21GRD05 Met4H2

D5 - Intercomparison on trace water in hydrogen standards over the nominal range from 0.5 µmol mol^{-1} to 50 µmol mol^{-1} with conclusions and recommendations for future improvements

Organisation name of the lead participant for the deliverable:
National Physical Laboratory (UK)

Due date of the deliverable: 30th September 2025

Actual submission date of the deliverable: 28 November 2025

Confidentiality Status: PU - Public, fully open (remember to deposit public deliverables in a trusted repository)

Deliverable Cover Sheet

European Partnership
Co-funded by the European Union

The project has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States.

Task	Activity	Reporting date
3.2	3.2.6	30.09.2025

Title

Intercomparison on trace water in hydrogen standards over the nominal range from 0.5 µmol mol^{-1} to 50 µmol mol^{-1} with conclusions and recommendations for future improvements

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Key words

Hydrogen, humidity, trace water, trace moisture, inter-laboratory comparison, primary humidity standards

Acknowledgement

The project Met4H2 21GRD05 has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States.

Feedback

The consortium welcomes feedback. Please send your comments, suggestions or other feedback to the project coordinator, Dr. Adriaan van der Veen (VSL), avdveen@vsl.nl .

Summary

Water vapour is one of the key parameters for hydrogen quality in the supply chain. The requirement to monitor water vapour is a cross-cutting issue over the entire hydrogen supply chain (i.e. transport applications, production, injection into gas network or for heat application). Recent studies (e.g., FCH-JU HYDRAITE, 16ENG01 MetroHyVe) highlighted the challenges related to these measurements, with one of the main challenges to achieve or access a reliable and traceable water vapour standard in the range of 0.5 µmol mol^{-1} to 50 µmol mol^{-1} in hydrogen.

In this project the participants organised the first ever comparison involving dynamic generators of humidity in hydrogen. The objective was to provide the hydrogen community with reliable and proven systems to generate reference water vapour values and provide confidence in the use of primary humidity standards with hydrogen.

This report summarises the results of this pilot intercomparison and recommendations for future comparisons of this type based upon the lessons learnt.

Contents

1 Introduction

Water vapour measurement is one of the key parameters for hydrogen quality in the supply chain. The requirement to monitor water vapour is a cross-cutting issue over the entire hydrogen supply chain (i.e. transport applications, production, injection into gas network or for heat application). Recent studies (e.g., FCH-JU HYDRAITE, 16ENG01 MetroHyVe) highlighted the challenges related to these measurements, with one of the main challenges to achieve or access a reliable and traceable water vapour standard in the range of 0.5 $\mu mol\ mol^{-1}$ to 50 $\mu mol\ mol^{-1}$ in hydrogen.

The provision of humidity calibrations in hydrogen is an emerging area. In order to add confidence in this, a first ever interlaboratory comparison (ILC) of dynamic primary humidity standards operating with hydrogen gas was carried out. The objective was to provide the hydrogen community with a reliable and proven system to generate reference water vapour values.

This report summarises the results of the intercomparison work and it will be shared with the ISO/TC 197 in order to support further standardisation and developments in international standards.

2 Primary standard details

2.1 Summary of Primary standards

Table 1 : Participant NMI generator capabilities for dynamic generation of water vapour in non-air gases

Institute	**Dew/frost point temperature range / °C**	**Pressure range / MPa**	**Water Vapour Amount Fraction / µmol mol^{-1}**	**Max flow rate / l min^{-1}**	**Gas species compatibility**
NPL	-70 to +15	0.1 to 3	0.1 to >500 (at 3 MPa) 2.5 to >1000 (at 0.1 MPa)	5	H_2, N_2, Air, others
VSL	-80 to +20	0.1 to 6	0.01 to 390 (at 6 MPa) 0.5 to >2000 (at 0.1 MPa)	5	H_2, N_2, Air, Ar, CH_4
INRIM	-55 to -10	0.1 to 5.5	0.5 to 50 (at 5.5 MPa) 20 to >2000 (at 0.1 MPa)	3	H_2, N_2, Air

2.2 NPL (UK) Primary Standard

The NPL Multi-gas, Multi-pressure Primary Standard Humidity Generator operates in a single pass mode, fully saturating the test gas to a frost-point temperature defined by the controlling the temperature of a bath of ethanol that the saturator pipework assembly is immersed in. The reference dew point was determined from measurements made using a platinum resistance thermometer (PRT). Traceability of measurement is provided by calibration of this thermometer to the International Temperature Scale of 1990 (ITS-90) through NPL Temperature Standards.

Pressure is controlled in a range extending above atmospheric pressure and traceability of pressure measurement is provided through a digital pressure indicator calibrated against NPL standards for pressure.

In single-pressure mode the standard can be used to make a direct calibration in units of dew- or frost-point temperature (°C) for instruments that measure that quantity.

From measurements of dew-point temperature, t_d , and saturator pressure, P, a reference value of amount fraction of water vapour can be calculated, x (μmol mol^{-1}) for instruments that measure that quantity.

$$x = \frac{e(t_d)\cdot f(t_d,P)}{P} \tag{1}$$

Water vapour pressure, e , is calculated from the dew point measurement using the equations of Sonntag [1] and the water vapour enhancement factor, f , for the background gas being saturated must be known. Further information on the water vapour enhancement factor equations used in this ILC for nitrogen and hydrogen can be found in section 4.1.

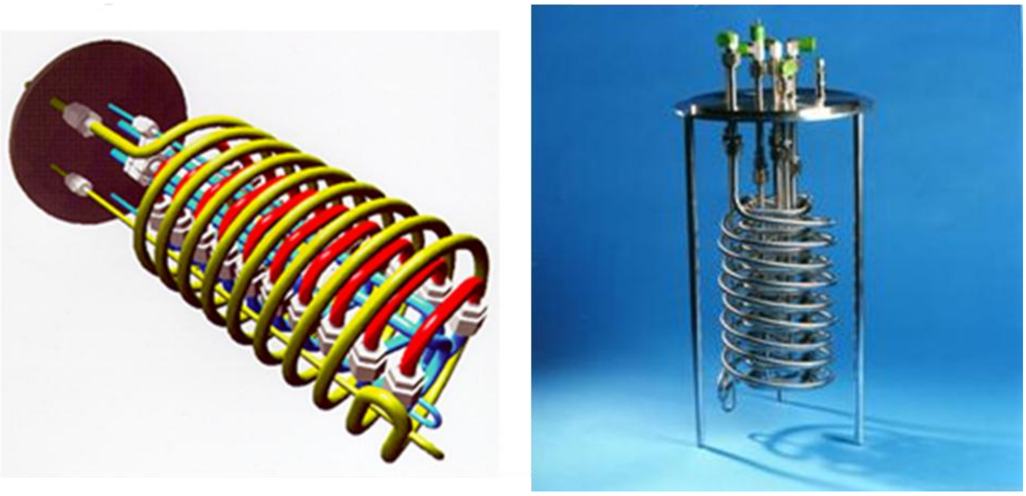


Figure 1: NPL Multi-gas, Multi-pressure Primary Standard Humidity Generator

2.3 VSL (Netherlands) Primary Standard

The VSL High-Pressure Dewpoint Generator (HPDG) operates in a single pass mode, fully saturating the test gas to a frost-point temperature defined by the controlling the temperature of a bath of ethanol in which it is fully submerged. The reference dew point was determined from measurements made using a standard platinum resistance thermometer (SPRT), which is traceable to the ITS-90 through the temperature standards of the contact thermometry laboratory of VSL. Temperature measurements are performed using a thermometric bridge which compares the resistance of the thermometer to a standard resistance. The latter is calibrated in comparison to a 25 Ω standard resistor in the primary thermometry laboratory of VSL, which in turn is traceable to the primary resistance standard of VSL. The pressure meters are calibrated against the primary standards of the pressure laboratory at VSL.

