METROLOGY for HYDROGEN VEHICLES 2

REPORT:

A2.4.4: Guideline report for laboratory-based validation and quality control of sensors

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Summary

This report was written as part of activity 2.4.4 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.

Confidentiality	Public

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Contents

Contents

1 - Abstract

Quality standards for hydrogen used for fuel cell electric vehicles such as ISO 14687 [1] or EN 17124 [2] specify maximal thresholds for some impurities which could damage the fuel cells. A complete analysis following ISO 14687 or EN 17124 standards is costly and it involves expensive analysers. Sensors could be a promising alternative to reduce the cost of quality control of hydrogen and provide information directly at the station. A review of state-of-the-art suitable sensors and analysers for detecting impurities in hydrogen [3] was done as part of metroHyVe 2 activity A2.4.1 and showed that currently, most of the low-cost sensors intended for use in hydrogen are for moisture analysis. Following this guideline, a laboratory evaluation of ATEX classified moisture sensors was considered as an appropriate next step. This report will present the result of the laboratory evaluation and describe the metric tested and the analytical protocols.

2 - Keywords

Hydrogen, ISO 14687, sensor, analyser, moisture

3 - 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 (i.e., boat, car, train, bike, engine, forklift). For fuel cell electrical vehicles (FCEV), high quality hydrogen is needed to ensure efficient energy conversion and to preserve the performance of fuel cells in the vehicles [4]. 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) [4].

The presence of impurities in hydrogen, like for example carbon monoxide, which is a catalyst poison, degrades cell performance. This degradation leads to a decrease of the electrical production efficiency. ISO14687 and EN17124 stipulate the maximum amounts of impurities acceptable in hydrogen, as shown in Table 1. The contaminants potentially present in the hydrogen are dependent on the process technology and on the further purification steps.

Table 1: Fuel quality specification for PEM fuel cell road vehicle application [1]

Compounds	Limits	
	minimum (%)	maximum (µmol/mol)
Hydrogen content (H_2)	99,97	/
Water (H_2O)	/	5
Hydrocarbon compounds (without methane)	/	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 (HCOH)	/	0,01
Formic acid (HCOOH)	/	0,2
Total Sulphur compounds (base H_2S)	/	0,004
Ammoniac (NH_3)	/	0,1
Total halogen compounds	/	0,05

In the project MetroHyVe 2, a state-of-the-art: “Review of the state of the art of online gas sensors/analysers'' [3] was done. This review shows that there is not a large selection of sensors/analysers with a purchase price below 5 k€. Many sensors are not sensitive enough to detect impurities in hydrogen at the level required in ISO 14687. This lack of commercially available sensors can be due to the contaminant itself, the hydrogen matrix and/or the stringent limits of detection required in the standards.

For the contaminants in table 1, an online analysis could ensure the quality of H_2-fuel while avoiding the drawbacks of an offline analysis. However, before implementing any sensor onsite, it is crucial to ensure that they will provide reliable measurements as important decisions would be made based on this (shut down of a station). The test of sensors can first be done in a laboratory environment, which is easier using a specially designed test rig. The most important metrics, including the response time, the accuracy and the precision can then be assessed.
To demonstrate how to test sensors, three moisture sensors using different measurement principles (phosphorus pentoxide sensor, aluminium oxide sensor and chilled mirror) were selected from the review of state-of-the-art [3] and their analytical performances were assessed for measurements close to the threshold in the standard.

The measurement of water is of high importance. As a reminder, at some points of the hydrogen refuelling stations (HRS), the hydrogen is cooled at -40°C and pressurised to 350 or 700 bar. In these conditions, water is an issue for hydrogen dispensing systems, for the on-board vehicle tank system and for fuel cell components due to the formation of ice [5].

This guideline is divided into two parts:

- the testing rig, the protocol and the analytical parameters for the laboratory-based validation of sensors.
- the technologies and the results obtained for each sensor in the laboratory condition.

4 - Glossary

Bara: it is the abbreviation for absolute pressure in bar unit for which the 0 corresponds to the vacuum.

Dew point: “temperature at which the vapour pressure of the vapour in a humid gas is equal to the saturation vapour pressure over pure liquid and at which condensation forms as liquid on cooling the gas. “

FCEV: fuel cell electrical vehicles

HRS: Hydrogen Refuelling Station

NPL: National Physical Laboratory

5 - Validation and/or verification of online sensors

The aim of this task is to highlight how and why it is important to perform a laboratory-based validation study of online sensors for the continuous measurement of impurities in gaseous hydrogen fuel in compliance with the hydrogen quality required by ISO 14687.

5.1 - Testing rig

The first step in the validation of online sensors is the design of a testing rig available with precise functions. The testing rig must include:
- Parallel distribution of the sampling gas,
- Several dilution level,
- Settings for the pressure,
- Settings for the flow rate,
- Purge line with nitrogen or neutral gas for safety issues during hydrogen works.

In 2021, no dedicated testing rig is available for validation of online sensors to measure impurities in hydrogen. During MetroHyve 2, Air Liquide has designed and developed a testing setup dedicated to the assessment of these types of sensor's metrics (fig. 1).

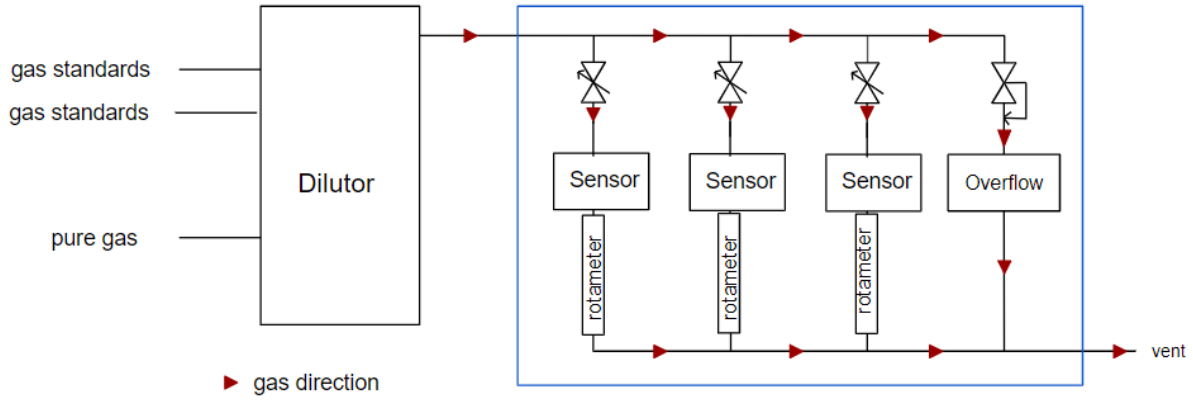


Figure 1: Testing rig

This testing rig is composed of:
- Parallel gas channels in order to test several sensors at the same time. For example, the different levels of concentration are tested at the same time on several sensors.
- Independent setting pressure and flow rate for each gas channel. Evaluation of a concentration level at the same time for each sensor but with their own optimised flow.
- A gas dilutor device, in this case, it was the Gasmix dilutor AIOLOS II. This instrument mixes the gases by controlling the gases' mass flow to dilute gas standards and generate several levels of dilution
- A neutral purge line to get to safety the testing rig.

The uncertainty of the mixture generated by the dilutor is calculated with the uncertainty of the cylinder (10 µmol/mol) and the uncertainty of flow deliver by the flow's mass controller in the dilutor (2%) with the following equation:

$$\frac{u_c(Z)}{Z} = \sqrt{\left(\frac{u(X_1)}{X_1}\right)^2 + \left(\frac{u(X_2)}{X_2}\right)^2 + \left(\frac{u(X_3)}{X_3}\right)^2}$$

with $u_c(Z)$: uncertainty of the mixture
Z: concentration of the mixture
$u(X_1)$: uncertainty of the cylinder
X1: H_2O concentration in the cylinder
$u(X_2)$: uncertainty of the H_2 mass flow
X_2: Mass flow of H_2
$u(X_3)$: uncertainty of the H_2O mass flow
X_3: Mass flow of the H_2O QS H_2

Then the uncertainty of the measurement is multiplied by factor equals to 2 to obtain the expanded uncertainty which contains 95% of the possible values. For all the concentrations, the uncertainty of the mixture analysed is 10% and it is essentially due to the uncertainty of concentration of water in the cylinder.

