

REPORT:

A2.4.1: Review of the state of the art of online gas sensors/analysers

Authors: Karine Arrhenius, Thomas Bacquart

Confidentiality: Public

Submission date: 10.02.2021

Revision: 16.04.2021

<https://www.sintef.no/projectwev/metrohyve-2>

Report A2.4.1: Review of the state of art of online gas sensors	
Funding European Metrology Program for Innovation and Research	Grant agreement no: 19ENG04
Project name Metrology for Hydrogen Vehicles 2	Project short name MetroHyVe 2
Author(s) Karine Arrhenius RISE karine.arrhenius@ri.se Thomas Bacquart NPL Thomas.bacquart@npl-co.uk	Pages 16 pages
<p>Summary</p> <p>This report was written as part of activity A2.4.1 from the EMPIR Metrology for Hydrogen Vehicles 2 (MetroHyVe2) project. The three-year European project commenced on 1st August 2020 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control, sampling and fuel cell stack testing). For more details about this project please visit website address.</p>	
Confidentiality	Public

This project “Metrology for Hydrogen Vehicles 2” (MetroHyVe 2) 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 under Grant agreement No [19ENG04].

EMPIR



The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Contents

1 - Introduction	3
2 - Gas sensors / analysers technologies and providers	3
3 – Sensors/analysers specifications.....	4
3.1 – Trueness.....	5
3.2 – Precision.....	5
3.3 - Response time.....	5
3.4 - Stability and Drift	6
3.5 - Selectivity or cross-sensitivity.....	6
3.6 - Sensitivity and nominal range.....	6
4 – Sensors/analysers operational conditions	6
4.1 – Operational temperature.....	6
4.2 – Operational pressure	7
4.3 – Operational flow range	7
5 - Identified sensors/analysers on the market	7
6 - State-of-the-art of tests of sensors performed for applications related to hydrogen purity testing	0
6.1 - MetroHyve 1	0
6.2 - Other projects.....	0
7 – Conclusions and criteria to select sensors/analysers to test for the other activities.....	1
References	1

1 - Introduction

The fuel cell (FC) system in a hydrogen vehicle can easily degrade if even parts-per-billion to parts-per-million level of some impurities are present in the hydrogen. EU Directive 2014/94/EU includes therefore a requirement to ensure that hydrogen supplied to fuel cell vehicles complies with the purity specifications set in standards (ISO14687:2019 [1], EN17124:2018 [2]).

Hydrogen fuel quality control can be performed either by sampling at the nozzle of the hydrogen refueling station (HRS) followed by offline analysis or by online monitoring at agreed points at the HRS. The advantages of online monitoring are at least twofold: real time measurement allowing quick response capability (i.e. stop delivering hydrogen fuel to vehicles if contamination of the hydrogen fuel is observed) and possibly cost reductions (as for instance there is no transport cost to send a cylinder back to the lab).

Online monitoring requires HRS operators to install sensors that can continuously monitor key contaminants to ensure that such contaminants never reach the FC vehicles. The sensors must continuously provide accurate measurements without drifting. Without quality control on online analysers and sensors, the stations cannot have confidence in the performance and accuracy of the online analysers, there is no guarantee that the instruments will provide correct measurements thus allowing harmful levels of contaminants to reach the hydrogen vehicle.

In this report, the state-of-art of the online gas sensors and gas analysers applicable to hydrogen purity testing have been updated to include information of instruments performance and specificities.

Most of the sensors and analysers are designed to respond to individual compounds. The individual impurities that need to be monitored (with the maximum authorized limit) are:

- Water, H₂O (max 5 µmol/mol)
- Methane, CH₄ (max 100 µmol/mol)
- Oxygen, O₂ (max 5 µmol/mol)
- Helium, He (max 300 µmol/mol)
- Nitrogen, N₂ (max 300 µmol/mol)
- Argon, Ar (max 300 µmol/mol)
- Carbon dioxide, CO₂ (max 2 µmol/mol)
- Carbon monoxide, CO (max 0.2 µmol/mol)
- Formaldehyde, HCHO (max 0.2 µmol/mol)
- Formic acid, HCOOH (max 0.2 µmol/mol)
- Ammonia, NH₃ (max 0.1 µmol/mol)
- Hydrogen sulphide, H₂S (actually included in total sulfur compounds, max 0.004 µmol/mol)
- Hydrogen chloride, HCl, hydrogen bromide, HBr, chlorine, Cl₂ (actually included in key halogenated max 0.05 µmol/mol)

After discussion with providers, the definition of the terms “sensor” and “analyser” appeared to be somewhat unclear. For example, some providers indicated that their gas analysers have sensors inside and the term “analysers” included the complete set of systems that introduce the sample gas into the instrument and then discharges or retrieves the gas. However, some providers are referring to gas sensor for instruments that can perform gas analysis and include inlet and discharge of gas. Discrepancies in the terminology used by providers to differentiate or designate gas sensors and analyser exist. Another distinction could be that gas analysers provide a multiplicity of outputs. To clarify the terminology, it was decided to consider the instruments as a whole and therefore use “sensors/analysers” through this report.

