MefHySto
Metrology for Advanced Hydrogen Storage Solutions

Deliverable D1

Report on the development of new metrology for the measurement of key impurities in hydrogen (water vapour and oxygen) produced from PEM water electrolysers, with fast response times of a few or tens of seconds

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Executive Summary

The aim of this work (Metrology for Advanced Hydrogen Storage Solutions - MefHySto 19ENG03) is to address the need for the assessment of the quality of hydrogen produced from PEM water electrolysis during rapidly imposed transient use periods. This work focuses on quality measurements with online gas analysers for two key impurities in hydrogen (water vapour and oxygen).

In order to meet this need, new metrology to test the response time of online instrumentation used for the measurement of water vapour and oxygen in hydrogen produced from PEM water electrolysers was developed. The metrology requires the ability to generate fast changes (of a few or tens of seconds - i.e. the timescale of surges in electricity demand and supply 0–100 %, 200 % peak) in the amounts of these key impurities, to test the response times of the instruments tested.

The online gas analysers for measuring water vapour and oxygen in hydrogen, were then evaluated using this new metrology. This report presents the validation results and discusses the findings.

Background

Advanced storage solutions are needed in parallel with hydrogen. Therefore, further investigation of new transformation processes, such as Power-to-Hydrogen, Power-to-Gas, or Gas-to-Power, is needed because:

• Impurities can provoke major performance losses in fuel cells during the conversion of hydrogen back to electrical power. As such, a detailed and systematic study of compounds/impurities on the performance of fuel cells under load cycling is needed to improve their durability.

• The intermittent operation of a water electrolysis cell for conversion of electrical power to hydrogen induces frequent start-stop transient periods with inherent, unstable, predefined idle conditions. The quality of the hydrogen produced during periods lacking excess electrical energy in the grid is also significantly affected.

The overall goal of this project is to provide traceable solutions for advanced hydrogen storage technologies which are required in order to achieve the ambitious new EU energy target for renewable energy by 2030, as per the Renewable Energy European Directive 2018/2001.

In general, electrolysis is currently well understood. However, detailed investigations on energy processes and load conditions are still lacking. This includes short-term peak energy loads of up to 200 %, which must be handled safely in order to prevent quality problems or damage to fuel cells (FC) and peripheral equipment. This project investigates the quality of hydrogen produced from proton-exchange membrane water electrolysis during rapidly imposed transient use periods. This was done with online gas analysers used for measuring key impurities (water vapour and oxygen). One of the objectives of this project is to obtain a better understanding of the parameters influencing water electrolysis under process conditions.

Electrolysers use electricity to chemically split water into oxygen and hydrogen. The electrolytic production of hydrogen as an energy carrier is possible without emissions at efficiencies of 50 % to 70 %. Power-to-gas or power-to-hydrogen plants are already successfully in operation, currently with capacities up to the Mega Watt range, and the first Giga Watt plants are being planned. However, the influence of load peaks of up to 200 % is still largely unknown as well as the quality parameters for gas generation, which inevitably affects subsequent elements in the production chain.

In order to assess the quality of hydrogen, the performance of online gas analysers for water vapour and oxygen typically used in measurements should be assessed so that any error found can be

corrected for. In this project new metrology has been developed in order to provide traceable references in hydrogen background gas for these key impurities at values and operating pressures reflective of use in hydrogen supply chain processes.

As rapid transients in impurity values are expected during short term peak demand periods the response time of the online gas analysers was assessed in newly developed facilities.

1 New metrology for the measurement of key impurities in hydrogen, with fast response times

1.1 Development of a metrologically compatible laser-spectrometric measurement method for fast H_2O impurity measurements in H_2 (PTB).

1.1.1 Introduction

In the recent years, there has been the need to perform accurate H_2O measurements in H_2 for quality control purposes. The limit value of H_2O in H_2 that can be used in PEM fuel cell or commercially is 5 µmol mol^{-1} according to ISO14687-2 [**1**]. For accurate H_2O measurements, laser spectroscopic methods are becoming prominent and have been demonstrated for accurate H_2O amount fractions measure-ments in a variety of studies [**2**] [**3**] Fast (a few or tens of seconds) online H_2O amount fraction measurements, employing, for example, laser spectroscopy, are now required to check the quality of H_2 produced from PEM water electrolysis during rapidly imposed transient use periods (0–100 %, 200 % peak) [**4**].

PTB has developed a metrologically compatible laser-spectrometric measurement method for H_2O impurity measurements in H_2. The method is based on cavity ringdown spectroscopy and can be applied for H_2O amount fraction measurements down to the range of nanomoles per mole.

1.1.2 Water vapour spectrometer validation set-up

The performance of the CRDS spectrometer in a background gas of hydrogen was evaluated using water vapour content reference gas mixtures of defined levels of H_2O in a matrix of H_2 prepared by NPL as described in Section 2.2.

Figure 1 shows a schematic diagram of the test set-up used to evaluate the performance of the spectrometer with the ability to purge the system with nitrogen humidified to appropriate levels before switching to pure hydrogen and then the reference gas mixtures which had certified water contents of 2 µmol mol^{-1}, 5 µmol mol^{-1} and 10 µmol mol^{-1} in a matrix of H_2.

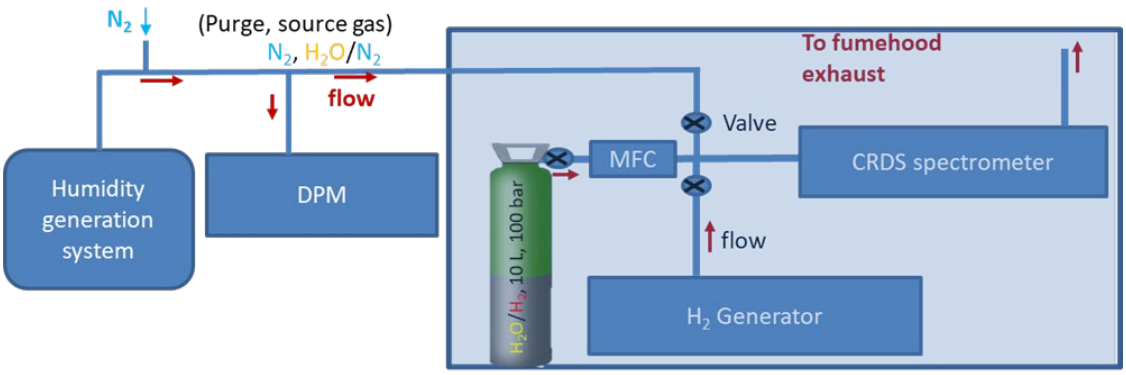

Figure 1 Schematic of test set-up at PTB for validation of CRDS spectrometer

The validation results of the spectrometer in a background gas of hydrogen are reported in Section 2.6.

1.2 Step-change facilities for applying fast step changes in water and oxygen contents of hydrogen. (NPL)

The response time of instruments to a step change in a measurand is often specified by manufacturers as either t_{63} or t_{90} – the time taken to reach 63 % or 90 % of the full step change between two stable measured values after a rapidly imposed transient. In order to evaluate response time experimentally, a facility would need to be developed that can rapidly impose transient changes in the measurand – faster than an expected response time of an instrument. In this work NPL established two separate response time testing facilities, for step changes in water vapour content and oxygen content in hydrogen, to impose fast step changes in times of the order of a few or tens of seconds.

It should be noted that the step changes imposed can either be rising or falling in nature and step changes in both directions are realisable with these facilities.

1.2.1 Facility for applying fast step changes in water content

1.2.1.1 Introduction

The water content step change facility developed by the NPL Humidity group took an approach where a continuous supply of two separate test gases with different levels of humidity were generated simultaneously and could be alternately switched between two test instruments. This enabled response time testing to rising step changes to be evaluated for one test instrument at the same time as the response time of another test instrument to falling step changes to be evaluated simultaneously as the supplies were switched between test instruments.

A range of hygrometers that utilised different measurement principles were loaned to the project by collaborators, for response-time testing. Measurement principles included metal oxide, quartz crystal resonance, surface acoustic wave, fibre optic and electrolytic. Two NPL-owned hygrometers were also tested, with condensation chilled-mirror and water vapour spectrometer measurement principles.

1.2.1.2 Method

The approach used enabled two humidity levels to be generated simultaneously at atmospheric pressure through:

a) direct saturation through the saturator of the NPL multi-gas, multi-pressure primary standard humidity generator to produce test gas with a humidity of nominally -40 ºC (100 µmol mol^{-1}) and

b) diluting the saturator output gas with appropriate flow rates of dry test gas to produce a mixture with a humidity of nominally -60 ºC (10 µmol mol^{-1}).

Gases a and b were flowed through the two inlet paths of a 4-way valve with two test instruments connected to the two outlet paths . Manually switching the 4-way valve swapped the outlet channel that was flowing to Test Instrument 1 to the outlet channel flowing to Test Instrument 2 and vice versa, imposing a rapid step change in the humidity of the test gas being measured.

In order to be an effective facility for testing instrument response time the volume of the tubing connecting the 4-way valve to test instruments was kept as low as possible by using short path lengths and small diameter (1/8” inch outer diameter) stainless steel tubing.

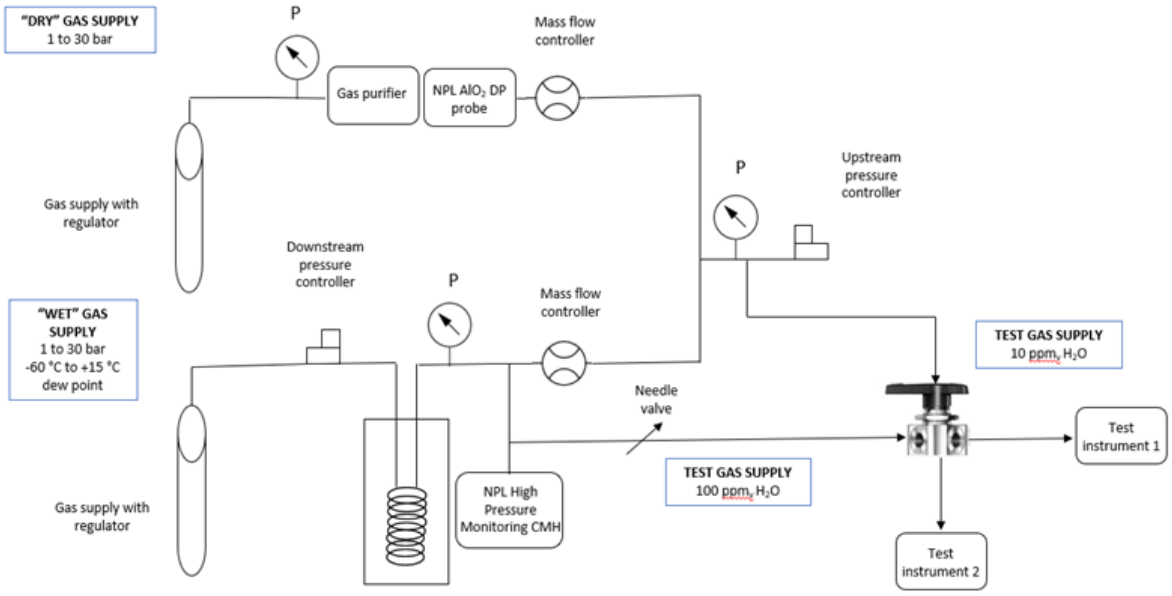

Figure 2 : Schematic diagram of NPL water vapour content step change facility

A platinum resistance thermometer (PRT) located in the centre of the ethanol fluid bath surrounding the saturator coil of the NPL generator gave a measurement of the dew-point temperature of the humidified hydrogen. Traceability of measurement was provided by calibration of this thermometer to the International Temperature Scale of 1990 (ITS-90) through NPL Temperature Standards.

A digital pressure indicator was used to measure the pressure of the gas in the saturator. This digital pressure indicator was calibrated with traceability to NPL standards for pressure.

1.2.1.3 Water vapour step change facility validation measurements

The instrument type expected to have the fastest response time (where the manufacturer’s response time claim was a few seconds) and a sampling interval of 0.3 seconds was used in order to evaluate whether the method of applying a step change in humidity was able to meet the aim of imposing transients of the order of a few or tens of seconds to test the response time of instruments.

Results obtained had a rising response time t_{90} of approximately 2 seconds, and a falling response time t_{90} of approximately 25 seconds. As a t_{90} value was realised within two seconds for the rising step change test, and part of this duration was due to the response time of the instrument used, it was concluded that the facility successfully met the objective of being able to apply transients in water vapour content within a few seconds.

1.2.1.4 MatLab response time evaluation software

A set of functions were written in MatLab by the NPL Data Science group to perform fits to data sets collected from instruments during response time testing to rising and falling step changes in humidity. Depending on the form of the data collected, sigmoid functions and exponential decay functions can be fitted by the user and response times are output at values of t_{63} and t_{90} with associated uncertainties in the estimated response time.

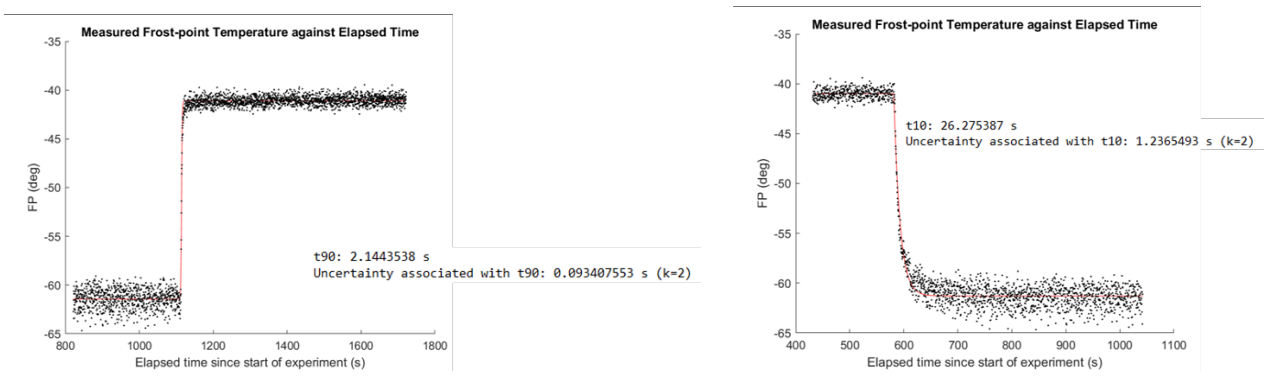

Figure 3 : Fits to measurements of rising and falling water vapour content step changes during evaluation of NPL facility

1.2.2 Facility for applying fast step changes in oxygen content

1.2.2.1 Introduction

A step-change facility for applying fast step changes in oxygen contents of hydrogen was developed by the NPL Gas Metrology group to enable response time testing to oxygen contents changes to be evaluated for online oxygen analyser instruments. A schematic of the facility set-up is shown in Figure 4.