5.2- Metrics

The metrics tested during the sensor evaluation are the sensitivity, the response time, the trueness, the intermediate precision and the cross sensitivity of CO on H_2O measurement:

- The **sensitivity** is the ability to detect the analyte of interest.
- The **response time** is how quickly the sensor reacts between the start of concentration variation to the stable measurement.
- The **linearity** is the link between the several concentrations obtained by using the method.
- The measurement '**trueness**' is an expression of how close the mean of a large number of results produced by the method is to a reference value. Trueness is expressed quantitatively by the bias.
- The **intermediate precision** is the precision under intermediate precision conditions (the same measurement procedure, same location, and replicate measurements on the same or similar objects).
- The **cross sensitivity** or **selectivity** is the ability to measure the analyte of interest in samples containing specific interferences. [6] [7]

5.3 - Protocols

To evaluate the metrics (sensitivity, response time, linearity, trueness and intermediate precision), a minimum of five concentrations close to the threshold are used (both higher and lower). The set of concentrations is repeated over several days. A set of analysis allows us to assess the sensitivity, the response time, the linearity and the trueness (bias):

- The **sensitivity**, a qualitative metric, is observed with the variation of the different concentrations used.
- The **response time** is defined by using two different attributes: the rising and the descending response time. The T90 rising response time is the time needed by an analytical device to reach 90% of the final value and the T10 descending response time is the time to reach 10% of the initial value.
- The **linearity** is obtained by correlating the mean of the measurements obtained in function of the theoretical concentration.

- The **intermediate precision** is assessed by using the standard deviation of the results over days of analyses sets.
- The **trueness** is based on the measurement of bias by using the comparison of the mean of the results obtained from the method and the reference value.
- The **selectivity** is acceptable if the effect of interference is examined by the analysis of mixtures containing suspected interferences in the presence of analytes of interest.

5.4 - Example of results

Three sensors are selected from a state-of-the-art: "Review of the state of the art of online gas sensors/analysers'' [3] and for each sensor, the metrics are evaluated: the sensitivity, the response time, the linearity, the trueness and the intermediate precision. In our case, the threshold of the analyte of interest is 5 µmol/mol. The following concentrations were used to assess the metrics: 0.5, 1, 3, 5, 8, 12 and 20 µmol/mol of H_2O with balance H_2.

5.4.1 - Sensor description

In this part, the technologies used in this report for the analysis of humidity in hydrogen are detailed, i.e., phosphorus pentoxide sensor, aluminium oxide sensor and chilled mirror.

5.4.1.1 **- Pentoxide phosphorus sensor**

The pentoxide phosphorus sensor uses the hygroscopic properties of the P_2O_5 leading to the absorption of humidity.
This sensor is composed of two platinum winding electrodes coated with a film of phosphorus pentoxide (fig.2). The water molecules present in the gas, pass through the P_2O_5 to be electrolysed by the electrodes. The current generated is directly proportional to the amount of water in the gas.
To use this sensor, a regular regeneration of the phosphorus pentoxide by a solution of phosphoric acid is necessary.

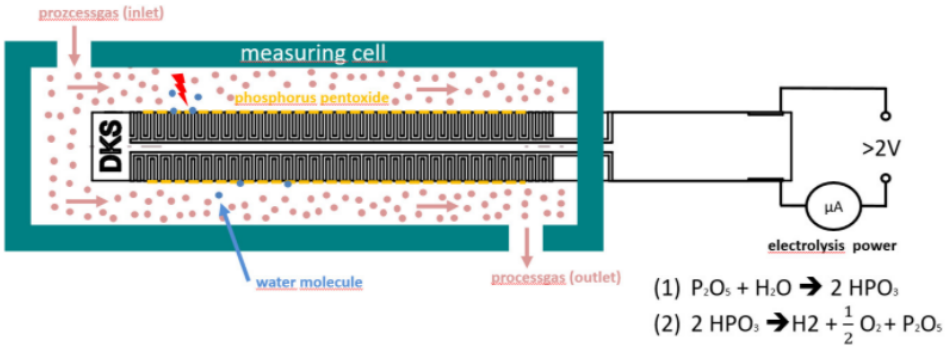


Figure 2: Scheme of the phosphorus pentoxide moisture sensor [8]

The pentoxide phosphorus sensor characteristics are described in table 2.

5.4.1.2 **- Aluminium oxide sensor**

The aluminium oxide sensor is composed of a permeable gold film and a porous film of Al_2O_3 on a ceramic medium which absorbs water (fig.3). The gold and the aluminium oxide are the electrodes of the sensor, and the size of the oxide film makes the sensor specific to H_2O. The absorption of water by the Al_2O_3 changes the sensor capacitance (its capacity to store energy as electric charges), which is used to calculate the water content in the gas.

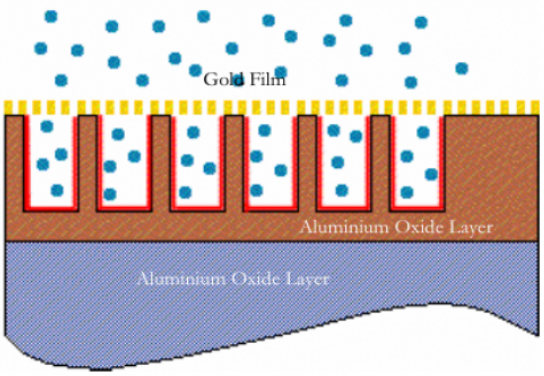


Figure 3: Scheme of the aluminium oxide moisture sensor [9]

The aluminium oxide sensor characteristics are described in table 2.

5.4.1.3 - Chilled mirror

The chilled mirror determines the dew point of a gas mixture by cooling it at constant pressure until the water condenses on a mirror. The condensation droplet is then detected by a photodetector and the mirror temperature is the temperature of the dew point of the gas which is dependent on the amount of H_2O in the gas (fig.4).

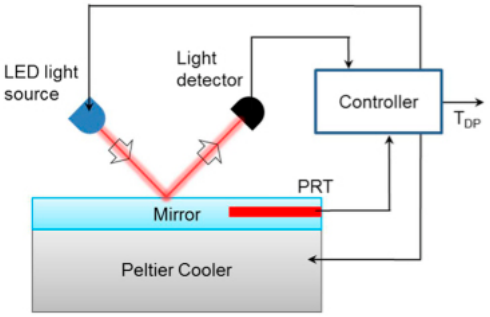


Figure 4: Scheme of a chilled mirror [10]

The chilled mirror characteristics are described in table 2.

5.4.2 - Comparison of the sensors

The following table gives the characteristics of the different sensors selected in this project.

Table 2: Characteristics of the sensors selected for the MetroHyVe 2 tests

Analytical technique	Pressure (bar)	Flow rate (L/min)	Predicted limit of detection (µmol/mol)	ATEX	Dimension (cm)	Price (k€)
P_2O_5	0.2-6.9	0.1	0.5	YES	13 x 7 x 6	<5
Al_2O_3	0-300	0.5-5	0.05	YES	12 x 3 x 3	<5
Chilled mirror	0-100	0.2-0.4	5	YES	31 x 31 x 20	10 - 20

5.4.3 - Sensors results

5.4.3.1 - Pentoxide phosphorus sensor

For the evaluation of the P_2O_5 sensor, the flow rate and the pressure are set at 100 mL/min and 2 bara, respectively. Figure 5 shows the results following exposure to 0.5, 1, 3, 5, 8, 12 and 20 µmol/mol of H_2O in balance H_2. The sensor is exposed to each concentration for 30 minutes and the flushing time (with pure H_2) between each concentration is also 30 minutes.

