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Deliverable D2 - Metrological guidelines for the validation, calibration and verification of hydrogen sensors used within the hydrogen supply chain for quality control

RISE, NPL, VSL

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**Deliverable Cover Sheet**

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## Summary

This document is intended to be a guideline for validation, calibration and verification of sensors used within the hydrogen supply chain. Three types of sensors are described as relevant for the hydrogen supply chain: safety hydrogen sensors, hydrogen purity sensors and sensors which measure hydrogen in gas mixtures (for example hydrogen/methane). Together with the rigs developed at NPL and RISE and the protocol, this is a good basis for reliable testing of sensors which is a prerequisite to demonstrate that any sensor is fit-for-purpose for a given application. In annex, the protocol developed during Met4H2 is given.

## 1 Introduction

Hydrogen from renewable sources is one of the clean, secure and affordable forms of future energy. Clean hydrogen is currently experiencing an unprecedented surge in political and business support. The number of countries with policies that directly support investment in hydrogen technologies is increasing, along with the number of sectors they target. Global spending on hydrogen energy research, development and demonstration by national governments has significantly risen over the past few years [1].

The supply chain for hydrogen comprises the processes necessary to produce, distribute, and dispense the hydrogen. Hydrogen is a very flammable gas and can cause fires and explosions if not properly handled. Hydrogen has a very broad flammability range (from 4 % to 74 % in air). Hence, keeping air from mixing with hydrogen, mostly in confined spaces, is very important to ensure the safety of system, staff and the public. The future of hydrogen supply chain depends directly on its safety and the safety of the facilities where hydrogen is produced, distributed or used. The installation of sensors which can quickly detect hydrogen is key to ensuring safety. Sensors have other applications; as contributing to ensure the lifetime of fuel cell electrical vehicles [2] or to measure hydrogen in a mixture, such as blending of hydrogen with natural gas [3]. In this case, the sensors serve as a mean to control hydrogen quality.

A chemical sensor responds to a particular analyte in a selective and reversible way. A gas sensor works by detecting the presence or concentration of a given gas in a given environment. The concentration is converted through changes in electrical or optical properties e.g., resistance, capacitance or current into an electronic signal which is analysed, and a microprocessor outputs the reading to a display [4]. Chemical sensors exist for a wide variety of components including hydrogen. In that case, sensors can be used to trigger alarms and activate ventilation or shut down systems to prevent hydrogen reaching flammable levels.

To ensure the correct function of sensors, it is important to independently and metrologically assess their performance to guarantee reliable readings. Different types of sensors exist, and development of new hydrogen sensors based on different/new technologies is ongoing. Each detection technology has its own advantages and disadvantages in terms of performance and operational conditions. Therefore, sensor needs to be chosen for a specific application depending not only on the ambient working conditions but also on the detection requirements and sensor performance capabilities. In each application, a sensor's ability to perform the required measurements must meet the end-user needs and be documented.

This document is intended to be a guideline for validation, calibration and verification of sensors used within the hydrogen supply chain. Three types of sensors are specifically relevant: safety hydrogen sensors, hydrogen purity sensors and sensors which measure hydrogen in gas mixtures (for example hydrogen/methane).

## 2 Sensor types

### 2.1 Safety hydrogen sensors

These types of sensors are used to monitor the level of hydrogen. Their working range usually covers up to the Lower Explosive Limit (LEL). Current applications were defined during the project H2Sense [5] and include room/area monitoring for safety where hydrogen leakage may occur e.g., battery, detection of leaked hydrogen, process monitoring and control (petrochemistry industry), stationary and mobile fuel cell applications.

### 2.2 Hydrogen purity sensors

Sensors can also be used to monitor the quality of hydrogen. An example of application is the quality control process to assess compliance with the requirements in the international standards ISO14687:2019 [6], EN 17124:2022 [7] and ISO19880-8:2024 [7] for hydrogen used as a fuel. For this application, sensors need to be able to detect low levels of components such as oxygen, carbon monoxide, hydrogen sulfide, water (low ppm<sup>1</sup>) in pure hydrogen. However, as hydrogen is a relatively new sector for sensors, manufacturers mainly propose existing solutions for other matrices (i.e., nitrogen or air). If a commercial sensor designed for another matrix gas is to be used for hydrogen application, it is important to ensure that the hydrogen itself will not give rise to a signal before further testing. Moreover, due to the flammability range of hydrogen, it is preferable that the sensors are intrinsically safe.

### 2.3 Hydrogen in gas mixtures sensors

The storage and transportation of hydrogen are challenging due to its low density and volumetric energy value [8]. A solution to this issue is to inject hydrogen into the existing natural gas network, where it can be transported to its consumers. The presence of hydrogen in the blend hydrogen/natural gas, or at 100 % in the grid might have several impacts associated to gas quality (i.e., end users or billing). Therefore, the amount of injected hydrogen must be controlled so that the hydrogen–natural gas mixture satisfies the gas quality requirements of the pipeline set by legislations and standards [8] (usually up to 10 %). Sensors can help detecting hydrogen in such a mixture. And hydrogen is usually produced by a steam methane reforming reaction in industry. The production gas from the reforming reaction contains 2 %- 10 % of methane as the residual. Thus, sensors that can measure a high amount fraction of hydrogen in mixture gas that contained hydrogen and methane are in demand [9].

