METROLOGY for
HYDROGEN VEHICLES

REPORT:

D6 : Report recommending the best strategies for developing and implementing low cost sensors for performing online measurement of impurities in hydrogen at refuelling stations

EMPIR EURAMET

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation programme.

16ENG01 WP3 - D6 Report recommending the best strategies for developing and implementing low cost sensors for performing online measurement of impurities in hydrogen at refueling stations

www.metrohyve.eu

This report was written as part of task 3.4 from the EMPIR Metrology for Hydrogen Vehicles (MetroHyVe) project. The three year European project commenced on 1st June 2017 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control and sampling). For more details about this project please visit www.metrohyve.eu.

This work has been carried out by:

Claire Beurey	**Air Liquide R&D**
Martine Carré	**Air Liquide R&D**
Marine Catry	**Air Liquide R&D**
Bruno Gozlan	**Air Liquide R&D**
Nathalie Luu	**Air Liquide R&D**
Janneke van Wijk	**VSL**
Heleen Meuzelaar	**VSL**
Stefan Persijn	**VSL**

Revision : July 17 2019

Table of contents

Introduction

In the next decade the EU's top priority is to decarbonize large parts of the energy system. This energy transition faces many challenges, in particular for a diverse market such as individual and collective mobility. One of the main current alternatives is the deployment of hydrogen (H_2) for the transport market (boat, car, train, bike, engine, elevator, etc ...). For vehicles high quality hydrogen is needed to ensure efficient energy conversion and to preserve the performance of fuel cells in vehicles. The supply chain should not add pollutants to the hydrogen and at the same time high quality hydrogen is needed to prevent degradation of upstream and downstream facilities throughout the supply chain.

To this end, rules and requirements are currently being implemented throughout the supply chain and include, of course, the quality monitoring of stations (risk analysis, quality control during development tests and during start and / or restart phases of processes and stations, implementation of quality assurance plan, audit, unannounced or scheduled checks, claim, incident, troubleshooting, etc...).

To allow a collective trust in hydrogen as a transport fuel by all market players (authorities, research institutes manufacturing process designer, hydrogen producer, distributor, station operator, vehicle manufacturers, final consumer), traceability is a must. Considering the expectations regarding purity and guarantee of hydrogen supply and distribution, online quality monitoring would bring greater transparency and it would enable to take timely action in case of non-conformance.

Taking into account the high costs of purchasing and operating H_2 purity analyzers, deployment of low-cost sensors would offer large cost benefits provided such sensors are sufficiently sensitive and long-term reliable. This report presents the results of an inventory of the current state of the art on existing commercial technologies and their possible transposition on hydrogen use.

Given the genesis of the H_2 mobility business model, the manufacturers of analyzers had so far not taken into account the need to offer low cost solutions and small footprint in ATEX environment. In fact, current regulations just require from the operators of station a methodology "to put in place the processes in order to guarantee the quality expected at the point of use" but without precising the methodology.

The producers of hydrogen for their mature market have long established means of monitoring and quality control. This market is characterised by large-scale production and limited distribution network, controlled by industrial hydrogen producers, making the traceability simple. However, H_2 quality control for fuel cell systems has different constraints. It necessitates the use of more advanced monitoring methods as it involves a few complementary impurities and/or some very low levels tolerances on already known impurities.

The number of hydrogen refueling stations in operation is steadily growing (example: in Germany more than 70 stations are already in operation in July 2019 and around 30 others are still planned for 2019 [1]). As a result, the current industrial model in which production, transport and quality control at the refueling station is in the same hand, is no longer viable. The use of the quite expensive laboratory equipment by individual station operators would condemn the market in a purely financial context referring to consumer sensitivity to the cost of energy.

Today, there are online analyzers that integrate with industrial installations, often with a measuring principle that is a consumable and that can be called a low-cost sensor at an intermediate or low speed. But until now, they were mainly used on networks of natural gas and biogas or on high purity gases such as in the electronics industry or in the fields of medical or food gases.

In all these cases, the continuous flow model prevails and therefore the specificity of hydrogen on the intermittence of vehicle loading was not a prerequisite in the design of technical solutions with two significant constraints related to sampling: very high pressure and low temperature.

The presence of impurities in hydrogen is one of the causes of the chemical degradation of the membrane of the PEM fuel cell. This degradation leads to a decrease of the electrical production efficiency. That's why an ISO standard of the quality control of hydrogen was established. The reference document is the standard ISO / DIS 14687 standard [2]. It stipulates the maximum amount of impurities in hydrogen, shown in table 1. The contaminants potentially present in the hydrogen are depending on the process technology and on the further purification steps.

Table 1. Extract from the ISO 14687 standard [2]

Compounds	**Limits**	
	Min.	**Max. (ppm)**
Hydrogen (H_2)	99.97 %	-
Water (H_2O)	-	5
Hydrocarbon compounds (excluding CH_4)	-	2
Methane (CH_4)	-	100
Oxygen (O_2)	-	5
Helium (He)	-	300
Nitrogen (N_2)	-	300
Argon (Ar)	-	300
Carbon dioxide (CO_2)	-	2
Carbon monoxide (CO)	-	0.2
Formaldehyde (HCHO)	-	0.2
Formic acid (HCOOH)	-	0.2
Total content of CO, HCHO and HCOOH	-	0.2
Total sulfur compounds (H_2S base)	-	0.004
Ammonia (NH_3)	-	0.1

The aim of this study is to identify the most interesting sensors of the market to be tested into the EMPIR project MetroHyVe.

1. Glossary

Gas sensor: Device able to detect a physical characteristic (analogical signal) and which transforms this signal into a measurable electrical signal using a transducer. The electrical signal is proportional to the gas concentration.

Technology Readiness Levels (TRL) [3]: scale evaluating the level of the technology in its development and industrialization. The scale ranges from the basic stage TRL 1 to the most mature stage TRL 9.

Selectivity: sensor ability to detect a specific gas and isolate it from the other gases.

Cross-sensitivity: sensitivity to one substance that predisposes an individual to sensitivity to other substances that are related in chemical structure.

Anode: Electrode where oxidation reaction happens (electrons are released).

Cathode: Electrode where reduction reaction occurs (electrons are acquired).

Electrolyte: A chemical compound that conducts ions from one electrode to the other.

Hydrogen sulfide (H_2S): Toxic at 10 ppm and unpleasantly odorous at a threshold of less than 1 ppb. According to ISO 14687-2, the limit for total sulfurs in hydrogen is 4 ppb [2].

Carbon monoxide (CO): Colourless, odourless and toxic with a threshold limit value of 25 ppm. CO is harmful to the performance of PEM batteries even at low concentrations. This molecule binds very strongly to platinum sites, thus preventing the oxidation of hydrogen. 0.2 ppm is the CO limit in ISO 14687-2.

Oxygen (O_2): Useful for the operation of the PEM but harmful if present in the fuel which can chemically degrade the membrane. Its specified limit in hydrogen is 5 ppm.