In A3.2.1 of the Met4H2 project VSL upgraded this generator to be used with hydrogen at pressures up to 6 MPa. The saturator was left unchanged and is described extensively in [2].

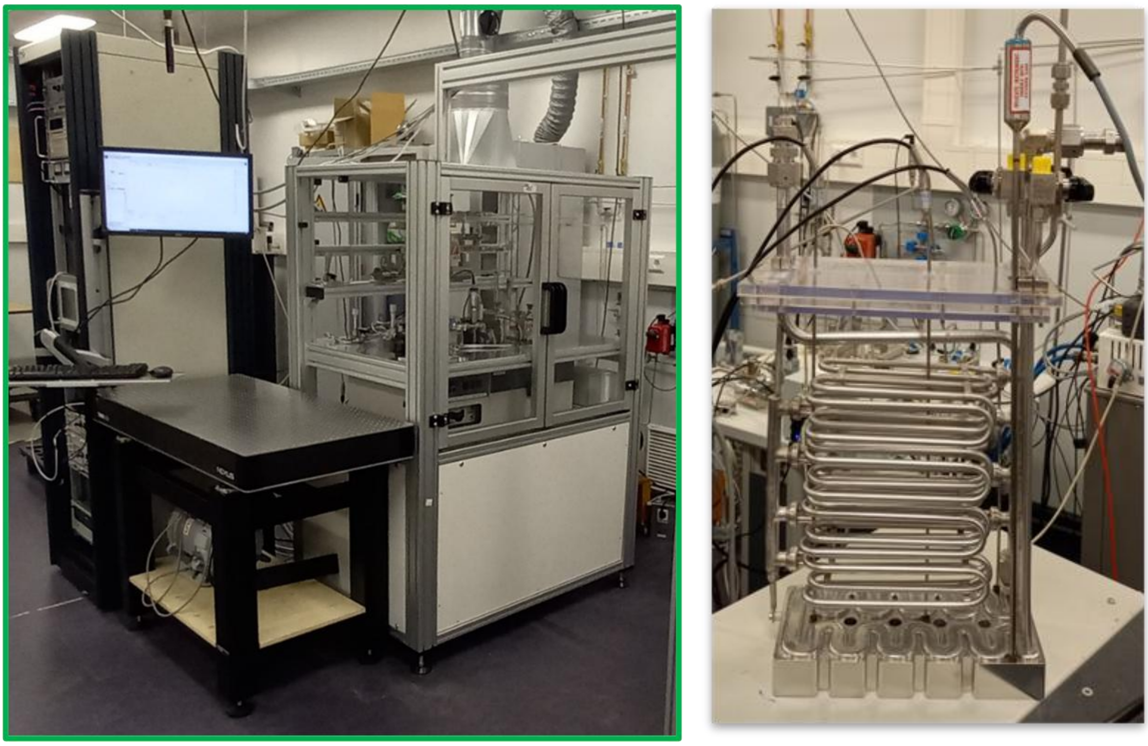


Figure 2 left panel: High-pressure Dew Point Generator (HPDG) modified for use with Hydrogen. Right panel: Saturator in use with the HPDG.

Similar to the NPL setup, in single-pressure mode, the standard can be used to make a direct calibration in units of dew-point temperature (°C) for instruments that measure in that unit. The amount fraction of water vapour units reference value is calculated using equation (1).

2.4 INRIM (Italy) Primary Standard

The INRIM transportable precision humidity generator (t-PHG) consists of a single-pass saturation-based generator capable of generating a moist hydrogen stream with an amount fraction of water between 0.5 µmol mol^{-1} and 50 µmol mol^{-1} at any pressure between 0.1 MPa and 5.5 MPa. This is equivalent to a dew/frost-point temperature at pressure between -55 °C and -10 °C. The temperature of the saturator is defined by controlling the temperature of a thermal bath where the saturator and the heat exchanger are hosted. The reference temperature is measured by means of a 25-ohm SPRT inserted into a thin-walled thermowell which is thermally clamped to the saturator outlet tubing via an isothermal copper block. The compact stand-alone design of the generator - where all control and measurement systems were assembled on a control panel placed on the top plate of the thermostat bath - allows for the transportability of the standard for on-site calibration at hydrogen end-use points. The generator can operate in both single temperature – single pressure (1T-1P) and in single temperature - two pressure (1T-2P) modes. The INRIM transportable precision humidity generator (t-PHG) was designed, developed and validated as part of the Met4H2 project activity A3.2.1.

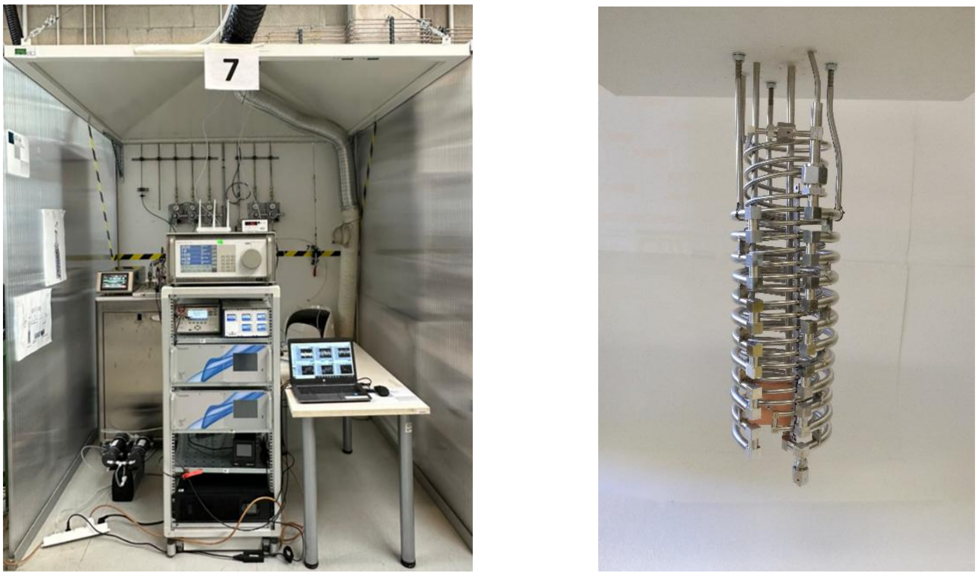


Figure 3 left panel: Transportable precision humidity generator (t-PHG) setup developed at INRIM for use with moist hydrogen. Right panel: Heat exchanger and saturator in use with the t-HPG.