## 3 Sensor's metrics

The main metrological criteria for sensors include trueness, precision, accuracy, response time (T<sub>90</sub>)/recovery time (T<sub>10</sub>), stability and drift, selectivity or cross-sensitivity, limit of quantification, sensitivity and linear range/measuring range/nominal range (saturation), resolution, hysteresis, reversibility, environmental effects and operation conditions (temperature, pressure, relative humidity, vibration). The definitions of these metrics are given below.

### 3.1 Trueness

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<sup>1</sup> Parts-per-million

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. Trueness is often reported as **accuracy** when manufacturer list the specifications of sensors/analysers. It may be advised to require detailed explanation from instrument manufacturer on the methodology used to determine accuracy and trueness.

### 3.2 Precision

The precision refers to the closeness of results to one another and is measured by the standard deviation of results obtained from replicate measurements. It evaluates the sensor's ability to deliver consistent results when exposed to identical gas concentrations under similar conditions. Measurement **repeatability** (when a measurement is performed by a single analyst using the same equipment over a short timescale) and measurement **reproducibility** (variability in results between laboratories) represents the two extreme measures of precision which can be obtained. In between, there is the **intermediate (measurement) precision** (different analysts, extended timescale, different pieces of equipment etc.). A highly repeatable sensor ensures measurements with minimal variation.

### 3.3 Accuracy

**Accuracy** is the closeness of agreement between a measured quantity and a true quantity value of a measurand. Measurement accuracy describes how close a single measurement result is to the true quantity value and therefore includes the effects of precision and trueness.

### 3.4 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 **T<sub>90</sub>** 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. The recovery Time **T<sub>10</sub>** is defined as the time for a sensor to return to baseline value after the step removal of the measured variable, usually specified as time to fall to 10% of final value after step removal of measured variable.

### 3.5 Stability and Drift

Drift is a temporal change in the response of an instrument to a constant concentration. Most instrument show drift over long period of time. It is generally due to sensor's aging, but it can also be caused by dust and variations of measurement conditions (i.e., pressure, temperature, humidity). Drift implies that the performance of a measuring instrument changes, and re-calibration must be performed. The manufacturer should provide guidance on the frequency of recalibration (or replacement) in correlation with instrument drift over time.

### 3.6 Selectivity or cross-sensitivity

Sensors are designed to be selective to a compound or to specific classes of compounds. Selectivity refers to a sensor's ability to distinguish the target gas from other gases present in the environment. 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.

### 3.7 Limit of quantification

The limit of detection can be described as the smallest measure that can be detected with reasonable certainty [10]. The limit of quantification (LOQ) is derived from the smallest measure that can be quantified with reasonable certainty for a given analytical procedure.

### 3.8 Sensitivity, nominal range, saturation

**Sensitivity** measures how well a sensor can detect even the smallest changes in the concentration of the target gas. High sensitivity means that even small concentration changes can be detected [4]. 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.

Saturation is a state in which the signal that needs to be measured is larger than the dynamic range of the sensor. In that case, the output of the sensor becomes the limiting value of the sensor range. This induces error between the true and estimated values.

### 3.9 Resolution

This resolution is the smallest detectable incremental change of input parameter that can be detected in the output signal. Resolution can be expressed either as a proportion of the reading (or the full-scale reading) or in absolute terms.

### 3.10 Hysteresis

A sensor should be capable of following the changes of the concentration regardless of which direction it increases or decreases; hysteresis is the measure of this property.

### 3.11 Reversibility

Reversibility is the ability of a sensor to recover, or return to its original background/baseline condition, after exposure to an analyte.

### 3.12 Environmental effects and operational conditions

The sensor response and/or the interpretation of the sensor response may be influenced by various environmental parameters, such as humidity, temperature, flow rate, vibration and pressure. These factors can affect the accuracy and reliability of the sensor's readings. Moreover, sensors generally work effectively under specific conditions. Therefore, it is crucial to control and maintain the environmental parameters within the specified limits to ensure the sensor functions effectively and provides accurate data.

#### Temperature

It is the normal operating temperature or temperature range. Operating gas sensors in a lower or 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.

### **Pressure**

It is the normal operating pressure or pressure 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. In addition, there are few sensors which are sensitive to pressure change (typically working at ambient pressure). Any changes that cause pressure elevation will lead to incorrect measurement. Therefore, it is crucial to control and monitor the pressure in sensor performance evaluation.

### **Flow range**

The flow rate should be controlled and maintained within the recommended operational range to avoid damages and incorrect measurement. To ensure that the conditions are in the correct ranges, sensors can be completed with so called sample system.