The facility consists of three sections: step-change device (dynamic system), sensor testing and external control. The dynamic system is the core part in the facility. To enable evaluation of instruments' response time (typically within tens of seconds claimed by manufacturers), the step-change device must be capable to rapidly impose transient changes in the measurand which should be faster than the expected response time of instruments. This was realised by two calibrated mass flow controllers, referred to as diluent (high purity hydrogen ≥ 99.999%) and NPL's primary reference materials (see Section 2.2). A step change (rising or falling) can be easily achieved by rapidly adjusting the flow ratio between the diluent and the primary reference materials.

Another important part within the facility is the external quality control which consists of a gas chromatograph with a pulsed discharge ionization detector (GC-PDHID). The amount fraction of oxygen in hydrogen before and after step change was verified simultaneously in the GC-PDHID while the gas mixture was delivered to the online gas analyser instruments to ensure the meas-urement traceability. The GC-PDHID was calibrated externally using NPL primary reference mate-rials to ensure the reliability and traceability of the results.

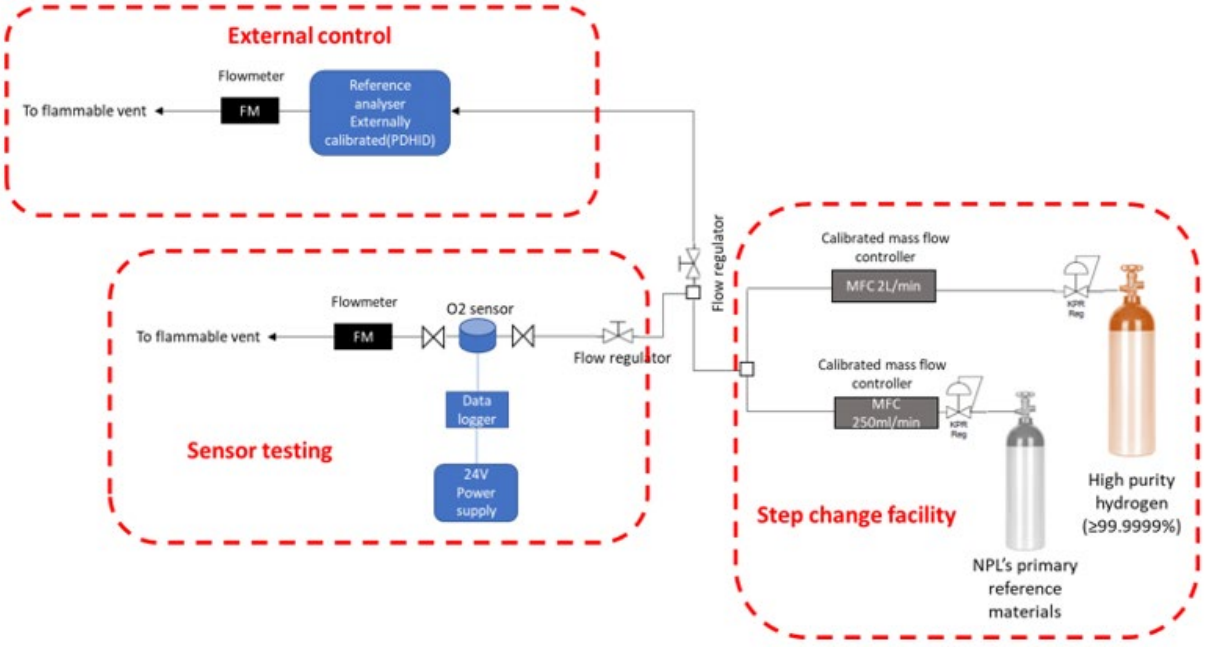

Figure 4 : Schematic diagram of NPL oxygen content step change facility

1.2.2.2 Method

The response time of the dynamic system to oxygen contents step change was evaluated by using the GC-PDHID. The target oxygen amount fraction is 10 µmol mol^{-1} and the step change is 5 µmol mol^{-1}.

Various response times were assessed for the dynamic system. As there is a load time of the loop for 12 seconds as part of the GC method, this time needs to be added onto any timing to assess the true response time. If testing time below 12 seconds, the GC run needs to be started and then the amount fraction changed after timing. The procedure for each response time testing described as follows:

1. Run 5 µmol mol^{-1} O_2 in H_2 on the dynamic system, change to 10 µmol mol^{-1} on the start system, then start timer, start run on GC after 1 minute on timer – response time is 1 minute + load time 12 s

2. Repeat as in step 1, but start the run on the GC after 30 s on timer - response time is 30 s + load time 12 s

3. Repeat again but start the run on the GC after 20 s on timer - response time is 20 s + load time 12 s

4. Repeat again but start the run on the GC after 10 s on timer - response time is 10 s + load time 12 s

5. Repeat again but start the run on the GC after 5 s on timer - response time is 5 s + load time 12 s

6. Repeat again but start the run on the GC after 2 s on timer - response time is 2 s + load time 12 s

Table 1 : Experimental plan for response time assessment of the dynamic system

Time / s	72	42	32	22	17	14	7*	1*
Load time / s	12	12	12	12	12	12	(12 -5)	(12-11)
Flow rate / ml min^{-1}	30	30	30	30	30	30	30	30
Loop size / ml	1	1	1	1	1	1	1	1

* In order to perform measurement between 0 to 12 seconds, the GC run would have to be started first, then the MFC change is realised after at the desired time. In this way, the concentration on the dynamic system changed after the desire time. For example, regarding the response time testing of 1 second, the oxygen contents were changed on the dynamic system after 11 seconds when the GC method is started.

1.2.2.3 Response time of step change facility for oxygen

In total eight response times were tested on the dynamic system and the GC. The peak area of oxygen was used to evaluate and confirm the 90% step change of oxygen amount fraction is achieved. It can be observed from Figure 5 that a step change from 5 µmol mol^{-1} to 10 µmol mol^{-1} (as showed as black dot line) by using the dynamic system could be achieved at approximate 7 seconds as the peak areas from experiments with 7 seconds and onwards are stabilised.

Another aspect is the length or volume of the system between the fast-changing facility and the analyser. The pipeline volume needs to be limited to ensure fast transfer of the gas. In this case study, the pipeline volume was minimised by using 1/16in OD pipe and less than a metre.

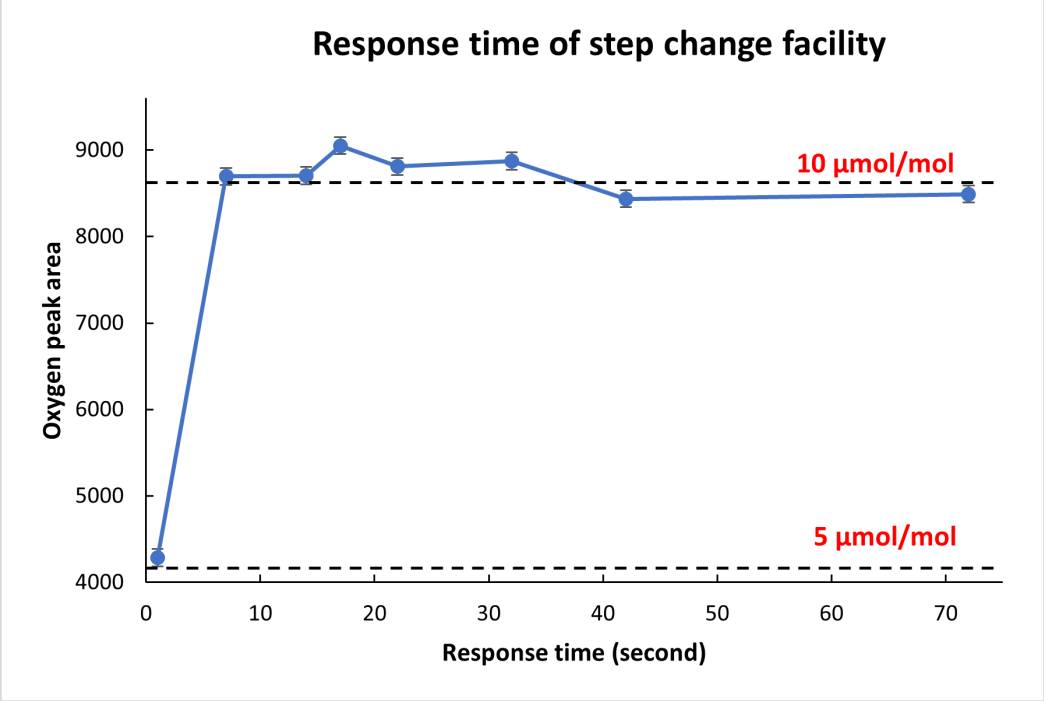

Figure 5 : Response time of step change facility for oxygen contents

The dynamic system has successfully been demonstrated to apply fast step change in oxygen contents of hydrogen and met the target response time requirements (≤ 20 seconds). However, as there were no data points available between 1 second and 7 seconds, it is recommended to conduct further tests at a shorter response time to confirm a t_{90} value.

1.3 Establishment of PEM water electrolyser test systems (single cell) with online impurity measurement at the cathode (NPL / CEA).

1.3.1 PEMWE Single Cell with Online Oxygen Measurement at NPL

1.3.1.1 Introduction

The electrolysis of water in a PEMWE electrolyser produces hydrogen at the cathode and oxygen at the anode. If the electrolyser is well designed such that the materials used in its construction do not release impurities and if it is operated correctly i.e., the water supplied to it is high purity (typically ASTM Type II or better) and the system is appropriately purged then the only impurities present in the supplied hydrogen are oxygen and water and trace gases dissolved in the supplied water. When the hydrogen exits the electrolyser cell it is saturated with water with a dew point approximately the temperature of the stack (ca. 60-90 °C) and will have oxygen present from the reaction on the anode. The concentration of this oxygen is critical as it must be maintained below ~4 % to prevent the formation of explosive mixtures and will consume hydrogen during purification, reducing system efficiency.

In a PEMWE the anode and cathode are separated by an ion exchange membrane typically 125-150 µm thick. The thinner the membrane the more efficient the electrolyser, however one of the roles of this membrane is to limit crossover from anode to cathode, and vice versa, Figure 7a. Quantification of the oxygen crossover in operating cells is therefore important to identify materials and conditions that maximise efficiency while maintaining low concentrations of oxygen in the product hydrogen. In real electrolyser systems a recombination catalyst is used to combust the trace oxygen and water is removed with a standard drying process. The concentrations of impurities existing from a commercial system are therefore well controlled and it is necessary to do this testing on a single cell. Here we report the system established at NPL to make these measurements.

1.3.1.2 Experimental Setup

1.3.1.2.1 Materials

The porous transport layers (PTLs) used on both the anode and cathode sides were circular porous sintered titanium discs (32 mm diameter x 1 mm, Bekeart, UK) coated in 100 nm Pt (Teer Coatings, UK). The catalyst coated membrane was a circular (35 mm diameter) Nafion^{TM} 117 membrane coated in 1.0 mg cm^{-2} Pt on advanced carbon for the cathode side, and 2.0 mg cm^{-2} Ir on the anode side (CCM-CC-E35D-N117, Quintech, Germany) which was used as received. All water used was a ASTM Type I supplied directly from a laboratory deionisation system (Purelab Chorus, ELGA). Argon was used as a carrier gas (Pureshield, BOC). Nitrogen was used for cell compression (BOC industrial grade).

1.3.1.2.2 Equipment

The PEMWE cell used for this experiment had an active area of 8 cm^2 and was constructed of PEEK with a platinum coated piston without flow field. The cell body was tightened to 1 Nm with 4 M6 bolts, spring washers and nuts and the piston used to compress the active area of the cell was pressurised to 20 barg using nitrogen. Deionised water was circulated to both the anode and cathode from a

temperature-controlled glass jacketed reservoirs (Radleys, UK and Huber Ministat 230, DE) with a peristaltic pump (323, Watson-Marlow, UK). The temperature of the water at the anode inlet of the cell was controlled to 60 °C.

Electrochemical measurements were made using a Potentiostat/Galvanostat (Gamry Reference 3000 potentiostat equipped with a Gamry 30 K booster). The cathode outlet gas was split into two with ~ 30 ml min^{-1} passed through a dehumidifier (EPC1000C, M&C) and droplet separator (ADS-SS, M&C) before overflowing a µGC (micro GC, 990, Aglient) with a 10 m long 5 Å molecular sieve column (MS5A SS 10mx0.25 mmx30um,BF,RTS) and thermal conductivity detector the overflow rate was monitored by a digital rotameter (MV-191-H2, Bronkhorst). This is shown schematically in Figure 6.

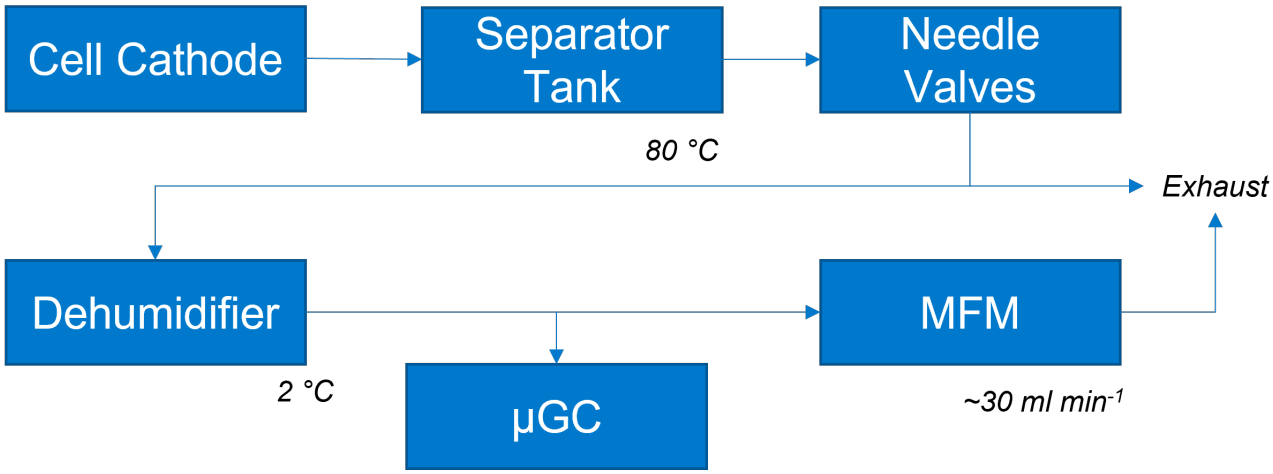

Figure 6: Schematic of gas analysis system connected to PEMWE single cell cathode at NPL.

