX at the vent point in air) or a reintroduction at a low pressure point of the system (i.e., it may require additional compression steps).

Implementing sensors where hydrogen is stored (storage banks) benefits from a large volume of hydrogen and more stable conditions (pressure at 200 bar or 900 bar). If located at the bottom or top of the storage bank and if a really low number of refueling events occurs per day, segregation can occur as the gas is not moving into the system. Placing the sensors close to the outlet of the storage tank would, therefore, be more suitable as it better represents the hydrogen fuel going to the nozzle.

Only a few sensors are designed to operate at higher pressure (>100 bar). Examples of those are sensors for water, such as Systech Illinois (MM300) [29], General Electric HygroPro [32], or Vympel FAS-W [34]. Sensors for oxygen named in this study all operate at low pressure (<10 bar). Sensors after the compression stage are required to monitor potential leakages of components due to the compression itself (such as compressor oil). In that case, sensors for hydrocarbons would be best suited but these sensors will then need to operate at high-pressure or would require a bleed line. Depending on the type of compressors (i.e., ionic liquid, mechanical, cryogenic, metal hydride, electrochemical, or adsorption compressor), it may require other types of sensors to reflect the potential contaminants introduced during the compression sensors (i.e., liquid droplet or particulate).

In many cases, the implementation of sensors will require modification of the HRS hardware. Except for the ATEX classified sensors which, in addition, are suitable for high-pressure measurements, most sensors would require implementation on a dedicated line with pressure reduction, including at least a pressure relief valve and a shutoff valve to enable the isolation of the sensor. Sensors which are not ATEX classified must be implemented outside of the ATEX zone at the HRS and the line must include a safety vent for the exhaust, possibly with connections to reuse the exhaust gas if the measurement principle is non-destructive. In most systems, depressurized hydrogen could only be reintroduced back into the system by implementing a compression stage after the sampling point. This would then cause another possible contamination source for hydrogen. The implementation of a specific line for the sensor without the possibility to reuse the exhaust gas implies a loss of hydrogen and a new ATEX area linked to the safe venting of the sensor exhaust. Most of the sensors require a flow of 0.2 to 5 L/min. It would represent a release of 20 to 500 g of hydrogen per day if not reintroduced into the system. It is important information to consider especially for small HRS systems.

4. Performance Testing of These Sensor Technologies

Before implementing any sensor, it is crucial to ensure its performance has fully been validated. To identify sensor technologies that would be best suited for hydrogen fuel quality control, and to understand the performance of the sensor technologies, sensors must be tested according to testing protocols, preferably standardized. The performance attributes or metrics that need to be assessed are accuracy, baseline, cross-sensitivity or selectivity, drift, environmental effects, final indication, hysteresis, limit of quantification, linear range/measuring range, noise, operation range (temperature, pressure, relative

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humidity), uncertainty, response/recovery time, reversibility, resolution, saturation, and sensitivity [14].

The performance parameters are slightly different than classical laboratory analyzers, as defined in ISO 21087 (measurement uncertainty, precision, trueness, working range, limit of detection and quantification, selectivity, and robustness). It reflects the fact that the sensor will be implemented for a long period of time performing measurements continuously and requiring a control check and,, possibly calibration with relatively larger time intervals (not calibrated on a daily based as is the case with many laboratory analyzers).

4.1. Testing Protocols

A recent work [15] from EPA underlines the lack of standard testing protocols, metrics, or targets to evaluate the performance of air sensors uniformly. It is, therefore, safe to assume that the same applies to sensors for hydrogen quality control, which are not yet as commonly used as air sensors. This lack of guidelines leads to uncertainties of how well sensors perform, how to operate (e.g., calibrate) them, and how well they need to perform to be fit for a given purpose. To remediate this issue for air sensors, EPA just produces a technical report containing testing protocols, metrics, and target value for ozone air sensors which contains two parts: a base testing (in the field) and enhanced testing (in the laboratory). The enhanced testing consists of operating and examining at least three replicate ozone air sensors in controlled laboratory conditions to understand the effect of interferents, temperature, and relative humidity in addition to drift and accuracy at higher concentration levels [15]. The testing is performed in an exposure chamber that can control environmental conditions and requires the use of calibration cylinders (preferably reference materials) containing known amount of interferents.