### **Vibration**

Sensors shall be constructed to withstand the vibrations expected in its use.

## **3.13 Compliance to ATEX Environmental effects and operational conditions**

Additional parameters such as compliance to ATEX requirements for hydrogen specific applications need to be taken into consideration. However, this is not a metric of the sensor. If there is no possibility to install the sensors in non-ATEX designated areas, then the sensors have to comply to a certain ATEX -related requirements.

## **4 Validation of a sensor**

Validation implies demonstrating that a sensor is able to perform the measurements that it is intended to do (fit-for-purpose) with a required performance. This performance can be formulated in terms of one or more of the metrics defined in chapter 3. Sensor validation involves evaluating different metrics and comparing the results with the end-user's needs for each given application, with the results then being documented. This evaluation should be done after defining the scope and in a laboratory environment.

## **5 Verification of a sensor**

While validation is the process of checking whether a product meets the need for which it was created, verification can be defined as the process of ensuring that the data provided by the sensors remains accurate and consistent over time. In that case, specific metrics can be measured over time.

Another definition of verification is the process of checking the performances against specifications provided by the sensor's developers. This process could be performed together with the validation.

Finally, verification could entail to check some of the sensor's metrics onsite (site verification).

## **6 Calibration and adjustment of a sensor**

Calibration is the operation performed on a sensor that, under specified conditions

- 1) Established a relation between the values with associated uncertainties provided by measurement standards and corresponding indications with associated uncertainties of the sensor

2) Uses this information to establish a relation for obtaining a measurement result from an indication given by the sensor

Adjustment is the process that entails adjusting the response of a sensor to align its output accurately with its input by a recognized reference. This operation can be needed if the sensor's output show a bias or a drift of response with time. Adjustment can be done in a laboratory or onsite.

## 7 Step-by-step procedure for validation, verification and calibration

### 7.1 Selection of relevant tests

Some performance characteristics will be more important than others and testing all performance characteristics may not be needed. This should be a discussion between the manufacturer, the independent party performing the tests and/or the end-users in order to define how the testing shall be conducted. Example of relevant questions to be discussed:

- What is the purpose of the testing: Lab validation, lab verification, site verification or instrument development?
- Depending on the answer: should the manufacturer provide some testing results (if a verification is intended) or should end users validate the metrics by defining the testing? All metrics? End-users can, for example, define acceptance tests of the performances stated by the manufacturer.
- What should be the measuring environment conditions, such as pressure, temperature or flow during testing?

The results of the discussion will allow to define who bears the responsibility of the testing and what to do if the sensor does not fulfil the requirements. The following table needs to be agreed upon beforehand:

Parameters	Provided by the manufacturer	Required by the end-users	Lab verification	Site verification	Measuring environment
Precision					
Trueness					
Response time					
Stability					
Cross-sensitivity					
Limit of quantification					
Nominal range					
Resolution					
Hysteresis					
Reversibility					

### 7.2 Selection of protocols, reference standards and testing rigs

Testing of sensors requires protocols, reference standards and test rigs (test facilities) to evaluate the performance of sensors uniformly, the exception to the latter being when test is performed onsite. Without

guidance or protocols in place, uncertainties arise regarding 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

## 8 Protocols

Protocols are intended primarily for validation and define test methods to assess a given metric. A protocol has been developed as part of Met4H2 activity A1.3.2 and is given in Annex of this guideline. The tests proposed in this protocol are based on ISO 26142:2010 [11] which defines the performance requirements and test methods of hydrogen detection devices designed to measure and monitor hydrogen concentrations in stationary applications and on the standard hydrogen test protocols for the NREL [12] sensor testing laboratory together with considerations from the Eurachem guide - the fitness for purpose of analytical methods [13] in order to fulfil metrological assessment of the performances.

Some studies and protocols exist for sensors measuring concentrations of hydrogen.

ISO standard 26142:2010 [14] defines the performance requirements and test methods of hydrogen detection apparatus that is designed to measure and monitor hydrogen concentrations in stationary applications. It is intended to cover situations where the user desires the ability to detect hydrogen leaks and monitor hydrogen concentrations relevant to safety, primarily for hydrogen detection apparatus at vehicle refuelling stations but also to other stationary installations. The standard is intended to be used for certification purposes. It contains general requirements about construction, labelling and marking, instruction manual and vibration. Finally, the standard describes the tests to perform to control the performance requirements.

The National Renewable Energy Laboratory (NREL) has developed a variety of test protocols to quantitatively assess the performance specifications for hydrogen sensors [15] which is similar to ISO 26142 but more rigorous. Specific protocols were developed for linear range, short-term stability and the impact of fluctuations in temperature (-20 °C, 0 °C, 25 °C, 50 °C and 85 °C), pressure (0.8 bar to 1.2 bar), relative humidity (25 %, 50 % and 85 %) and chemical environment (CO, NO<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>, NH<sub>3</sub>, CO<sub>2</sub>). Typical range is 0 % to 2 % hydrogen in air. that is not relevant either for H<sub>2</sub> utilization as a fuel (gas grids or motors) or as a component in various power-to-X (PtX) applications.