1.3.1.2.3 Methods

The cell was conditioned by flowing deionised water at 60 °C and approximately 260 ml min^{-1} and holding the cell at 1 A cm^{-2} for 3 h and then at 0.5 A cm^{-2} for 3 h. The cell was then cycled for 3 h between 1 A cm^{-2} and 0 A cm^{-2} with each current density held for 10 s. This was followed by further operation at a constant current density of 1 A cm^{-2} for 3 h and then and 0.1 A cm^{-2} for a final 3 h.

Gas analysis was performed continuously throughout the experiment with a sampling time of 20 s, an injection time of 80 ms, an elution time of 89 s and a backflush time of 11 s. The column pressure was 25.0 Psi and column temperature 80 °C while the inlet temperature was 50 °C. Calibration was performed done at a single point against air with an assumed concentration of 20.9 % introducing significant uncertainty into the quantification of the oxygen content.

1.3.1.3 Example Results & Discussion

An example of the gas chromatograph data obtained with the µGC method chosen is shown in Figure 7a. The separation between oxygen and matrix gases hydrogen and nitrogen is sufficient to allow quantification. Argon elutes from the column with the same retention time as oxygen, so argon is chosen as a carrier gas to exclude its potential influence, though the limit of detection is expected to be higher (ca. 10 µmol mol^{-1}) than when helium is used.

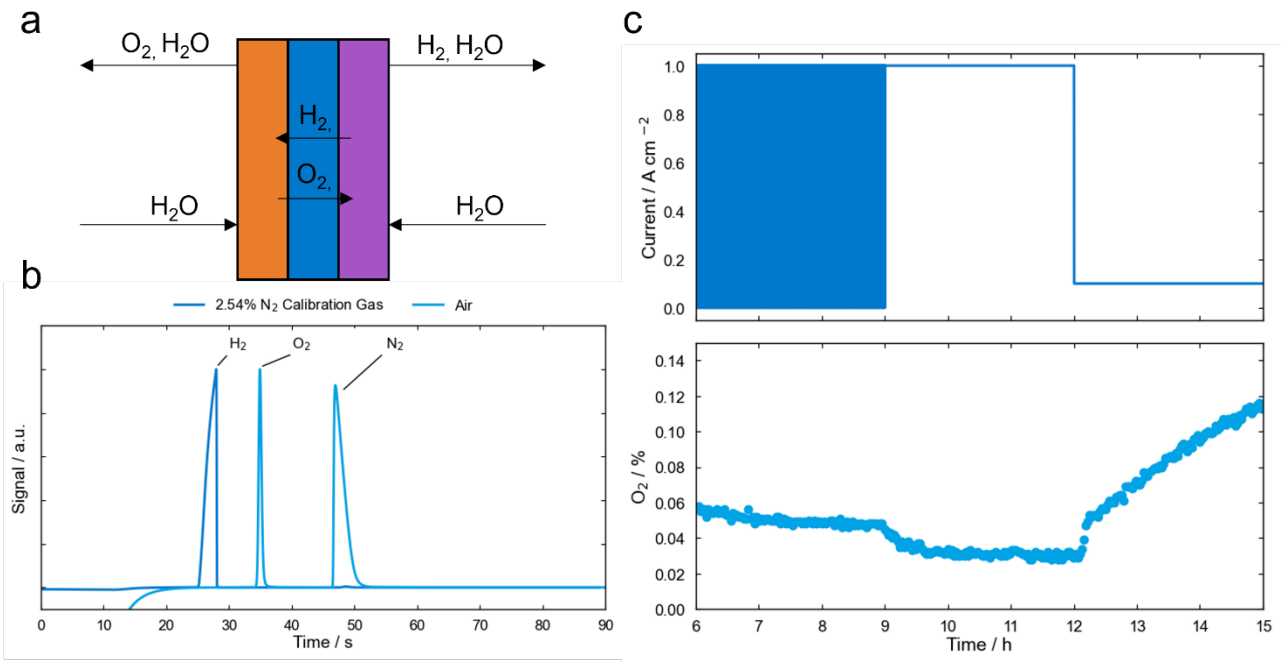

Figure 7 a) schematic of cell showing crossover of anode and cathode gasses b) example of the gas chromatogram showing separation between H_2, O_2 and N_2 c) current profile applied to the cell and corresponding oxygen concentration in the cathode gas.

Figure 7c shows the current profile applied to the cell and the resulting oxygen concentration. The results show that the oxygen concentration depends on the applied current density and are consistent with an approximately constant rate of oxygen concentration. When the current density is increased from an average of 0.5 A cm^{-2} to 1 A cm^{-2} the concentration equilibrates to approximately 0.03% from 0.06%, This change is due to the doubled rate of hydrogen production at higher current densities. At a low current density of 0.1 A cm^{-2} the concentration increases but does not equilibrate within the 3 h experiment, likely because the low production rate of hydrogen is insufficient to rapidly purge the volume of the separator vessels.

1.3.2 PEMWE Single Cell with Online Oxygen Measurement at CEA

1.3.2.1 Introduction

As mentioned in Section 1.3.1, hydrogen produced in a PEM electrolyser typically is not only contaminated by oxygen produced at the anode but also by contaminants coming from supplied water and dissolved trace gases, most notably carbon dioxide. The latter can also be present due to the corrosion of carbon catalyst support at the cathode. While NPL successfully demonstrated the suitability of gas chromatography for the quantification of oxygen present in the hydrogen product, at CEA, differential electrochemical mass spectroscopy (DEMS) has been used to detect contaminants in the hydrogen product stream, since this technique is known to offer suitable detection limits. Here we report the system established at CEA to measure contamination in hydrogen produced at the cathode of a PEMWE cell, while at the same time quantifying crossed-over oxygen along similar lines to the work done at NPL.

1.3.2.2 Experimental Setup

1.3.2.2.1 Materials

The catalyst-coated membrane is a circular (2.8 cm diameter) Tion™ 5-W PFSA membrane coated with 0.5 mg cm^{-2} Pt on advanced carbon for the cathode side, and 2.0 mg cm^{-2} Ir-black on the anode side, used as received. All water used is ultra-pure (typically 18 MΩ cm^{-1} at 25 °C) and pre-heated to 80 °C and supplied at a flow rate of 50 cm^3 min^{-1} to the anode compartment, from which it returns to the source reservoir, along with the produced oxygen, forming a closed loop.

1.3.2.2.2 Equipment

The PEMWE cell used for this experiment has an active area of 25 cm^2 and was composed of a Ti plate with no flow-field, a small Ti mesh used to fill the cell, two large Ti meshes (ITM), one Pt-coated porous Ti current collector, the MEA (Fuel Cell Store), the same current collector that is used on the anode side, a large Ti mesh (ITM), a small Ti mesh and a Ti plate. The cathode outlet gas is passed through a dehumidifier and out of the exhaust, with a T-junction employed to allow the mass spectrometer (Pfeiffer Vacuum) to take samples for measurement. This latter precaution is necessary because the mass spectrometer cannot withstand more than 1-2 cm^3 min^{-1} of gas.

1.3.2.2.3 Methods

The cell was conditioned by cycling for 2.5 h between 2 A cm^{-2} and 0 A cm^{-2} with each current density held for 10 s. This initial step was followed by further operation at a constant current density of 2 A cm^{-2} for 2.5 h and then 0.1 A cm^{-2} for a final 2.5 h. Gas analysis was performed continuously throughout the experiment.

1.3.2.3 Results & Discussion

Using the conventional settings for the DEMS equipment, it is found that oxygen content in the hydrogen flow could be measured. Figure 8 shows the results of this test when the cell ran at high (2 A cm^{-2}) and then low (0.1 A cm^{-2}) current-densities. At high current density, the level of O_2 in H_2 is in the same range (between 0.015 and 0.02%) compared to NPL results obtained by gas chromatography.

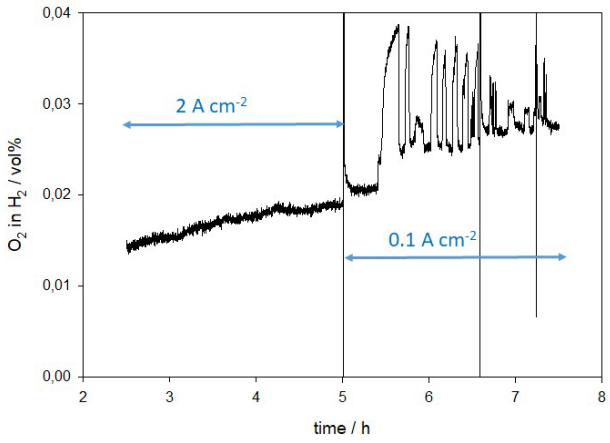

Figure 8: Oxygen contamination in hydrogen stream measured using DEMS connected to a 25 cm^2 PEM electrolysis cell, as a function of current-density. Operating conditions: 80°C, H_2O supply, 50 cm^3 min^{-1}, P_{atm}

The data shows the expected increase in the oxygen/hydrogen ratio when the current-density is decreased. However, there is huge variation in the O_2 level (between 0.02 and 0.04%) at 0.1 A cm^{-2}. These instabilities could come from the low flow rate of H_2 produced (17 cm^3 min^{-1}) related to the flow derived for the DEMS (1 - 2 cm^3 min^{-1}) and the volume buffer at H_2 cell outlet (pipes, gas separator with periodic purge, dehumidifier). Consequently, the H_2 flow rate must remain sufficient to ensure stable and reliable DEMS measurements. Adding a precise digital flow controller to get a constant flow at DEMS inlet could help to improve the quality of the measurement.

Since our DEMS equipment allows a sensitive measurement mode, this technique could be also used to try to detect transient CO and CO_2 traces coming from the corrosion of cathode carbon support in Pt/C catalyst (during operation or after shut-down period for instance). So far, first results have been obtained but further work is required before to be able to conclude reliably on this point.

2 Testing and validation of instruments for measuring key impurities in hydrogen

A number of collaborators loaned hygrometers and oxygen concentration analysers to be calibrated against NPL standards and have their response time evaluated using the facilities developed in the project and described in sections 1.2.1 and 1.2.2.

The performance of five hygrometer types from five different manufacturers with measurement principles including metal oxide, quartz crystal resonance, surface acoustic wave, fibre optic and electrolytic was validated. Two NPL owned hygrometers were also tested with condensation chilled-mirror and water vapour spectrometer measurement principles.

The performance of two oxygen concentration analysers utilising a galvanic fuel cell sensor type from two different manufacturers was validated.

The results of the validation testing are reported with anonymity.

2.1 Test protocol for the evaluation of performance of instruments for measuring impurity levels (principally water vapour and oxygen) in hydrogen as a function of operating conditions.

A test protocol was agreed that encompassed pressures, humidities and oxygen concentration levels expected to be encountered in quality measurements of the hydrogen throughout the production, transport and storage processes as listed in Table 2 below.

Table 2 : Expected test pressures, oxygen content and water vapour contents in various locations of the hydrogen supply chain

Location	Sub-location	Pressure / barg	Oxygen Content	Oxy-gen limit	Water Vapour	water limit	typically Measure-ment point
		barg	ppmv	ppmv	mg/m³	mg/m³	
salt cavern (≥99,96 % H_2)	cavern itself	30 - 300	0 - 10		saturated at cavern tem-perature = 300 - 1000[1]		
	gas treatment facility (input)	**40** (30 - 80)	0 - 10		300 - 600		
	gas treatment facility (Output)	**40** (30 - 80)	0 - 10	1 / 5[2]	1 - 5	4	x
Gas Mixture up to 99,96 % H_2 (Salt cavern or pore reservoirs/aqui-fers)	gas treatment facility (input)	**40** (30 - 80)	0 - 10		300 - 600		
	gas treatment facility (Output)	**40** (30 - 80)	0 - 10	10	20 - 50	50	x
Exhaust of NPL's single cell lab setup		0	<5%		100% RH @ 70 °C		x
Outlet of Hogen S2 Generator (CEA and NPL lab gen-erator)		15 bar	< 1 ppmv		<5 ppmv		x
Backbone of UK national grid (Based off Hy4Heat Specs)		80 bar	< 0.2%		-10 degree dew point		x
Local grid / com-bustion equip-ment spec (Based off Hy4Heat Specs)		1 bar	< 0.2%		-10 degree dew point		x
Refuelling Station Output (ISO14787)		1000 bar	5ppm		5 ppm		x
Total range en-countered		1 bar to 1000 bar	l ppm to < 5 % O2	1 - 10 ppm	5 ppm to 1000 mg / m3	4 - 50 mg / m3	

[1] depending on temperature + pressure
[2] 1 only for chemical Industry

Where it was within the operating range of the standards these conditions were realised to test the instruments. Test values which covered the range of pressures and impurity levels expected to be produced in the hydrogen from the Hogen electrolysers for which quality measurements were to be made in Task 1.3 were covered.

The NPL multi-gas, multi-pressure standard humidity generator has a dew-point temperature range of -60 °C to +15 °C and a pressure range of 0.1 MPa to 3 MPa.

The following humidity test matrix was used: dew-point temperatures of -60 °C, -40 °C, -20 °C and -5 °C at pressures of 0.105 MPa and 3 MPa in background gases of air, nitrogen and hydrogen.

Values of 5 µmol mol^{-1} ,10 µmol mol^{-1} and 15 µmol mol^{-1} of oxygen in hydrogen were chosen to test the oxygen concentration analysers. Mixtures at this level would be unstable if prepared gravimetrically so the values were realised through dilution of the 500 µmol mol^{-1} oxygen concentration in hydrogen parent mixture that was prepared as described in section 2.2.

2.2 Preparation and validation at least two different types of high-precision gas mixtures (gravimetric preparation and validation using analytical techniques) for oxygen and water in hydrogen. (NPL)

NPL has prepared two types of primary reference materials (PRMs) for water and oxygen in hydrogen and in total seven PRMs for the project (one in addition to the protocol requirement of six).