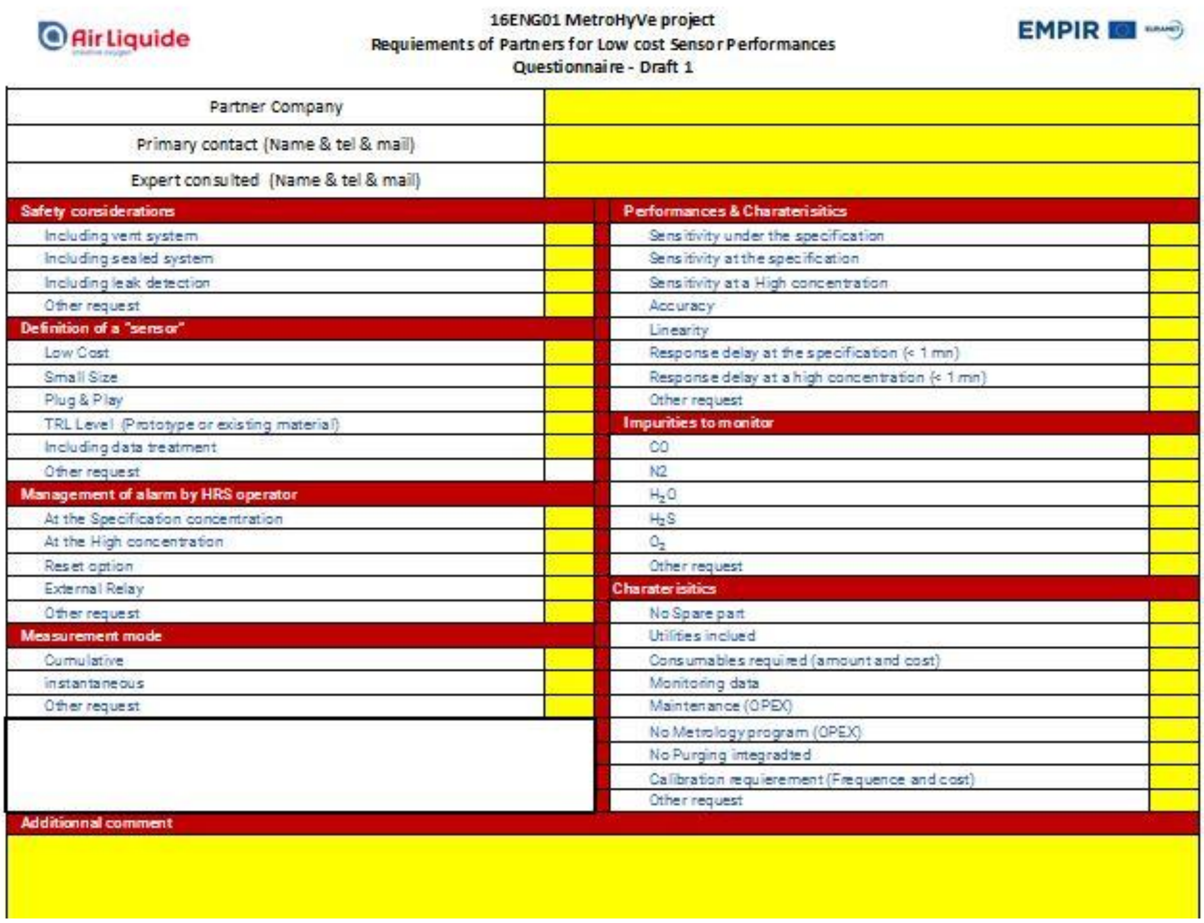
Moisture (H_2O): According to ISO 14687-2, the H_2O limit is 5 ppm.

EMPIR: European Metrology Programme for Innovation and Research

2. Study

The first step of this project was to understand the industrial needs. For this, a study was carried out with the other 28 participants in order to know what they expect: expected cost, technological readiness (TRL), size, target molecules, etc. The questionnaire below (figure 1) was sent to them. Participants had to answer by choosing between 1 and 3 according to the importance of the criteria.

Only one participant has sent an answer which is not informative enough and that is why the information given on the conclusion is based on literature research.



16ENG01 MetroHyVe project
Requiements of Partners for Low cost Sensor Performances
Questionnaire - Draft 1

Partner Company	
Primary contact (Name & tel & mail)	
Expert consulted (Name & tel & mail)	

Safety considerations

Including vent system
Including sealed system
Including leak detection
Other request

Definition of a "sensor"

Low Cost
Small Size
Plug & Play
TRL Level (Prototype or existing material)
Including data treatment
Other request

Management of alarm by HRS operator

At the Specification concentration
At the High concentration
Reset option
External Relay
Other request

Measurement mode

Cumulative
instantaneous
Other request

Performances & Charateristics

Sensitivity under the specification
Sensitivity at the specification
Sensitivity at a High concentration
Accuracy
Linearity
Response delay at the specification (< 1 mn)
Response delay at a high concentration (< 1 mn)
Other request

Impurities to monitor

CO
N2
H_2O
H_2S
O_2
Other request

Charateristics

No Spare part
Utilities inclued
Consumables required (amount and cost)
Monitoring data
Maintenance (OPEX)
No Metrology program (OPEX)
No Purging integradted
Calibration requierement (Frequence and cost)
Other request

Additionnal comment

Figure 1. Questionnaire about low cost sensor expectations

3. Gas sensors technologies

Because the survey and the discussion at the stakeholder advisory board did only present a broad idea about what a 'low cost sensor' comprises, the study brings together a wide spectrum of devices ranging from the simple electrochemical cell to the analyzer. Indeed, "sensor" can be equivalent to "detector" or cell/probe. A sensor is defined as a device which can quantitatively measure a certain physical quantity. However, a cell cannot be used alone in a hydrogen refueling station, it has to be associated with a transducer (a device which converts one physical quantity to another form of physical quantity), to be ATEX certified etc. The price is between a few euros (for the cell/ probe only) and several hundred euros.

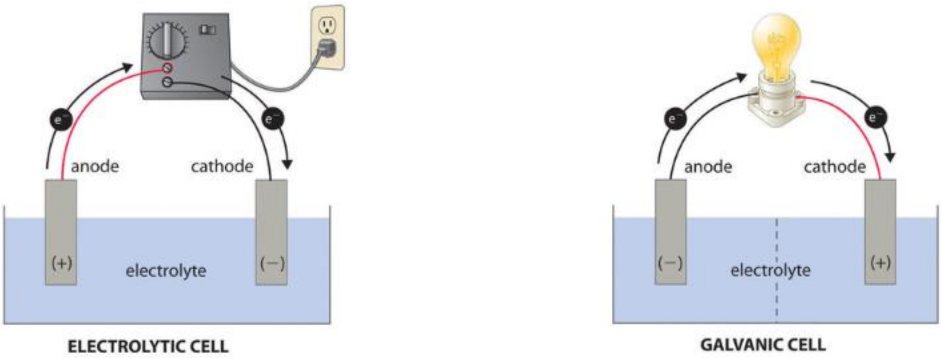
In this part, the technologies encountered at the manufacturers will be detailed. Firstly, the operating principles of technologies will be presented. Then an evaluation why it can be used (or not) for H_2 purity control. Finally, the average price and the list of models encountered (non-exhaustive list) are provided.

3.1. Electrochemical sensor

Two kinds of electrochemical gas sensors exist: electrolytic (electrical energy is consumed) and galvanic (electrical energy is produced) [4], illustrated in figure 2 below. Electrolytic cell is divided into several types:

- Amperometric (measure current): the most used, detailed in section 3.1.1.
- Potentiometric (measure voltage)
- Conductometric (measure conductivity)

An electrochemical cell typically consists of electronic conductors (also called electrodes) and an ionic conductor (called an electrolyte).



Electrolytic cell	Galvanic cell
Energy used to drive non-spontaneous redox reactions	Energy released by spontaneous redox reactions
Electrical energy is converted into chemical energy in the cell	Chemical energy is converted into electrical energy in the cell
The electrodes are present in the same compartment	The electrodes are present in different compartments

Figure 2. Comparison of electrolytic and galvanic principles [5]

A major advantage of electrochemical cells is their low power consumption. However, a minimum amount of O_2 is necessary to ensure a proper working of the cells.

3.1.1. Amperometric sensors

An amperometric sensor is composed of an electrolyte and of 2 or 3 electrodes (figure 3):

- A sensing/working electrode: reacts with the target gas to generate a current;
- A counter electrode;
- A reference electrode (usually Ag/AgCl) provides a fixed potential.

When gas comes in contact with electrodes, oxidation-reduction process occurs and the resulting current is measured (proportional to the gas concentration).