The results show that the sensor reacts rapidly to the changes in H_2O concentration. P_2O_5 is sensitive to moisture.

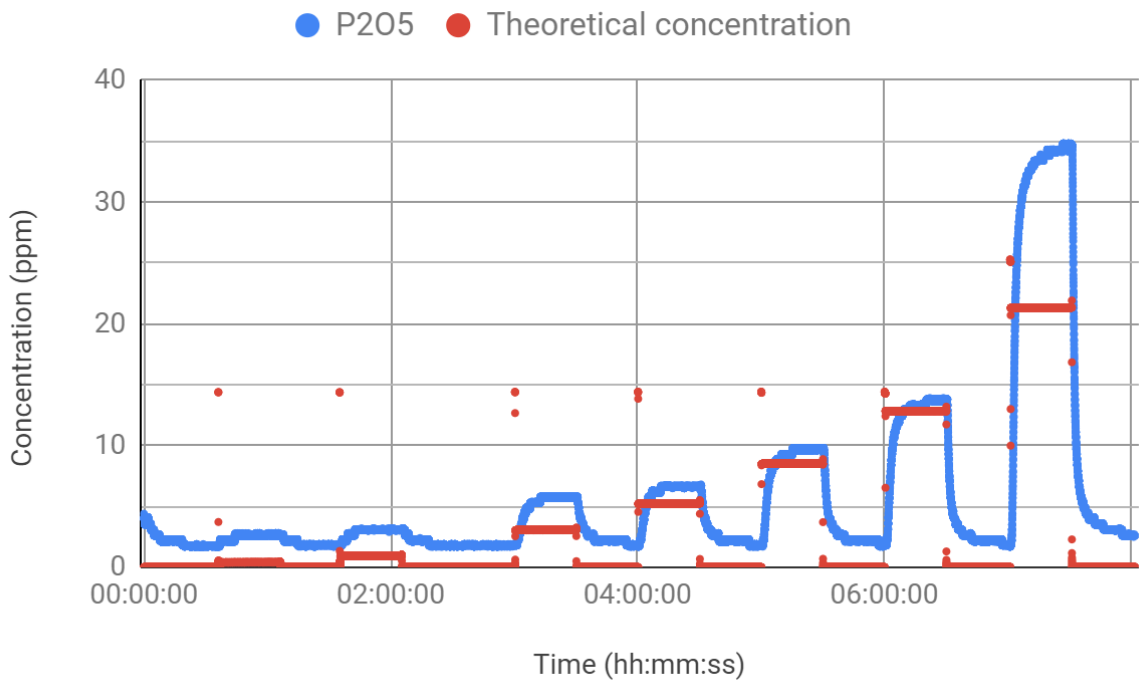


Figure 5: Analysis of various concentrations of H_2O in H_2 matrix (0.5, 1, 3, 5, 8, 12 and 20 µmol/mol) by the P_2O_5 sensor with a flow rate of 0.1 L/min and a pressure of 2 bara.

A) Response time

The response time is evaluated on five different days (rising: average time needed to reach 90% of the stable reading (T90) and descending: average time to reach 10% of the stable reading (T10) during the return to the baseline) for each concentration (fig.6). The results show that T90 decreases with concentration increases, with an average value of 9 minutes (540 seconds) while T10 increases between 0.5 and 5 µmol/mol and decreases from 5 µmol/mol to 22 µmol/mol, with an average value of 6 minutes (360 seconds). The P_2O_5 sensor can therefore detect low levels of moisture in the hydrogen matrix relatively rapidly.

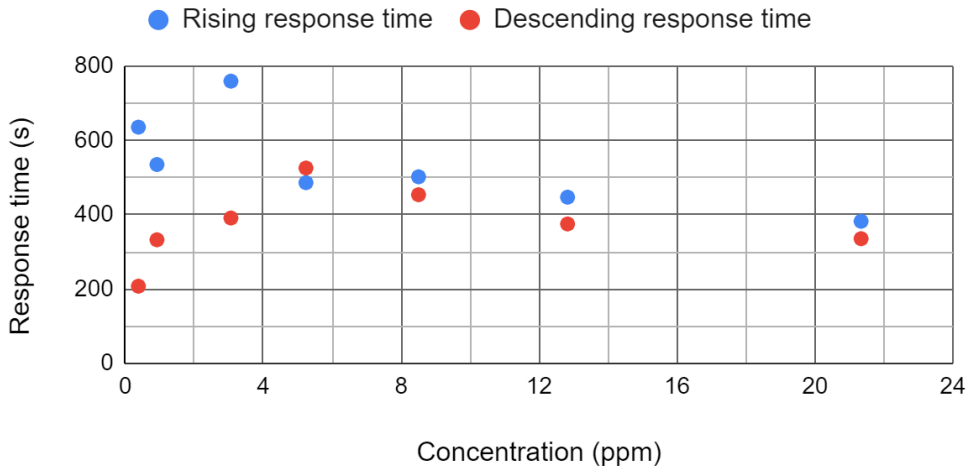


Figure 6: The average T90 and T10 on 5 different days of the P_2O_5 sensor in function of the amount fraction of water in µmol/mol

B) Linearity

The linearity is evaluated by using the average concentration measured for each concentration on 5 different days (fig.7). As it can be seen on figure 7, the sensor is linear all over the range, from 0.5 to 20 µmol/mol with a correlation coefficient (R^2) higher than 0.99, i.e., 0.995 in fig7.

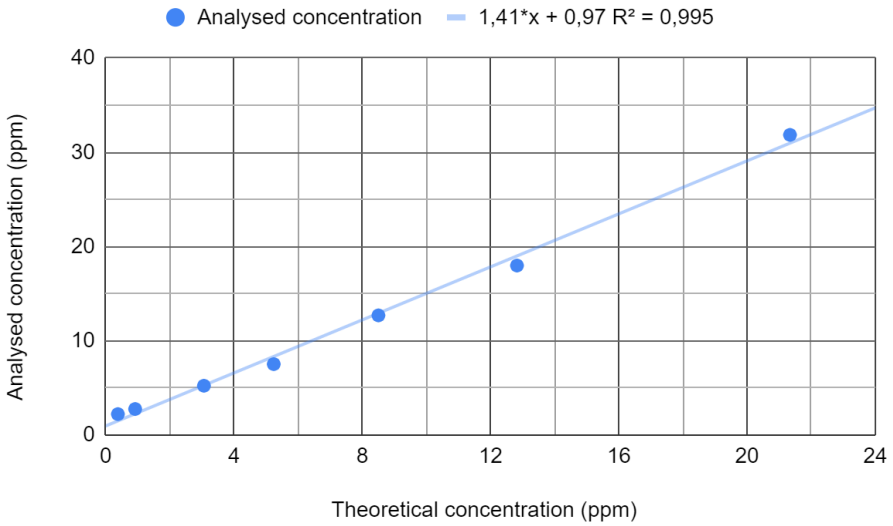


Figure 7: The linear calibration curve of P_2O_5 sensor

C) Trueness

The average bias (difference between the expected concentration and the measured concentration) is used to evaluate the trueness of the P_2O_5 sensor at each concentration. The absolute bias calculated on five different days is found to be around 2 µmol/mol for concentrations between 0.5 to 5 µmol/mol (fig.9). The absolute bias then increases to reach around 10 µmol/mol for a concentration of 20 µmol/mol.