3 Transfer Standard Instrumentation

Table 2 : Transfer standard hygrometers used.

Manufacturer	Model	Serial number	Measurement principle	Operating range	Inlet pressure range / MPa	Compatible gas species
MBW	373 LX-HP	14-0610	Chilled-mirror condensation	-60 °C to +20 °C	0.1 to 3	Air, N_2, H_2 others
Tiger Optics	F7702	8295	CRDS water vapour spectroscopy	0 − 1750 µmol mol^{-1}	0.2 to 0.96	Air, N_2, H_2 others
DTU	Proto-type	n/a	Far-UV spectroscopy	1 - 300 µmol mol^{-1}	0.1 to 4 (H_2) 0.1 to 10 (N_2)	N_2, Ar, H_2

3.1 Chilled-Mirror Hygrometer

A condensation principle hygrometer measures the temperature at which a condensate forms on the surface of a small mirror giving an indication of the dew-point temperature of the test gas.

Figure 4: A photo of an MBW 373 chilled mirror hygrometer (source Process Insights).

The MBW 373 LX-HP model used in these measurements is able to measure test gas at elevated pressures up to 20 MPa (200 bar). Flow rate was manually controlled using a rotameter with a needle valve assembly on the outlet of the instrument.

3.2 Cavity Ring-down Water Vapour Analyser

A cavity ring-down water vapour spectrometer measures the water content amount fraction of the test gas through measuring the absorption of laser light passed through the measurement cell based on the rate of decay of light multiply reflected within the cell.

Figure 5: A photo of a Tiger Optics Cavity Ring-down Water Vapour Analyser (source Process Insights).

The Tiger Optics SPARK H_2O Trace Level Moisture Analyser model F7702 used in these measurements was used in conjunction with a Swagelok High-Purity, High-Flow Gas Regulator (HF Series) which limited the maximum inlet pressure to the measurement cell of the analyser to 0.45 MPa absolute. Flow rate was manually controlled using a rotameter with a needle valve assembly on the outlet of the instrument.

3.3 Prototype far-UV water vapour analyser (DTU)

A prototype far-UV water vapour analyser that measures the water amount fraction in the test gas through measuring the absorption of far-UV light passed through the measurement volume (cell).

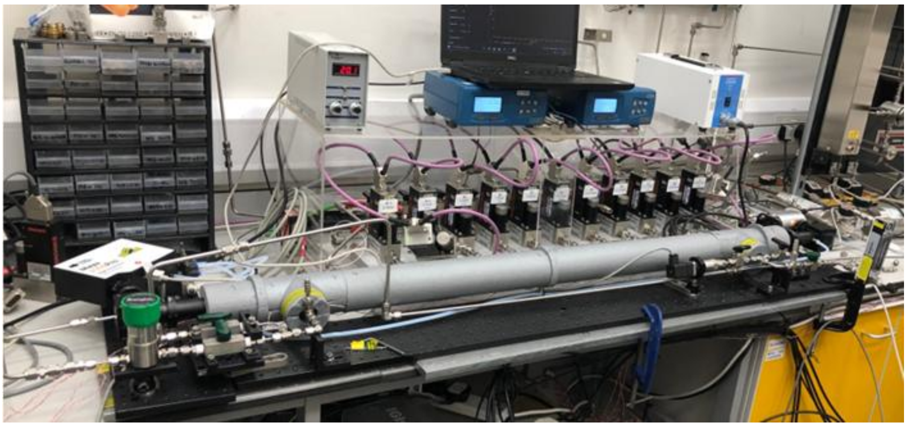


Figure 6: A photo of the DTU prototype far-UV Water Vapour Analyser used.

Cells in different lengths can be used upon an application. The length of the measurement cell in the configuration used in the ILC work was 100.5 cm. The cell and all components of the analyser in direct contact with the test gas from gas inlet side are coated by DURSAN® coating (SilcoTek®) which has an excellent water repellence characteristic. The cell can be pressurised up to 10 MPa (100 bar). In the ILC work the maximum test gas pressure was 3 MPa (30 bar). Temperature and pressure in the cell were measured by a calibrated (absolute) pressure sensor and four uniformly distributed thermocouples over the cell length respectively. The test gas flow rate was manually controlled using needle valves and was kept at around 0.5 LPM. The outlet from the analyser was connected to the exhaust vent of the participant laboratory.

4 Inter-laboratory comparison protocol development

The participants discussed the common frost-point temperature and operating pressure ranges of their standards and agreed an ILC protocol that would be applicable to the transfer standard instruments listed in Section 3. The nominal range of -60 °C to -15 °C frost-point temperature at pressures of 0.2 MPa and 3 MPa was chosen which equates to water vapour amount fractions in the range 0.5 µmol mol^{-1} to 50 µmol mol^{-1}, a range of interest for hydrogen quality measurements.

The agreed humidity values were measured with all three circulating hygrometers in hydrogen and nitrogen at the following nominal frost-point temperatures. The corresponding nominal water vapour amount fractions are shown in Tables 3 and 4 for nitrogen as the carrier gas.

Table 3 : Measurement values at 0.2 MPa test pressure:

Nominal Frost-point temperature / °C	Nominal equivalent water vapour amount fraction / µmol mol^{-1}
-60.7	5
-52.3	15
-42.3	50

Table 4 : Measurement values at 3 MPa test pressure:

Nominal Frost-point temperature / °C	Nominal equivalent water vapour amount fraction / µmol mol^{-1}
-59.0	0.5
-40.0	5
-17.3	50

Full details of the ILC protocol can be found in Metrology for the hydrogen supply chain Report Number Met4H2-A3.2.3 [3]. Instruments were connected in parallel to the generator at each laboaraotry using internally electropolished stainless steel tubing.

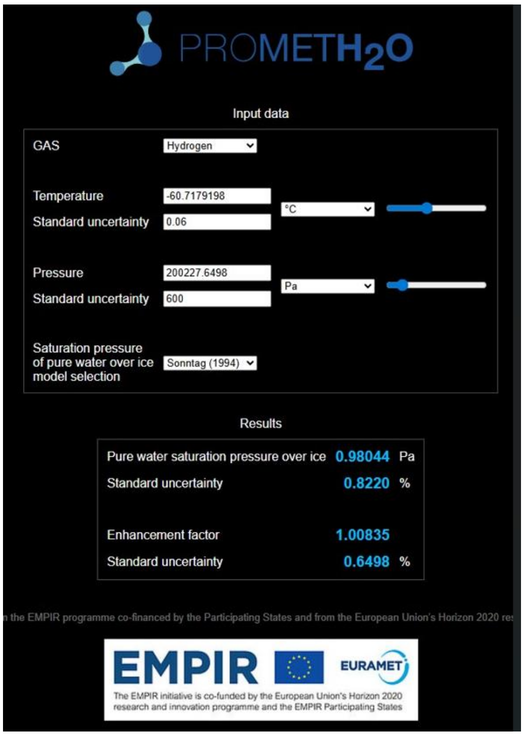
4.1 Reference dew-point temperature to amount fraction value conversion considerations

When calculating amount fraction of water vapour (x) from dew-point temperature (t_d) and total pressure measurements (P) or vice versa, the water vapour enhancement factor (f) is needed in the calculations as per Eqn. 1 in Section 2.2.