Primary reference standards of water in hydrogen were prepared from pure water in the liquid phase (purity > 95%, Sigma-Aldrich, Gillingham, UK) in accordance with ISO 6142-1 [**5**]. The pure water was deionised water with less than 18 mΩ resistivity. Pure water was added to a transfer loop via syringe injection. The transfer loop consisted in a piece of 1/8-inch external diameter tubing with Swagelok fittings on one end and a three-way valve on the other. All the parts of the transfer loop were made of Swagelok stainless steel 316. The transfer loop and the valve were evacuated to a pressure of 1×10^{-6} mbar to ensure no contaminants or air were pre-sent in the system. The evacuated transfer loop and valve were then weighed on a balance (Sartorius Research, Epsom, UK). Pure formic acid was then transferred into a syringe equipped with a two-way valve (Hamilton, Giamata, RO). The syringe was connected to the three-way valves on the transfer loop. The volume within the connection between the three-way valve and the syringe was evacuated to a pressure of 1×10^{-6} mbar to remove contaminants and air. The water was then transferred from the syringe into the transfer loop. The transfer loop, filled with water, was then weighed again. An empty gas cylinder (10 L aluminium with Spectraseal passivation, BOC, Woking, UK), with an NPL-designed outlet diaphragm valve (Rotarex Ceodeux, Luxembourg) was evacuated below 5×10^{-7} mbar using a turbo molecular pump (Leybold Vacuum, Chessington, UK) for at least 12 hours. The cylinder valve included an internal screw thread to minimise dead volume. The gas cylinder was connected to the transfer loop using a minimum dead volume connection. The volume within the connection between the transfer loop and the minimum dead volume fitting was evacuated to a pressure of 1×10^{-6} mbar to ensure no contaminants or air were present. The water was then transferred from the transfer loop into the cylinder. After the transfer, the transfer loop was weighed again. The cylinder was weighed on a balance (XPE26003LC, Mettler Toledo, Leicester, UK) using an automated weighing facility (KRISS, SK). The cylinder was filled with 6 MPa to 10 MPa (60 bar to 100 bar) of hydrogen (purity > 99.9999%, BIP+, Air Products, Walton-on-Thames, UK). The pure hydrogen had less than 10 nmol mol^{-1} of water amount fraction. The cylinder was then weighed and homogenised through rolling for a further two hours.

Due to the limitation of the mass of water that can be transferred using the method described above, the reference materials of water at 2 µmol mol^{-1}, 5 µmol mol^{-1} and 10 µmol mol^{-1} in hydrogen gas

were prepared via dilution. These were prepared in the same cylinder type as the higher amount fraction gas standards. The gas cylinders were conditioned using a NPL proprietary treatment. The compounds were added to the cylinder being filled by direct transfer of a NPL primary reference materials (prepared as described above from pure water) via a length of 1/16 inch stainless steel tubing (Swagelok, Kings Langley, UK) that had undergone Silcosteel® passivation (Thames Restek, Saunderton, UK). The cylinder was weighed on balance (XPE26003LC, Mettler Toledo, Leicester, UK) after each transfer, and finally filled with 6 MPa to 10 MPa (60 bar to 100 bar) (purity > 99.9999%, BIP+, Air Products, Walton-on-Thames, UK). Upon completion of preparation, the gas standards were homogenised by rolling along the vertical axis for two hours.

Due to the limitation of the safety for mixing oxidant and flammable, the oxygen in hydrogen mixture was prepared from the dilution of a safety premix of oxygen in helium. The NPL PRM of oxygen in helium was prepared from pure oxygen in pure helium. The reference materials of oxygen at 5 µmol mol^{-1}, 50 µmol mol^{-1} and 500 µmol mol^{-1} in hydrogen gas were prepared via dilution therefore will contain a significant amount of helium. These were prepared in the same cylinder type as the higher amount fraction gas standards. The gas cylinders were conditioned using a NPL proprietary treatment. The compounds were added to the cylinder being filled by direct transfer of a NPL primary reference materials (prepared as described above from pure water) via a length of 1/16 inch stainless steel tubing (Swagelok, Kings Langley, UK) that had undergone Silcosteel® passivation (Thames Restek, Saunderton, UK). The cylinder was weighed on balance (XPE26003LC, Mettler Toledo, Leicester, UK) after each transfer, and finally filled with 6 MPa to 10 MPa (60 bar to 100 bar) of hydrogen (purity > 99.9999%, BIP+, Air Products, Walton-on-Thames, UK). Upon completion of preparation, the gas standards were homogenised by rolling about the axis for two hours.

The compositions of the gas standards (amount fraction and associated uncertainty) were calculated from the masses of formic acid and hydrogen introduced in each cylinder using the software package 'GravCalc2' [**6**] (NPL, Teddington, UK). The amount fraction with uncertainty for each compound was validated and verified by using different analytical techniques including Cavity Ring-Down Spectroscopy (CRDS) and gas chromatography with a pulsed discharge ionization detector (GC-PDHID).

Three water gas mixtures with various amount fraction have been prepared for PTB between 2 µmol mol^{-1} and 10 µmol mol^{-1} of water in hydrogen as detailed in Table 3 below. Several PRMs of oxygen in hydrogen were prepared for evaluating performance of oxygen analysers at NPL. Due to instability of low amount fraction oxygen in hydrogen, oxygen gas mixtures at amount fraction below 20 µmol mol^{-1} were realised through dilution of the 500 µmol mol^{-1} oxygen in hydrogen parent mixture and used shortly after to avoid any decay. The details of oxygen in hydrogen gas mixture are listed in Table 3 below.

Table 3 : Oxygen in hydrogen gas mixtures (n.a., not available as not present in the mixture)

Cylinder number	D914174	D914233	D306725	D386411R	3083	3084	3078
O_2 (µmol mol^{-1})	498.93 ± 0.42	502.09 ± 0.45	50.9 ± 0.08	5.004 ± 0.026	n.a.	n.a.	n.a.
He (µmol mol^{-1})	125545 ± 105	125255 ± 110	12687 ± 17	1238.0 ± 3.2	n.a.	n.a.	n.a.
H_2O (µmol mol^{-1})	n.a.	n.a.	n.a.	n.a.	9.68 ± 0.02	4.86 ± 0.02	1.98 ± 0.01
H_2 (µmol mol^{-1})	balance	balance	balance	balance	balance	balance	balance

2.3 Assessment of online gas analyser instruments for selectivity and pressure-dependence (NPL).

The performance of five hygrometer types from five different manufacturers with measurement principles including metal oxide, quartz crystal resonance, surface acoustic wave, fibre optic and electrolytic was validated. Two NPL owned hygrometers were also tested with condensation chilled-mirror and water vapour spectrometer measurement principles. The results of the validation testing are reported with anonymity.

Error, as shown in the results, is defined as: Measured value of the instrument – Reference value.

2.3.1 Hygrometer background gas species effect on measurement error

Instruments B and E were only specified to operate at atmospheric pressure and so could only be evaluated for background gas species error dependence in this work.

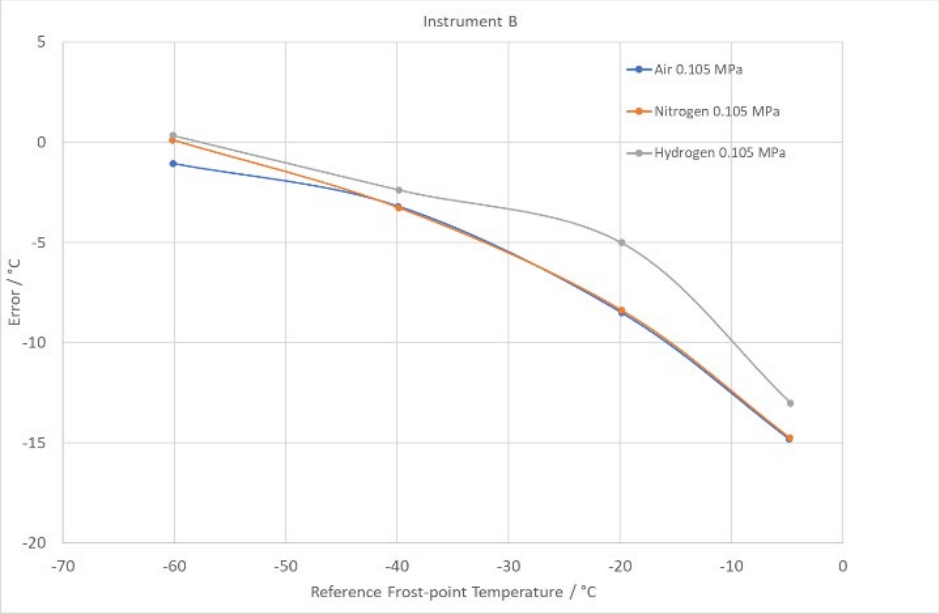

Figure 9 : Instrument B demonstrating background gas species measurement error dependence at near atmospheric pressure

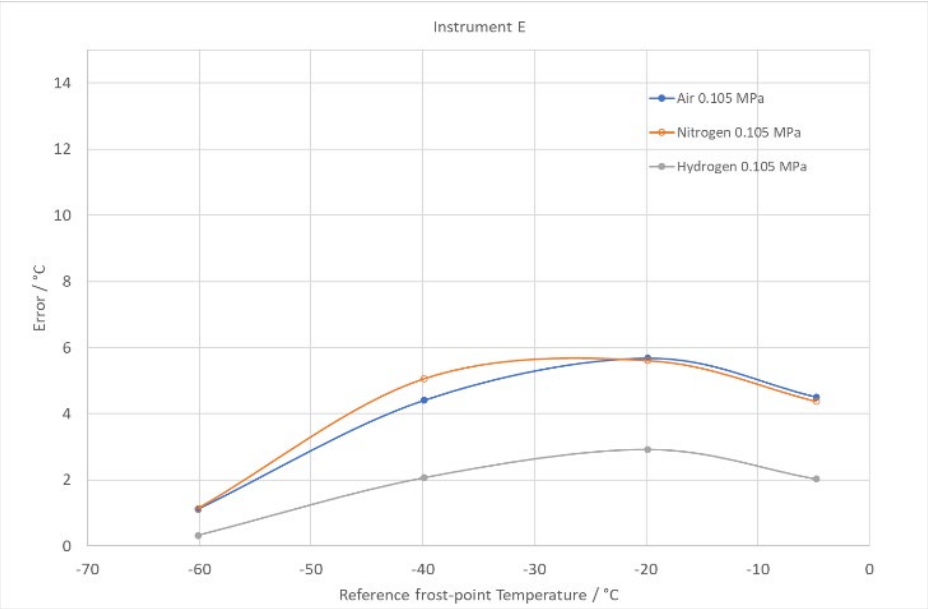

Figure 10 : Instrument E demonstrating background gas species measurement error dependence at near atmospheric pressure

For both instruments the measurement errors for air and nitrogen background gas were consistent but when the background gas was changed to hydrogen a shift in measurement error was observable. The instruments incorporated different measurement principles and it is interesting to notice that the shift in error due to hydrogen background gas is towards over-reading for instrument B but towards under-reading for instrument E.

2.3.2 Hygrometer test pressure effect on measurement error

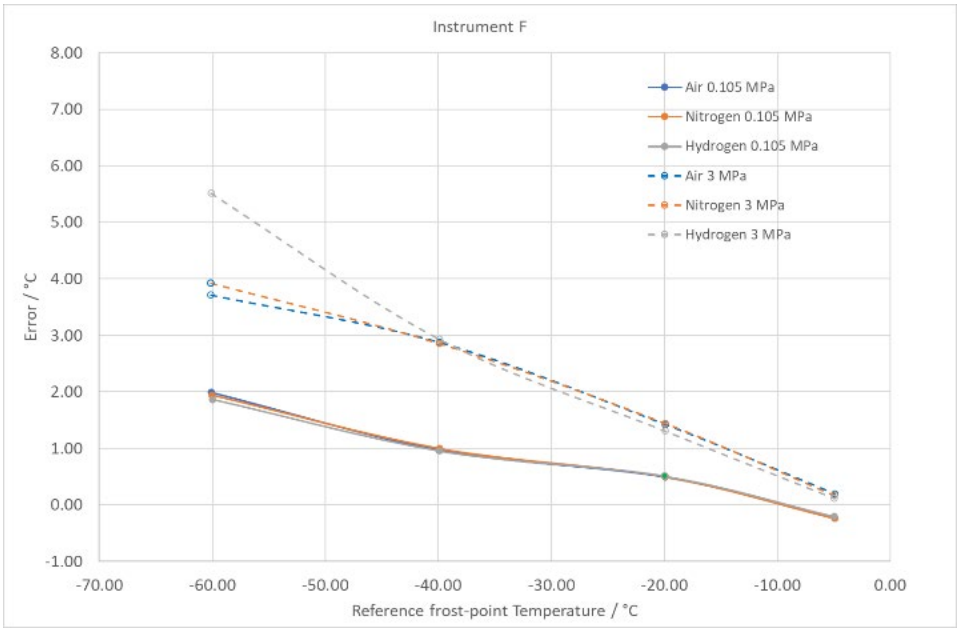

Figure 11 : Instrument F demonstrating pressure and background gas species measurement error dependence

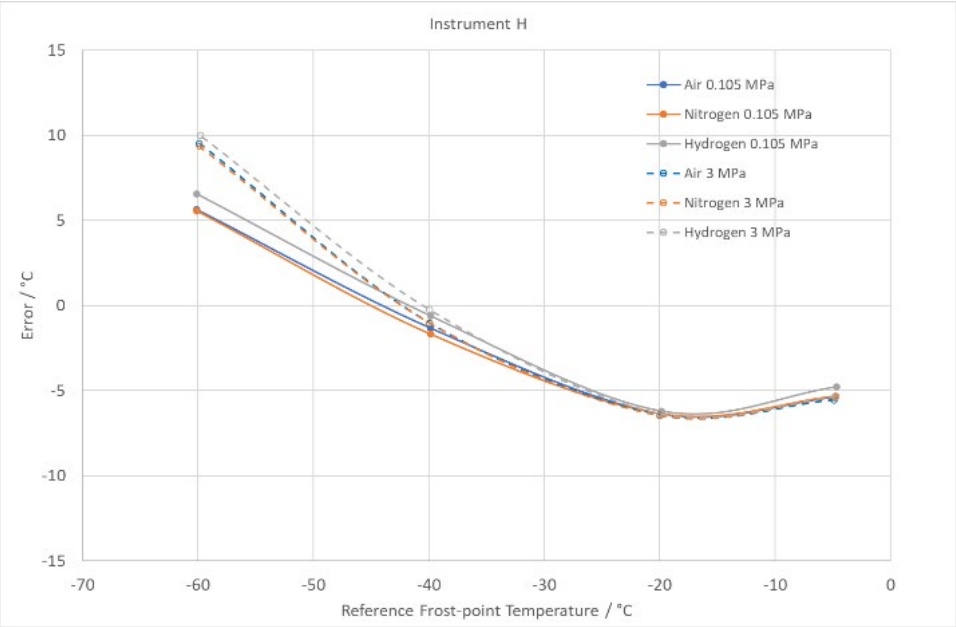

Figure 12 : Instrument H demonstrating pressure and background gas species measurement error dependence

In Figure 11, the measurement error of instrument F demonstrated no background gas dependency at the test pressure close to atmospheric pressure. However, the results when the test pressure was increased to 3 MPa show a clear pressure dependency measurement error of instrument F with over-reading increasing with increasing pressure. At the elevated pressure at dew-point temperatures below -40 ºC the results in hydrogen background gas also showed a further increase in error compared to those in air and nitrogen at this pressure.