2 - Gas sensors / analysers technologies and providers

Different types of sensors/analysers to measure key impurities have been listed in the recently produced report D6 “Report recommending the best strategies for developing and implementing low cost sensors for performing online measurement of impurities in hydrogen at refueling stations” [3]. The operating principles were explained

in the report. In the same manner, different technologies of multi-components analysers were presented in the report D3 “Assessment report of a multi-component analyser with optimised sampling analysis that meets the required detection limits as per business ISO/TC197 and CEN/TC268” [4] produced during the EMPIR project “Metrology for sustainable hydrogen energy applications” (2016-2019). The technologies identified in these projects are electrochemical sensors, catalytic gas sensors, metal oxides semiconductor sensors, chilled mirror hygrometer, aluminum oxide moisture sensors, phosphorus pentoxide moisture sensors, paramagnetic oxygen sensors, zirconium oxide sensors, acoustic sensors and optical sensors, Fourier Transform Infrared Spectroscopy (FTIR), Cavity Ring Down Spectroscopy (CRDS), Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS) and Broadly Tunable Laser technique (BTL).

The following providers have been mentioned in the reports previously mentioned: Alphasense, Figaro, Analytical industries, Southland Sensing Ltd, Systech Illinois, Aeroqual, DD Scientific, SGX Sensortech, City Technology, Dräger, AMI, Kane, Honeywell, Hanwei Electronics, Mitchell Instruments, GE Company, Baker Hughes, MEECO, Servomex, DKS for sensors and Tiger Optics, MKS, AP2E and Blue Industry and Science for gas analysers. New providers have also been identified: as for example Mettler Toledo for a technique called Tunable Diode Laser (TDL) and Agilent or Siemens for micro-GC. Some of these sensors / analysers use techniques that have not been described in the previous reports [3] and [4] such as TDL or GC-IMS. These principles are briefly described below.

Principle of Tunable diode laser: A diode laser emits a beam of near-infrared light, which passes through the process gas and is then reflected back into the detector by an optical device. The wave-length of the laser diode output is tuned to a gas specific absorption line. The laser continuously scans the absorption lines with a high spectral resolution. For analysis, absorption, strength and line shape of the return signal is used. The influence of cross interferences from background gases is negligible, since the wavelength specific laser light is absorbed very selectively by only one specific molecule. The minimum detectable limit, the accuracy and the resolution is dependent on the optical path length, the process temperature and pressure.

Principle of Gas Chromatography Ion Mobility Spectrometry (GC-IMS) is an analytical technology to separately detect gaseous compounds in a mixture of analytes. The separation is based on the specific drift times, that ionized compounds need to pass a fixed distance (drift tube) in a defined electric field. Ionization of molecules can be obtained by several techniques as for example by soft chemical-ionization initiated by a low-radiation tritium source.

3 – Sensors/analysers specifications

The performance of all above-mentioned sensors / analysers may be characterized by their signal-to-noise (S/N) ratio, minimum detectable limit (MDL) or sensitivity, selectivity, response time and frequency of measurements. Another classification of gas sensors and analysers could be based on their sampling method: by diffusion, pumped transport or via remote optical sampling. In order to ensure that the instruments are properly functioning they must be provided with a required flow and pressure of hydrogen.

The issue of cost is also a great importance. Costs cover not only the instrument itself but also costs for commissioning, installation, training, utilities, expensive for quality control such as calibration and finally costs for maintenance.

To ensure that sensors /analysers continuously provide accurate measurements, it is of high importance to study the instruments precision, trueness and drift.

Finally, as instruments will be used in a flow of hydrogen, they should preferably be ATEX certified.

The procedure to establish that instruments/methods are fit-for-purpose is covered in detail in ISO21087:2019 [5] for analyses done in laboratories after the sampling of hydrogen. However, the standard does not cover online monitoring. But for discussion purposes, we have chosen to apply the same criteria for some performance characteristics of online sensors/analysers than those presented in ISO21087 for offline methods.