By this factor the deviation of a real gas mixture from pure water vapour is accounted for. Widely accepted data for water vapour enhancement factor exists for air, but is only emerging for other gas species.

It was agreed in this ILC for the pilot to apply a consistent water vapour enhancement factor values to calculate x values from all participants reference measurements of t_d and P.

The f-calculator [4] created in the EMPIR project 20IND06 PROMETH2O was used to calculate the 0.2 MPa values (as the use of this calculator is limited to pressures up to 1 MPa).



Input data

GAS: Hydrogen

Temperature: -60.7179198 °C

Standard uncertainty: 0.06

Pressure: 200227.6498 Pa

Standard uncertainty: 600

Saturation pressure of pure water over ice model selection: Sonntag (1994)

Results

Pure water saturation pressure over ice 0.98044 Pa

Standard uncertainty 0.8220 %

Enhancement factor 1.00835

Standard uncertainty 0.6498 %

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

Figure 7: Example 0.2 MPa calculation in PROMETH2O f-calculator.

NPL experimental data from the evaluation of water vapour enhancement factor ratios in hydrogen from the EMPIR project Metrology for Advanced Hydrogen Storage Solutions (MefHySto) [5] was used for estimates of water vapour enhancement factor f at 3 MPa.

5 Results - Frost- point temperature using chilled-mirror hygrometer

5.1 Frost-point temperature at 0.2 MPa

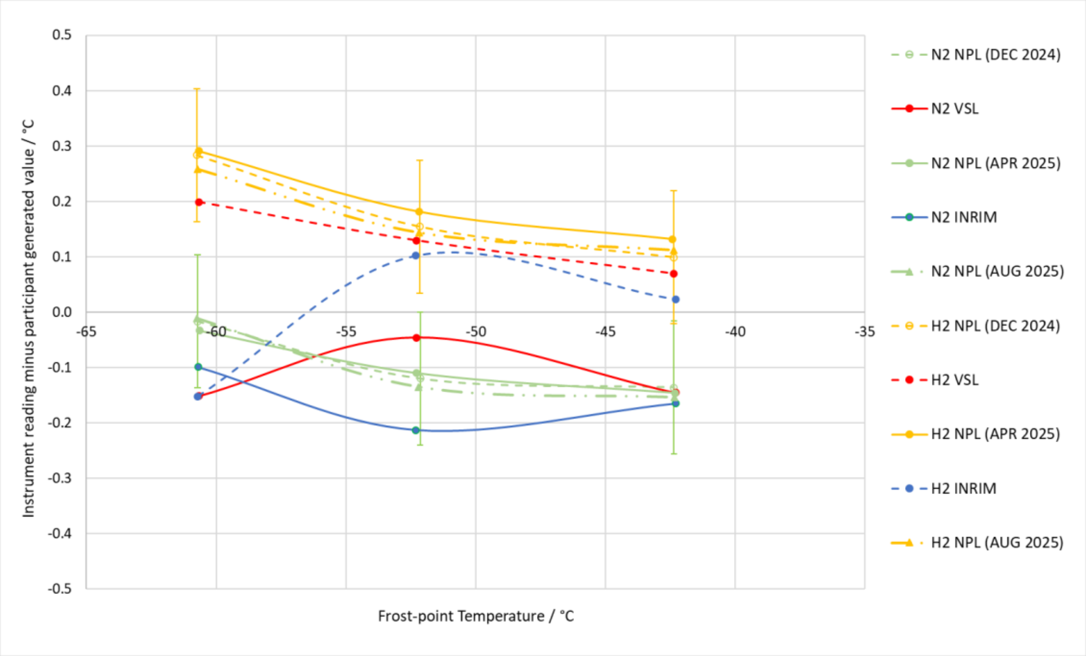

Figure 8: Single-pressure dew-point temperature comparison results at 0.2 MPa.

5.2 Frost-point temperature at 3 MPa

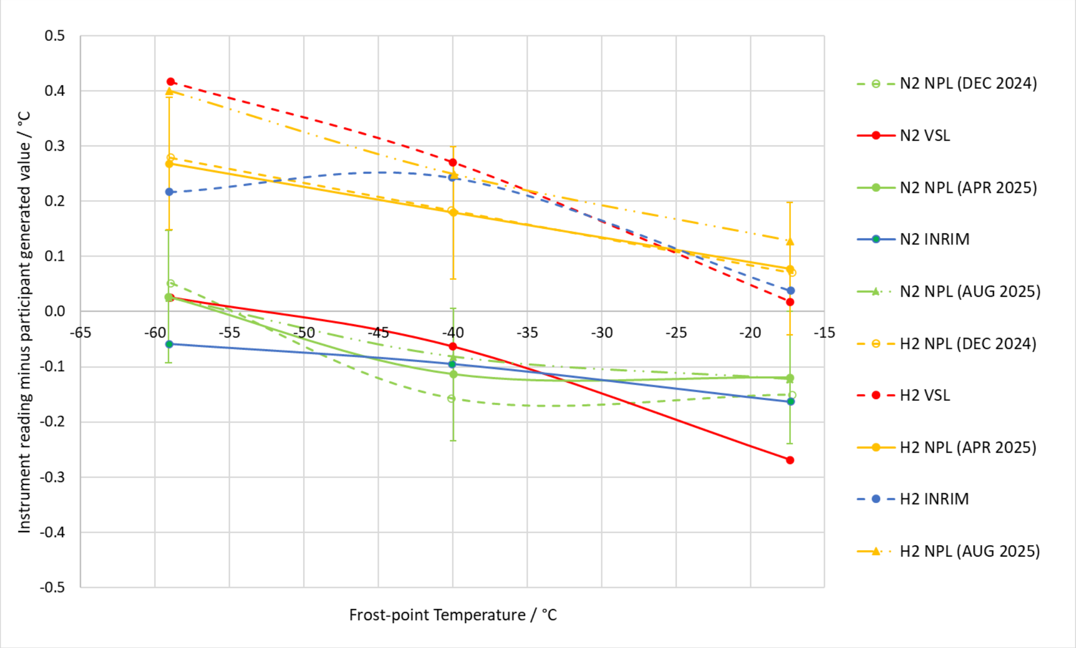

Figure 9: Single-pressure dew-point temperature comparison results at 3 MPa.