The measurement error of instrument H, as shown in Figure 12 demonstrated a pressure dependant over-reading with increasing background pressure at dew-point temperatures of -40 ºC and below.

Instrument G when tested showed minimal effect from changing background gas species and test pressure as shown below in Figure 13.

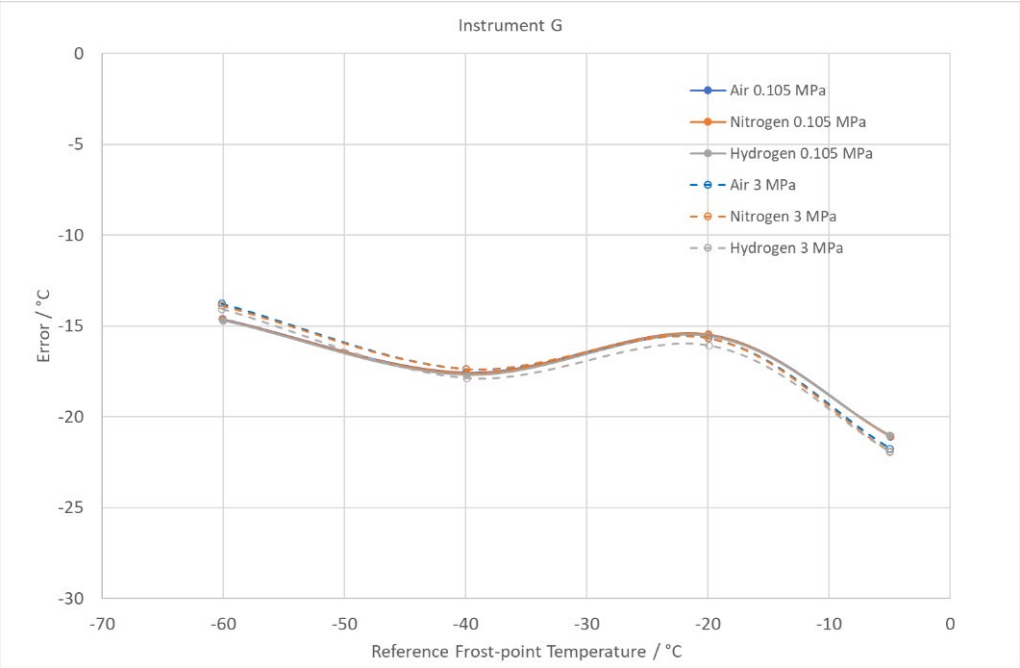

Figure 13 : Instrument G demonstrating minimal pressure and background gas species measurement error dependence

2.3.3 Evaluation of performance of online gas analysers for oxygen measurement in hydrogen

The performance of two online gas analyser instruments for oxygen measurement in hydrogen were assessed in terms of pressure dependence, linearity, repeatability, trueness, and selectivity. The testing result of each metric is described and discussed as follows.

2.3.3.1 Assessment of pressure dependence of oxygen analysers

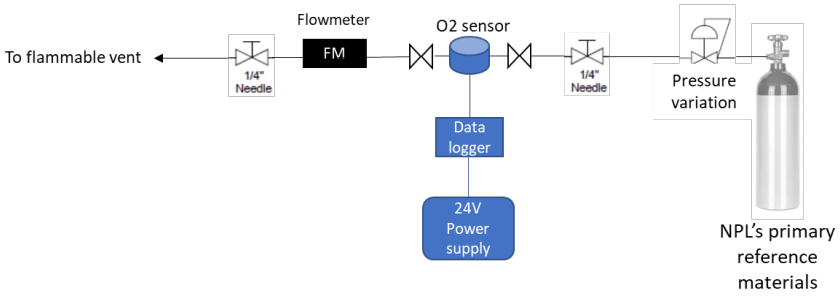

Figure 14 : Facility set-up for assessment of pressure dependence of oxygen analyser

A new facility was developed by the NPL Gas Metrology group and dedicated to evaluating the influence of pressure on the performance of oxygen analyser. The set-up is mainly consisting of NPL's primary reference material to ensure measurement traceability, calibrated pressure and flow meters which can be used to read pressure value and flow rate and needle valves to regulate and restrict flow (function as back pressure regulator).

Even if an instrument or sensor has a specific pressure operating range, it can be useful to evaluate their behaviour within or outside of the pressure range. For example, instrument A and B should operate at atmospheric pressure, nevertheless, it was recommended by the manufacturer to perform

pressure dependence test on the instrument B. The experiments were performed using the facility described in the Figure 14 above and results are presented in Figure 15 below.

The procedure for the pressure dependence test was for the sensor to be purged with pure H_2 (regions where the PRM value is 0 in Figure 15) under atmospheric pressure and once the reading of purged sensor reached baseline and was stable, 5 µmol mol^{-1} O_2 in H_2 was delivered to the sensor and the test pressure was set to the values shown in the red text in Figure 15 through simultaneous back pressure regulation from the needle valves shown in Figure 14. The black dotted lines in Figure 15 are used to indicate the periods when each test pressure was applied to the sensor.

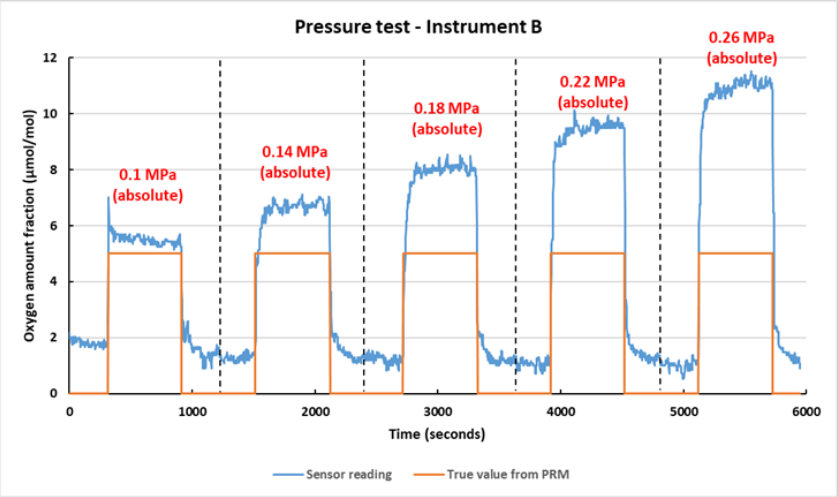

Figure 15 : Results of influence of pressure on oxygen analyser performance

Increasing test pressure has a significant effect in measurement error (see Figure 15 above). It is interesting to notice the measurement value of oxygen amount fraction is proportional to the elevated oxygen partial pressure in hydrogen. Therefore, the inlet pressure of the gas in the sensor is critical to get accurate value and would lead to positive bias if increased.

2.3.3.2 Assessment of linearity of oxygen analysers

The linearity of oxygen analysers was assessment with the facility described in Section 1.2.2. The results of the linearity tests are presented in Figure 16.

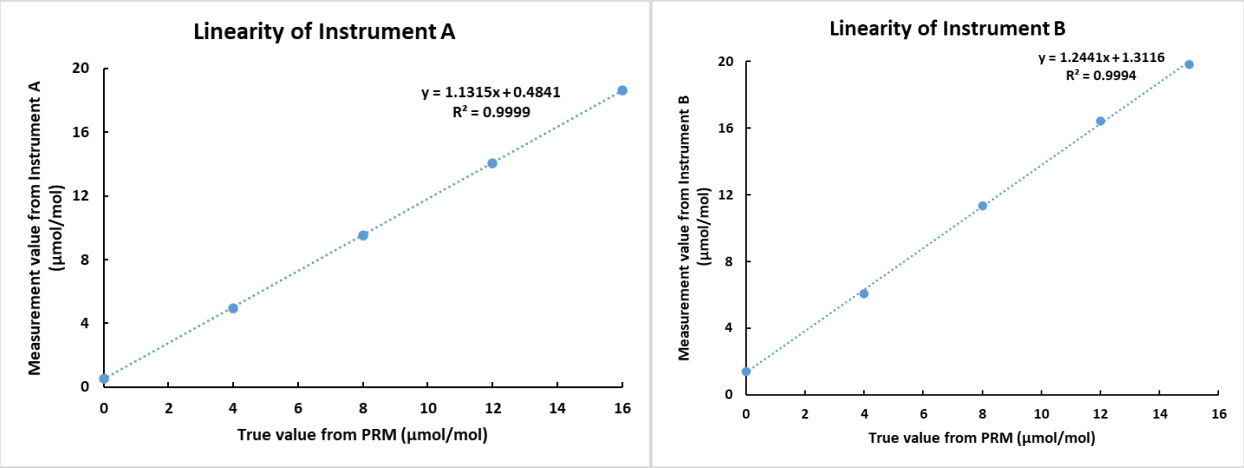

Figure 16 : Results of linearity tests for oxygen analysers

It can be observed there was a good linearity of measurement value of oxygen amount fraction over the range 0-20 µmol mol^{-1} in hydrogen of both instrument A and instrument B.

2.3.3.3 Assessment of repeatability and trueness of oxygen analysers

The repeatability and trueness of oxygen analyser were assessed with the facility described in Section 1.2.2. A gas mixture of 5 µmol mol^{-1} oxygen in hydrogen was delivered from the dilution of a NPL's primary reference material with the dynamic system and used for evaluating the repeatability and trueness of oxygen analysers. Between each repeat run, the oxygen analysers were purged under high-purity hydrogen condition to mitigate the measurement error caused by oxygen content residue in the line and instrument itself.

The results are showed in Figure 17 and Table 4. The measurement of oxygen contents in hydrogen was repeated three times and five times on the instrument A and instrument B, respectively.

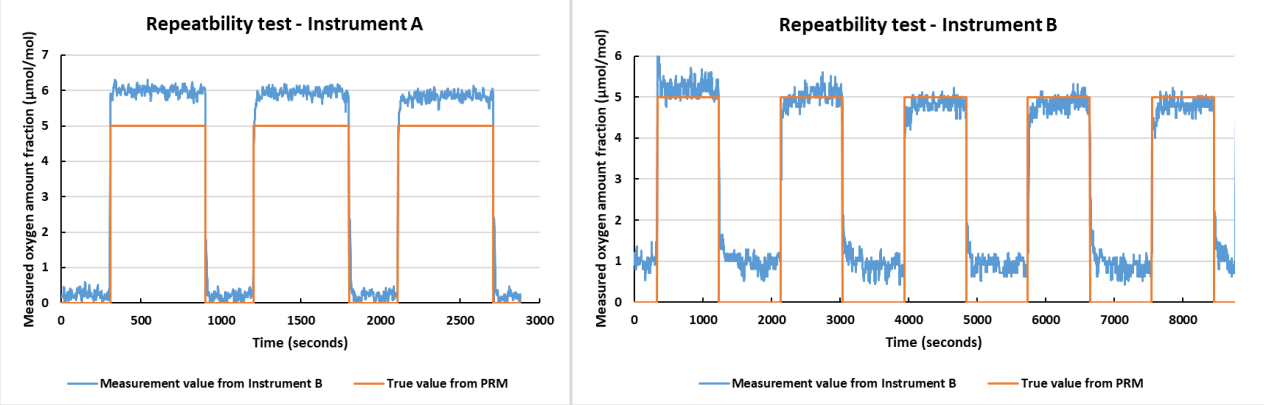

Figure 17 : Results of repeatability test for oxygen analysers

Table 4 : Measurement results of oxygen contents in hydrogen. The uncertainty is provided expanded with *k*=2

	True value from PRM	Instrument A			Instrument B				
		1st results	2nd results	3rd results	1st results	2nd results	3rd results	4th results	5th results
Oxygen amount fraction / µmol mol^{-1}	4.971 ± 0.253	5.991 ± 0.311	5.931 ± 0.295	5.813 ± 0.333	5.195 ± 0.309	5.148 ± 0.292	4.837 ± 0.205	4.817 ± 0.274	4.785 ± 0.250

From Table 4, it can be observed that the measurement value from the instrument A demonstrated a good repeatability (less than 2% variability) while the measurement value from the instrument B has a good but higher variability (approximately 4%)

On the other hand, the instrument B is accurate and achieve true value measurement while the instrument A is biased reporting around 16% higher results than the reference value. Therefore, the instrument A requires dedicated calibration. Therefore, it is critical to calibrate the instruments prior to being utilised for measurement. The calibration of both oxygen analysers is performed in Section 2.5.3.

2.3.3.4 Assessment of selectivity of oxygen analysers

The selectivity of oxygen analysers was assessed with the facility showed in Figure 18. The facility was modified on the basis of the step change facility in Section 1.2.2. An additional injection line was added that enable the static gas mixture with different background gas (i.e., helium or nitrogen) to be delivered from the individual injection line.