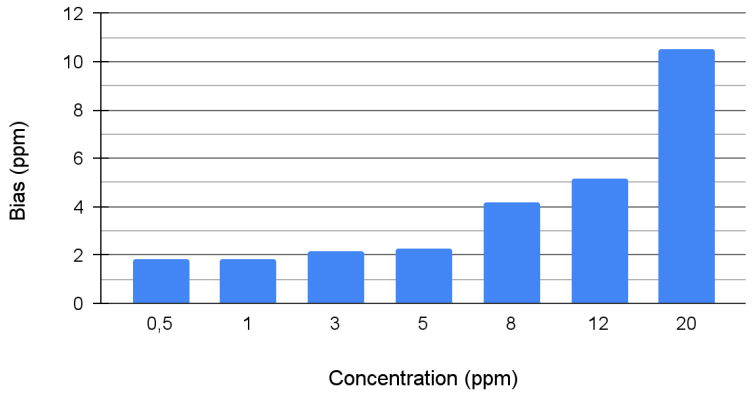


Figure 9: The mean absolute bias of the P_2O_5 for the analysis of H_2O on 5 different days

The relative bias calculated on five different days decreases with the concentration from 490% to 45% between 0.5 and 5 µmol/mol and between 5 and 20 µmol/mol, the relative bias is between 40 and 50% (fig.10).

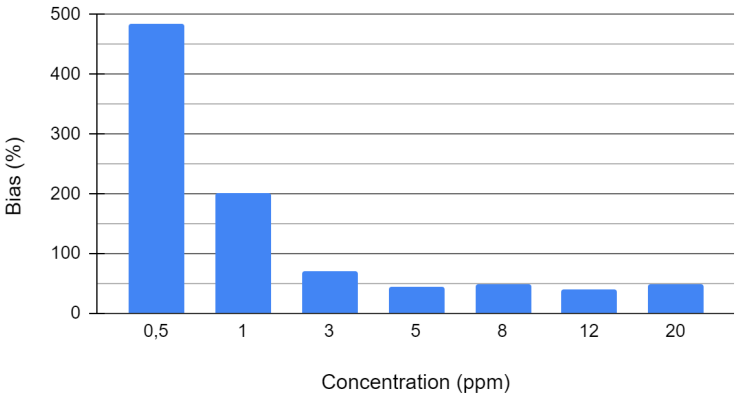


Figure 10: The mean relative bias of the P_2O_5 for the analysis of H_2O on 5 different days

D) Intermediate precision

The absolute standard deviation of the measurements obtained over 5 days at each concentration is used to determine the intermediate precision. The absolute standard deviation increases with the concentration (fig. 11).

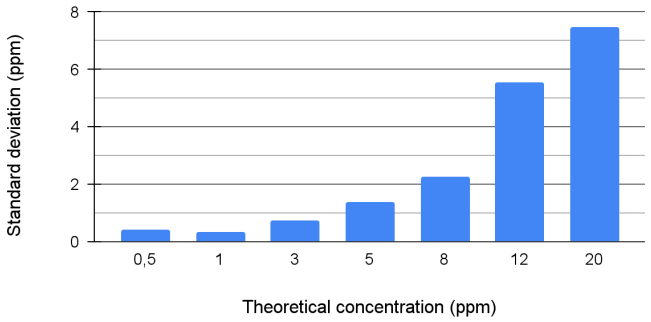


Figure 11: The absolute standard deviation on 5 different days of the P_2O_5 response

For all the concentrations between 0.5 and 20 µmol/mol, the relative standard deviation is between 10% and 30% (fig. 12).

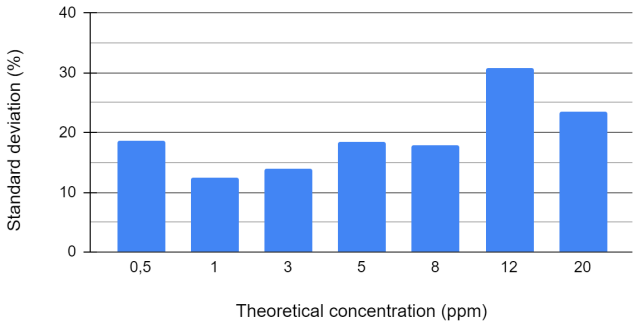


Figure 12: The relative standard deviation on 5 different days of the P_2O_5 response

E) Certified cylinder analysis

A gas mixture of 4.04 ± 0.22 µmol/mol of H_2O in H_2 gas balance is provided by NPL. This standard is diluted to 1 µmol/mol and it is analysed with the phosphorus pentoxide sensor in the same conditions as the previous analyses. The results obtained are compared to the previous analysis at 1 µmol/mol in table 3.

The analysis of 1 µmol/mol of H_2O in balance H_2 from the NPL cylinder is included in the interval of the intermediate precision of the concentration. The P_2O_5 sensor gives similar results with different gas suppliers.

Table 3: Comparison of the results for the analysis of water at 1 µmol/mol in hydrogen matrix

Mean concentration of 1 µmol/mol H_2O generated with the gas dilutor (µmol/mol)	**Intermediate precision (µmol/mol)**	**Mean concentration of the NPL cylinder diluted at 1 µmol/mol (µmol/mol)**	**Intermediate precision (µmol/mol)**
2.76	0.35	2.62	0.35

F) Selectivity

The effect of CO (threshold 200 nmol/mol according to EN 17214 [2]) on the moisture measurement is evaluated by using a gas standard cylinder from the NPL of 4.30 ± 0.22 µmol/mol H_2O and 200 ± 10 nmol/mol CO balance H_2. This standard is diluted to 1 µmol/mol of H_2O, and it is analysed with the phosphorus pentoxide sensor and it is compared to the previous results obtained for a mixture of 1 µmol/mol H_2O in balance H_2 (with only water in the hydrogen) in table 4.

In table 4, the results show that the measurement of 1 µmol/mol H_2O in H_2 is not affected by the presence of 50 nmol/mol CO.

Table 4: Comparison of the results for the analysis of a mixture of H_2O at 1 µmol/mol and CO at 50 nmol/mol in hydrogen matrix

Mean value of the mixture of 1 µmol/mol H_2O balance H_2 (µmol/mol)	**Intermediate precision calculated (µmol/mol)**	**Mean value of the gas standard cylinder 1 µmol/mol H_2O and 50 nmol/mol CO in balance H_2 (µmol/mol)**
2.8	0.4	2.2

The presence of CO doesn't inhibit the quantification of the analyte of interest, H_2O.

G) Conclusion

The P_2O_5 sensor provides reasonable rising and decreasing response times (T90 = 9 min and T10 = 6 min) for the measurement of H_2O in H_2. Moreover, the sensor is linear all over the range (0.5 to 20 µmol/mol) but a relatively high bias is observed especially at low concentration (490% of the value at 0.5 µmol/mol). Moreover, for all the concentration, the bias (between 45% and 490%) is higher than the uncertainty of the mixture analysed (10%) which showed that the bias is due to the sensor and not to the gas dilution. The presence of 50 nmol/mol of CO doesn´t interfere with the measurement of water.

5.4.3.2 - Aluminium oxide sensor

For the evaluation of the Al_2O_3 sensor evaluation, the flow rate and the pressure are set at 1 L/min and 2 bara, respectively. Figure 13 shows the results following exposure to 0.5, 1, 3, 5, 8, 12 and 20 µmol/mol of H_2O respectively in H_2. Each concentration runs for 30 minutes with a pure hydrogen flush time of 40 minutes.

This sensor reacts rapidly to the changes in H_2O concentration. The sensor reacts rapidly to the changes in H_2O concentration leading to a positive detection of the analyte of interest. Al_2O_3 is sensitive to moisture.