5.3 Frost-point temperature results discussion

This chilled-mirror hygrometer over-read in hydrogen compared to nitrogen background gas when measuring test gas from the generators of all of the participating laboratories. As this is a consistent effect in hydrogen for all participants this meant that the results were still useable measurements for ILC purposes.

The response of chilled-mirror hygrometer to a change to hydrogen background gas was observed to take many hours to stabilise at trace moisture values.

Some participants were able to operate in hydrogen background gas overnight, other participants only operated in hydrogen background gas during hours when staff were present. A different error would result if these measurements were left to equilibrate for longer. In some cases, slightly different readings would probably have resulted.

The chilled-mirror hygrometer error appears to have drifted to over-reading in hydrogen over the duration of the ILC according to final repeat results at the pilot laboratory NPL. This could also be simply because of irreproducibility of this transfer standard, and uncertainty contributions for this were evaluated and applied to degree of equivalence (DoE) analysis.

6 Results - Water vapour amount fraction using cavity ring-down (CRDS) moisture analyser

6.1 CRDS moisture analyser water vapour amount fraction at 0.2 MPa

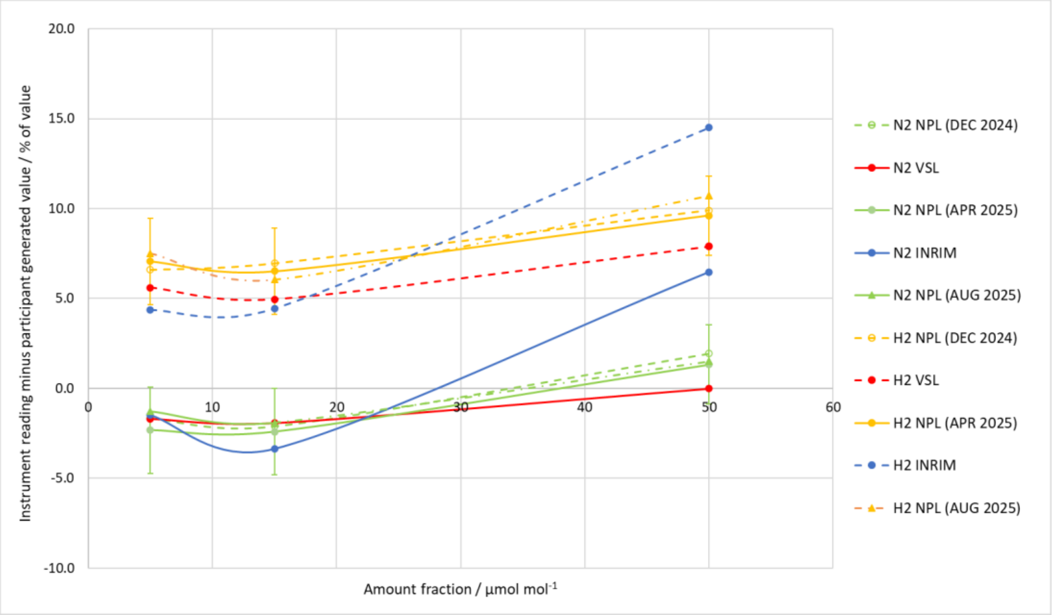

Figure 10: CRDS moisture analyser water vapour amount fraction comparison results at 0.2 MPa.

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6.2 CRDS moisture analyser water vapour amount fraction at 3 MPa

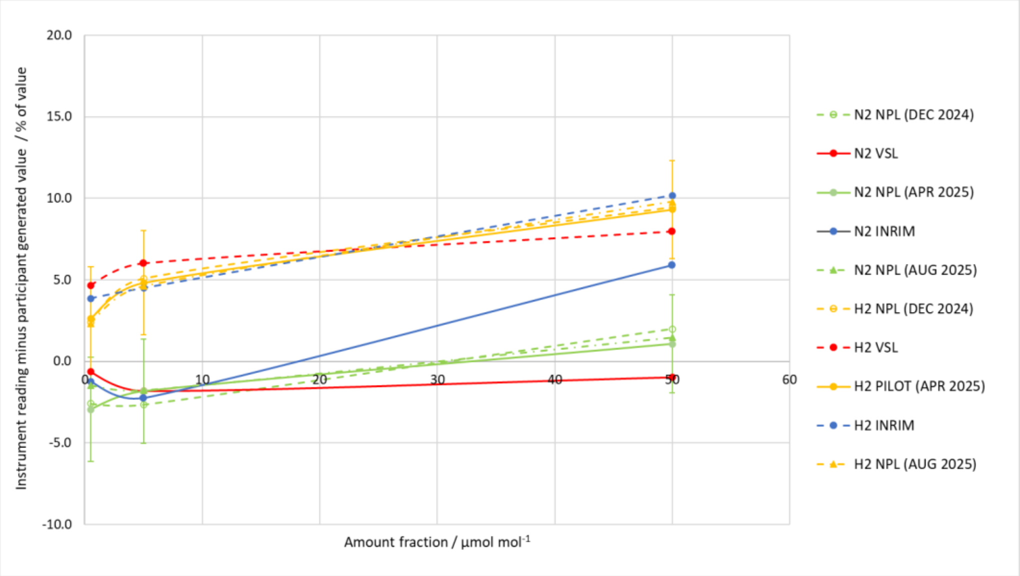

Figure 11: CRDS moisture analyser water vapour amount fraction comparison results at 3 MPa.

6.3 CRDS moisture analyser water vapour amount fraction results discussion

Conversion of reference frost point to amount fraction would be affected by the choice of water vapour enhancement factor (WVEF). In this ILC the pilot applied the same WVEF calculation to convert each participant's reference measurements of dew-point temperature and total pressure.

Hydrogen measurement values for the analyser appear to be over-reading compared to measurements in nitrogen at the same water content values. At 0.2 MPa deviations between measured and generated H_2O amount fractions (calculated as described in section 4.1) varied from about -4 % to 15 % of value

This error is not due to the operator using an incorrect background gas "mode" as it is known that the error due to this is much larger than that observed in the ILC results.

It is not possible at this stage to distinguish if this is a measurement error due to the background gas change in the generator, the choice of WVEF equation used to calculate reference values or an instrumental error due to background gas dependence.

However, as this is a consistent effect in hydrogen for all participants, the results are still useable measurements for ILC purposes.