In order to evaluate the specifications of a sensor/analyser, it is important to define properly the terms used to assess those. In the following section, definitions are taken from different sources such as ISO21087:2019 [5] or from the application note 181223 SemeaTech (Electrochemical gas sensor specifications) [6].

However, if sensors/analysers are only used to warn if the signal is above threshold, it is not necessary to check all the parameters described below. It will depend on the level of accuracy expected and/or if ISO21078 can apply.

Other documents that of interest are:

- General verification protocol for portable multigas analysers, Environmental Technology Verification Program, Advanced Monitoring Systems Center, EPA, 2003 [7] which has a section for the experimental design (which recommend to test two identical analysers operated side by side), and a section for test procedures (i.e. linearity, response time, detection limit...).

- Protocol of evaluation and calibration of low-cost gas sensors for the monitoring of air pollution, JRC Technical Reports, 2013 [8] which has been written as part of the EMRP project “Metrology for Chemical Pollutants in Air (MacPoll) which includes sections “experiments within the protocol of validation of sensors” and “test report”.

- Air Sensor Performance Targets and Testing Protocols [9]. The Environmental Protection Agency (EPA) has been engaged in a variety of activities to help advance the understanding of air sensors. These activities underline the lack of standard testing protocols, metrics, or targets to evaluate the performance of air sensors uniformly leading 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).

3.1 – Trueness

Describes the closeness of agreement between the value (or the mean value of a series of measurements) and an accepted reference value or conventional true value and is a measure of the systematic error (also called bias) of measurement of an instrument. In ISO21087:2019, it is stated that the bias shall be small enough to have a relative combined standard uncertainty below 10% of the concentration for amount fractions equal or above 10 nmol/mol and below 50% for amount fractions equal or below 10 nmol/mol. Trueness is often called **accuracy** when manufacturer list the specifications of sensors/analysers.

3.2 – Precision

The precision describes the closeness of results to one another and is a measure of the standard deviation of results obtained by carrying replicate measurements. In ISO21087:2019, it is stated that the precision shall be small enough to have a relative combined standard uncertainty below 10% of the concentration for amount fractions equal or above 10 nmol/mol and below 50% for amount. The precision can be expressed as **repeatability**.

3.3 - Response time

The response time is defined as the speed of response to an input signal change and is often expressed in seconds. The response time is often also dependent upon test conditions, such as calibration gas flow rate and ambient temperature. Typically, the response time can be measured by changing the gas concentration and monitoring the sensor output as change of concentrations (increase and decrease) are introduced. The response

time **T90** is commonly used by the sensors industry and corresponds to the time taken to reach 90% of the applied target gas concentration or its stable reading.

3.4 - Stability and Drift

Drift is a temporal change in the response of an instrument to a constant concentration. Drift implies that the performance of a measuring instrument changes and re-calibration must be performed. It is generally due to sensor's aging, but it can also be caused by dust and variations of pressure, temperature, humidity.

3.5 - Selectivity or cross-sensitivity

Sensors are designed to be selective to a compound or to specific classes of compounds. However, in the presence of some non-targeted compounds, a signal may be produced leading to errors in the measurement of the target compound; this is called cross-sensitivity. The manufacturer can sometimes provide a list containing common gases and the typical effect they would have at a given concentration on the signal of sensors.

3.6 - Sensitivity and nominal range

Sensitivity refers to the sensor output signal per $\mu\text{mol/mol}$ of the target gas. The **nominal range** is also often a specification for sensor and corresponds to the range where the gas sensor outputs show the best linearity. This can be measured by successively increasing the concentration from the lowest detectable level and recording the outputs.

4 – Sensors/analysers operational conditions

The sensor response and/or the interpretation of the sensor response may depend on many environmental parameters, such as temperature, flow rate and pressure. Moreover, sensors only work effectively under specific conditions of temperature, pressure and flow rate. These parameters are important as hydrogen may be subject to significant temperature variation depending on the location (in northern country, $-10\text{ }^{\circ}\text{C}$ or southern country $+40\text{ }^{\circ}\text{C}$). The hydrogen at refueling station can be sampled at various pressure from low pressure (close to atmosphere) to high pressure (350-700 bar).

4.1 – Operational temperature

It is the normal operating temperature or temperatures range. Operating gas sensors in a lower and higher temperature environment than the operational temperatures may result in slower (or faster) response time. It also may damage the sensors permanently. Some gas sensors may have a transient response to sudden temperature changes, and it may result in false alarming for a short time on the instrument using such sensors. In between this range, the sensor output can be dependent upon the temperature. In this case, the signal is corrected for the average temperature dependence. Figure 1 below shows tests performed by Alphasense on the sensor H2S-B4 in the operational temperature ranges (-30 to $50\text{ }^{\circ}\text{C}$) and shows the sensitivity dependency of the output of the sensor for a typical batch of sensors.