ATSM WK64899 "New Practice for Performance Evaluation of Ambient Air Quality Sensors and Other Sensor-Based Instruments" [41] is under development within this ASTM Committee D22 (Air Quality). This standard intends to establish standardized tests and assessment criteria for the performance evaluation of sensor-based continuous instruments for ambient air quality measurements. A similar approach needs to be undertaken before chemical sensors for hydrogen quality control can be implemented at HRS.

Some studies are available for sensors measuring concentrations of hydrogen. In a recent report on hydrogen measuring sensors for safety applications [42], the authors compared evaluating sensors using "flow through test" methods with the more common "chamber test" methods. The first methods are efficient, cost-effective alternatives for sensor performance assessment as many sensors can be simultaneously tested, in series or in parallel. However, these methods also present challenges associated with the ability to control environmental parameters (humidity, pressure, and temperature) during the test and changes in the test gas composition induced by chemical reactions with upstream sensors. It is important to investigate similar topics to determine the best testing protocols for sensors measuring contaminants in hydrogen.

4.2. Testing Facilities

Development of sensors must be done in parallel with the development of dedicated testing facilities where specific conditions for the pressure, temperature, flow, and gas composition can be chosen. Due to hydrogen specificity when used in HRS: pressure up to 900 bar, low temperatures (as low as $-50\,^{\circ}$ C), high purity requirements (very low amount fractions of contaminants acceptable as specified in ISO14687), building testing capabilities in a laboratory environment is economically more advantageous than testing sensors directly at a HRS and allows to verify that the sensor is indeed suitable for this given application. Examples of existing facilities are provided below.

4.2.1. The Shared Sensor Technology User Facility (SSTUF)

SSTUF, which was built by the Sensor Research Group of the International Center for Sensor Science and Engineering [43], is one of the best known facilities designed

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to test chemical sensors. The SSTUF has a gas-mixing system that provides different concentrations of targeted analytes in different matrices. It operates from sub-ambient temperature up to $450\,^{\circ}\text{C}$ and from sub-atmospheric pressures to several bar. The test chamber is cylindric (10 cm diameter, 25 cm long). Nitrogen, hydrogen, carbon dioxide, and carbon monoxide can be introduced in any proportion.

4.2.2. Air Liquide Facility

Air Liquide developed a simple testing setup (Figure 2) for chemical sensors detecting impurities in hydrogen during the course of the MetroHyVe project [17]. This testing facility was designed to work with varying compositions. For this purpose, a Gasmix dilutor was used to mix gas standards with hydrogen or nitrogen. The outlet of the dilutor was set at 500 mL/min. The sensors were mounted in series using $\frac{1}{4}$ inch stainless steel tubing. The sensor assembly was enclosed in a plastic chamber continuously flushed with 5 L/min of nitrogen for safety purposes due to the presence of electronics in combination with a potential explosive mixture of hydrogen and oxygen from air.

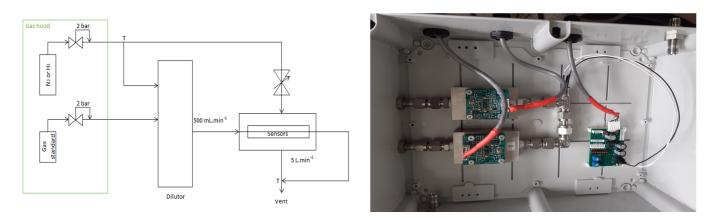


Figure 2. Diagram of the sensor testing setup and picture of the enclosure with sensor ready for testing.

This set-up (Figure 2) was used during the course of the project MetroHyVe [17] to trial several sensors. A CO-B4 sensor from Alphasense was connected to a gas hood with standard Swagelok 1/4-inch connections in stainless steel. The sensor was pressed to the gas hood using screws and an O-ring was used as tight gas seal. A potentiostat (electronic hardware required to control a three-electrode cell) was used to provide the input power and readout of the sensor. This potentiostat was an Individual Sensor Board obtained from Alphasense, dedicated to measurements at low amount fractions (μ mol/mol).