7 Results - Water vapour amount fraction using far-UV moisture analyser

7.1 Far-UV moisture analyser water vapour amount fraction at 0.2 MPa

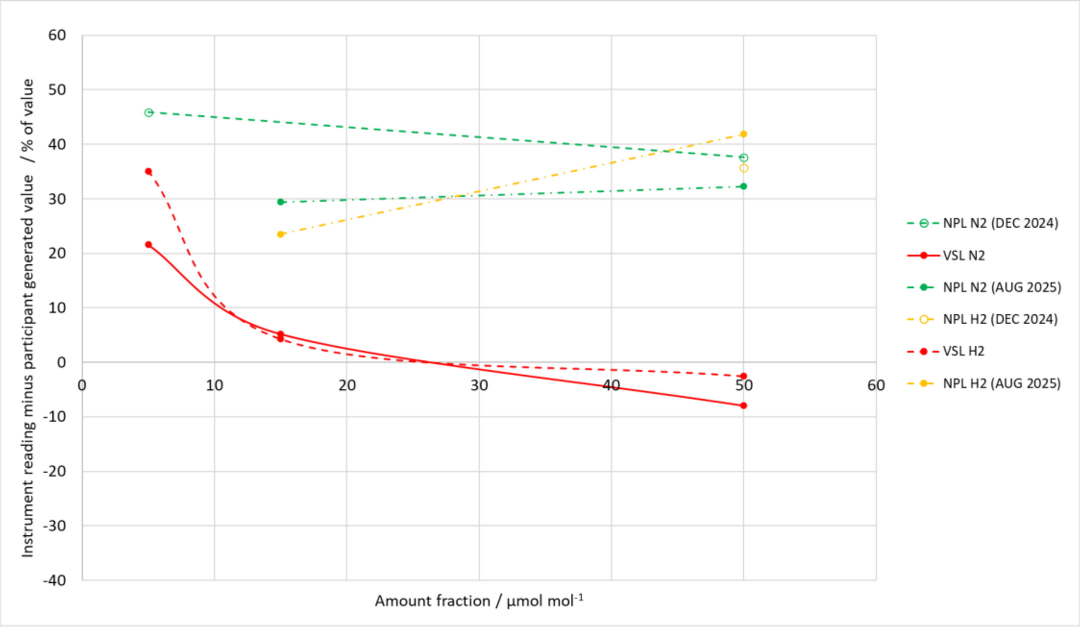

Figure 12: Far-UV moisture analyser water vapour amount fraction comparison results at 0.2 MPa.

7.2 Far-UV moisture analyser water vapour amount fraction at 3 MPa

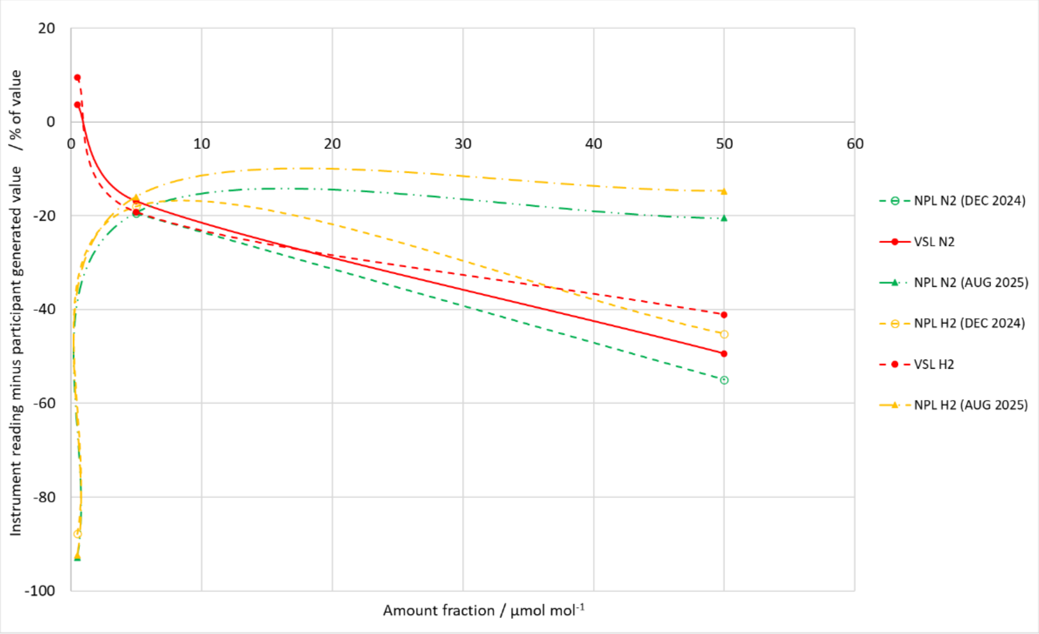

Figure 13: Far-UV moisture analyser water vapour amount fraction comparison results at 3 MPa.

7.3 Far-UV moisture analyser water vapour amount fraction results discussion

Due to time constraints INRIM were not able to set up and use the far-UV moisture nalyser in their laboratory and therefore no measurements were made at INRIM with this analyser. Data processing for the prototype far-UV analyser was performed after measurements had been made, remotely by the analyser developer. Access to real-time moisture measurement data would have allowed the participants to react to any anomalous data (e.g. to look for leaks in connecting pipework) during the measurements in the laboratory.

At 0.2 MPa the VSL results for the far-UV analyser are broadly consistent with those for the SPARK analyser in Figure 10 except the 5 µmol mol^{-1} point. The deviations at 50 µmol mol^{-1} are within 10 % of value but for the SPARK at this value they were larger than this at are around 15 % of value.

The NPL results are far off compared to VSL ones which might be attributed to other side effects in the complex measurement set up at NPL, for this instrument. Figure 12 shows that besides the analyser itself, the way the analyser is connected to the generator (together with other analysers) is important in low-H_2O level measurements.

Not all of the far-UV analyser measurement results obtained at NPL were reportable due to the non-stabilised water amount fraction conditions in the analyser while the stable conditions in the time that stable chilled mirror and SPARK analyser measurements had been achieved.. The instrument developer believed this can be explained by different reasons. Firstly, the presence of oxygen in small but significant amount fractions (far above the nominal trace O_2 values as in N_2(6.0) or H_2(6.0) grade carrier gases) in the test gas affects the water measurements and may indicate the presence of dead volumes not being fully purged prior the start of the measurements or leaks in the connections to the analyser or in connections between different analysers used in ILC work at NPL.

In general, results in both nitrogen and hydrogen showed consistent errors showing the instrument did not show a background gas dependent measurement error. Moreover, once the measurements with the test gas were completed, the so-called “base line” measurement of the analyser always returned to its zero.

As the differences in generated and measured water amount fractions with far-UV analyser were larger than the uncertainties in the generated water amount fraction values as a stand-alone units this meant that at 3 MPa some transient effects can happen. the results are not useable measurements for ILC purposes and further work to understand this is required.

As one can see from the Figure 13, the VSL data are very consistent for both N2 and H2, while the NPL data have large deviations for both N2/H2 between the two times when the measurements had been done.

Comparing Figure 11 and Figure 13 show that the far-UV results are systematically giving a negative deviation with respect to expected water amount fraction, while the SPARK results are always in positive domain, in the similar way as in Figure 10 vs. Figure 12.