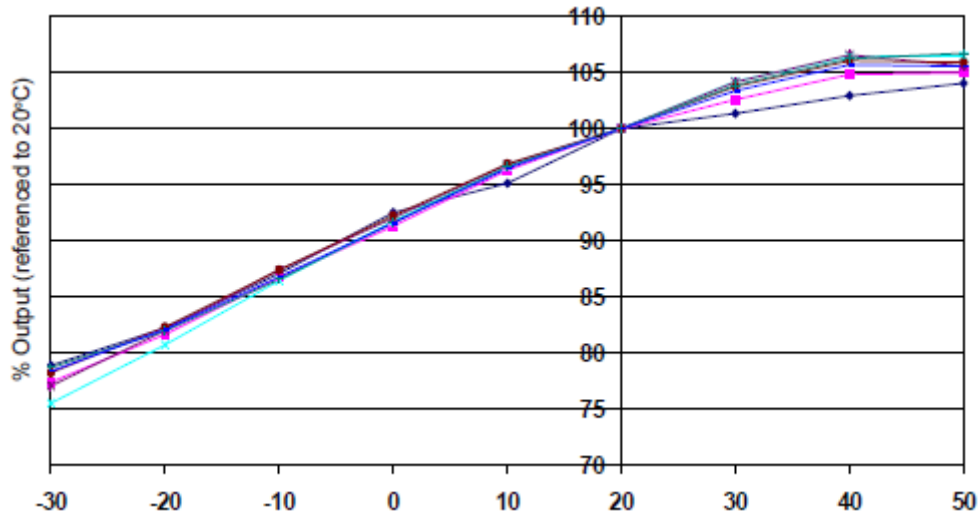


Figure 1 - Sensitivity dependency in the operational temperature range

4.2 – Operational pressure

It is the normal operating pressure or pressures range for the gas sensors. Some gas sensors may have a transient response to sudden pressure changes, and it may result in false alarming for a short time on the instrument using such sensors.

4.3 – Operational flow range

The flow rate should be low enough to avoid damaging the sensor without being so low as to extend the system response time to an unacceptable level.

To ensure that the conditions are in the correct ranges, sensors can be completed with so called sample system.

5 - Identified sensors/analysers on the market

In the previous EMPIR projects MetroHyVe1 and Hydrogen, sensors / analysers for hydrogen purity testing were identified. The sensors models presented in the report [3] were evaluated for their applicability to hydrogen purity testing and costs. In the same manner, a list of multi-component analysers was produced in [4]. In the tables below (Table 1 for sensors/analysers, Table 2 for multi-component analysers), this information is summarized; and the sensors/analysers that were dismissed (for different reasons but mostly because they were not sensitive enough for the application at hand or not compatible with hydrogen) are not reported here. When available, specifications for the sensors/gas analysers are given. Most of the information have been found on the website of the providers (references given after the name of the models) or after contact with the providers.

Table 1. Gas sensors/analysers for hydrogen purity testing listed in [3] with additional information obtained by contacting providers (All Information from providers unless specified otherwise)