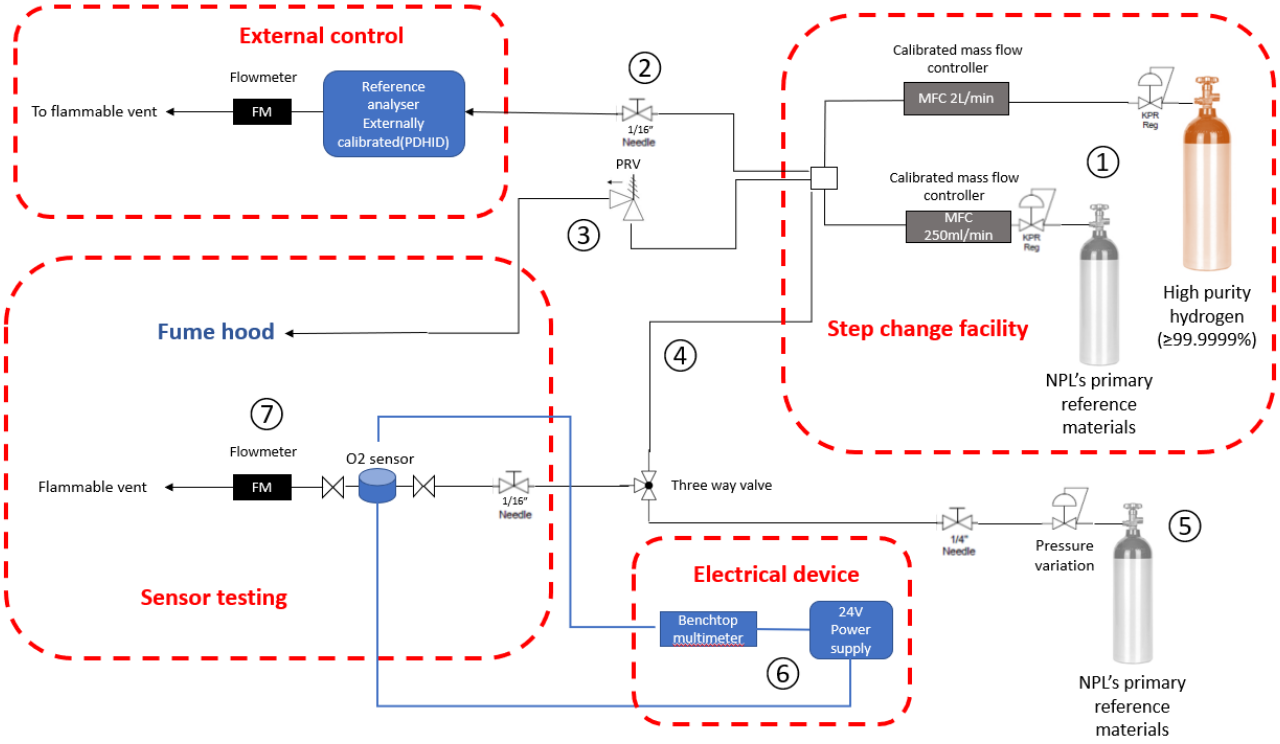

Figure 18 : Facility for assessment of selectivity of oxygen analysers

The results of selectivity tests are presented in Figure 19 and Figure 20 for instruments A and B respectively. Calibration using reference materials in inter gas (i.e., N_2 and He) is appealing as it simplifies safety gas handling (i.e., flammable).

Three different balance gas (H_2, He, N_2) were used to assess instrument A. Based on the reading of oxygen contents in hydrogen and helium matrix, the results for instrument A agreed well. However, a significant difference is noticeable when balance gas changed from hydrogen to nitrogen. The bias is towards under-reading. Regardless the type of other background gas, the response time to achieve 90% step change to a stable value is significantly longer than the one with hydrogen.

For instrument B, two balance gas (H_2, He) were assessed. As observed with instrument A, the response time to achieve 90% step change to a stable value is significantly longer in helium than in hydrogen. A significant bias was observed between the results from oxygen in helium compared to oxygen in hydrogen. The bias due to balance gas change from hydrogen to helium is towards over-reading for instrument B.

It is quite interesting to notice a discrepancy on the selectivity of instrument A and B when using helium as balance gas.

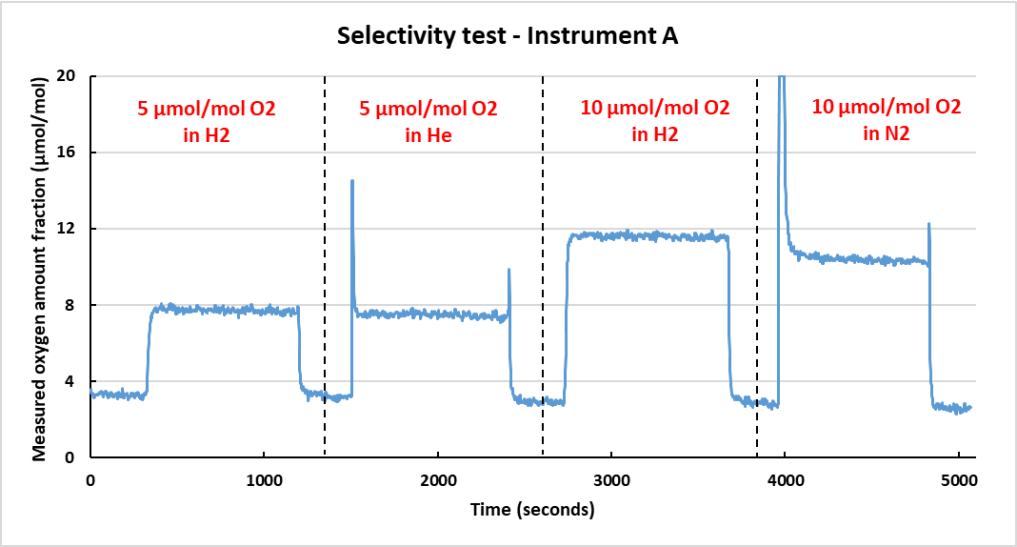

Figure 19 : Evaluation of Instrument A sensor selectivity for oxygen amount fraction as a function of balance gas (He, N_2 and H_2)

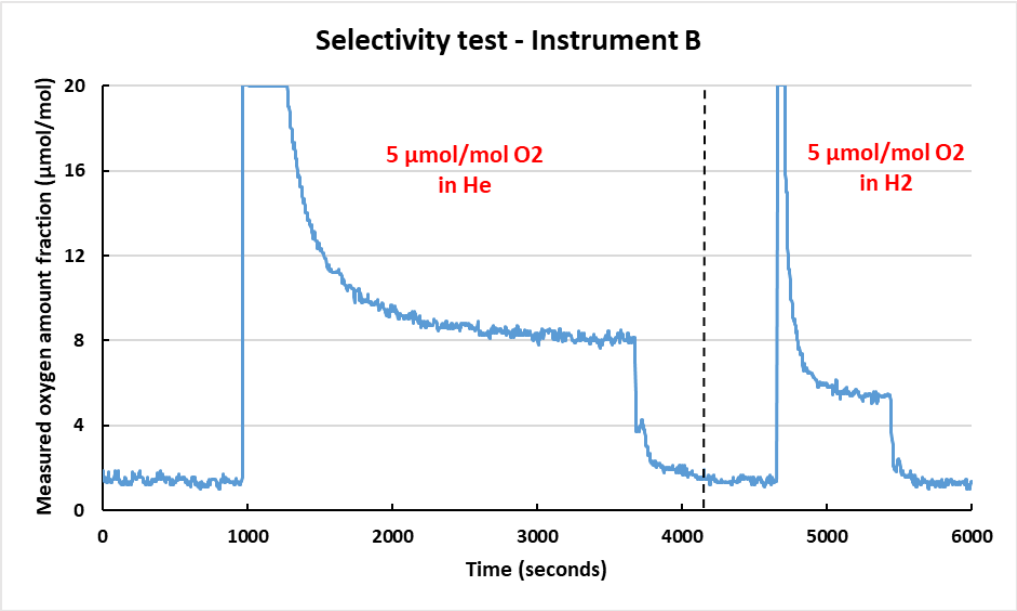

Figure 20 : Evaluation of Instrument B sensor selectivity for oxygen amount fraction as a function of balance gas (He, N_2 and H_2)

The results highlight that selectivity is related to the measurement technology and requires proper evaluation for each sensor.

2.4 Assessment of the response time of online gas analysers and sensors of water vapour and oxygen (NPL).

2.4.1 Hygrometer response time testing

Using the facility described in Section 1.2 for water content response time testing, rising step changes from -60 °C to -40 °C frost-point temperature (10 mol mol^{-1} to 100 mol mol^{-1}) were rapidly imposed on the test instruments. Data was logged from the instrument under test at the shortest sampling interval possible during its response to the rapidly imposed transient in water content level.

The MatLab functions described in Section 1.2.1.4 were used to estimate t_{90} for after rising and falling step changes were applied to the data logged from the instrument under test.

In Figure 21 and Figure 22 below the measurements of all test instruments are normalised to the same timeline such that the manual valve switch causing the step change was made at a time of 30 seconds.

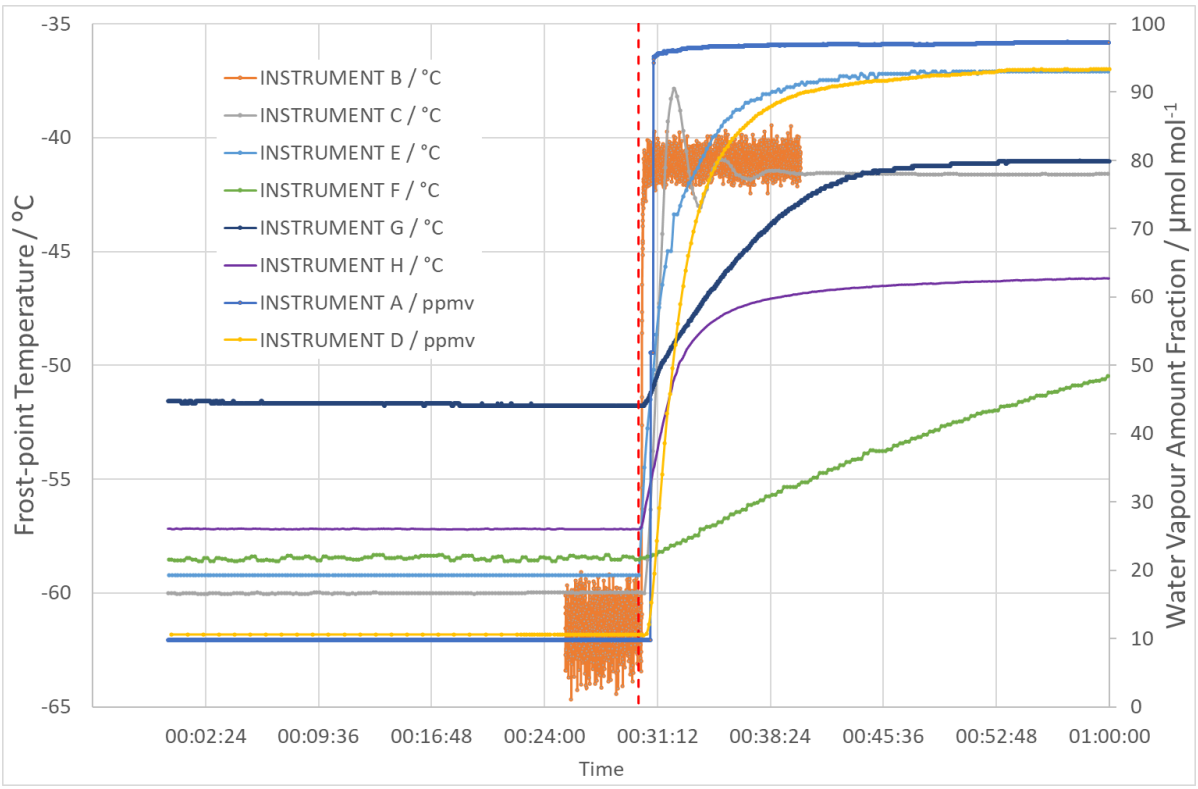

Figure 21 : Measurement response of test hygrometers A to H to a rising step change in humidity from -60 °C (10 mol mol^{-1}) to -40 °C (100 mol mol^{-1})

The results in Table 5 below show the t_{90} response time of the eight instrument types tested to a rising step change in humidity from -60 °C (10 mol mol^{-1}) to -40 °C (100 mol mol^{-1}).

Table 5 : Measurement response times of test hygrometers A to H to a rising step change in humidity from -60 °C (10 mol mol^{-1}) to -40 °C (100 mol mol^{-1})

Instrument	t_{90} response time / s
INSTRUMENT A	19.30
INSTRUMENT B	2.14
INSTRUMENT C	26.83
INSTRUMENT D	164.8
INSTRUMENT E	306.1
INSTRUMENT F	6872
INSTRUMENT G	786.6
INSTRUMENT H	402.7

A wide range of t_{90} response times were found ranging from two seconds (Instrument B) to nearly two hours (Instrument F) taken for the instrument under test to reach 90 % of the step change to a final stable measured value.

The t_{90} response times for the instruments tested for rising step changes found in this work were compared to response time values that had been specified in manufacturer's technical data sheets. Where response times were specified, it was not stated if this was the time taken to respond to a rising or falling step change in humidity or the magnitude of the applied step change.

Table 6 : Comparison of measured response time to rising step change to manufacturer's specified response time for instrument type (where given)

Instrument	Manufacturer specification response time / s
INSTRUMENT A	Met
INSTRUMENT B	Met
INSTRUMENT C	Not given
INSTRUMENT D	Not given
INSTRUMENT E	Not given
INSTRUMENT F	Not given
INSTRUMENT G	Not met
INSTRUMENT H	Not met

The response time of the test instruments to falling step changes from -40 °C to -60 °C frost-point temperature (100 mol mol^{-1} to 10 mol mol^{-1}) were also analysed. The t_{90} response times to a falling step change in humidity were longer in duration for every instrument tested when compared to t_{90} response times for the same rising step change in humidity.