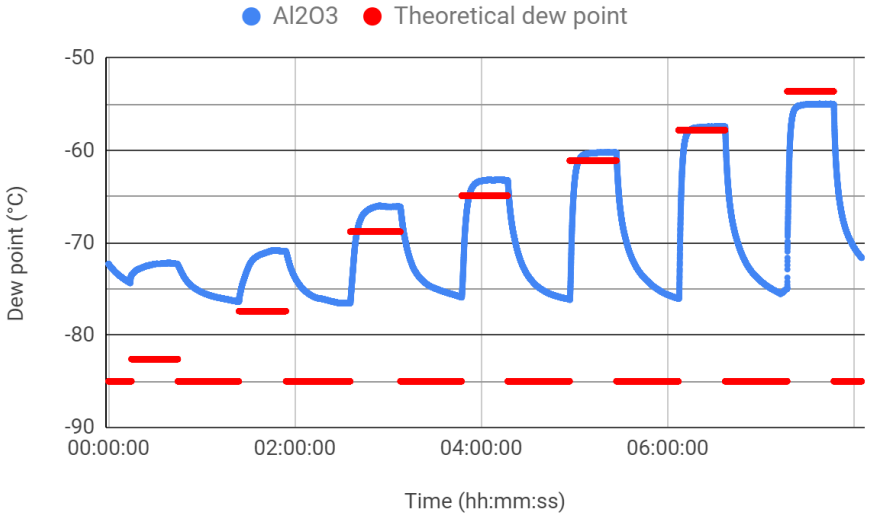


Figure 13: Analysis of various concentrations of H_2O in H_2 matrix (0.5, 1, 3, 5, 8, 12 and 20 µmol/mol) by the Al_2O_3 sensor with a flow rate of 1 L/min and a pressure of 2 bara

A) Response time

The response time is evaluated on five different days by calculating T90 and T10 when analysing moisture at each concentration (fig.14). T90 decreases with concentration, with an average value of 6 minutes while T10 increases with the concentration, with an average value of 19 minutes. The Al_2O_3 sensor can detect relatively rapidly low levels of moisture in hydrogen matrix but needs a relatively long time to return to the baseline after exposure to the decreasing high concentrations. This phenomenon can be explained by the saturation of the sensor which is more important at high concentrations than at low concentrations.

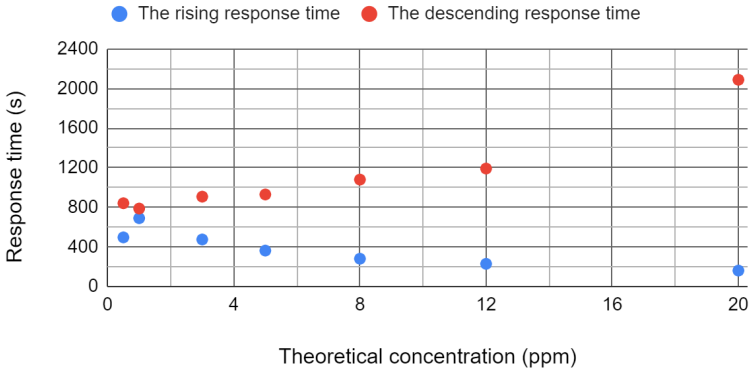


Figure 14: The average T90 and T10 on 5 different days of the Al_2O_3 sensor in function of water amount fraction in µmol/mol

B) Linearity

The linearity is evaluated by using the average dew point for each concentration on 5 different days (fig.15). The sensor response in function of the concentration is not linear but it can be represented by a second order polynomial with an R^2 higher than 0.99, i.e., 0.992 in fig15.

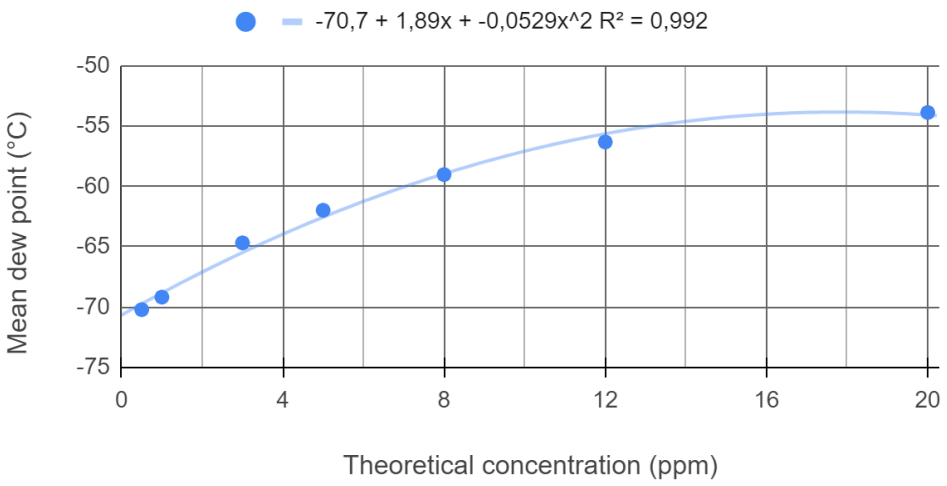


Figure 15: The second order polynomial calibration curve of Al_2O_3 sensor mean dew point (°C) in function of water amount fraction (µmol/mol)

C) Trueness

The average absolute and relative bias (difference between the expected concentration and the measured concentration) is used to evaluate the trueness of the Al_2O_3 sensor at each concentration. On figure 17, the absolute bias calculated on five different days is relatively stable with the concentration (increases only from 2 µmol/mol to 3 µmol/mol for concentrations between 0.5 and 12 µmol/mol and decreases to 0.2 µmol/mol for 20 µmol/mol). The bias is significant at low concentrations and smaller at higher concentrations.

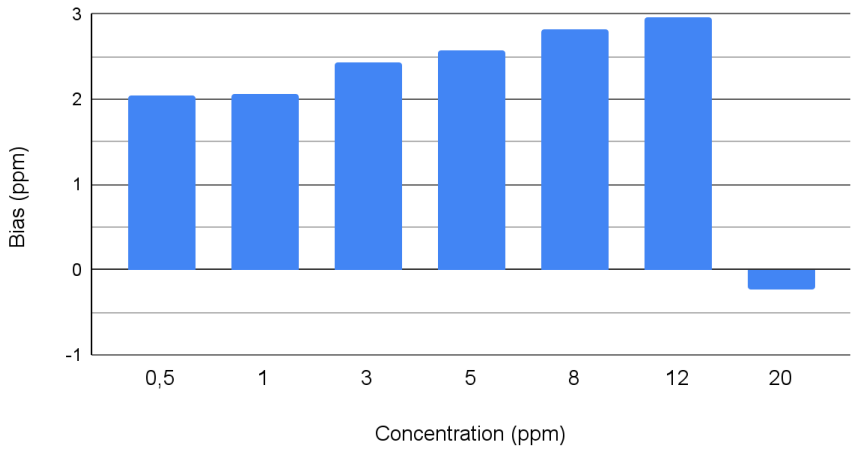


Figure 17: The mean absolute bias of the Al_2O_3 response on 5 different days

Figure 18 shows that between 0.5 and 20 µmol/mol, the relative bias decreases rapidly with the concentration from 540% at 0.5 µmol/mol to 1% at 20 µmol/mol.

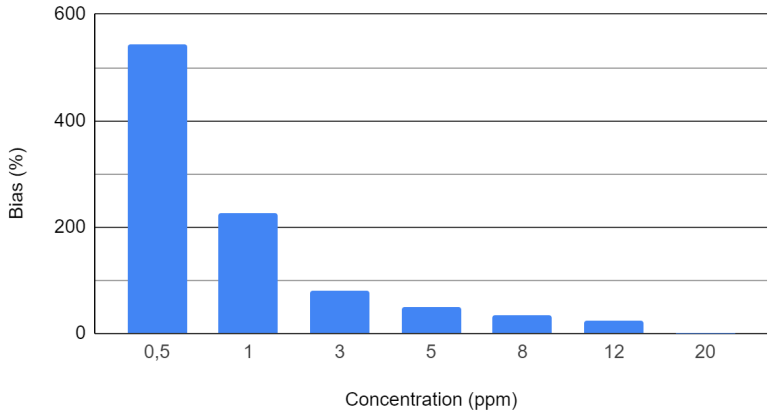


Figure 18: The mean relative bias of the Al_2O_3 response on 5 different days

D) Intermediate precision

The standard deviation over 5 days at each concentration is used to determine the intermediate precision. The absolute standard deviation for each dew point is around 1.5 °C (fig. 19). The Al_2O_3 sensor possesses the same intermediate precision over all the analytical range.