Underestimated water amount fraction from far-UV measurements which is decreasing with pressure increase (from about – 8 % to about - 50 % at 50 µmol/mol) can be attributed to physical phenomena for which enhancement factors are used: less H2O molecules in the gas phase and more molecules adsorbed on the walls). This may indicate that the real pressure-dependence in enhancement factors may differ than one used in 4.1).

8 Bilateral degree of equivalence analysis for chilled-mirror dew point measurements and CRDS moisture analyser measurements

Bilateral degree of equivalences at each dew point were calculated from differences D_{ij} between participants i and j, where:

$$D_{ij} = R_{lab\ i} - R_{lab\ j}$$

The bilateral degree of equivalence (DoE) is determined as:

$$\left(D_{ij}\ , U_{ij}\right) = \left(D_{ij}\ , ku\left(D_{ij}\right)\right)$$

where the coverage factor $k = 2$ provides a coverage probability of 95 % for sufficiently large effective number of degrees of freedom of $u(D_{ij})$.

In this case, $u(D_{ij})$ is given by

$$u^2\left(D_{ij}\right) = u^2\left(R_{lab\ i}\right) + u^2\left(R_{lab\ j}\right) + u^2{}_{drift}$$

where u^2_{drift} is the uncertainty in the comparison due to drift of both hygrometers at a given dew point value. u^2_{drift}, is assigned a single generalised value at each dew point, irrespective of whether participants measured in immediate succession or separated in time, based on the differences observed in repeat measurements at the pilot laboratory.

The DoE was calculated for each pair of participants at each nominal measurement point. The results are summarised in tables 6.1 to 6.4. DoE is expressed as (D_{ij}, U_{ij}) in degrees Celsius for the chilled-mirror hygrometer results and in µmol mol^{-1} for the SPARK CRDS moisture analyser results. An estimate for instrument drift uncertainty is included in the uncertainty shown.

8.1 Degree of Equivalence results at 0.2 MPa in hydrogen (using chilled-mirror hygrometer)

Table 5 : Degree of equivalence between the participants at the frost-point temperature -60.7 °C at 0.2 MPa. DoE is expressed as ($\mathbf{D}_{ij}$, U_{ij}) in degrees Celsius:

-60.7 °C	NPL		VSL		INRIM	
NPL			**0.085**	0.131	**0.436**	0.131
VSL	**-0.085**	0.131			**0.351**	0.056
INRIM	**-0.436**	0.131	**-0.351**	0.056		

Table 6 : Degree of equivalence between the participants at the frost-point temperature -52.3 °C at 0.2 MPa. DoE is expressed as ($\mathbf{D}_{ij}$, U_{ij}) in degrees Celsius:

-52.3 °C	NPL		VSL		INRIM	
NPL			**0.025**	0.131	**0.052**	0.131
VSL	**-0.025**	0.131			**0.028**	0.058
INRIM	**-0.052**	0.131	**-0.028**	0.058		

Table 7 : Degree of equivalence between the participants at the frost-point temperature -42.3 °C at 0.2 MPa. DoE is expressed as ($\mathbf{D}_{ij}$, U_{ij}) in degrees Celsius:

-42.3 °C	NPL		VSL		INRIM	
NPL			**0.029**	0.131	**0.076**	0.131
VSL	**-0.029**	0.131			**0.047**	0.056
INRIM	**-0.076**	0.131	**-0.047**	0.056		

8.2 Degree of Equivalence results at 3 MPa in hydrogen (using chilled-mirror hygrometer)

Table 8 : Degree of equivalence between the participants at the frost-point temperature -59.0 °C at 3 MPa. DoE is expressed as ($\mathbf{D}_{ij}$, U_{ij}) in degrees Celsius:

-59.0 °C	NPL		VSL		INRIM	
NPL			**-0.138**	0.262	**0.062**	0.263
VSL	**0.138**	0.262			**0.200**	0.236
INRIM	**-0.062**	0.263	**-0.200**	0.236		

Table 9 : Degree of equivalence between the participants at the frost-point temperature -40.0 °C at 3 MPa. DoE is expressed as $(\mathbf{D}_{ij}, U_{ij})$ *in degrees Celsius:*

-40.0 °C	NPL		VSL		INRIM	
NPL			**-0.087**	0.136	**-0.060**	0.139
VSL	**0.087**	0.136			**0.028**	0.075
INRIM	**0.060**	0.139	**-0.028**	0.075		

Table 10 : Degree of equivalence between the participants at the frost-point temperature -17.3 °C at 3 MPa. DoE is expressed as $(\mathbf{D}_{ij}, U_{ij})$ *in degrees Celsius:*

-17.3 °C	NPL		VSL		INRIM	
NPL			**0.052**	0.138	**0.032**	0.139
VSL	**-0.052**	0.138			**-0.020**	0.079
INRIM	**-0.032**	0.139	**0.020**	0.079		

8.3 Degree of Equivalence results at 0.2 MPa in nitrogen (using chilled-mirror hygrometer)

Table 11 : Degree of equivalence between the participants at the frost-point temperature -60.7 °C at 0.2 MPa. DoE is expressed as $(\mathbf{D}_{ij}, U_{ij})$ *in degrees Celsius:*

-60.7 °C	NPL		VSL		INRIM	
NPL			**0.135**	0.127	**0.082**	0.128
VSL	**-0.135**	0.127			**-0.052**	0.050
INRIM	**-0.082**	0.128	**0.052**	0.050		

Table 12 : Degree of equivalence between the participants at the frost-point temperature -52.3 °C at 0.2 MPa. DoE is expressed as $(\mathbf{D}_{ij}, U_{ij})$ *in degrees Celsius:*

-52.3 °C	NPL		VSL		INRIM	
NPL			**-0.074**	0.127	**0.093**	0.128
VSL	**0.074**	0.127			**0.167**	0.051
INRIM	**-0.093**	0.128	**-0.167**	0.051		

Table 13 : Degree of equivalence between the participants at the frost-point temperature -42.3 °C at 0.2 MPa. DoE is expressed as $(\mathbf{D}_{ij}, U_{ij})$ *in degrees Celsius:*

-42.3 °C	NPL		VSL		INRIM	
NPL			**0.010**	0.127	**0.029**	0.129
VSL	**-0.010**	0.127			**0.019**	0.052
INRIM	**-0.029**	0.129	**-0.019**	0.052		

8.4 Degree of Equivalence results at 3 MPa in nitrogen (using chilled-mirror hygrometer)

Table 14 : Degree of equivalence between the participants at the frost-point temperature -59.0 °C at 3 MPa. DoE is expressed as $(\mathbf{D}_{ij}, U_{ij})$ *in degrees Celsius:*

-59.0 °C	NPL		VSL		INRIM	
NPL			**0.026**	0.134	**0.110**	0.127
VSL	**-0.026**	0.134			**0.084**	0.063
INRIM	**-0.110**	0.127	**-0.084**	0.063		

Table 15 : Degree of equivalence between the participants at the frost-point temperature -40.0 °C at 3 MPa. DoE is expressed as $(\mathbf{D}_{ij}, U_{ij})$ *in degrees Celsius:*

-40.0 °C	NPL		VSL		INRIM	
NPL			**-0.094**	0.154	**-0.062**	0.154
VSL	**0.094**	0.154			**0.031**	0.099
INRIM	**0.062**	0.154	**-0.031**	0.099		

Table 16 : Degree of equivalence between the participants at the frost-point temperature -17.3 °C at 3 MPa. DoE is expressed as $(\mathbf{D}_{ij}, U_{ij})$ *in degrees Celsius:*

-17.3 °C	NPL		VSL		INRIM	
NPL			**0.118**	0.128	**0.012**	0.130
VSL	**-0.118**	0.128			**-0.106**	0.057
INRIM	**-0.012**	0.130	**0.106**	0.057		

In general the difference between participant results is lower than the associated uncertainty for the chilled mirror hygrometer measurements at the majority of points, except for the lowest humidity values at both pressures.