Technology		Model	Response time (T90)	Selectivity	Sensitivity/range	Stability	Temperature range (°C)	Pressure range (bar)	Flow rate	Costs	
Electrochemical sensor	Alphasense (H ₂ S)*	H2S-B4 [10]	From 0 to 2 µmol/mol <60s	@ 5 µmol/mol Cl ₂ <-10 @ 5 µmol/mol CO <-3 @ 100 µmol/mol H ₂ <50 @ 20 µmol/mol NH ₃ <0.1 @ 5% CO ₂ <0.1	H ₂ S: 1 nmol/mol [3] Linearity tested from 0 to 200 nmol/mol every 20 nmol/mol*	<20% change/year in air	-30 to 50	0.8 to 1.2		++[3]	
	Alphasense (CO)	CO-B4 [11]	From 0 to 60 µmol/mol <60s*	@ 5 µmol/mol H ₂ S <1 @ 5 µmol/mol Cl ₂ <-1 @ 100 µmol/mol H ₂ <0.5 @ 20 µmol/mol NH ₃ <0.1 @ 5% CO ₂ <0.1	CO: 4 nmol/mol [3]	<10% change/year in air	-30 to 50	0.8 to 1.2		++[3]	
	Analytical industries (O ₂)	GPR-1500 series [12]	<10s	No info	O ₂ : 0.05 to 10 µmol/mol [3]	No info	-10 (or 5) to 45*	0.3 to 2	30-60 l/h	++[3]	
	DSK GmbH	OxyTransII or Oxymaster II	<45s	No info			0 to 50	0.1 to 1		+	
	Southland Sensing Ltd (O ₂)	TO2-133 [13]	7s	No info	O ₂ : 0(?) to 10 µmol/mol	No info	0 to 50	No info	15-150 l/h	++[3]	
	Systech Illinois (O ₂)	EC91 [14] (analysers)	20s	No info	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	
	Aeroqual (CO)*	ECM [15]	60s (not specified T90)	@25 µmol/mol NH ₃ 1 @ 100 µmol/mol CO: 200 @1000 µmol/mol CO ₂ : 0 @1 µmol/mol Cl ₂ : 0 @100 µmol/mol H ₂ :100 @5000 µmol/mol CH ₄ : 0	CO: 0.05 to 25 µmol/mol	No info	0 to 40	No info	No info	++[3]	
	AMI (O ₂)	T Series [16] (T2)	<25 s for 0 to 10 µmol/mol	No info	O ₂ : 0.05 µmol/mol to			-4 to 46	0.03 to 10.3	3 to 60 l/h	++[3]

					5/10000 µmol/mol					
Chemical-optical sensor	Presens (O ₂)	Oxy-1 SMA-trace-RS232	No infor	No info	O ₂ : down to 0.5 µmol/mol					+
Phosphorus pentoxide moisture sensor	DKS (H ₂ O)	Aquatrace IV [17]	Dry to wet: < 5s Wet to dry <15 min	<10 µmol/mol H ₂ S	H ₂ O: 0.05 to 2000 µmol/mol		5 to 65	Approx 0.2 above the measuring cell inlet	20 or 100 NI/h	+ [3]
	DSK GmbH	Aquatrace ATT500	Dry to wet: < 5s Wet to dry <15 min	Not compatible with ammonia	H ₂ O: 0 to 500 µmol/mol		-10 to 60	0-20	1-300 NI/h	+
	Systech Illinois (H ₂ O)	MM50 [18]	Within 60 s		H ₂ O: 0.1 to 1000 µmol/mol	No info	No info	No info	No info	
	MEECO (H ₂ O)	Uber M-I [19]	5 min		H ₂ O: 0.5 to 5000 µmol/mol		0 to 60	0.2 to 7		+
	Systech Illinois (H ₂ O)	MM300 [21]	< 5min	Annual calibration recommended	Dewpoint: -100 to 20 °C	No compatible with HCl, NH ₃ , Cl ₂	-40 to 60	450	30 to 420 NI/h	+without sampling system) 0: with
	Dr. Wernecke	Humitrace II			0 to 2000 ppm		5 to 65	1 to 5	20 NI/h, 100 NI/h	
Chilled mirror	Vympel (H ₂ O)	Cong Prima 2M	5-15 min (0.3 – 2 NI/min	"No drift"	Dewpoint: -30 to 30 °C			160-300	0.3 to 2 NI/min	00
	Vympel (H ₂ O)	FAS	5-15 min		Dewpoint: -80 to 60 °C (3 different ranges)		-20 to 80	<100	0.2 to 2 NI/min	00
	Vympel (H ₂ O)	Hygrovision			Dewpoint: -50 to 30 °C		-10 to 50	<100	0.2 to 2 NI/min	
	Baker Hughes (H ₂ O)	Optica			Dewpoint: -80 to 15 °C (1311-XR)		0 to 35	1 to 8	0.25 to 2.5 l/min	00
Metal oxide dew-point	Vympel (H ₂ O)	FAS-SW			Dewpoint: -100 to 20 °C (2 different ranges)		-40 to 60	<300	0.5 to 5 NI/min	
	Baker Hughes (H ₂ O)	HygroPro [23]	15s		Dewpoint: -110 to 20 °C		-20 to 60	to 345		+ (excl. sample system)
	Baker Hughes (H ₂ O) (aluminum oxide)	M Series Probe [20] or IQ probe??	No info		Dewpoint: -110 to 60 °C overall in 3 ranges (ex: -110 to -50 °C)		0 to 60	<0.01 to 345		
	Servomex (H ₂ O) (info asked 200923) (aluminium oxide)	Aquaxact 1688 [22]			Dewpoint: -100 to 20 °C	No info	No info	No info	No info	No info
Surface Acoustic wave	Ball Wave (H ₂ O)	FT-300WT	<1s		H ₂ O: 1-4000 µmol/mol		10-40	Atmospheric pressure	0-1 l/min	0