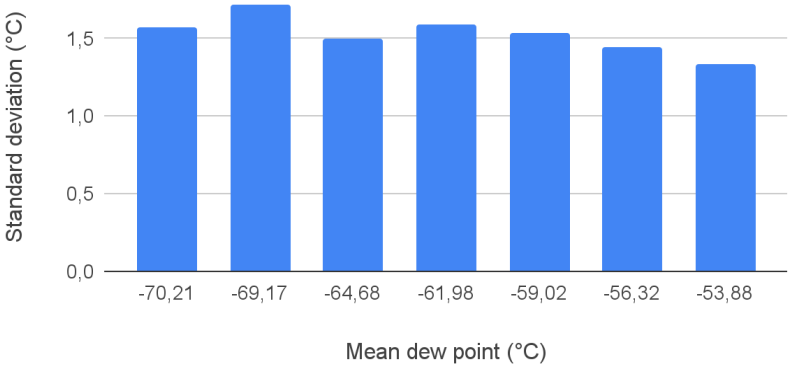


Figure 19: The absolute standard deviation of the dew point on 5 different days of the Al_2O_3 response

The absolute standard deviation, calculated in µmol/mol (fig. 20), increases from 0.6 µmol/mol to 3.3 µmol/mol between 0.5 and 20 µmol/mol. The conversion of the standard deviations in µmol/mol shows that the dispersion of the results increases with the concentration.

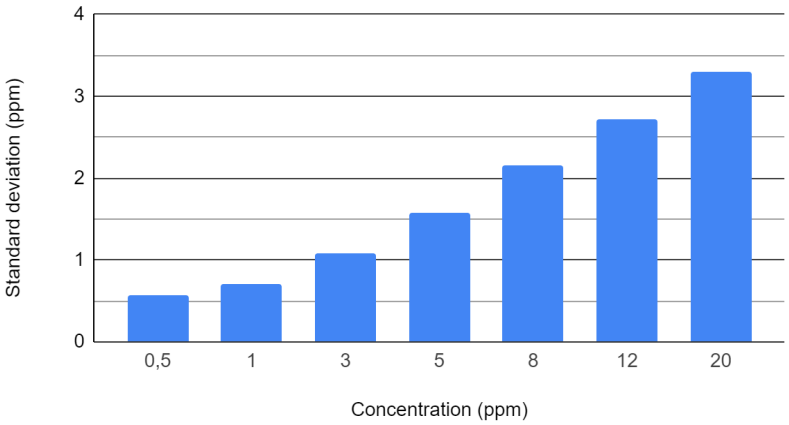


Figure 20: The absolute standard deviation of the concentration on 5 different days of the Al_2O_3 response

The relative standard deviation for each theoretical concentration decreased with the concentration from 25% at 1 µmol/mol to 16% at 20 µmol/mol (fig. 21).

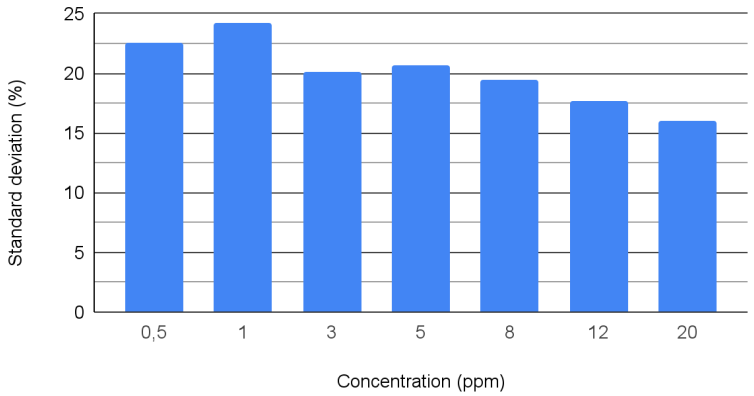


Figure 21: The relative standard deviation on 5 different days of the Al_2O_3 response

E) Certified cylinder analysis

A gas mixture of 4.04 ± 0.22 µmol/mol of H_2O in balance H_2 is provided by the NPL. This standard is diluted to 1 µmol/mol and it is analysed by the aluminium oxide sensor in the same conditions as the previous analyses. The results obtained are compared to the previous analysis at 1 µmol/mol in table 5.

The analysis of 1 µmol/mol of H_2O in the H_2 matrix from the NPL cylinder is included in the interval of the intermediate precision of the concentration. The Al_2O_3 sensor gives similar results with different gas suppliers.

Table 5: Comparison of the results for the analysis of water at 1 µmol/mol in hydrogen matrix

Mean concentration of 1 µmol/mol H_2O generated with the gas dilutor (°C)	**Intermediate precision (°C)**	**Dew point of the NPL cylinder diluted at 1 µmol/mol (µmol/mol) (°C)**
-69,172	1,5	-68,09

F) Selectivity

A test is carried out to verify if the presence of carbon monoxide (threshold 200 nmol/mol in hydrogen according to ISO 14687,[1]) interferes with the measurement of H_2O when using the Al_2O_3 sensor.

The evaluation of the effect of CO (threshold 200 nmol/mol according to EN17214,[2]) on the moisture measurement is evaluated by using a gas standard cylinder from the NPL of 4.30 ± 0.22 µmol/mol H_2O and 200 ± 10 nmol/mol CO in balance H_2. This standard is diluted to 1 µmol/mol and it is analysed with the aluminium oxide sensor and it is compared to the previous results obtained for a mixture of 1 µmol/mol H_2O in balance H_2 (with only water in the hydrogen) in table 6.

The analysis of a mixture of 1 µmol/mol of H_2O and 50 nmol/mol of CO in balance H_2 by the aluminium oxide sensor is included in the interval of the intermediate precision of concentration of the previous analyses. Moisture analysis by the Al_2O_3 sensor is not influenced by the carbon monoxide.

Table 6: Comparison of the results for the analysis of a mixture of H_2O at 1 µmol/mol and CO at 50 nmol/mol in hydrogen matrix

Mean dew point of the mixture of 1 µmol/mol H_2O balance H_2 (°C)	**Intermediate precision calculated (°C)**	**Mean dew point of the gas standard cylinder 1 µmol/mol H_2O and 50 nmol/mol CO balance H_2 (°C)**
-69,172	1,5	-70,23

G) Conclusion

The Al_2O_3 sensor measures relatively rapidly the increase of the concentration (T90 = 6 min) but the signal decreases slowly after exposure (T10 = 19 min) of humidity in hydrogen gas balance, the saturation of the sensor is more important at high concentrations than at low concentrations. Moreover, the sensor is not linear over the range and the bias is important at high concentration and relatively low at higher concentration whereas the standard deviation is acceptable all over the range. Moreover, at low concentration, the bias (160% for 0.5 µmol/mol) is higher than the uncertainty of the mixture analysed (10%), which showed that the bias is due to the sensor and not to the gas dilution. The presence of 50 nmol/mol of CO doesn´t interfere with the measurement of water.