For calibration, gas sensor manufacturers may provide specific calibration procedures and recommendations for their products.

## 9 Testing rigs

There are at least two distinct methods to test sensors, the “flow-through test” method (more adapted to sensors for hydrogen quality assessment) and the “chamber test” method (more adapted to fugitive/emission measurement). The chosen rig must be compliant with the requirements set by the protocol and the chosen tests. In a recent study [16], authors have compared testing different sensors using the two methods. The results show that the performance of the sensors was similar but not identical with both methods.

During Met4H2 project, two testing rigs were developed, one at RISE and one at NPL.

(shall we add the scheme of the rigs?)

## 10 Interpretation and reporting of the results

During measurement planning, the relevant testing parameters (gas composition, flow, pressure, temperature, humidity) shall be specified and agreed with the relevant partners (sensor provider, laboratory testing the device...) for each metric.

The used parameters shall then be notified in the final report, and all quantifiable results shall be given preferably as a table. The final report should include all valid data.

Only valid data should be reported and subjected to statistical treatment. Valid data purged of all outliers are those data that would be reported as resulting from the normal performance of the sensor; they are not marred by method deviations, instrument malfunctions, unexpected occurrences during testing, or by clerical, typographical and arithmetical errors.

## 11 Conclusions

This document is intended to be a guideline for validation, calibration and verification of sensors used within the hydrogen supply chain. Three types of sensors are specifically relevant: safety hydrogen sensors, hydrogen purity sensors and sensors which measure hydrogen in gas mixtures (for example hydrogen/methane).

This document defines these three types of sensors, the different metrics of a sensor, the concept of validation, verification and calibration/adjustment of a sensor and then gives a step-by-step procedure for the validation, verification and calibration/adjustment of a sensor including the selection of rigs, and how to define the scope of the testing.

In annex, the protocol developed during Met4H2 is given.

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# Annex 1: protocol to evaluate sensors

## Preparation and equipment

The sensor to be tested will be prepared and mounted in a manner representative of the typical application, in accordance with the instruction or operation manual. There are at least two distinct methods to test sensors, the “flow-through test” method (more adapted to sensors for hydrogen quality assessment) and the “chamber test” method (more adapted to fugitive/emission measurement).

In the flow-through testing method, the interface of the sensors to the gas line is hermetically sealed to assure that the sensors are subjected to the proper gas composition without any leaks. With this method, several sensors can be tested simultaneously, in parallel or in series (some sensors consume the component they measure).

Examples of flow-through test set-up are shown on Figure 1 (ISO 26142) and on Figure 2 [4].