Tunable diode laser absorption spectroscopy	Baker Hughes (H ₂ O)	Aurora	<2		H ₂ O: 2-1000 μ mol/mol		-20 to 65	Max 14	5-30 l/min	00
Spectrometry laser photoacoustic	MirSense (H ₂ O, NH ₃ , CH ₂ O) In development: CO, CO ₂ , CH ₄	Multisense	<30-60s	Very high due to wavelength laser selection	H ₂ O: 1 μ mol/mol NH ₃ : 100 nmol/mol CH ₂ O: 50-100 nmol/mol	Recalibration (verification) every 6 months	-20 to 100	0,5-2 (abs)	10-80 ml/min	1 gas: 0 4 gas: 00
MID infra red	Intelligent Spectroscopy Solutions Inc	VX1169	<30s	High	H ₂ O: (1 μ mol/mol) CO (20 nmol/mol)	Calibration not required for 2 years	-40 to 50	0.8 to 1.2	1 Sl/min	+
Direct reading tubes (chemical reaction)	Draeger		Some seconds to several minutes	Interferences are different for each type of tubes	NH ₃ : (2.5 μ mol/mol) CO (2 μ mol/mol) H ₂ O (60 μ mol/mol)	-		Close to atmospheric		++

*if a signal is observed even at low amount fraction of hydrogen, it is very likely that the signal will be saturated in almost 100% hydrogen

The prices are indicated by ranges

++: < 1000€

+: 1000 – 5 000€

0: 5001 – 10000€

00 >10000€

Table 2. Multi-component analysers for online monitoring of hydrogen purity (all information from providers unless specified otherwise)

Technology	Response time	Sensitivity	Selectivity	Stability	Flow rate	Pressure	Price range
FTIR (MKS)		H ₂ O 0.1 μ mol/mol CO 0.01 μ mol/mol CO ₂ 10 nmol/mol HCHO 20 nmol/mol HCOOH 0.1 μ mol/mol NH ₃ 20 nmol/mol CH ₄ : 30 nmol/mol	As each chemical compound is comprised of a unique combination of atoms, no two compounds produce the exact same IR spectrum.		30-60 l/h		00
CRDS (Tiger Optics)		H ₂ O: 1-6 nmol/mol O ₂ : 2.5 nmol/mol CO ₂ : 50-250 nmol/mol	Very high, typical H ₂ sample purity	Short-term: \pm 0.75%, 1 σ	Typical 30-60 l/h, flow as low as 3	1 bar typical (gauge pressure), models for	00

		CO 150-250 nmol/mol (50 nmol/mol is in development) HCHO: 6 nmol/mol NH ₃ : 1 nmol/mol CH ₄ : 1-2 nmol/mol HCl: 1 nmol/mol	has no known interference	Long-term: ± 1% over one year (99% confidence) [†]	l/h possible for CO, CO ₂ , CH ₄	lower pressure available on request	
OFCEAS/CEAS (AP2E)		H ₂ O 1 nmol/mol O ₂ 0.5 µmol/mol CO ₂ 2 nmol/mol CO 1 nmol/mol HCHO 1 nmol/mol HCOOH 5 nmol/mol NH ₃ 10 nmol/mol CH ₄ : 1 nmol/mol H ₂ S 2 nmol/mol HCl	Very good as the measurement principle allows the identification of absorption peaks with a very narrow spectral width		10-20 l/h		00
BTL		H ₂ O CO ₂ HCHO HCOOH					
TDL	<4s (H ₂ O in N ₂)	H ₂ O 1 µmol/mol CH ₄ 1 µmol/mol	Very good as the wavelength specific laser light is absorbed very selectively by only one specific molecule	Negligible drift (<2% of measurement range between maintenance intervals)		0.8-2 bar	0
Micro-GC (Agilent 990 Micro GC)	1-2 min	Ar 5-10 µmol/mol O ₂ 5 µmol/mol N ₂ 5-10 µmol/mol CO 5-10 µmol/mol CH ₄ 5-10 µmol/mol CO ₂ 5-10 µmol/mol	Very good due to the GC separation	Negligible. Calibration interval depends on application (can be very day, every 100 injections...)		1 bar (pressure can be reduced)	00