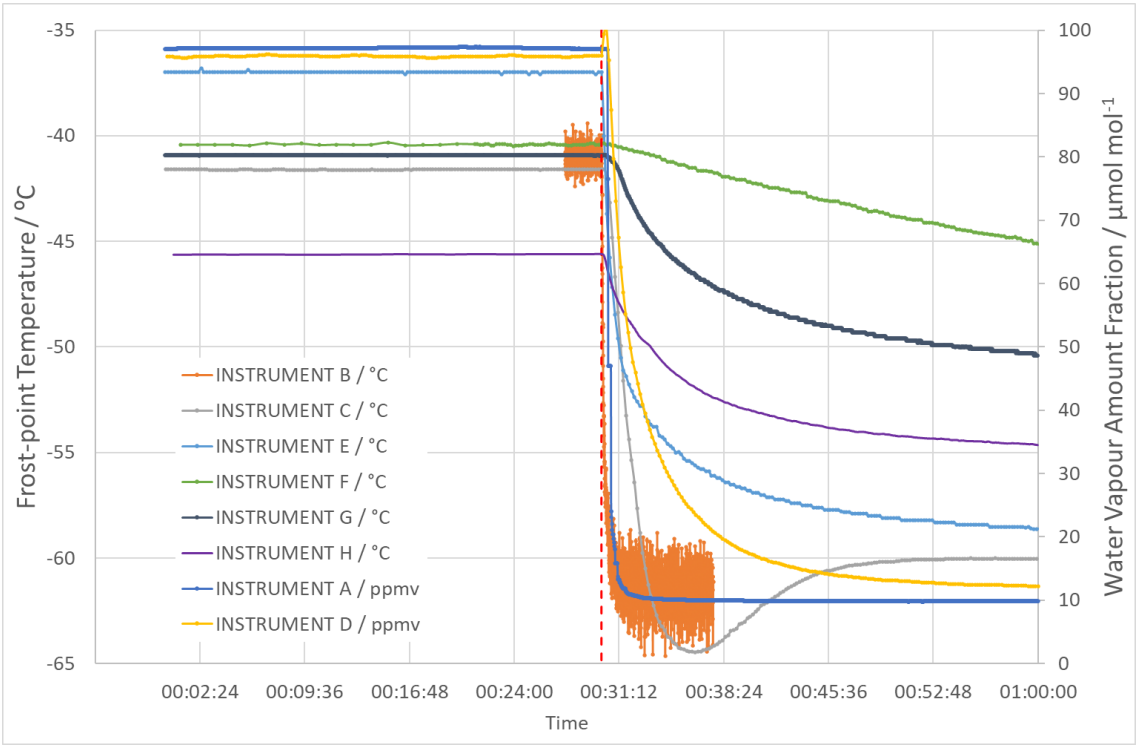

Figure 22 : Measurement response of test hygrometers A to H to a falling step change in humidity from -40 °C (100 mol mol^{-1}) to -60 °C (10 mol mol^{-1})

Again a wide range of response times were found for the response times to falling step changes ranging from 26 seconds to nearly four and a half hours taken for the instrument under test to reach 90 % of the step change to a final stable measured value as shown in Table 7 below.

Table 7 : Measurement response times of test hygrometers A to H to a falling step change in humidity from -60 °C (10 mol mol^{-1}) to -40 °C (100 mol mol^{-1})

Instrument	t_{90} response time / s
INSTRUMENT A	28.32
INSTRUMENT B	26.28
INSTRUMENT C	117.9
INSTRUMENT D	417.8
INSTRUMENT E	449.5
INSTRUMENT F	16822
INSTRUMENT G	3452
INSTRUMENT H	2580

2.4.2 Oxygen analyser response time testing

The response time of online gas analyser instruments for measuring oxygen in hydrogen was assessed with the step change test facility developed in Section 1.2.2. Two instruments (A and B) were loaned from the collaborators and used for response time testing. A series of experiments were performed with rising and falling step changes including nominally 0 µmol mol^{-1} to 10 µmol mol^{-1}, 5 µmol mol^{-1} to 10 µmol mol^{-1}, 10 µmol mol^{-1} to 5 µmol mol^{-1} and 10 µmol mol^{-1} to 0 µmol mol^{-1}.

The response time results of instruments can be found in Figure 23 and Figure 24. Detailed information of response time measurement in rising and falling step changes are reported in Table 8. The measurement of both instruments was amended by taking the response time of the dynamic system (7 seconds) into account.

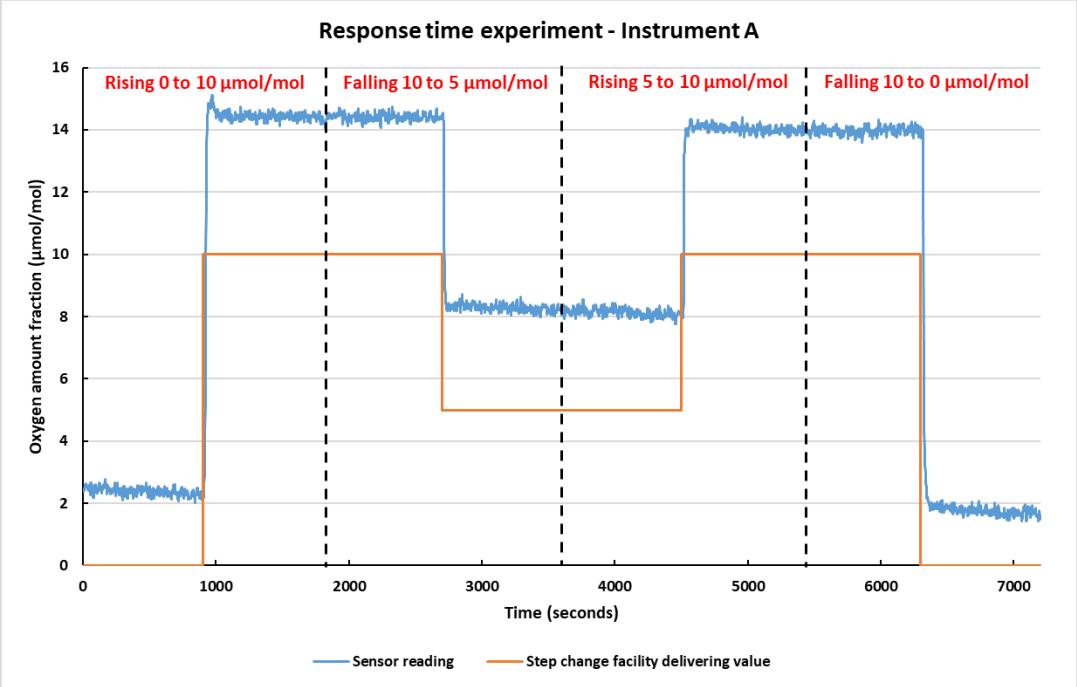

Figure 23 : Response time assessment of Instrument A for oxygen measurement

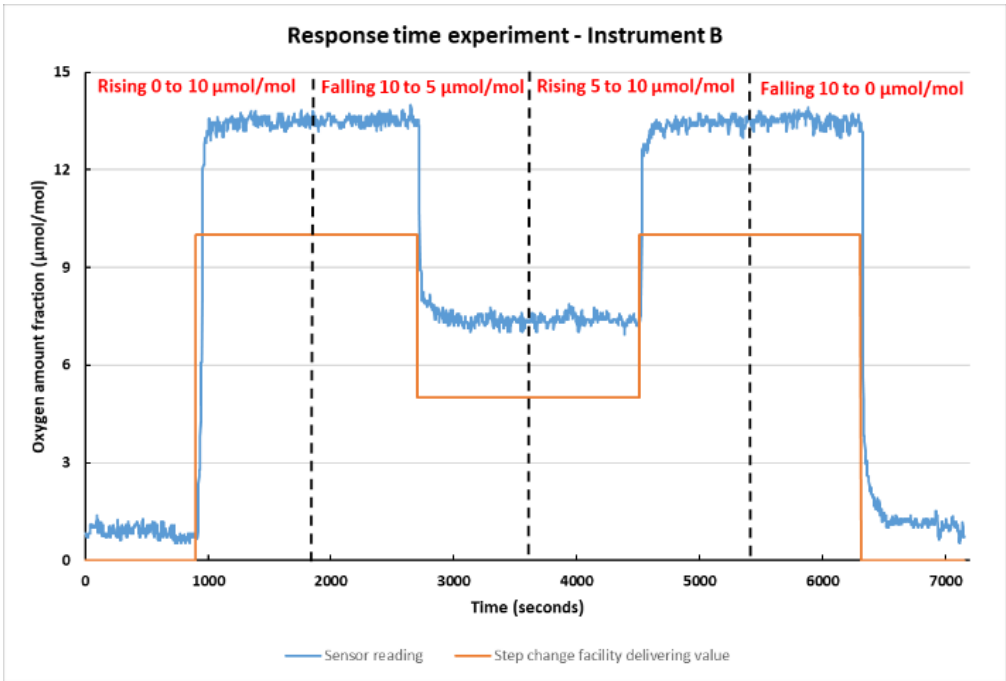

Figure 24 : Response time assessment of Instrument B for oxygen measurement

It can be observed from Table 8 the response time to either rising or falling step changes is within tens of seconds to reach 90 % of the step change to a final stable measured value except the response time to falling step change from 10 µmol mol^{-1} to 0 µmol mol^{-1} for the instrument B. Instrument

A showed similar response times when responding to oxygen contents change in hydrogen, measuring both rising and falling step changes, with good reproducibility within 25 seconds.

For instrument B, a significant difference in response time is observed between small and large step changes of oxygen in hydrogen. By comparing the response times in different step changes being applied to the instrument B, instrument B responded twice as fast to a smaller values of step change than to larger changes.

Table 8 : Results of response time (t_{90}) testing to step changes in oxygen contents of hydrogen

	Instrument A				Instrument B			
	Rising step change		Falling step change		Rising step change		Falling step change	
	0-10 µmol/mol	5-10 µmol/mol	10-5 µmol/mol	10-0 µmol/mol	0-10 µmol/mol	5-10 µmol/mol	10-5 µmol/mol	10-0 µmol/mol
t_{90} (s)	23	24.5	24.5	24.5	51.5	32	27	114.5

2.5 Calibration of existing online gas analyser instruments for measuring water vapour and oxygen in hydrogen. (NPL)

2.5.1 Hygrometer calibrations: dew-point temperature

Examples of the measurement error observed during calibration in hydrogen at different humidities and background pressures can be seen in Section 2.3. Measurement uncertainties are also applicable to each of the results.

The instruments that output values in dew-point temperature units were calibrated directly against the multi-gas, multi-pressure primary standard humidity generator in single-pressure mode. The standard uncertainty of the generated dew-point temperature is calculated by combining the estimated uncertainties arising from the calibration, drift, self-heating and measurement of the reference PRT, the saturation efficiency, temperature conditioning, pressure measurement and pressure differences in the calibration system, the temperature variations in the generator bath, and the effects of leaks, desorption and contamination.

The standard uncertainty of measurement is calculated by combining the standard uncertainties of the generated dew-point temperature, the standard deviation of the recorded readings of the instrument under test, its resolution and an estimate of its reproducibility during calibration.

The reference uncertainty of this generator in dew-point temperature units is 0.11 °C in the range -60 °C and +15 °C and high-performance instrument types like chilled mirror hygrometers (Figure 25) would expect expanded measurement uncertainties (coverage factor $k = 2$, providing a coverage probability of approximately 95 %) of 0.12 °C once their contributions to the uncertainty are added.

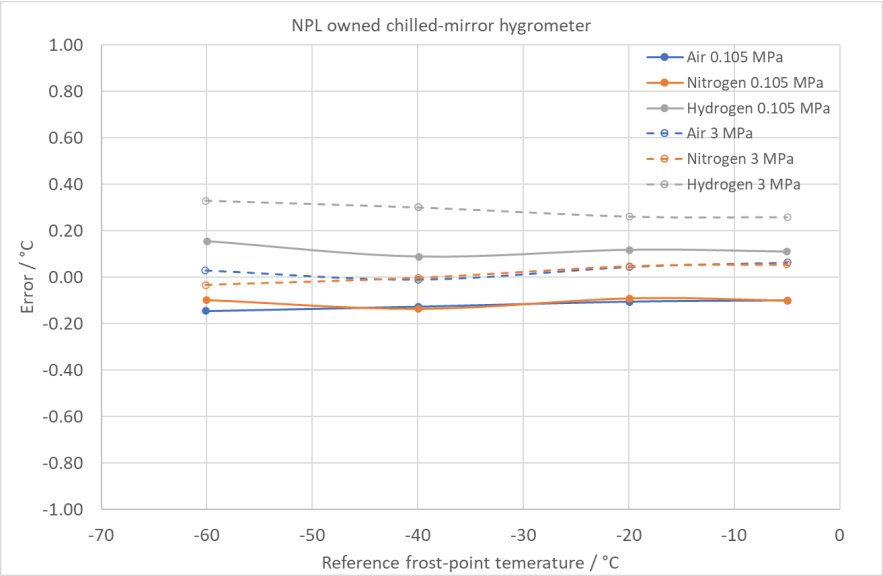

Figure 25 : Calibration of NPL owned chilled-mirror hygrometer

For other instrument types, uncertainty contributions to the measurement uncertainty from irreproducibility of the instrument under test increase the measurement uncertainty considerably. Measurement uncertainties of the order of a few degrees Celsius can be expected when the measurement error of the instrument under test is found to be irreproducible by amounts of this magnitude during calibration.

The hygrometers were loaned to the project for the majority of the project duration so it was possible to check long-term drift of the measurement error over time. For instruments C and F the measurement drift was low at the repeat calibrations. Figure 26 shows an example of measurement drift for instrument type G and Figure 27 shows an example of measurement drift for instrument type E between two calibrations nearly one year apart. It should be noted that the two instruments are of different measurement principles and the measurement error of instrument G drifted towards under reading by approximately 15 °C across the calibrated range and the measurement error of instrument E drifted towards over reading by a similar magnitude in the same time period.

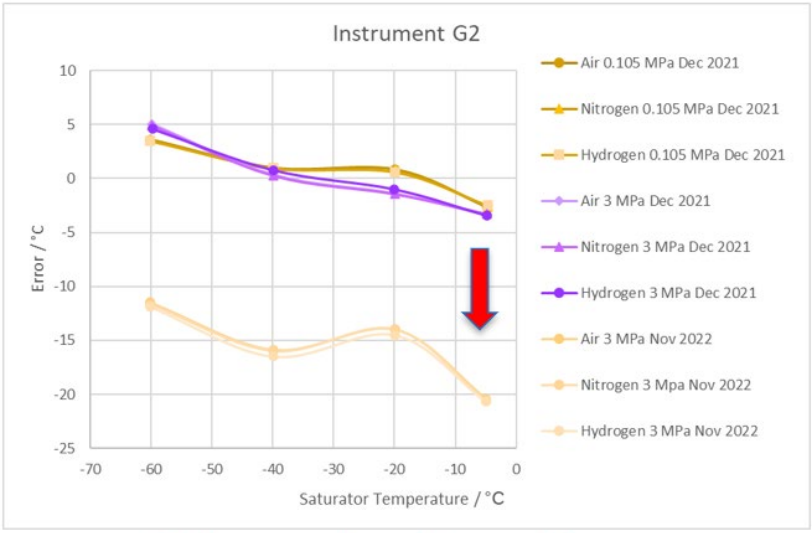

Figure 26 : Long-term drift of measurement error of instrument G between two calibrations nearly one year apart

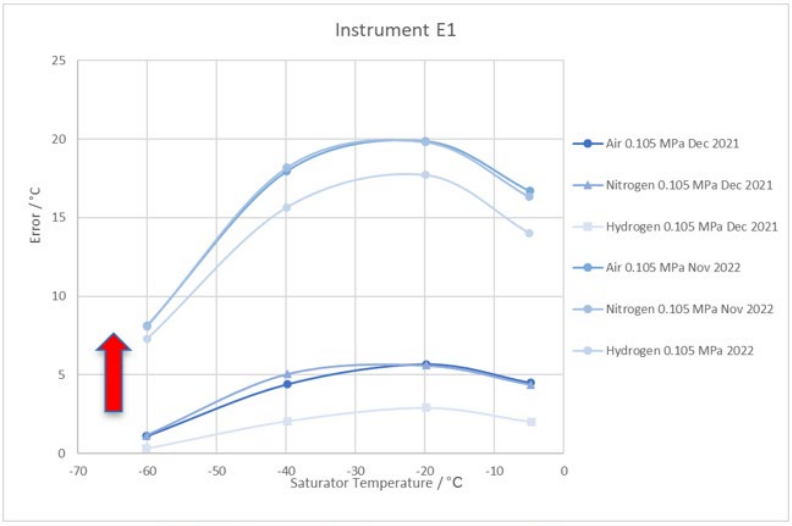

Figure 27 : Long-term drift of measurement error of instrument E between two calibrations nearly one year apart

When considering the measurement uncertainty of a calibrated hygrometer, an estimation of the long-term drift in use should be made and incorporated into the uncertainty budget. This estimation can be made when the calibration history of an instrument is known.