Tests were first performed in a nitrogen matrix and afterwards in a hydrogen matrix. A gas standard in nitrogen containing 50 μ mol/mol of carbon monoxide (CO) and 20 vol-% of oxygen (necessary for the electrochemical cells and the metal oxide sensor) was then diluted with nitrogen [44]. The amount fractions tested were 0, 2, 5, and 10 μ mol/mol (see Figure 3a). The test dilutions conducted with hydrogen (Figure 3b) directly showed an overloaded sensor independently of the concentration of CO. These tests clearly demonstrated the importance to test sensors under realistic conditions, especially when switching applications or matrices.

A phosphorus pentoxide sensor and an aluminum oxide sensor were simultaneously trialed with the testing setup shown in Figure 4 to measure water in hydrogen. Their response time (Figure 5) were determined at different concentrations of water ranging from 0.5 to $20~\mu mol/mol$.

The results showed that, at concentration equal to or above 3 μ mol/mol, the aluminum oxide sensor responded significantly faster than the phosphorus pentoxide sensor (at least 20% faster). These results provide a good ground to select the more suitable sensors to

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implement onsite (i.e., in that case, the sensor giving a fastest response as it is a requirement in this particular application).

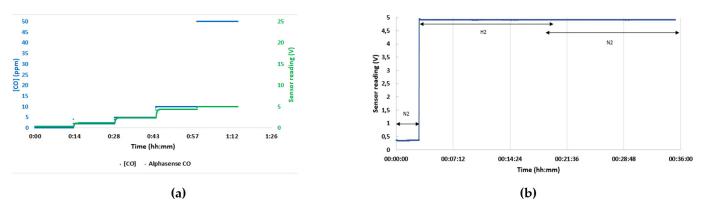


Figure 3. Results of sensor testing at Air Liquide facility (a) CO measurements in nitrogen, resulting in an expected response from the sensor, and (b) pure hydrogen, overload.

A new testing rig was developed by Air Liquide during the course of the MetroHyVe2 project [45]. With this rig, several sensors mounted in parallel can be tested simultaneous under varying compositions and at different flow rates, as shown in Figure 4.

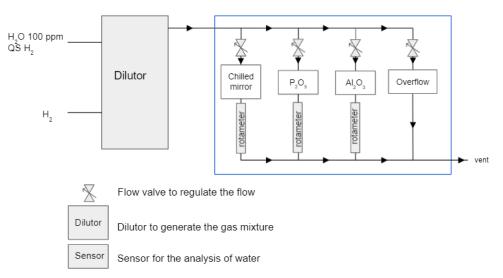


Figure 4. Testing rig developed by Air Liquide facility for simultaneous testing of several sensors.

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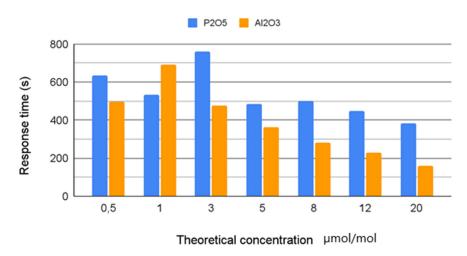


Figure 5. Comparative response time (T90) for two sensors measuring water concentrations (from 0.5 to $20 \mu mol/mol$) in hydrogen.

5. Identification of the Gaps in Current Sensor Technologies

For hydrogen quality control, high sensitivity, integration parameters and low cost are the most important requirements before sensors can be implemented at a HRS. Response time is also of high importance but is not as critical as for sensors used for safety purposes.

A number of sensors are able to detect impurities in hydrogen [44]. However, these are not often sensitive enough to detect them at the level required in ISO14687. The lack of commercially available sensors for all gaseous contaminants mentioned in ISO14687:2019 can be due to the contaminant itself, the matrix (hydrogen), and/or the stringent limits of detection required in the standards. Most of the commercial sensors mentioned in this study (Table 1) are for water and oxygen, which are two critical contaminants when hydrogen is produced by electrolysis. However, other contaminants, such as carbon dioxide, nitrogen, and hydrocarbons [40], may also be present in an HRS supplied by an electrolyzer and it will be important to measure those contaminants using sensor technology as well. For other hydrogen production methods, such as steam methane reforming (i.e., the most susceptible contaminant CO, N₂, and CH₄), for a specific supply chain (i.e., pipeline transport), or for really harmful contaminants to FCEV (i.e., H₂S), no or very few commercial sensors are available under 5000–10,000€ to monitor the relevant species. It is important to notice that even if sensors below 10,000€ are not available, other analyzers (mentioned in Section 2.8) are available. However, the cost and the complexity of these analyzers (implementation and operation) are two challenges to overcome to successfully implement analyzers at every HRS in the future.