GC-IMS	Typically 10-90 s	HCHO 59 nmol/mol HCOOH 42 nmol/mol NH ₃ 1.4 nmol/mol H ₂ S 0.2 nmol/mol SO ₂ 4 nmol/mol C ₂ H ₄ S 4 nmol/mol Halogens Oils fats	Very high, through combination of two orthogonal separation methods (1. Fast GC, 2. IMS)	2-4 % per year	Typical 20-100 ml/min (laboratory usage)	0-0.5 bar	00
--------	-------------------	--	--	----------------	--	-----------	----

6 - State-of-the-art of tests of sensors performed for applications related to hydrogen purity testing

6.1 - MetroHyve 1

Alphasense CO-B4 sensor: the results in nitrogen were satisfactory with rapid reactions to different CO concentrations (2, 5 and 10 $\mu\text{mol/mol}$ increasing and decreasing) and good linearity in the range 2 to 10 $\mu\text{mol/mol}$, the signal was overloaded at 50 $\mu\text{mol/mol}$ CO in nitrogen. The signal was directly overloaded in hydrogen.

Figaro TGS3870 sensor was tested during the project MetroHyVe. The signal was directly overloaded in hydrogen.

Alphasense H2S-B4 sensor was tested during the project MetroHyVe. The signal was directly overloaded in hydrogen.

AP2E OFCEAS has been tested at the RISE in the laboratory for H_2S , CO, CO_2 , O_2 and H_2O . The instrument has also been tested online.

Two CRDS analyzers (one for H_2O , one for O_2) were part of the intercomparison done by NPL as part of MetroHyVe 1; both analyzers passed the test criteria.

Shell was developing a sensor in collaboration with Princeton for H_2O and CO to be installed at a HRS. The sensor was tested during MetroHyVe1. However, Shell has now decided to not move forward with the development of the sensor.

6.2 - Other projects

The U.S. National Renewable Energy Laboratory (NREL) tested CRDS among other analyzers for analysis of fuel-cell hydrogen in 2015; CRDS finished top in the test. The Korean Gas Safety Corporation (KGSC) uses CRDS analyzers to sample fueling station and developing methods to do this on a larger scale. California regulators use CRDS for H_2O , NH_3 and CH_2O detection in their fuel cell labs in Sacramento and Anaheim to test real samples from hydrogen fueling stations (research not available yet). A GC-IMS were tested by EMCEL online at HRS in Ulm and in Limburg for DAIMLER and H2 Mobility. The results are confidential but some fluctuations of the hydrogen quality was observed.

One of the deliverables of the HYDRAITE project was about the testing of online analysers for hydrogen fuel quality control [23]. In this work, the utilisation of a PEM (proton Exchange Membrane) type sensors was discussed. The idea is that although a PEM-sensor system will not be selective, it would give an indication in case impaired fuel is dispensed at the HRS. Some preliminary tests have been performed during Hydraite and the results showed that more work is needed before implementing these kinds of sensors at a HRS (inclusive the evaluation of irreversible degradation, sensor lifetime, automation...) The concept is being also tested by LANL (Los Alamos National Laboratory) as part of a project having as scope to develop a device using a MEA (Membrane Electrode Assembly) to measure impurities in a dry fuel stream of hydrogen at and above the SAE J2719 levels [24] with a quick response ($t < 5$ min). A Nafion based electrochemical hydrogen contaminant detector was tested at a HRS in Burbank, USA with promising results (effective detection of CO down to 1 $\mu\text{mol/mol}$). To our knowledge, none of these sensors are yet commercially available.

7 – Conclusions and criteria to select sensors/analysers to test for the other activities

Based on the Table 1, it appears that there is not a large selection of commercial sensors/analysers in the price range under 5000€. This is probably because the demand is not yet sufficient for sensors/analysers providers to develop products. However, it is likely that all existing sensors/gas analysers have not been identified at the time this report was produced and it is also possible that new sensors/analysers will soon be developed.

However, a discussion platform between sensors/analysers providers and the hydrogen industry may be relevant to develop in order to share information, discuss research and development requirements and develop a better collaboration between both parts.

The choice of the sensors to be tested can be based on the compounds. For instance, some compounds are important to directly analyse onsite to be sure that detect eventual leakage (H₂O, O₂, N₂). The choice of relevant compounds can also be based on results from studies where hydrogen has been analysed, (selection of the impurities that have actually been found in real hydrogen samples).

As stated in the protocol, stable impurities shall be chosen. Another important criterion is as mentioned above, the price range as the goal was initially to test “low-cost” sensors. However, due to the limited number of sensors/analysers identified at a cost of less than 5000€, the final selection of sensors/analysers to be tested may include some more expensive models.