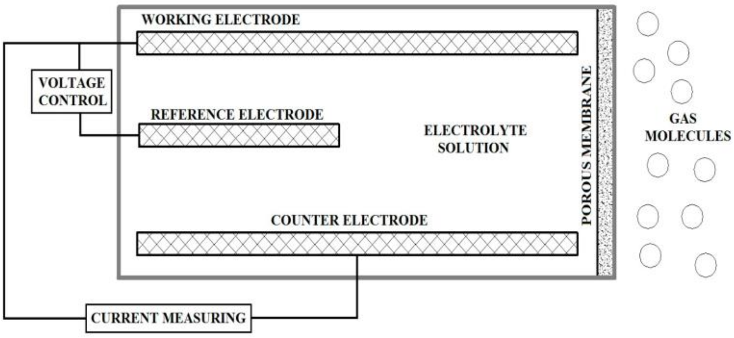


Figure 3. Amperometric sensor principle [6]

Hydrogen application: because oxygen is required in the reaction with the target gas, electrochemical sensors are widely used for the monitoring of indoor air quality and gas leaks. If the oxygen supply to the counter-electrode is cut off, the current cannot be sustained. Therefore, for the sensor to operate a minimum amount of O_2 needs to be provided.

Concerning CO or H_2S sensors:

- Usually, they are designed to be used in standard atmospheric air (20.9% O_2).
- But sometimes, CO and H_2S sensors need oxygen to function only as much as the target gas. For example, if the need is to measure 100 ppm CO, only 100 ppm of O_2 must be present.
- Another major drawback of this technology is its cross-sensitivity: CO and H_2S sensors are cross-sensitive to CO, H_2S, H_2, CO_2 and other molecules, according to the datasheets of reviewed sensors. The cross-sensitivity to H_2 is an issue for detecting ppm levels in hydrogen matrix, although some manufacturers offer models with low cross-sensitivity to H_2.

This technology is not usable for the detection of CO or H_2S in high hydrogen matrix.

Concerning the oxygen detection:

- For some sensors the resolution is not sufficient as these are only designed to measure in increments of 0.1% (which is equivalent to 1000 ppm), so the required accuracy cannot be reached.

Average cost: between 30 € and 200 € the cell.

The following table gives references for H_2S, CO and O_2 sensors using amperometric technology. For each company, only the model which is the closest to the ISO specification is given.

Table 2. Sensors using amperometric technology

Brand	H_2S - control threshold 4 ppb	CO - control threshold 0.2 ppm	O_2 - control threshold 5 ppm
Aeroqual	EHS/EHS2, from 0.04 to 10 ppm [7]	ECM, from 0.05 to 25 ppm [8]	/
Figaro	FECS50-100, from 0.1 to 100 ppm [9]	FECS40-1000, from 1 to 1000 ppm [10]	/
DD Scientific	GS+4DT, from 0.5 to 200 ppm [11]	GS+4CO2H, from 2 to 500 ppm [12]	designed for % measurement [13]
SGX Sensortech	SGX-7H2S, from 0.5 to 50 ppm [14]	SGX-7CO, from 2 to 1000 ppm [15]	EC410, designed for % measurement [16]

City Technology	4HLM CiTiceL, from 0.2 to 100 ppm [17]	4CF+ CiTiceL, from 2 to 500 ppm [17]	CNLH CiTiceL, from 0 to 2 ppm [17]
Dräger	H_2S, detection limit at 0.5 ppm [18]	CO, detection limit at 5 ppm [18]	O_2 LS, detection limit at 0.2% [18]
AMI	3010 BR, detection limit at 50 ppb [19]	/	T series, detection limit at 0.05 ppm [20]
Kane	/	KANE9206, until 4000 ppm [21]	/
Honeywell	/	PS-RM04H [22]	/

3.1.2. Galvanic sensors

Galvanic cells (also called voltaic cells or Micro Fuel Cell) are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. The sensor consists of an anode (usually Pb for oxygen), a cathode and an electrolyte, together with a diffusion limiting capillary.

Hydrogen application: like amperometric sensors, a minimum amount of oxygen is required.

Average cost: 200 - 400 €

The following table gives references for H_2S, CO and O_2 sensors using galvanic technology. For each company, only the model which is the closest to the specification is given.

Table 3. Sensors using galvanic technology

Brand	H_2S - control threshold 4 ppb	CO - control threshold 0.2 ppm	O_2 - control threshold 5 ppm
Alphasense	H2S-B4, noise level: 1 ppb [23]	CO-B4, noise level: 4 ppb [24]	designed for % measurement [9]
Figaro			SK-25F, up to 30% O_2 [12]
Analytical Industries			GPR-1500 Series, from 0.05 to 10 ppm [25]
Southland Sensing Ltd.			TO2-133, from 0 to 10 ppm [26]
Systech Illinois			EC91, from 0 to 20 ppm [27]

3.2. Catalytic gas sensors

Catalytic sensors are mainly used to detect combustible gases, CH_4, H_2, H_2S, or hydrocarbons. The sensor consists of a detector cell (platinum wire coil) coated with an oxidation catalyst such as alumina and a reference cell. These two cells are placed in a Wheatstone bridge circuit used to indicate the resistance change (figure 4).

In air, the detector cells are designed to have equal electrical resistance: no current flows through the meter. When a sample containing detectable gases reacts with the catalyst, the electrical resistance increases proportionally with the gas concentration [28].

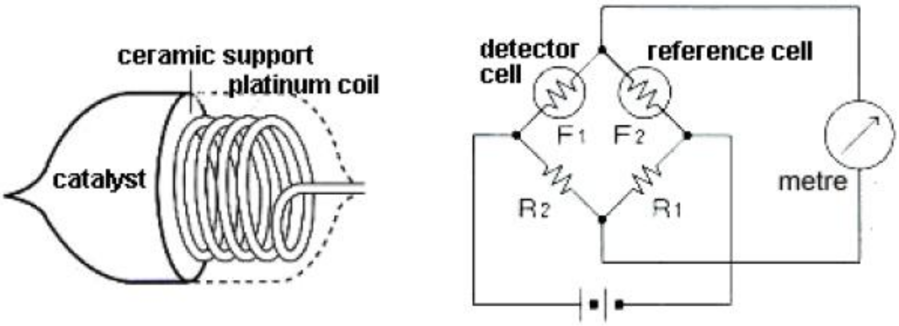


Figure 4. Catalytic sensor principle [29]

Hydrogen application: Because it's not a selective sensor and because a minimum level of O_2 is necessary for oxidation, catalytic sensors are not adapted to our application.

Average cost: 20-40 €

The following table gives references for CO sensors using catalytic technology. For each company, only the model which is the closest to the specification is given.

Table 4. Sensor using catalytic technology

Company	Alphasense	SGX sensortech
Model	CH-A3 [30]	VQ500 or VQ600 Series, designed for 0.1 to % measurements [31]

3.3. Metal Oxides Semiconductor sensor (MOS)

Carbon monoxide concentration in air can be detected by measuring the resistance change of MOS-type gas sensors. Metal Oxide Semiconductor is an electrical conductivity sensor, composed of a sensitive conducting layer (a metal oxide) applied to a non-conducting substrate (silicon) between two electrodes. Most sensors have been based on tin dioxide (SnO_2) which reacts under the presence of combustible gases such as CH_4, C_3H_8, CO and H_2.

In ambient air, oxygen is adsorbed at the surface of the semiconducting material. The substrate is heated to cause reaction between the gas and the material. Its resistance will change with the absorption of gas at the surface: decrease in presence of reducing gases such as CO (figure 5). This change is proportional to the concentration of the gas to be detected [32].

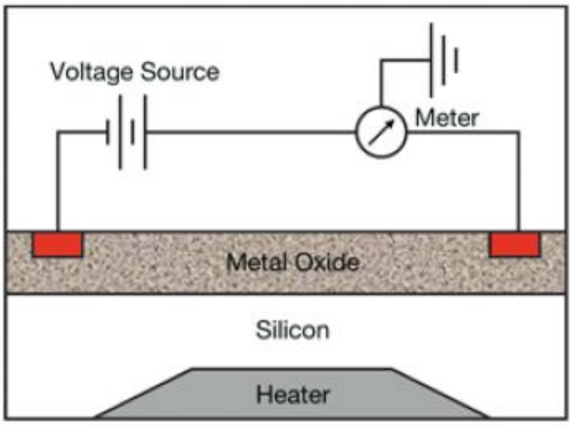


Figure 5. MOS sensor principle [33]

Hydrogen application: Because it's not a selective sensor and because they require the presence of ambient oxygen (21%) in their operating environment in order to function properly, we cannot use this sensor for our application, unless by providing a minimum amount of O_2.