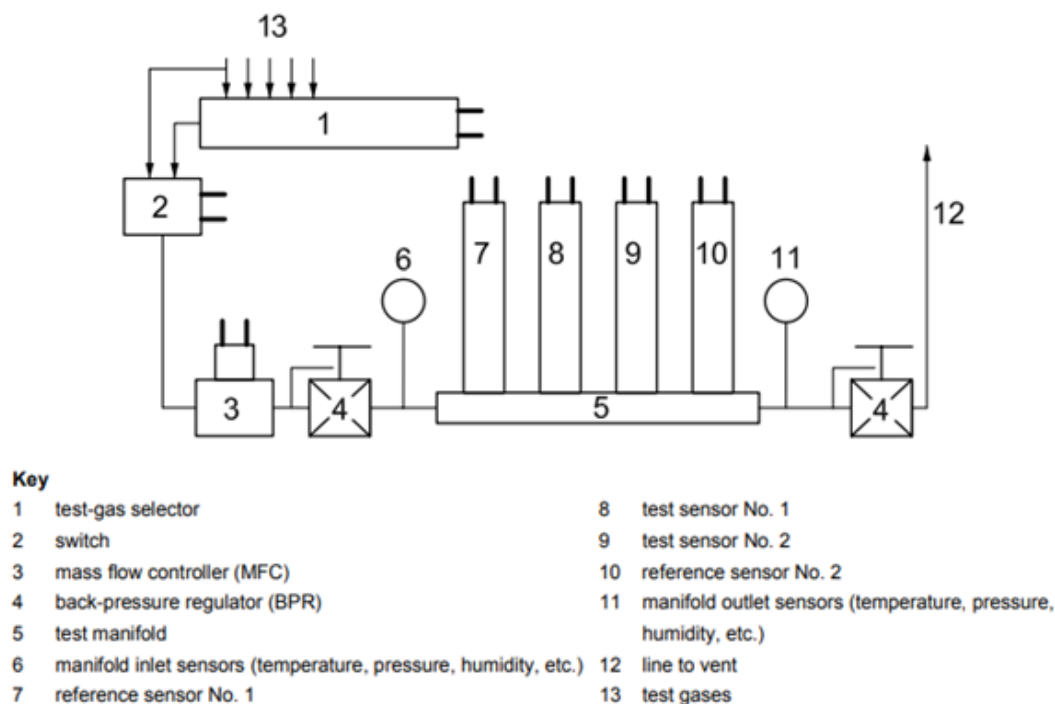


Figure 1 - Set-up for a flow-through test according to ISO26142

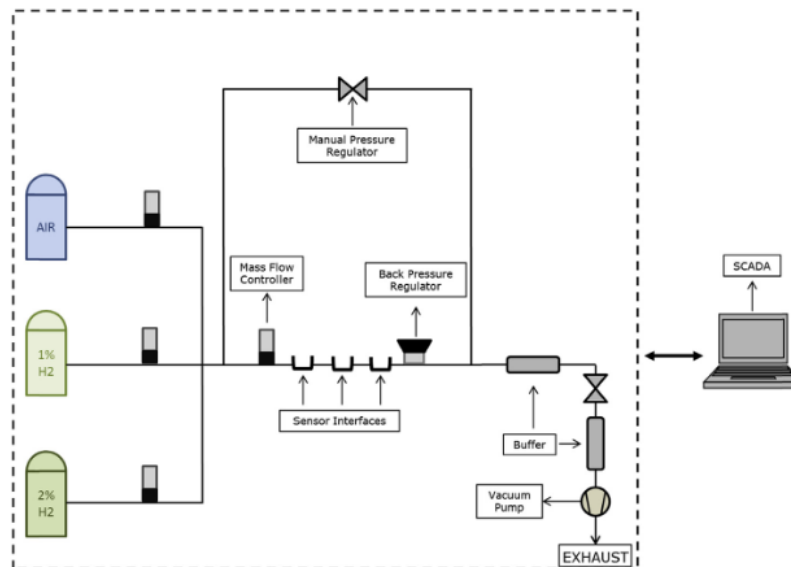


Figure 2 - Set-up for a flow-through test

In the “chamber test” method, the sensors are placed in a micro-chamber where flow-through conditions are simulated. The environmental parameters can be easily controlled. The number of sensors that can be tested simultaneously depends upon the size of the chamber. An example of chamber test set-up is shown on Figure 3.

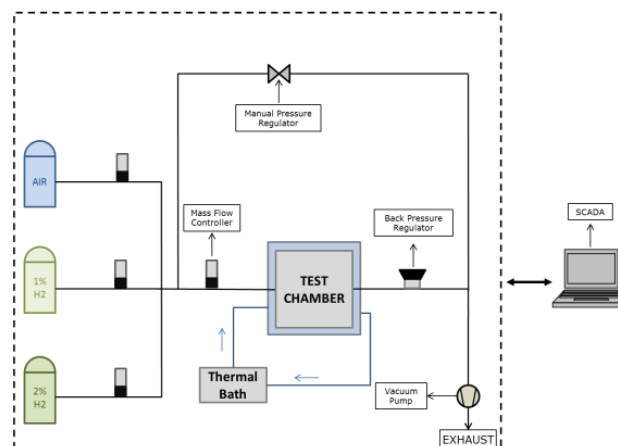


Figure 3 - Set-up for a chamber test

Independently of the method chosen, the rig must include test gases, mass flow, temperature, pressure, and humidity controllers/monitors, control system and safe flow path including vent, pressure relief. All measurements with gases should be performed in well-ventilated areas, preferably located in a fume cupboard. If the test gases include reactive/corrosive gases (e.g.  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{HF}$  etc.), the testing area should be suitable to handle any release (i.e., suitable extraction, personal protective equipment, handheld guard sensor).

## Test gases

The two key parameters are the origin and the amount fraction of the test gas and number of test gas required.

All gases used should preferably be certified reference material (provided values with traceability links to units of the International System (SI)). Test gases can be generated from blending certified gas mixtures with synthetic air (safety sensors), hydrogen (quality control sensors) or methane (H<sub>2</sub>/NG blend sensors). In the protocol developed by NREL [5], the test gas concentrations are mixed within  $\pm 10\%$  of the nominal concentration but are known to within  $\pm 2\%$ . When blending certified gas mixtures with a pure gas (i.e., hydrogen), the purity of the pure gas needs to be determined to avoid any bias due to contaminant presence (i.e., presence of CO in the pure hydrogen gas while testing CO sensor would lead to an inaccurate response).

The working range of the sensor will provide indication regarding the amount fraction and number of test gas required:

- Safety sensors: ISO 26142 states that the tests shall be conducted using a single test gas per one order of magnitude in the measuring range with a hydrogen volume fraction at the midpoint of that order. If the measuring range is less than two orders of magnitude, then the test shall be conducted with a single test gas having a hydrogen volume fraction at the midpoint of the measuring range. If the measuring range is between two to three orders of magnitude, two test gases shall be used.
- Quality control sensors: the conditions stated above should also apply for quality control sensors. The tests shall be conducted using a single test gas per one order of magnitude in the measuring range with a volume fraction for the targeted compound at the midpoint of that order. If the measuring range is less than two orders of magnitude, then the test shall be conducted with a single test gas. If the measuring range is between two to three orders of magnitude, two test gases shall be used.