5.4.3.3 - Chilled mirror

For chilled sensor evaluation, the flow rate and the pressure are set at 0.2 L/min and 2 bara, respectively. Figure 22 shows the results following exposure to 0.5, 1, 3, 5, 8, 12 and 20 µmol/mol of H_2O in H_2. Each concentration runs for 30 minutes with a flushing time of 40 minutes in between.

The chilled mirror cannot detect µmol/mol of moisture in hydrogen matrix meaning that this sensor is not sensitive enough to moisture. It is possible to analyse these amounts of water by cooling down the gas to analyse µmol/mol of H_2O by putting the chilled mirror in a refrigerator.

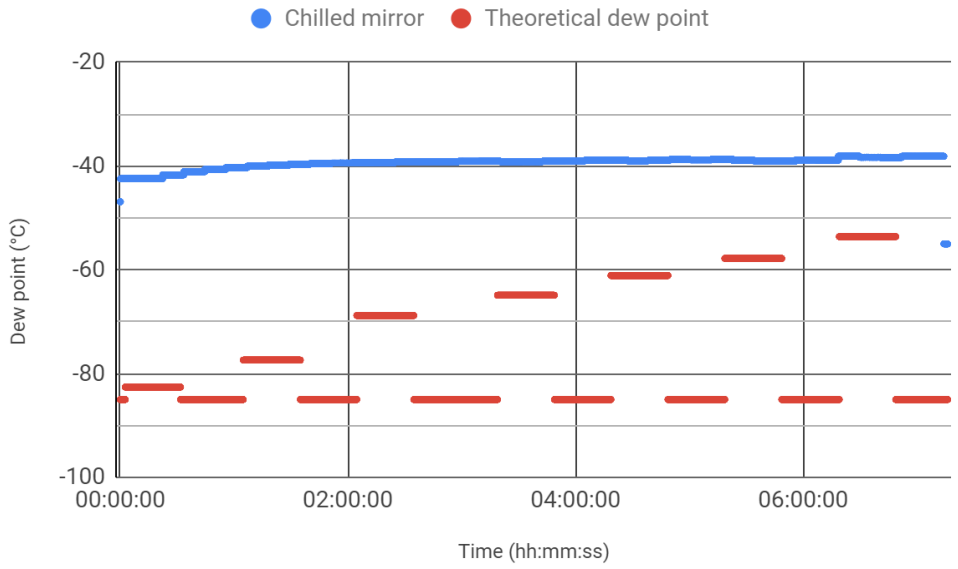


Figure 22: Analysis of different concentrations of H_2O in H_2 matrix (0.5, 1, 3, 5, 8, 12 and 20 µmol/mol) by the chilled mirror with a flow rate of 0.2 L/min and a pressure of 2 bara

Because the cooling device is not available at the time of the tests, the evaluation is stopped in the MetroHyVe 2 project.

5.4.3.4 Sensors comparison

To compare the performance of the P_2O_5 sensor and the Al_2O_3 sensor, the response time, the trueness and the intermediate precision of each sensor previously introduced are compared.

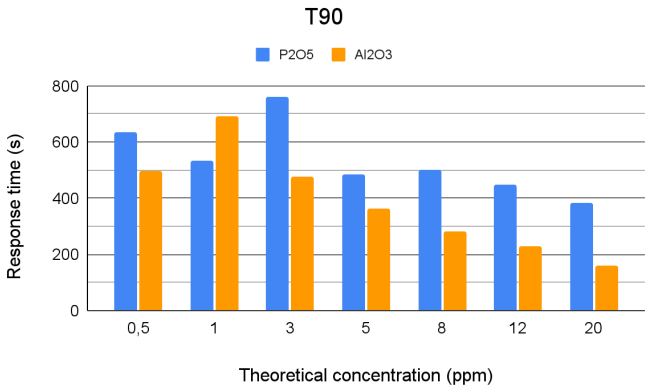
A) Response time

The T90 and T10 of the Al_2O_3 and P_2O_5 sensors are compared in table 8. The T90 of the phosphorus pentoxide sensor is slightly higher than the aluminium oxide sensor but the standard deviation intervals are overlapping. The T10 of the aluminium oxide sensor is higher than the T10 of the phosphorus pentoxide sensor with no overlap of the intervals.

Table 8: Comparison of the mean rising and descending response time of the Al_2O_3

Sensor	T90 (min)	T10 (min)
Al_2O_3	6 - SD = 3	19 - SD = 7
P_2O_5	9 - SD = 2	6 - SD = 2

The T90, at each concentration except at 1 µmol/mol, the P_2O_5 sensor is higher than for the Al_2O_3 sensor. Concerning the T10, at each concentration, it is higher for Al_2O_3 than for P_2O_5.



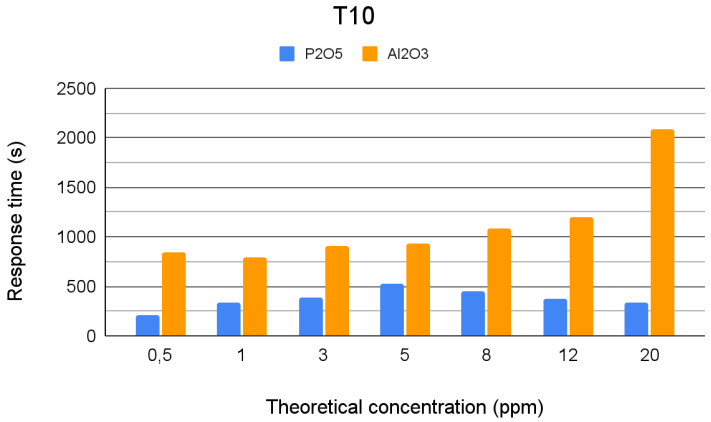


Figure 23: Comparative response time of T90 and T10 of the P_2O_5 and Al_2O_3 sensors measuring water concentrations from 0.5 µmol/mol to 20 µmol/mol in hydrogen.

B) Trueness

The bias obtained for the P_2O_5 sensor and the Al_2O_3 sensor are used to compare the trueness. The absolute biases analysed by the P_2O_5 and Al_2O_3 sensors are similar for concentrations under 5 µmol/mol while for concentrations higher than 5 µmol/mol, the bias is smaller for the Al_2O_3 sensor (fig. 24).

At the threshold, i.e., 5 µmol/mol, the trueness of the analysis of humidity by the 2 sensors is similar. For higher concentrations, best results are obtained with the Al_2O_3 sensor.

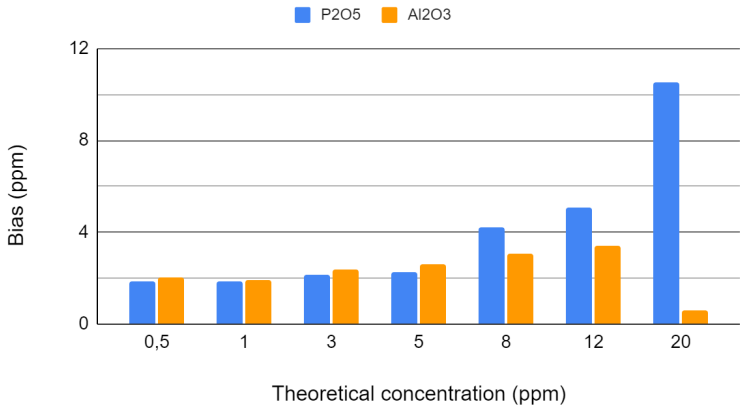


Figure 24: Comparative absolute bias of the P_2O_5 and Al_2O_3 sensors measuring water concentrations from 0.5 µmol/mol to 20 µmol/mol in hydrogen

Figure 25 shows that for both sensors, the relative bias decreases with the concentration, but for the P_2O_5 sensor, the relative bias is stabilised around 50% from 5 µmol/mol while the relative bias of the Al_2O_3 sensor continues to decrease with the concentration.