Average cost: 2€

The following table gives references for CO sensors using MOS technology.

Table 5. CO sensors using MOS technology

Company	Hanwei electronics	Figaro	SGX sensortech
Model	MQ-7 from 20 to 2000 ppm [34]	TGS3870-B00, from 50 to 1000 ppm [35]	MiCS-5524, from 1 to 1000 ppm [36]

3.4. Chilled mirror hygrometer

Dew point is the temperature at which the atmosphere is saturated with water vapour, when it is cooled without changing its pressure or vapour content. Chilled mirror hygrometers determine the dew point by cooling, at constant pressure, a reflective condensation surface until water begins to condense. The condensed fine water droplets are detected optically by a photodetector and in this condition the temperature of the mirror (measured by a platinum resistance thermometer: PRT) is equal to the dew point temperature of the gas [37], as shown on the figure 6.

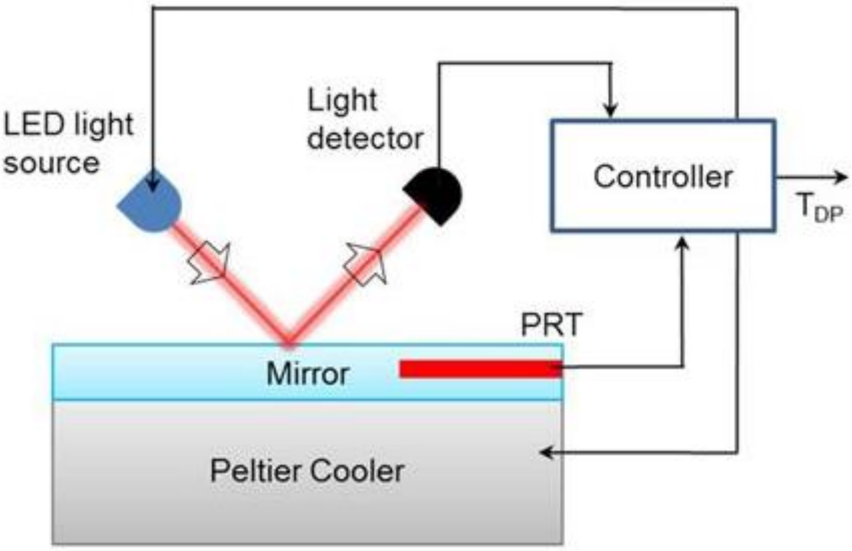


Figure 6. Hygrometer sensor principle [38]

Hydrogen application: The drawbacks of this sensor are the stabilization time (around minutes, not always true for new technologies) and the absence of ATEX certification.

Average cost: > 8 k€

The following table gives references for H_2O sensors using chilled mirror hygrometer technology.

Table 6. H_2O sensors using chilled mirror hygrometer technology

Company	Michell Instruments	GE Company
Model	S4000 TRS, from -100 to 20°C [39]	Optica [40]

3.5. Aluminium oxide (Al_2O_3) moisture sensor

The aluminium oxide sensor (also called Alox or Impedance hygrometer) provides accurate determination of ppm humidity in most industrial gases. It is based on two electrodes, a porous aluminium oxide layer (which absorbs H_2O) and a permeable gold film, as illustrated in figure 7 below. The capacitance of the sensor varies with the absorption of moisture [41].

The thinness of the active layer enables a low response time, a few seconds.

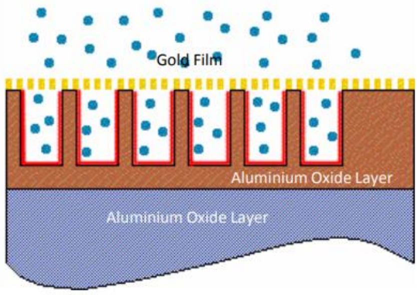


Figure 7. Alox sensor principle [41]

Hydrogen application: These cells drift over time, so they must be changed or calibrated at regular intervals.

Average cost: 20 €

The following table gives references for H_2O sensors using Alox technology.

Table 7. H_2O sensors using Alox technology

Company	Baker Hughes, a GE company	Systech Illinois	Servomex	General Electric
Model	M Series Probe, from -110 to 60°C [42]	MM400, from -100°C to 20°C [43]	Aquaxact 1688, from -100 to 20°C [44]	HygroPro, from -110 to 20°C [45]

3.6. Phosphorus pentoxide (P_2O_5) moisture sensor

This sensor exploits the hygroscopic properties of phosphorus pentoxide (P_2O_5). A winding of two platinum electrodes is coated with a film of phosphorus pentoxide. H_2O molecules are attracted by the film, pass through it and are electrolysed on the electrodes under a direct current voltage. The current measured is directly proportional to the water content in the gas, at a given flow rate.

Hydrogen application: hydrogen and oxygen can react with electrolysis products to form water, leading to false high results but some manufacturers can compensate for this effect. It is suitable to measure water traces. A constant flow and a regular regeneration of the coating are required.

Average cost: 2 k€

The following table gives references for H_2O sensors using P_2O_5 moisture technology. According to their manufacturers, they are suitable for H_2O measurement in hydrogen.

Table 8. H_2O sensors using P_2O_5 moisture technology

Brands	DKS	Systech Illinois	MEECO
Model	AQUATRACE - IV with P_2O_5 sensors, from 0.05 to 2000 ppm [46]	MM500, from 0.01 to 1000 ppm [47]	Uber M-I, from 0.5 to 1000 ppm [48]

3.7. Paramagnetic oxygen sensor

Oxygen is a paramagnetic gas (with a magnetic susceptibility higher than for other gas molecules), which means that it is attracted by a magnetic field. A paramagnetic O_2 sensor contains a measurement cell with two glass spheres filled with N_2 gas which are suspended by a metal wire. When O_2 molecules flow through the cell, the O_2 molecules are pulled towards the stronger magnetic field zone and the spheres are moved away from the zone. The resulting deviation of the spheres is detected with the light receiving element (figure 8). The signal obtained is directly proportional to the O_2 concentration in the gas mixture.

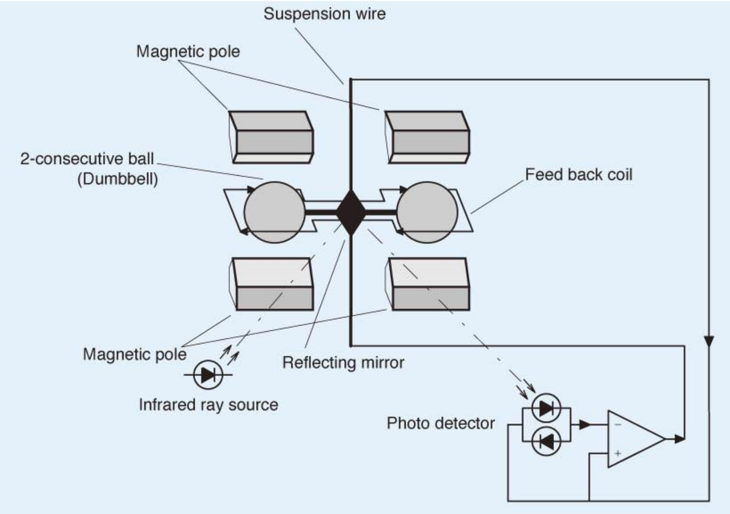


Figure 8. Paramagnetic sensor principle [35]

Hydrogen application: because the difference in magnetic susceptibility between the sphere and the gas sample is negligible for low oxygen concentrations, this method cannot be used for trace level (low ppm) O_2 measurements as required for ISO 14687-2.

Average cost: from 2 k€ to 8 k€

The following table gives references for O_2 sensors using paramagnetic technology.