Change of gas: the rig to test sensors should be equipped with components to allow to effectively change the test gas. It can be systems a dilutor or a mixing device. The composition of the resulting gas should be verified using a reference analytical instrument.

## Mass flow controllers

The mass flow controllers (MFC) should be appropriate for the pressure and flow of the sensor (range of flow 10-100% of the full flow controller). The MFC should be calibrated with the corresponding gas it will measure.

## Temperature controllers

The temperature during any test should be controlled. A typical range would be from 0 °C to 50 °C. A temperature monitor should be implemented to record the gas temperature supplied to the sensor. The temperature monitor should have an accuracy of typically 0.5 °C.

The temperature controller and monitor may be the same instrument as long as the accuracy is suitable.

## Pressure controllers

The pressure during any test should be controlled. It could be realized using a pressure regulator or back pressure regulator. A typical range would be from (0.5 to 100) bar gauge. A pressure monitor (i.e., pressure transducer) should be implemented to record the gas pressure supplied to the sensor. The pressure monitor should have an accuracy of 1% of span (full scale).

Some flowmeters can measure mass flow and pressure simultaneously.

The pressure controller and monitor may be the same instrument as long as the accuracy is suitable.

## Humidity controllers

The humidity during any test should be controlled. It could be realized using dry gas or through humidification system. A humidity monitor (i.e., humidity transducer) should be implemented to record the gas humidity supplied to the sensor. The humidity monitor should have an accuracy of 1% of span. The pressure humidity controller and monitor may be the same instrument as long as the accuracy is suitable.

## Control system

A control system is needed to collect data from the sensor. The data-collecting interval should be low enough to allow determining response time and recovery time.

## Line to vent

The vent line should be made of suitable material (chemically inert tubing, pressure rating suitable for the operating condition), should reach a safe release point (i.e., allowed to release flammable gas), and should include a non-return valve.

## Conditioning of the system (reaching zero condition) prior to testing

## Performance test methods

Many performance criteria are developed to define how a sensor performs: precision, trueness/accuracy, response time (T90)/recovery time (T10), stability and drift, selectivity or cross-sensitivity, limit of quantification, sensitivity and linear range/measuring range/nominal range (saturation), resolution, hysteresis, reversibility, environmental effects and operation conditions (temperature, pressure, relative humidity, vibration),. The definition of some of these metrics has been listed in a report done as part of EMPIR project MetroHyVe2 [6]. The definition of the metrics is given below:

## 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. The precision can be expressed as **repeatability**.

In ISO26142, it is recommended to perform five consecutive tests of 150 s each with 300 s exposure to clean air in between each test. NREL's protocol recommends performing consecutive cycles without clean air in between (0%, 0.2%, 1%, and 2% hydrogen at a constant flow rate of 1 l/min) for 1 hour. This is then performed nine times over a three-day period (short-term stability).

The EURACHEM guide; the fitness for purpose of analytical methods [7] recommends 6 to 15 replicates during a short timescale for the determination of the repeatability standard deviation.

What to do	Evaluation of results	Pressure conditions	Comments
6-15 replicates for at least for a duration of at least 10 times the response time during a short timescale using a single test gas having a volume fraction at the midpoint of the measuring range using a flow at the midpoint of the flow interval. Calculate the standard deviation	Calculate the standard deviation of the replicates	0.8 to 1.2 bar, kept constant within $\pm 0.1$ bar throughout the duration of the test 15°C and 25°C kept constant within $\pm 2$ °C throughout the duration of the test 20 % and 80 % within $\pm 10$ % throughout the duration of the test.	For "sticky" impurities*, the duration of the test should be extended (to the time needed to obtain a stable signal). A reference analytical instrument can be used to confirm that the sensor is exposed to the amount of analyte present in the test gas

\*General comment: this affects several other performance parameters.

## Trueness/Accuracy

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. Trueness is often called **accuracy** when manufacturer list the specifications of sensors/analysers.

**Accuracy** is the closeness of agreement between a measured quantity and a true quantity value of a measurand. Measurement accuracy describes how close a single measurement result is to the true quantity value and therefore includes the effect of both precision and trueness.

In ISO 26142, the sensor is exposed in an ascending order to each hydrogen volume fraction of the test gas for 3 min without exposure to clean air (air that is free of flammable gases, interfering or contaminating substances, and dust) between the hydrogen volume fractions. Following the highest hydrogen volume fraction, the sensor shall be exposed to clean air for 10 min. This operation shall be carried out three times consecutively. For all measurements, the variation of the final indication from the hydrogen volume fraction of the test gas is compared to the indication of the sensor.