2.5.2 Hygrometer calibrations: water vapour amount fraction

To convert reference dew-point temperature values at a given test pressure to water vapour amount fractions requires knowledge of a water vapour enhancement factor for hydrogen. Research completed by NPL in this project has helped lower the uncertainty in the estimation of this quantity. For hydrogen, where there are few or no accepted data or equations for water vapour enhancement

factor, values were approximated based on NPL experimental measurements in the same temperature and pressure range. An uncertainty was allowed made to account for this approximation.

2.5.3 Oxygen concentration analyser calibrations

Based on the performance evaluation of oxygen analysers in Section 2.3.3, it is important to calibrate the oxygen analysers to ensure the measurement value is accurate. The NPL's primary reference material was used to ensure its measurement traceability. The calibration results of two instruments are shown in Figure 28 and Figure 29. The high R-squared values indicate the calibration curves are good fits to the data.

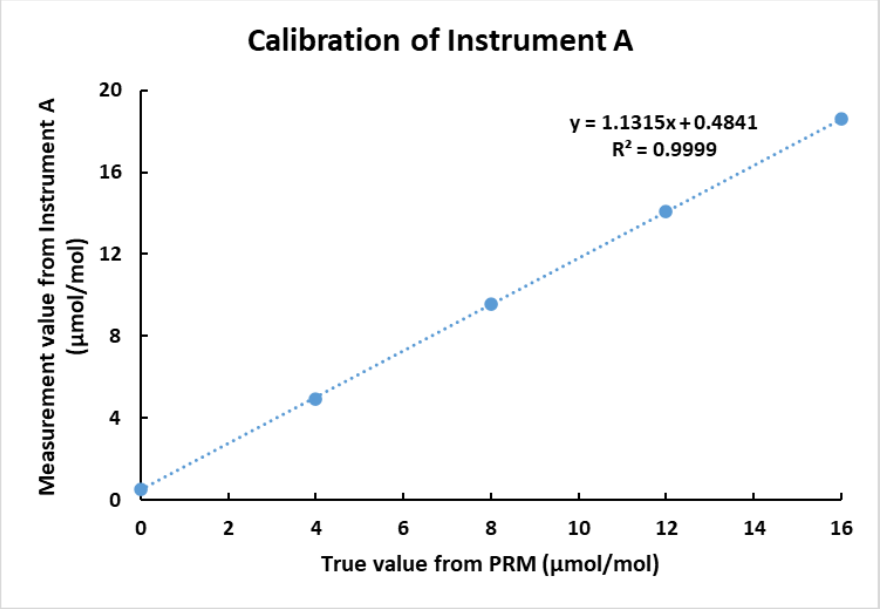

Figure 28 : Calibration results of Instrument A

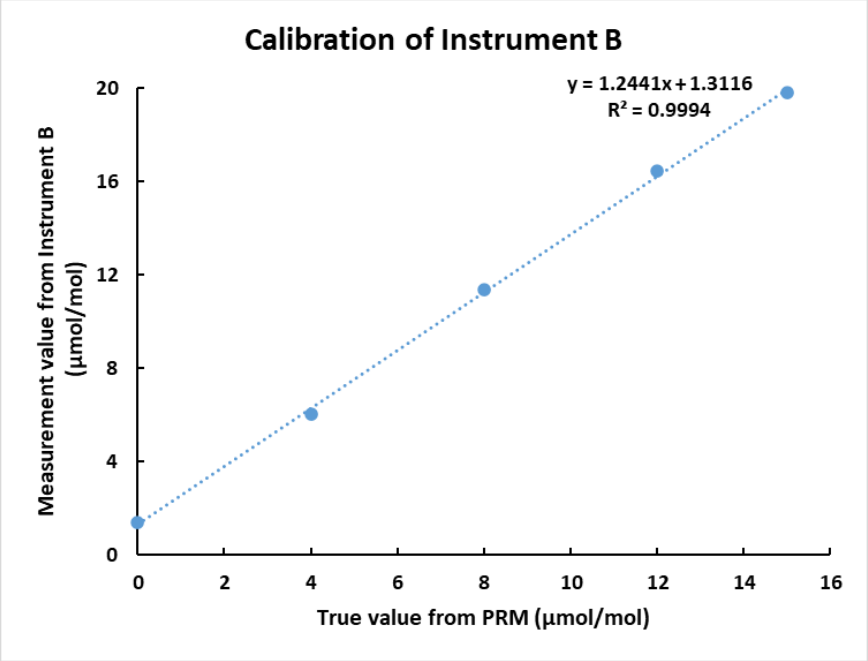

Figure 29 : Calibration results of Instrument B

2.6 Testing and validation of the spectroscopic method developed in 1.1 for H2O impurity detection in H_2, including response time assessments. (PTB)

After verifications and corrections, the spectroscopic method (based on CRDS) was validated against NPL gravimetric standards at 2 µmol mol-1, 5 µmol mol-1 and 10 µmol mol-1 water vapour in hydrogen using the test set-up shown in Section 1.1.2. Figure 30 depicts a plot of the CRDS H2O amount fraction results as a function of the values provided for the NPL mixtures. A generalized linear regression is applied to the data in Figure 30, leading to a good linearity (slope value of 0.996 ± 0.016, k = 1) and an insignificant intercept value (intercept uncertainty is larger than the intercept value).

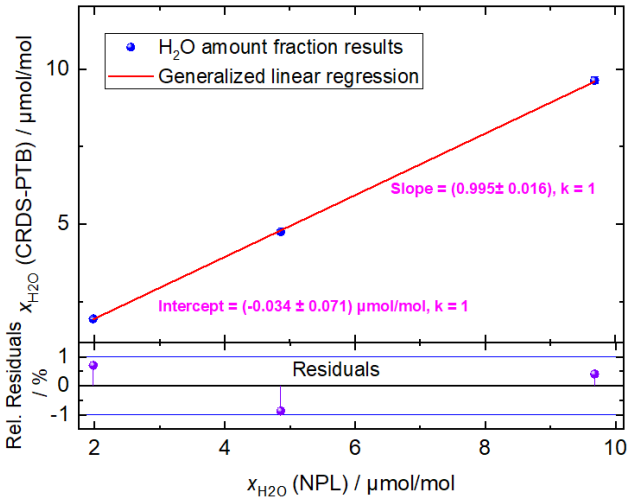

Figure 30 : Results of H_2O amount fraction in H_2 when reference mixtures of 2 µmol mol^{-1}, 5 µmol mol^{-1} and 10 µmol mol^{-1} water vapour in hydrogen

Figure 31 depicts example H_2O amount fraction measurements near the ISO14687-2 limit value of 5 µmol mol^{-1} showing the capability of the spectroscopic method.

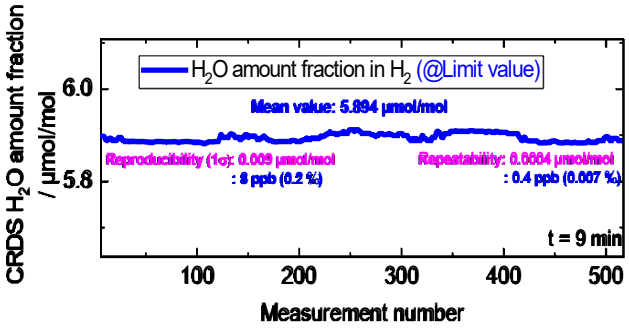

Figure 31 : Results of H_2O amount fraction in H_2 around the limit value of 5 µmol mol^{-1}

The measurement frequency of the data in Figure 31 is 1 Hz. The repeatability, expressed as the standard deviation of the mean, of the results is 0.4 nmol mol^{-1} (relative: 0.007 %). The reproducibility (expressed as the standard deviation) is 9 nmol mol^{-1} (relative: 0.2 %). The spectroscopic method developed at PTB will be presented at the GAS 2024 conference [**7**].

3 Conclusions

PTB has developed a metrologically compatible laser-spectrometric measurement method, based on cavity ringdown spectroscopy (CRDS), for H_2O impurity measurements in H_2. CRDS is a highly sensitive spectroscopic techniques and was employed by PTB to perform H_2O amount fraction measurements down to the nmol/mol range in N_2 and H_2 gas matrices. The spectroscopic H_2O amount fraction measurement method was validated against reference gas mixtures from NPL in the amount fraction range between 1 and 10 µml/mol. The performance of the CRDS instruments at the limit value of 5 µmol mol^{-1} of H_2O in H_2 was investigated, resulting to a good repeatability of the measurements at the limit value and thus demonstrating the capability of the spectroscopic measurement method for H_2O quality control measurements in hydrogen.

A step change facility that can apply fast step changes in the water content of hydrogen was developed at NPL with the ability to apply rising or falling step changes within approximately two seconds.

The results of testing the response time of a range of hygrometers, utilising different sensing principles, showed response times to a step change from 10 µmol mol^{-1} to 100 µmol mol^{-1} water content ranging from the order of two seconds to nearly two hours. It is important to consider response time when choosing instruments for online hydrogen quality measurement. Using an instrument with too slow a response time will delay feeding back an impurity rise information to process control systems, delaying any action to bring the hydrogen quality back to levels that meet required specifications. Conversely, a slow response time to a falling step change in water vapour content could lead to extra time and energy spent needlessly drying hydrogen which had already met required water content levels.

It is anticipated that this facility can be used to validate new sensor technologies for hydrogen water content measurement, supporting sensor manufacturers and industry.

Calibration of hygrometers at NPL revealed that whilst the measurement performance of some instruments tested was relatively unaffected by a change of background gas, the output of other instruments exhibited dew-point temperature changes of as much as a few to five degrees Celsius dew-point temperature when the background gas was changed from air or nitrogen to hydrogen.

Where available, a calibration in a background gas of hydrogen for hygrometers is recommended to address any gas-dependency not identified in the factory calibration performed in a background gas of air or nitrogen. It cannot be assumed that corrections based on the results of factory calibration certificates are applicable to a hygrometer used to measure the humidity of hydrogen.

For the hygrometers that could be tested at elevated pressure, the calibrations of the hygrometers at different pressures revealed that whilst the measurement error of some instruments tested was relatively unaffected by a change of test pressure, the measurement error of other instruments exhibited changes of as much as a few to five degrees dew-point temperature when the test pressure was changed from 0.105 MPa to 3 MPa.

Where available, a calibration in hydrogen at the elevated pressure reflecting hygrometer use in an application should be performed to address any pressure-dependency not identified in the factory calibration performed at atmospheric pressure in air or nitrogen.

The calibration drift of hygrometers was evaluated over the duration of project. Calibration drift of as much as 15 °C (dew-point temperature) was observed in some of the instruments tested in a period of a year. This has significant implications for hygrometers such as these if they are to be used in hydrogen quality measurement. Under-reading could lead to false assumption of the quality of hydrogen and over-reading could lead to needless extra time and energy spent on drying processes when in reality the hydrogen is already of acceptable quality for the process.

A fast-step change facility was developed and validated by NPL for oxygen amount fraction in hydrogen. The facility was able to realise step change of 100% at the range 0 – 10 µmol mol^{-1} within less than 7 seconds (upward and downward). The fast-step change facility was applied to validate new sensor technologies with quick response time. Moreover it will support sensor manufacturer and potentially allow onsite calibration following further development.

Primary reference materials play an important role in ensuring measurement traceability. Often, industry relies on calibration gas instead of PRMs, it is critical to check the stability and shelf time of gas mixtures, particularly the ones containing reactive compounds (e.g., oxygen) as any decay or reaction will cause the loss of these contaminants and consequently lead to false measurement or biased calibration. NPL demonstrated that water and oxygen PRMs can be prepared as part of the project.

The validation of sensors is critical and using the fast-step changing facility further sensor validation exercises were realised. Sensors and online analysers may have to operate in more complex conditions than analytical laboratories. Sensors may operate at various system pressures therefore the effect of pressure on sensor response is important and should be evaluated. The pressure dependence tests realised in this study showed that sensor responses were pressure sensitive. Large measurement bias was caused by elevated pressure for sensor B. Therefore, it is critical to calibrate sensors under a range of pressures to get accurate values when gas sample pressure is variable. It will help to define the boundaries of application of the sensor for reliable measurements.

Selectivity assessment of the oxygen sensors tested revealed that the measurement value was significantly affected by a change of the balance gas species. The sensor responses varied for oxygen amount fraction if the balance gas was nitrogen, helium or hydrogen. It should be noted that the effect was technology dependent (sensor A and B showed different selectivity toward helium).

It is recommended to calibrate oxygen sensors with the matrix gas used for the online analysis (hydrogen). Corrections based on the results of factory calibration certificates performed in alternative balance gas may not be applicable to an oxygen sensor used to measure oxygen in hydrogen except if relevant evidence are provided showing agreement between hydrogen and the factory calibration balance gas.

The overall study on sensor validation and fast step change facility demonstrated that sensor validation is challenging and require further study to support a fast-growing industry. This first study will provide a good basis for further research as part of ongoing project as Met4H2 [**8**]. Further calibration or validation activities will be discussed with the industry and provide more case study application towards standardisation of sensor and online analyser validation for hydrogen quality.

4 References

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