References

- [1] ISO14687:2019 - hydrogen fuel quality – product specification
- [2] EN17124:2018 -Hydrogen fuel - Product specification and quality assurance - Proton exchange membrane (PEM) fuel cell applications for road vehicles
- [3] MetroHyVe D6 “Report recommending the best strategies for developing and implementing low cost sensors for performing online measurement of impurities in hydrogen at refueling stations”
- [4] Hydrogen D3 “Assessment report of a multi-component analyser with optimised sampling analysis that meets the required detection limits as per business ISO/TC197 and CEN/TC268”
- [5] ISO21087:2019
- [6] SemeaTech Note 181223 (Electrochemical gas sensor specifications) [6].
- [7] General verification protocol for portable multigas analysers, Environmental Technology Verification Program, Advanced Monitoring Systems Center, EPA, 2003 [
- [8]. Protocol of evaluation and calibration of low-cost gas sensors for the monitoring of air pollution, JRC Technical Reports, 2013
- [9] Air Sensor Performance Targets and Testing Protocols," 17 march 2021. [Online]. Available: <https://www.epa.gov/air-sensor-toolbox/air-sensor-performance-targets-and-testing-protocols>.
- [10] « Hydrogen Sulfide », *Alphasense*. [En ligne]. Available online: <http://www.alphasense.com/index.php/products/hydrogen-sulfide-safety/>. [visited 200922].
- [11] « Carbon Monoxide », *Alphasense*. [En ligne]. Available online: <http://www.alphasense.com/index.php/products/carbon-monoxide-safety/>. [visited 200922].

- [12] « Trace Oxygen Analyzer: sample panel or wall-mounted GPR-1500 Series », *Analytical Industries Inc.* [En ligne]. Available online: <https://www.iii1.com/products/trace-oxygen-analyzer-for-wall-and-panel-installations.htm>. [visited 200922]
- [13] « Southland Sensing Ltd. - Southland Sensing O2 Sensors (Gas) Available online: <http://www.sso2.com/products/industrial-oxygen-sensors>. [visited 200922]
- [14] « EC91 ATEX o2 analyzers », *Systech Illinois* Available online: <https://www.systechillinois.com/en/products/ec91-safe-oxygen-analyser>. [visited 200922]
- [15] « Carbon Monoxide Sensor 0-25µmol/mol », *Aeroqual*. Available online: <https://www.aeroqual.com/product/carbon-monoxide-sensor-0-25µmol/mol>. [visited 200922]
- [16] « Oxygen Sensors & Gas Sensors by AMI », *Advanced Micro Instruments inc.* Available online <https://www.amio2.com/oxygen-sensors>. [visited 200922]
- [17] « AQUATRACE® - IV Typ - W wall unit - Gas Detection, trace moisture, gas humidity », *DKS engineering*. Available online: [s](https://www.dks-engineering.com/aquatrace). [visited 200923]
- [18] « MM500 Moisture Detector for use in process gas analysis », *Systech Illinois*. Available online <https://www.systechillinois.com/en/products/mm500-moisture-analyzer>. [visited 200923]
- [19] « UBER M-I », *MEECO*. Available online: <http://meeco.com/meeco/wp-content/themes/meeco/pdf/english/M-i.pdf> [visited 200923]
- [20] https://www.bakerhughesds.com/sites/g/files/cozyhq596/files/2020-09/IQ.probe%20Aluminum%20Oxide%20Moisture%20Probe_CS.pdf (to update from D6)
- [21] « MM400 Moisture Analyzer for process gas measurement », *Systech Illinois*. Available online: <https://www.systechillinois.com/en/products/mm400-moisture-analyzer>. [Consulté le: 22-mars-2019].
- [22] « AquaXact 1688 - SERVOPRO Safe Area - Product Ranges - Gas Analyzers | Servomex ». Available online: <https://www.servomex.com/gas-analyzers/product-ranges/servopro/aquaxact-1688> [visited 200923]
- [23] « HygroPro », *General Electric*. Available online: https://www.gemeasurement.com/sites/gemc.dev/files/hygropro_datasheet_english.pdf [visited 200923]
- [24] HYDRAITE – Hydrogen Delivery Risk Assessment and Impurity Tolerance Evaluation, D3.2: Initial report on testing of inline analysers for hydrogen fuel quality control, T. A. Aarhaug, A. Kabza, R. Herrera, T. Bacquart, J. Viitakangas, S. Escribano, 2019
- [25] SAEJ2719 – Hydrogen Fuel Quality for Fuel Cell vehicles, 2020