In the NREL protocol, the “accuracy of Response Test” (Linear Range Test) is performed by exposing the sensor to a gas mixture whose hydrogen concentration is changed stepwise between 0% and 2% hydrogen (maximum) by mixing with synthetic air – purity not specified (concentration established by independent gas analysis).

What to do	Evaluation of results	Pressure conditions	Comments
Expose the sensor 10 times for a duration of at least 10 times the response time to the test gas having a volume fraction at the midpoint of the measuring range (it is possible to use the data produced for the “precision” evaluation). Other concentrations (for example, close to the limit of quantification) can be tested in the same manner	Calculate bias (b), relative bias, b(%) or the relative recovery R(%) (apparent recovery). $b = \bar{x} - x_{ref}$ $b(\%) = \frac{\bar{x} - x_{ref}}{x_{ref}} \cdot 100$ $R(\%) = \frac{\bar{x}}{x_{ref}} \cdot 100$	(0.8 to 1.2) bar, kept constant within $\pm 0.1$ bar throughout the duration of the test 15°C and 25°C kept constant within $\pm 2$ °C throughout the duration of the test 20 % and 80 % within $\pm 10$ % throughout the duration of the test.	For sticky” impurities, see section 3.2

## 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. The recovery Time **T10** is defined as the time for a sensor to return to baseline value after the step removal of the measured variable, usually specified as time to fall to 10% of final value after step removal of measured variable.

According to ISO26142, the sensor shall be switched on in clean air and, after an interval corresponding to at least two times the warm-up time, the sensor shall be subjected to the standard test gas and from standard test gas to clean air.

What to do	Evaluation of results	Pressure conditions	Comments
6-15 replicates starting with clean air or hydrogen, expose the sensor to the standard test gas at the midpoint of the measuring range followed by clean air or clean hydrogen. Let the	Evaluate T90 and T10 as the average of the replicates	(0.8 to 1.2) bar, kept constant within $\pm 0.1$ bar throughout the duration of the test 15°C and 25°C kept constant within $\pm 2$ °C	

sensor reach stability in each step. Other concentrations (relevant for the application) can be tested in the same manner to evaluate if the response time depends on the concentration of the measurand		throughout the duration of the test 20 % and 80 % within $\pm 10$ % throughout the duration of the test.	
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### 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.

As it can be challenging to expose sensor continuously to a gas during a long period, the following options are proposed:

option 1: sensor is used only at the beginning and at the end of the test period,

option 2: sensor is used every week during 4 hours and the signal is only measured in the beginning and at the end of the test period,

option 3: sensor placed at the client's facility is tested at the end of the test period,

option 4: client's decision of methodic

What to do	Evaluation of results	Pressure conditions	Comments
Expose the sensor to three levels of concentration: midpoint of the working range, close to the lower limit of quantification, close to the upper limit of the working range after a period of time (ex: a month, three months, six months, a year)	Calculate bias and compare with the bias obtained when started testing the sensor. If the bias increases, the response of the sensor is not stable	(0.8 to 1.2) bar, kept constant within $\pm 0.1$ bar throughout the duration of the test 15°C and 25°C kept constant within $\pm 2$ °C throughout the duration of the test 20 % and 80 % within $\pm 10$ % throughout the duration of the test.	

### Selectivity or cross-sensitivity

Sensors are designed to be selective to a specific compound or to a certain type 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; the signal of target compounds being affected (either higher or lower than predicted); 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.

According to NREL's protocol, the sensor shall be subjected to two exposure cycles of the interferent gas at the test concentration. Following the second interferent exposure and recovery in air, the sensor is exposed continuously to 1% hydrogen while the interferent exposure cycles are repeated two or more times. The concentration of the interferent is not changed. Following the second interferent exposure, the sensor is allowed to stabilize in 1% hydrogen followed by a recovery time in air. Following the recovery, the sensor response to 1% hydrogen in air is measured twice. Some of the proposed interferents may be poisons (i.e., vapors that induce irreversible effects on sensor behavior). The proposed interferents are carbon monoxide (50  $\mu\text{mol/mol}$ ), nitrogen dioxide (5  $\mu\text{mol/mol}$ ), hydrogen sulfide (20  $\mu\text{mol/mol}$ ), methane (1 vol-%), ammonia (50  $\mu\text{mol/mol}$ ), and carbon dioxide (5000  $\mu\text{mol/mol}$ ).

According to ISO 26142, the sensor shall be exposed to methane (500  $\mu\text{mol/mol}$ ), isooctane (500  $\mu\text{mol/mol}$ ), and carbon monoxide (500  $\mu\text{mol/mol}$ ) and other species enhanced by the sensor's manufacturer, individually in air.

What to do	Evaluation of the results	Pressure conditions	Comments
List suspected interferences and adequate test concentrations. Analyse test gases containing suspected interferences at increasing concentrations (repeat the test with decreasing concentrations).	Examine effect of interferences. Is the Interference causing a bias by increasing or decreasing the signal? Can the sensor recover when not exposed anymore to the interference?	(0.8 to 1.2) bar, kept constant within $\pm 0.1$ bar throughout the duration of the test 15°C and 25°C kept constant within $\pm 2$ °C throughout the duration of the test 20 % and 80 % within $\pm 10$ % throughout the duration of the test.	