Table 9. O_2 sensors using paramagnetic technology

Company	Michell Instruments	Systech Illinois	Servomex
Model	XTP601, from 0.01 to 100% [49]	PM700, from 0.01 to 100% [50]	Designed for % measurements [51]

3.8. Zirconium Oxide (ZrO_2) Oxygen Sensor

This sensor measures oxygen concentration by using the conductivity of zirconia ceramic cells.

This sensor measures oxygen concentration by using the conductivity of zirconia ceramic cells (figure 9). The A side is exposed to reference gas (air in general) and the B side to the sample gas. A zirconia ceramic lets only oxygen pass above 450°C, O_2 ions move from the side with the highest concentration of oxygen to that with the lowest concentration. Ion movement generates an electro motive force depending on the oxygen content of the sample.

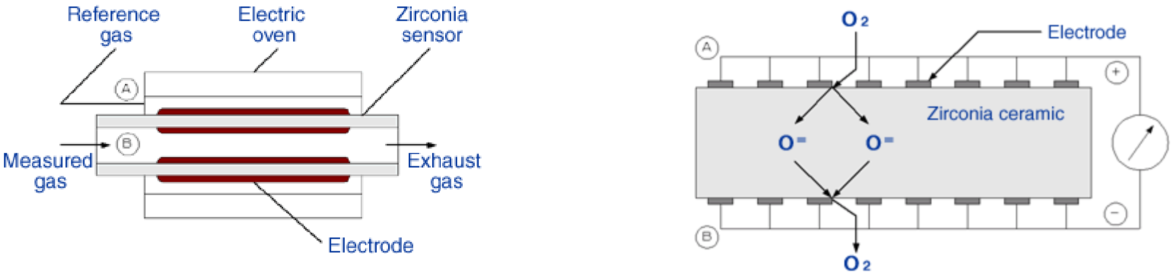


Figure 9. Zirconium oxide sensor principle [52]

Hydrogen application: because flammable gases cannot be used (it will cause a combustion reaction, so a measurement error), we cannot take advantage of this type of sensors [53].

Average cost: 20 € (for cars)

The following table gives references for O_2 sensors using zirconium oxide technology. They cannot be used in hydrogen matrix.

Table 10. O_2 sensors using ZrO_2 technology

Company	DKS	Michell Instruments	Systech Illinois
Model	ZIROX Minisonde SS27/MS27, from 0.13 ppm to 20.6% [54]	XZR400, from 0.1 ppm to 25% in pure inert gases [55]	ZR800, from 0.1 ppm to 100% [56]

3.9. Other technologies

The Thermal Conductivity Detector (TCD) compares the thermal conductivities of two gas flows: a pure carrier gas (also called the reference gas) and a carrier gas plus sample components. It is a non-destructive technique but it is non-specific. However, in hydrogen quality control it could be a marker of an impurity: if a TCD delivers a different signal than in pure hydrogen, it could be a warning.

4. Potential low-cost sensors

This section focuses on few technologies which are currently expensive or still under academic research but show a potential to become low cost sensors.

4.1. Acoustic sensors

4.1.1. Ultrasonic methods

Three categories can be found in the ultrasonic methods: speed of sound, attenuation and acoustic impedance. The most employed is the measurement of velocity using the Time of Flight (ToF), which uses the travel time of ultrasound at a given distance to calculate the propagation velocity of ultrasonic waves.

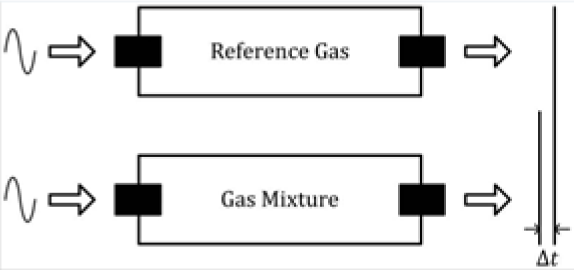


Figure 10. Ultrasonic detection principle [57]

Figure 10 shows the principle of the detection. Two channels alike respectively measure ultrasonic waves parameters (e.g., time difference Δt or phase) in the reference gas and the target gas mixture. The standard of reference speed of sound is determined with the relationship between speed of sound in the air and the air temperature. The gas concentration is proportional to the time difference Δt.

The ultrasonic detection has high precision however it is hard to ensure that the impacts of environment on the two channels are identical [57].

4.1.2. Surface Acoustic Wave (SAW) gas sensors

A surface acoustic wave (SAW) is an acoustic wave propagating along the surface of a solid material. Its amplitude decays rapidly, often exponentially, through the depth of the material. SAWs are utilized in many kinds of electronic components, including filters, oscillators, and sensors. SAW sensors belong to the MEMS category.

A SAW sensor is composed of two interdigitated transducers (IDT) etched onto a piezo-electric substrate, covered with a thin film (figure 11). The mass of the film increases as its material selectively adsorbs gas molecules. This causes a shift in resonance to a slightly lower frequency and thus information about the amount of species in the air.

The space between the IDTs, across which the surface acoustic wave will propagate, is known as the delay-line. This region is called the delay line because the signal, which is a mechanical wave at this point, moves much slower than its electromagnetic form, thus causing an appreciable delay.

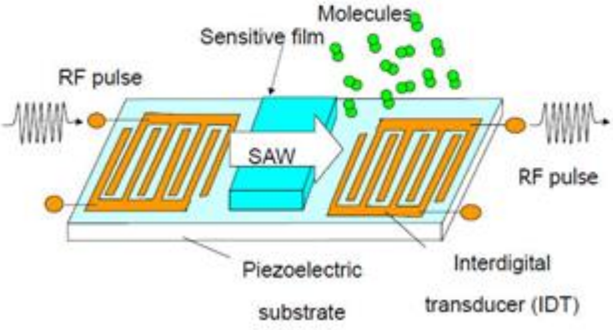


Figure 11. Principle of SAW sensors (RF = Resonance Frequency) [58]

The acoustic wave travels from the first IDT across the surface of the substrate to the other IDT, converting the wave back into an electric signal by the piezoelectric effect. Any change that was made to the mechanical wave will be reflected in the output electric signal. As the characteristics of the SAW (amplitude, phase, frequency, time-delay) can be modified by changes in the surface properties of the substrate, sensors can be designed to quantify any phenomenon which alters these properties.

4.1.3. Photoacoustic (PA) detection

Photoacoustic (PA) spectroscopy is a technique to measure trace gases at parts-per-million (ppm) or parts-per-billion (ppb) level using an infrared (IR) light source. The PA method is based on the generation of an acoustic wave in a gas excited by a modulated IR light beam at a wavelength corresponding to an absorption line of the gas species, and on the detection of this sound using a sensitive microphone, as shown in figure 12.

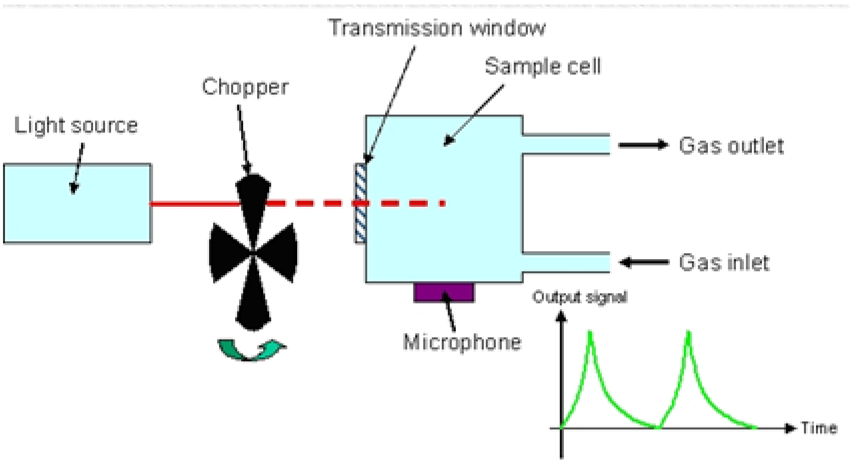


Figure 12. Photoacoustic gas sensor principle [59]

In low cost systems the infrared (IR) source is mostly a heated black body and a mirror focuses the light onto the window of the sample cell after it has passed the chopper (a slotted disk that rotates and switches the light on and off). In some systems a laser is used instead of a black body leading to a higher sensitivity albeit at a higher price.