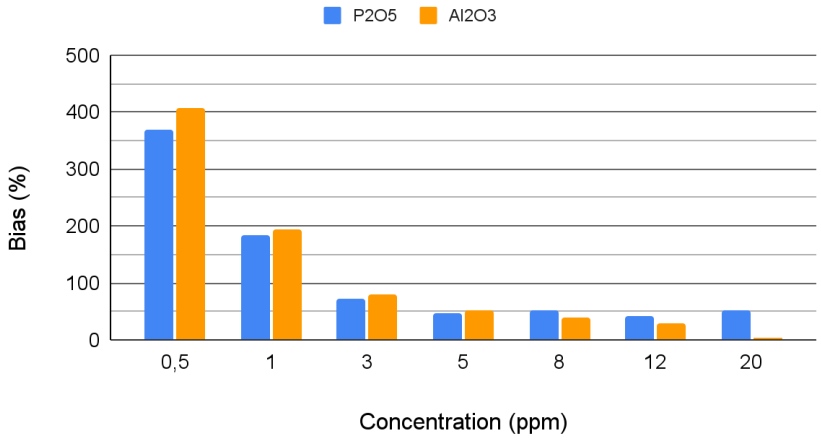


Figure 25: Comparative relative bias of the P_2O_5 and Al_2O_3 sensors measuring water concentrations from 0.5 µmol/mol to 20 µmol/mol in hydrogen

C) Intermediate precision

The standard deviation over 5 days of each concentration compared for the P_2O_5 sensor and the Al_2O_3 sensor. Between 0.5 and 8 µmol/mol, the absolute standard deviations of the two sensors are similar and from 12 µmol/mol, the deviation of the P_2O_5 results is more important than the deviation of the Al_2O_3 results (fig. 26).

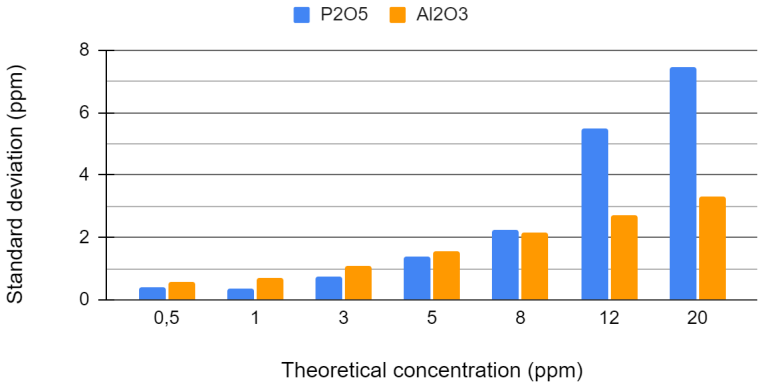


Figure 26: Comparative standard deviation over 5 days of the P_2O_5 and Al_2O_3 sensors measuring water concentrations from 0.5 µmol/mol to 20 µmol/mol in hydrogen

For the P_2O_5 sensor, the relative standard deviation is included between 10% and 30% while the relative standard deviation of the Al_2O_3 sensor is oscillated between 15% and 25% and decreases with the concentration (fig. 27). The P_2O_5 analysis is more reproducible than the Al_2O_3 analysis below 8 µmol/mol and the Al_2O_3 sensor is more reproducible from 8 µmol/mol.

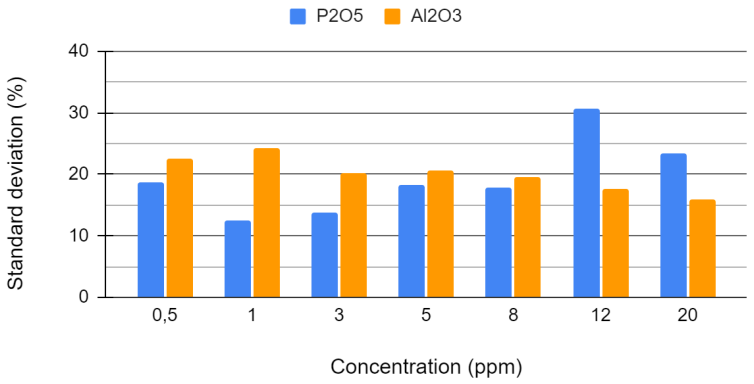


Figure 27: Comparative standard deviation over 5 days of the P_2O_5 and Al_2O_3 sensors measuring water concentrations from 0.5 µmol/mol to 20 µmol/mol in hydrogen

The two sensors are reproducible at low concentrations while at higher concentrations, the Al_2O_3 measurements are more reproducible than for the P_2O_5.

5.4.3 - Conclusion of the results

Three moisture sensors using different measurement principles (phosphorus pentoxide sensor, aluminium oxide sensor and chilled mirror) were selected from the state-of-the-art [3] and their analytical performances were assessed. The evaluation was not conducted on the chilled mirror

because it requires another device to cool the gas to measure µmol/mol of H_2O in hydrogen matrix, which was not available at the time of the measurements. The performances of the two other sensors are compared in table 9.

Table 9: Comparison of the performance of the Al_2O_3 sensor and the P_2O_5 sensor

Sensor	Positive point	Negative point
P_2O_5	- Low T10 - Lower intermediate precision over 5 days for low concentration - No CO cross-sensitivity	- High T90 - Significative bias at low concentration
Al_2O_3	- Low T90 - No CO cross-sensitivity	- High T10 - Significative bias at low concentration - Higher intermediate precision over 5 days for low concentration

For both sensors, the bias is significant, especially at low concentration for which the bias is higher than the uncertainty of the water dilution in hydrogen balance gas, which showed that the bias is due to the sensor. This observation confirms that standard gas must be used to determine the bias.

Thanks to these tests, the P_2O_5 supplier, Meeco, decided to perform some tests to understand the high bias of its sensors. The conclusion of these additional tests, contrary to the information in the operator manual, is that the P_2O_5 sensor has to operate at a pressure of 1.3 bara because at higher pressure, there is a recombination increasing the concentration analysed.

Even if the 2 sensors allow to analyse the moisture around the threshold, these tests bring into light issues with the reliability of the measurement and more developments have to be done on the moisture sensors before they can be used at an HRS to control the water concentration at the hydrogen refuelling station.

6 - General conclusion

An online analysis could ensure the quality of H2-fuel while avoiding the drawbacks of an offline analysis. However, before implementing any sensors onsite, it is crucial to ensure that they will provide reliable measurements and are properly validated as important decisions would be made based on this (shutdown of a station).

The test of sensors can first be done in a laboratory environment, which is easier using a specially designed test rig. The testing rig must include:

- a parallel distribution of the mixture to analyse the same mixture,
- several dilution levels,
- setting the pressure and the flow rate
- neutral gas purge line for safety issues during hydrogen works.

The most important metrics, including the response time, the accuracy and the precision can then be assessed. To evaluate these metrics, a minimum of five concentrations close to the threshold are used (both higher and lower). The analyses need to be repeated over several days.

The previous results obtained during the sensor's evaluation were then shared with the supplier in order to improve the reliability of the measurement and get the supplier and the operator's feedback. Thanks to the discussion between the two parts, the most important recommendations are:

- Improve the accuracy of the sensor especially by reducing the bias under the threshold of 5 µmol/mol, to increase the reliability of the measurement
- Decrease the response time (T10 and T90), to allow the HRS operators to faster react to increasing or decreasing water concentrations.

During the MetroHyVe 2 project, sensors will be implemented at an HRS to continuously measure the hydrogen fuel quality. The choice of the sensors will be dependent upon the probability of occurrence of contaminants (which depends upon the source of the hydrogen) and the availability of analysers or sensors. For example, an HRS with electrolyser feedstock should target the following contaminants as a minimum: N_2, O_2, H_2O, CO_2. Additional information will be gathered from these experiments on operation and performance of sensors at HRS and in real-life operation.

7 - Bibliography

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