### Limit of quantification

According to UIPAC [8], the limit of detection is derived from the smallest measure that can be detected with reasonable certainty. The limit of quantification (LOQ) is derived from the lowest signal that can be quantified with reasonable certainty for a given analytical procedure.

What to do	Evaluation of the results	Measuring conditions	Comments
Option 1: Expose the sensor to decreasing concentration starting from (for example) half the volume fraction at the midpoint of the measuring range followed by clean air or clean hydrogen until no signal can be recorded. Increase this concentration slowly until the signal is detected again  Option 2 for the starting point: Use information provided by the sensor's developer regarding the LOQ and start testing at 2 times this value	Record the outputs. LOQ is obtained at the lowest concentration tested that gives a signal with acceptable bias	(0.8 to 1.2) bar, kept constant within $\pm 0.1$ bar throughout the duration of the test 15°C and 25°C kept constant within $\pm 2$ °C throughout the duration of the test 20 % and 80 % within $\pm 10$ % throughout the duration of the test.	

### Sensitivity, nominal range, saturation

**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.

Saturation is a state in which the signal that needs to be measured is larger than the dynamic range of the sensor. In that case, the output of the sensor becomes the limiting value of the sensor range. This induces error between the true and estimated values.

What to do	Evaluation of the results	Measuring conditions	Comments
Expose the sensor to increasing concentration from the lowest detectable level to at least the upper level of the working range	Record the outputs. Saturation is reached when the bias between the true value and the output from the sensor differ by	(0.8 to 1.2) bar, kept constant within $\pm 0.1$ bar throughout the duration of the test	

indicated by the sensor's manufacturer	more than 2 times the bias at lower range	15°C and 25°C kept constant within $\pm 2$ °C throughout the duration of the test 20 % and 80 % within $\pm 10$ % throughout the duration of the test.	
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## Resolution

This resolution is the smallest detectable incremental change of input parameter that can be detected in the output signal. Resolution can be expressed either as a proportion of the reading (or the full-scale reading) or in absolute terms.

What to do	Evaluation of the results	Measuring conditions	Comments
Expose the sensor to smaller and smaller changes of concentration around the mid-point or start close to the value provided by the software or readings	Record the outputs, the resolution is the value when the sensor actually reacts to a small change in concentration	(0.8 to 1.2) bar, kept constant within $\pm 0.1$ bar throughout the duration of the test 15°C and 25°C kept constant within $\pm 2$ °C throughout the duration of the test 20 % and 80 % within $\pm 10$ % throughout the duration of the test.	

## Hysteresis

A sensor should be capable of following the changes of the input parameter regardless of which direction the change is made; hysteresis is the measure of this property.

What to do	Evaluation of the results	Measuring conditions	Comments
Expose the sensor to increasing amounts of the measurand (6-10 concentrations evenly spaced across the linear range). Expose the sensor to decreasing amounts of the measurand	Plot results and study if the signals overlap (no hysteresis) or differ (hysteresis)	(0.8 to 1.2) bar, kept constant within $\pm 0.1$ bar throughout the duration of the test 15°C and 25°C kept constant within $\pm 2$ °C throughout the duration of the test 20 % and 80 % within $\pm 10$ % throughout the duration of the test.	

## Reversibility

Reversibility is the ability of a sensor to recover, or return to its original background/baseline condition, after exposure to a target gas (an analyte).

What to do	Evaluation of the results	Measuring conditions	Comments
Expose the sensor to increasing amounts of the measurand (6-10 concentrations evenly spaced across the linear range). Expose the sensor to decreasing amounts of the measurand (same as above).	Plot results and study if the signal measured during the descending series differs from the signal measured during the ascending series when the sensor is exposed to no measurand	(0.8 to 1.2) bar, kept constant within $\pm 0.1$ bar throughout the duration of the test 15°C and 25°C kept constant within $\pm 2$ °C throughout the duration of the test 20 % and 80 % within $\pm 10$ % throughout the duration of the test.	For the exposure time, see comment in 3.1

## Environmental effects and 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.

### 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.

### 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. In addition, there are few sensors which are sensitive to pressure change (typically working at ambient pressure). Any changes cause pressure elevation will lead to wrong value in impurity measurement. Therefore, it is crucial to control and monitor the pressure in sensor performance evaluation.

### 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 a dedicated sample system.

### Vibration

Sensors shall be constructed to withstand the vibrations expected in its use.

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## **Compliance to ATEX requirements**

Additional parameters such as compliance to ATEX requirements for H2 specific applications need to be taken into consideration. However, this is not a metric of the sensor.

General: Non-ATEX areas installations preferable

If there is no possibility to install the sensors in non-ATEX designated areas then the sensors has to comply to a certain ATEX -related requirements.