When the wavelength is chosen to coincide with an absorption line/band of the target gas, the gas molecules will absorb part of the light. The higher the concentration of gas in the cell, the more light will be absorbed. As the gas absorbs energy, it is heated and therefore expands and causes a pressure rise. As the light is chopped, the pressure will alternately increase and decrease - an acoustic signal is thus generated.

All molecules have unique sets of allowed states, as predicted by quantum theory, which gives each molecule a unique fingerprint. So, it is possible to detect specific molecules with high selectivity.

The sample volume is small (down to 10 mL) due to the sample cell volume [60].

The most suited light source for gas detection is one which emits radiation in the infrared region of the electromagnetic spectrum, particularly between 650 and 4000 cm^{-1}.

This kind of sensors has been developed for use in the field of atmospheric pollution monitoring, the semiconductor industry, medical applications and life science applications.

Providers:

Laser PAS [61]

4.2. Optical sensors

4.2.1. Infrared (IR) gas sensors

Some gases absorb IR radiation at specific wavelengths, for example most hydrocarbons are known to absorb at wavelength of 3.4 µm while H_2O and CO_2 are nearly transparent in this same region. The principle of IR sensors is based on the absorption of IR radiation at a specific wavelength when it passes through the gas. The absorption is proportional to the concentration of the absorbing molecules.

The sensor is composed of a light source and a detector (figure 13). The source emits light at two different wavelengths, one at the absorption wavelength and the other outside the absorption area. The detector compares the signal strengths of the two beams of light and the gas concentration is determined. In presence of an absorbing gas between the source and detector, the intensity of IR radiation falls.

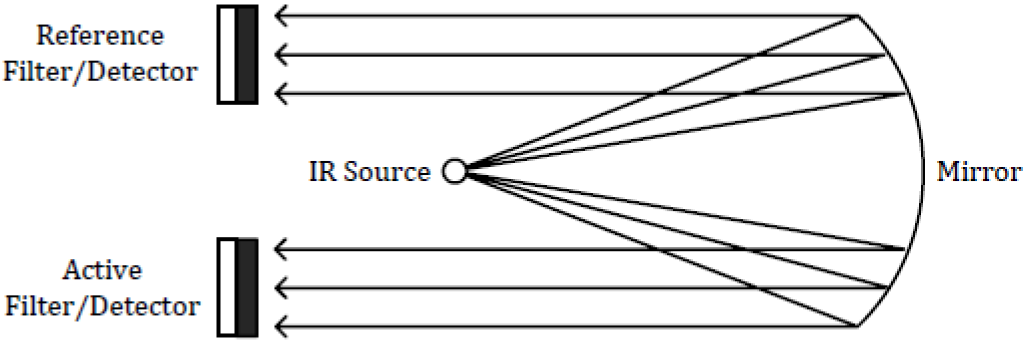


Figure 13. IR-based gas sensor principle [57]

These sensors are very selective, maintenance is limited, they can function without O_2 and their price is decreasing. Although they are sensitive, they can be used only for water, hydrocarbons and CO_2 measurement at levels required by ISO 14687-2. However, they require a large volume of gas. The recent use of Micro Electro-Mechanical Systems (MEMS) technology enabled the miniaturization of IR-based sensors which led to an increasing demand for this type of sensors.

IR sensors are often employed in corrosive and reactive gas detection because they do not directly interact with the gas. They are also used for toxic and combustible gas monitoring applications, CH_4, CO_2, hydrocarbons and VOCs detection.

IR sensors can detect CO, H_2S and H_2O, but not infrared transparent gases like H_2, N_2 and O_2.

Providers:

- Aeroqual (New Zealand)
- Alphasense (UK)
- City Technology (UK)
- SGX Sensortech (UK)
- UST Sensor (Germany)

4.2.2. Photo Ionization Detection (PID)

A PID is composed of an ultraviolet (UV) lamp which will ionize molecules provided the energy of the UV photons is higher than the ionization potential of the molecule. Then, these ions are directed by a bias electrode and accumulated at a collecting electrode. This will create an ion current which is amplified and which is a measure for the gas concentration (figure 14).

This kind of detection is non-destructive as ions recombine after passing the detector. The response time is low, around a couple of seconds.

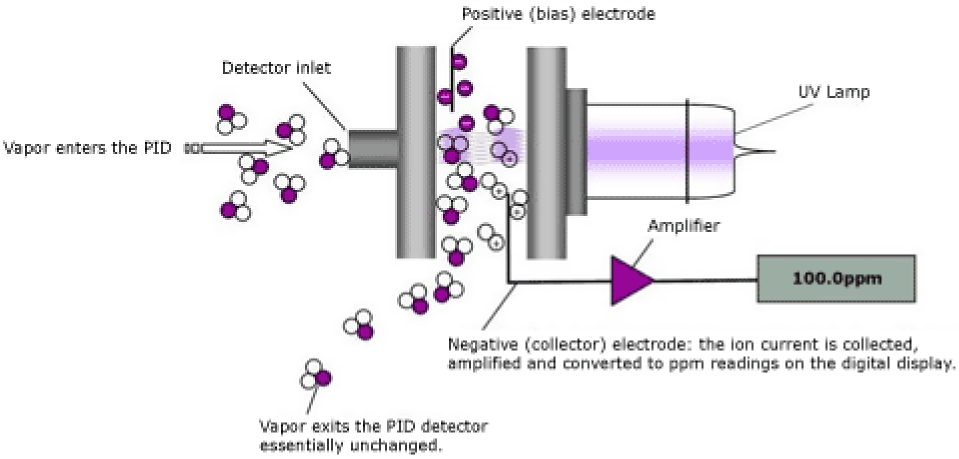


Figure 14. PID principle [62]

Lifespan of the lamps depends on the use and their maintenance.

PID sensors are mainly employed in detection of H_2S, NH_3 and VOC. Moreover, they can detect explosive gases and hydrocarbons below the lower explosive limit.

However, PID sensors cannot detect CO or light hydrocarbons (CH_4).

They are mainly used as monitoring devices, leak detectors in closed rooms or confined areas.

Providers:

- Alphasense (UK)
- City Technology (UK), Honeywell
- Wolf Sensing Solutions, Ltd (Ireland)
- Ion Science Ltd (UK)

Discussion

Even if it was not possible to validate between partners what is the expected definition of a low-cost sensor (technical and financial expectations), we can nevertheless say that today, the implantation of sensors on HRS would be a benefit on several aspects:

- Complementarity between online and offline analysis: for the commissioning of a station a full scope analysis in a lab is mandatory. But before that, it could be useful to check at the noozle regarding the specification using an online sensor response.
- Review measurement: following a complaint/incident/maintenance while the station is running but closed to customers; it may be useful to monitor the evolution of observable impurities to ensure a back to normal operation in order to plan the re-commissioning of the station.

Having in mind the different steps of the process into a station, it could be interesting to install the same sensor at several points of the unit in order to elaborate a mapping of the process to be able to:
- locate the entry point of a contamination
- check when and/or how the migration of an impurity occurs
- afford to have a defective sensor and have an online tool gathering and processing data from all sensors rather than considering each sensor as indispensable/critical.

Regarding the state of the art, it appears today that the identified sensors are at very different levels of maturity and that on an industrial level there are not yet solutions that can meet all the criteria which should be met for operation on a HRS.
In addition, there is no specific offer of sensors for a hydrogen matrix today. This means that short-term tests must be performed in laboratory to:
- confirm that in a hydrogen matrix their operation is not impaired
- check if in the presence of other potential impurities, the measure of the expected contaminant is not affected
- evaluate the speed of wear and/or loss of sensitivity.

Then,it would also be interesting to think:
- to evaluate the selected sensors in real life conditions of a station
- to carry out periodic qualification campaigns of the new low-cost sensors.