The challenge for the scientific community is, therefore, to develop sensors that are more sensitive and able to detect other impurities besides water and oxygen. Some new sensor developments are ongoing as, for example, with CO [46], methane [47–49], sulphur compounds [50], or hydrocarbons [51]. These sensors must be enough sensitive, fast and accurate to respond to the industry needs.

6. Challenge in Sensors Calibration

Sensors implemented at a HRS will operate permanently; it is, therefore, critical to consider how the sensors can be calibrated and how their performance can be verified (i.e., for drift, accuracy, precision, or response time). Sensor calibration is challenging for several reasons: calibration will require either use of reference materials at the HRS (most of the time, in 10 L or 50 L cylinders containing the targeted impurities in hydrogen at a certain pressure; typically, 50–100 bar) or to safely remove the sensors from the HRS for calibration in a laboratory. The first option would require defining a safe environment for the implementation of the reference materials, an additional line dedicated to the sensor calibration and ensuring that the reference materials are stable in the environmental

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conditions at the HRS (i.e., potential low temperature in winter). The presence of cylinders containing compressed hydrogen at refueling stations necessitates adequate space and an additional ATEX zone. Moreover, this option is only possible if reference materials are commercially available and stable (suitable lifetime, i.e., more than a year). Finally, the cylinder size may be important at HRS due to safety concerns and potential research may be required to reduce the calibration cylinders size down to 1L, for example. For compounds such as reactive compounds (formaldehyde, formic acid, or ammonia), reference materials are not currently available with suitable lifetime (more than a year); only the second option (calibration in laboratory) is then possible. The second option involving sensor calibration in laboratory will require capability for testing and calibrating sensors in conditions, similar to those existing at the HRS, and coherent to the sensor implementation point (i.e., pressure, flow rate, or temperature) as discussed in Section 4.2.

As no standardized testing protocol exists, the time interval between calibrations is currently unknown. There is a critical need for research in this field to avoid delaying the implementation of sensors at HRS.

Furthermore, if a sensor is sent for calibration in a laboratory, it must be replaced by another calibrated sensor during the time of the maintenance, which implies that each HRS needs to have multiple sensors with different calibration dates.

7. Conclusions

Hydrogen is receiving serious consideration as an alternative energy source. FCEVs are fully carbon dioxide emission free, but their deployment in the daily life requires the development of a refueling infrastructure. As for all technologies, there is a need of minimizing potential issues that could lower the general acceptance for this market. Sensor technology can ensure the safe and efficient implementation of the emerging global hydrogen market. Chemical sensors which respond to a particular analyte in a selective and reversible way could be used to indicate the presence of impurities harmful for the fuel cell system allowing the HRS to take rapid actions.

Only a few sensors with the required specifications have been found, showing there is a need to develop sensors specifically for the hydrogen industry. Several sensors for detecting oxygen and water have been identified, and different principles of measurement allow the detection of low μ mol/mol for these two species in hydrogen. Sensors for other compounds, such as carbon monoxide, carbon dioxide, methane, hydrogen sulfide, ammonia, formaldehyde, formic acid, and hydrocarbons, seem to not yet be available at the target costs (5000 euros). To the cost of the sensing element itself, it is usually necessary to add costs for complementary components/spare parts (such as temperature probe, gas sampling system, etc.).

For economical and safety reasons, there is a need to test sensors first in an exposure chamber (laboratory testing) and then at a HRS. But there is currently a lack of testing capability, and support (time and investment) should be provided to develop facilities, such as the SSTUF, with the ability to test under these relatively harsh conditions. However, it will first require the development of standardized testing protocols and targets for the metrics. Here, a similar approach to the one undertaken by EPA for air sensor is recommended.

Based on the sensor unavailability and current cost, it will be necessary to first establish the industrial needs for these sensors before a development is conceivable. Therefore, the development of a discussion platform between sensor providers and the hydrogen industry may be relevant to share information, discuss research and development requirements, and encourage a better collaboration between both parts.

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