Finally, the implementation of onsite analyzers or low-cost sensors requires to think about the implementation of gas:

- how to adapt the flow, the pressure and the temperature of the analyzed gas
- how to maintain fast measurement information given purge volumes related to high pressure of the station.

Based on this report, it is possible to carry out a first low cost sensor test campaign for the four molecules selected within the MetroHyve project, but it would be obviously useful in a future project to deepen this work.

The table below presents the sensors best suited for the four molecules.

Table 11. Recommendations of sensors per molecule for H_2O, H_2S, CO and O_2

H_2O	H_2S	CO	O_2

GE M Series Probe [42] Aluminium oxide sensor	Alphasense H2S-B4 [23] Galvanic sensor	Alphasense CO-B4 [24] Galvanic sensor	AMI T series [20] Amperometric sensor
MEECO Uber M-I [48] Phosphorus pentoxide sensor			Analytical Industries GPR-1500 Series [25] Galvanic sensor (down to -10°C possible, but device so more expensive - ATEX possible)

Bibliography

[1] « H2.LIVE: Hydrogen Stations in Germany & Europe », *H2 Mobility*. [En ligne]. Disponible sur: https://h2.live/en. [Consulté le: 17-juill-2019].

[2] ISO/TC 197 Hydrogen technologies, « ISO 14687 Hydrogen fuel -- Product specification -- Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles », sept. 2018.

[3] « ISO 16290:2013 Space systems -- Definition of the Technology Readiness Levels (TRLs) and their criteria of assessment ». nov-2013.

[4] School of Engineering - University of Connecticut, « Basic Concepts in Electrochemistry ». .

[5] « Electrolytic Cells », *Chemistry LibreTexts*, 02-oct-2013. [En ligne]. Disponible sur: https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Electrolytic_Cells. [Consulté le: 20-mars-2019].

[6] B. Szulczyński et J. Gębicki, « Currently Commercially Available Chemical Sensors Employed for Detection of Volatile Organic Compounds in Outdoor and Indoor Air », *Environments*, vol. 4, nº 1, p. 21, mars 2017.

[7] « Hydrogen Sulfide Sensor 0-10ppm », *Aeroqual*. .

[8] « Carbon Monoxide Sensor 0-25ppm », *Aeroqual*. [En ligne]. Disponible sur: https://www.aeroqual.com/product/carbon-monoxide-sensor-0-25ppm. [Consulté le: 22-mars-2019].

[9] « FECS50-100 : Gas Sensors & Modules - Products - Figaro Engineering Inc. » [En ligne]. Disponible sur: https://www.figaro.co.jp/en/product/entry/fecs50-100.html. [Consulté le: 21-mars-2019].

[10] « FECS40-1000 : Gas Sensors & Modules - Products - Figaro Engineering Inc. » [En ligne]. Disponible sur: https://www.figaro.co.jp/en/product/entry/fecs40-1000.html. [Consulté le: 22-mars-2019].

[11] « CO/H2S DT Sensor », *DD-SCIENTIFIC QUALITY GAS SENSORS*. [En ligne]. Disponible sur: http://www.ddscientific.com/coh2s-dt-sensor.html. [Consulté le: 22-mars-2019].

[12] « CO Sensors », *DD-SCIENTIFIC QUALITY GAS SENSORS*. [En ligne]. Disponible sur: http://www.ddscientific.com/co-sensors.html. [Consulté le: 22-mars-2019].

[13] « O2 Sensors », *DD-SCIENTIFIC QUALITY GAS SENSORS*. [En ligne]. Disponible sur: http://www.ddscientific.com/o2-sensors.html. [Consulté le: 22-mars-2019].

[14] « SGX-7H2S SGX Sensortech Gas Sensor - Electrochemical|SGX ». [En ligne]. Disponible sur: https://sgx.cdistore.com/ProductDetail/SGX7H2S-SGX-Sensortech/493197/pid=972#.VhIqMGeFP4g. [Consulté le: 22-mars-2019].

[15] « SGX-7CO SGX Sensortech Gas Sensor - Electrochemical|SGX ». [En ligne]. Disponible sur: https://sgx.cdistore.com/ProductDetail/SGX7CO-SGX-Sensortech/493196/pid=972#.VhIp_meFP4g. [Consulté le: 22-mars-2019].

[16] « EC410 SGX Sensortech Gas Sensor - Electrochemical|SGX ». [En ligne]. Disponible sur: https://sgx.cdistore.com/ProductDetail/EC410-SGX-Sensortech/333370/pid=972#.VhIpEWeFP4g. [Consulté le: 22-mars-2019].

[17] « City Technology Ltd, Global Leaders in Gas Sensor Technology ». [En ligne]. Disponible sur: https://www.citytech.com/index.html. [Consulté le: 22-mars-2019].

[18] « Toxic gas detection, toxic gas detectors, toxic gas, gas detection, gas detector, gas detectors », *Draeger Web App*. .

[19] « H2S Analyzer, Hydrogen Sulfide Analyzers by AMI », *Advanced Micro Instruments inc.* [En ligne]. Disponible sur: https://www.amio2.com/h2s-analyzers. [Consulté le: 22-mars-2019].

[20] « Oxygen Sensors & Gas Sensors by AMI », *Advanced Micro Instruments inc.* [En ligne]. Disponible sur: https://www.amio2.com/oxygen-sensors. [Consulté le: 22-mars-2019].

[21] « KANE9206 QUINTOX - Emissions Monitoring Solution », *Kane International Limited*. [En ligne]. Disponible sur: https://www.kane.co.uk/products/kane9206-quintox-emissions-monitoring-solution. [Consulté le: 22-mars-2019].

[22] « PS-RM04H Replacement Carbon Monoxide (CO) Sensor, H2 Resistant », *BW Technologies by Honeywell*. [En ligne]. Disponible sur: https://www.bw-gasmonitors.com/ps-rm04h.html. [Consulté le: 22-mars-2019].

[23] « Hydrogen Sulfide », *Alphasense*. [En ligne]. Disponible sur: http://www.alphasense.com/index.php/products/hydrogen-sulfide-safety/. [Consulté le: 21-mars-2019].

[24] « Carbon Monoxide », *Alphasense*. [En ligne]. Disponible sur: http://www.alphasense.com/index.php/products/carbon-monoxide-safety/. [Consulté le: 22-mars-2019].

[25] « Trace Oxygen Analyzer: sample panel or wall-mounted GPR-1500 Series », *Analytical Industries Inc*. [En ligne]. Disponible sur: https://www.aii1.com/products/trace-oxygen-analyzer-for-wall-and-panel-installations.htm. [Consulté le: 22-mars-2019].

[26] « Southland Sensing Ltd. - Southland Sensing O2 Sensors (Gas) ». [En ligne]. Disponible sur:

http://www.sso2.com/products/industrial-oxygen-sensors. [Consulté le: 22-mars-2019].
[27] « EC91 ATEX o2 analyzers », *Systech Illinois*. [En ligne]. Disponible sur: https://www.systechillinois.com/en/products/ec91-safe-oxygen-analyser. [Consulté le: 22-mars-2019].
[28] International Sensor Technology, « Catalytic Combustible Gas Sensors ». .
[29] « Catalytic combustion sensors », *GASTEC*. [En ligne]. Disponible sur: https://www.gastec.co.jp/en/product/detail/id=2205. [Consulté le: 15-févr-2019].
[30] « Pellistors », *Alphasense*. [En ligne]. Disponible sur: http://www.alphasense.com/index.php/products/pellistors/. [Consulté le: 22-mars-2019].
[31] « Need Gas Sensors? Try Our Sensor Selector | », *SGX Sensortech*. [En ligne]. Disponible sur: https://www.sgxsensortech.com/sensor-selector/. [Consulté le: 22-mars-2019].
[32] « Operating principle -MOS-type gas sensor », *Figaro*. [En ligne]. Disponible sur: https://www.figaro.co.jp/en/technicalinfo/principle/mos-type.html. [Consulté le: 15-févr-2019].
[33] Z. Yunusa, M. N. Hamidon, A. Kaiser, et Z. Awang, « Gas Sensors: A Review », *Sens. Transducers*, vol. 168, nº 4, p. 61‑75, avr. 2014.
[34] « Carbon Monoxide Sensor - MQ-7 - SEN-09403 - SparkFun Electronics ». [En ligne]. Disponible sur: https://www.sparkfun.com/products/9403. [Consulté le: 22-mars-2019].
[35] « TGS3870 : Gas Sensors & Modules - Products - Figaro Engineering Inc. » [En ligne]. Disponible sur: https://www.figaro.co.jp/en/product/entry/tgs3870.html. [Consulté le: 22-mars-2019].
[36] « MICS-5524 SGX Sensortech Gas Sensor - MetalOxide|SGX ». [En ligne]. Disponible sur: https://sgx.cdistore.com/ProductDetail/MICS5524-SGX-Sensortech/333420/pid=972. [Consulté le: 22-mars-2019].
[37] « Hygrometer: Principle of Operation CHILLED MIRROR HYGROMETERS », *Yankee Environmental Systems*. [En ligne]. Disponible sur: http://www.yesinc.com/products/data/cmh/index.html. [Consulté le: 15-févr-2019].
[38] J. Tao *et al.*, « An ultrahigh-accuracy Miniature Dew Point Sensor based on an Integrated Photonics Platform », *Sci. Rep.*, vol. 6, p. 29672, juill. 2016.
[39] « S4000 TRS Precision Dew-point Hygrometers - Michell Instruments | UK ». [En ligne]. Disponible sur: http://www.michell.com/uk/products/s4000_trs.htm. [Consulté le: 22-mars-2019].
[40] « Optica Chilled Mirror Hygrometer | Measurement & Controls », *sitenametest*. [En ligne]. Disponible sur: /measurement-sensing/moisture-gas-measurement/relative-humidity-transmitters/optica-chilled-mirror-hygrometer. [Consulté le: 22-mars-2019].
[41] Systech Illinois, « Aluminium Oxide (Al2O3) moisture sensor ». .
[42] « M Series - Aluminum Oxide Moisture Sensor Probe | Measurement & Controls », *Baker Hughes a GE Company*. [En ligne]. Disponible sur: /measurement-sensing/moisture-gas-measurement/moisture-analyzers-and-transmitters/m-series-aluminum-oxide-moisture. [Consulté le: 22-mars-2019].
[43] « MM400 Moisture Analyzer for process gas measurement », *Systech Illinois*. [En ligne]. Disponible sur: https://www.systechillinois.com/en/products/mm400-moisture-analyzer. [Consulté le: 22-mars-2019].
[44] « AquaXact 1688 - SERVOPRO Safe Area - Product Ranges - Gas Analyzers | Servomex ». [En ligne]. Disponible sur: https://www.servomex.com/gas-analyzers/product-ranges/servopro/aquaxact-1688. [Consulté le: 22-mars-2019].
[45] « HygroPro », *General Electric*. [En ligne]. Disponible sur: https://www.gemeasurement.com/sites/gemc.dev/files/hygropro_datasheet_english.pdf. [Consulté le: 09-mai-2019].
[46] « AQUATRACE® - IV Typ - W wall unit - Gas Detection, trace moisture, gas humidity », *DKS engineering*. [En ligne]. Disponible sur: s. [Consulté le: 21-mars-2019].
[47] « MM500 Moisture Detector for use in process gas analysis », *Systech Illinois*. [En ligne]. Disponible sur: https://www.systechillinois.com/en/products/mm500-moisture-analyzer. [Consulté le: 21-mars-2019].
[48] « UBER M-I », *MEECO*. [En ligne]. Disponible sur: http://meeco.com/meeco/wp-content/themes/mecco/pdf/english/M-i.pdf. [Consulté le: 09-mai-2019].
[49] « XTP601 Series Oxygen Analyzer - Michell Instruments ». [En ligne]. Disponible sur: http://www.michell.com/uk/products/xtp601.htm. [Consulté le: 22-mars-2019].
[50] « PM700 Process Oxygen Analysers », *Systech Illinois*. [En ligne]. Disponible sur: https://www.systechillinois.com/en/products/pm700-process-oxygen-analysers. [Consulté le: 22-mars-2019].
[51] « Gas Analyzers | Servomex ». [En ligne]. Disponible sur: https://www.servomex.com/gas-analyzers/filter/gas_sensed/oxygen-o/range/servotough-hazardous-area/technology/paramagnetic. [Consulté le: 22-mars-2019].
[52] « Oxygen analyzers | Zirconia analyzer & magnetic wind method », *Instrumentation and Control Engineering*,

30-mars-2018. .
[53] « Zirconia Oxygen Analysis », *Systech Illinois*. [En ligne]. Disponible sur: support/technologies/zirconia-oxygen-analysis. [Consulté le: 20-mars-2019].
[54] « ZIROX probe - Oxygen measurement in gases », *DKS engineering*. [En ligne]. Disponible sur: https://www.dks-engineering.de/en/products/oxygen-measurements/zirox-mini-probe-for-the-measurement-of-oxygen. [Consulté le: 21-mars-2019].
[55] « XZR400 Series Oxygen Analyzers - Michell Instruments | US ». [En ligne]. Disponible sur: http://www.michell.com/us/products/xzr400_touch_screen.htm. [Consulté le: 21-mars-2019].
[56] « ZR800 Oxygen Analyzers », *Systech Illinois*. [En ligne]. Disponible sur: https://www.systechillinois.com/en/products/zr800-oxygen-analyzer. [Consulté le: 21-mars-2019].
[57] X. Liu, S. Cheng, H. Liu, S. Hu, D. Zhang, et H. Ning, « A Survey on Gas Sensing Technology », *Sensors*, vol. 12, nº 7, p. 9635‑9665, juill. 2012.
[58] « Fundamental Technology of Ball SAW Device for Hydrogen Gas Sensor Established », *Tohoku University*. [En ligne]. Disponible sur: http://www.bureau.tohoku.ac.jp/kohyo/kokusai/06Feb3research-overview.htm. [Consulté le: 19-mars-2019].
[59] P. Michael, « ASA 148th Meeting Lay Language Papers - Chemical Detection With a MEMS Microphone », 16-nov-2004. [En ligne]. Disponible sur: http://acoustics.org/pressroom/httpdocs/148th/pedersen.html. [Consulté le: 20-mars-2019].
[60] « Photoacoustic Spectroscopy (PAS) », *LumaSense Technologies*. [En ligne]. Disponible sur: https://www.lumasenseinc.com/EN/products/technology-overview/our-technologies/pas/photoacoustic-spectroscopy.html. [Consulté le: 19-mars-2019].
[61] « H2S / H2O / CO2 in (natural) gas treatment », *Hobre.com*. .
[62] « PID - Photoionization detector », *ENVIEQ [STORE]*. .

Appendix 1: Companies/Providers

	Country	**Website**
Aeroqual	New Zealand	https://www.aeroqual.com/
Alphasense	UK	http://www.alphasense.com/
AMI	USA	https://www.amio2.com/
City Technology	UK	https://www.citytech.com/
DD Scientific	UK	http://www.ddscientific.com/
DKS	Germany	https://www.dks-engineering.de/de/
Dräger	Germany	https://www.draeger.com/fr_fr/Home
Figaro Engineering Inc	Japan	http://www.figaro.co.jp/en/
GE Company	Germany	https://www.gemeasurement.com/
Hanwei Electronics	China	https://www.hwsensor.com/
Honeywell	USA	https://www.honeywell.com/
Ion Science Ltd	UK	https://www.ionscience.com/
Kane International Ltd	UK	https://www.kane.co.uk/
Michell Instruments	Germany	http://www.michell.com/fr/
Servomex	UK	https://www.servomex.com/
SGX sensortech	UK	https://www.sgxsensortech.com/
Southland Sensing Ltd.	USA	http://www.sso2.com/
Systech Illinois	UK	https://www.systechillinois.com/fr/