8.5 Degree of Equivalence results at 0.2 MPa in hydrogen (using CRDS Moisture Analyser)

*Table 17 : Degree of equivalence between the participants at the water vapour amount fraction 5 µmol mol^{-1} at 0.2 MPa. DoE is expressed as (**D_{ij}**, U_{ij}) in µmol mol^{-1}:*

5 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**0.050**	0.226	**0.111**	0.161
VSL	**-0.050**	0.226			**0.062**	0.211
INRIM	**-0.111**	0.161	**-0.062**	0.211		

*Table 18 : Degree of equivalence between the participants at the water vapour amount fraction 15 µmol mol^{-1} at 0.2 MPa. DoE is expressed as (**D_{ij}**, U_{ij}) in µmol mol^{-1}:*

15 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**0.302**	0.711	**0.376**	0.461
VSL	**-0.302**	0.711			**0.074**	0.662
INRIM	**-0.376**	0.461	**-0.074**	0.662		

*Table 19 : Degree of equivalence between the participants at the water vapour amount fraction 50 µmol mol^{-1} at 0.2 MPa. DoE is expressed as (**D_{ij}**, U_{ij}) in µmol mol^{-1}:*

50 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**1.01**	2.13	**-2.30**	1.46
VSL	**-1.01**	2.13			**-3.31**	1.98
INRIM	**2.30**	1.46	**3.31**	1.98		

8.6 Degree of Equivalence results at 3 MPa in hydrogen (using CRDS Moisture Analyser)

*Table 20 : Degree of equivalence between the participants at the water vapour amount fraction 0.5 µmol mol^{-1} at 3 MPa. DoE is expressed as (**D_{ij}**, U_{ij}) in µmol mol^{-1}:*

0.5 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**-0.011**	0.036	**-0.007**	0.036
VSL	**0.011**	0.036			**0.004**	0.035
INRIM	**0.007**	0.036	**-0.004**	0.035		

Table 21 : Degree of equivalence between the participants at the water vapour amount fraction 5 µmol mol^{-1} at 3 MPa. DoE is expressed as ($\mathbf{D}_{ij}$, U_{ij}) in µmol mol^{-1}:

5 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**-0.047**	0.220	**0.029**	0.170
VSL	**0.047**	0.220			**0.076**	0.151
INRIM	**-0.029**	0.170	**-0.076**	0.151		

Table 22 : Degree of equivalence between the participants at the water vapour amount fraction 50 µmol mol^{-1} at 3 MPa. DoE is expressed as ($\mathbf{D}_{ij}$, U_{ij}) in µmol mol^{-1}:

50 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**0.74**	2.15	**-0.36**	2.15
VSL	**-0.74**	2.15			**-1.10**	2.09
INRIM	**0.36**	2.15	**1.10**	2.09		

8.7 Degree of Equivalence results at 0.2 MPa in nitrogen (using CRDS Moisture Analyser)

Table 23 : Degree of equivalence between the participants at the water vapour amount fraction 5 µmol mol^{-1} at 0.2 MPa. DoE is expressed as ($\mathbf{D}_{ij}$, U_{ij}) in µmol mol^{-1}:

5 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**0.001**	0.219	**-0.009**	0.153
VSL	**-0.001**	0.219			**-0.010**	0.198
INRIM	**0.009**	0.153	**0.010**	0.198		

Table 24 : Degree of equivalence between the participants at the water vapour amount fraction 15 µmol mol^{-1} at 0.2 MPa. DoE is expressed as ($\mathbf{D}_{ij}$, U_{ij}) in µmol mol^{-1}:

15 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**-0.026**	0.636	**0.187**	0.425
VSL	**0.026**	0.636			**0.213**	0.577
INRIM	**-0.187**	0.425	**-0.213**	0.577		

Table 25 : Degree of equivalence between the participants at the water vapour amount fraction 50 µmol mol^{-1} at 0.2 MPa. DoE is expressed as ($\mathbf{D}_{ij}$, U_{ij}) in µmol mol^{-1}:

50 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**0.98**	2.11	**-2.27**	1.41
VSL	**-0.98**	2.11			**-3.24**	1.92
INRIM	**2.27**	1.41	**3.24**	1.92		

8.8 Degree of Equivalence results at 3 MPa in nitrogen (using CRDS Moisture Analyser)

*Table 26 : Degree of equivalence between the participants at the water vapour amount fraction 0.5 µmol mol^{-1} at 3 MPa. DoE is expressed as (**D_{ij}**, U_{ij}) in µmol mol^{-1}:*

0.5 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**-0.010**	0.038	**-0.007**	0.038
VSL	**0.010**	0.038			**0.003**	0.037
INRIM	**0.007**	0.038	**-0.003**	0.037		

*Table 27 : Degree of equivalence between the participants at the water vapour amount fraction 5 µmol mol^{-1} at 3 MPa. DoE is expressed as (**D_{ij}**, U_{ij}) in µmol mol^{-1}:*

5 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**-0.041**	0.234	**-0.020**	0.178
VSL	**0.041**	0.234			**0.021**	0.163
INRIM	**0.020**	0.178	**-0.021**	0.163		

*Table 28 : Degree of equivalence between the participants at the water vapour amount fraction 50 µmol mol^{-1} at 3 MPa. DoE is expressed as (**D_{ij}**, U_{ij}) in µmol mol^{-1}:*

50 µmol mol^{-1}	NPL		VSL		INRIM	
NPL			**1.47**	2.28	**-1.96**	2.28
VSL	**-1.47**	2.28			**-3.44**	2.22
INRIM	**1.96**	2.28	**3.44**	2.22		

The only points where the difference between participant results is greater than the associated uncertainty for the CRDS Moisture Analyser measurements are the 50 µmol mol^{-1} INRIM points in hydrogen and nitrogen at 0.2 MPa when compared with both the NPL and VSL standards at these values and the 50 µmol mol^{-1} INRIM point in nitrogen at 3 MPa compared with with the VSL standard at this value.

9 Future recommendations

It would be beneficial to spend longer characterising transfer standards to better understand their response time. If no overnight operation is possible at a participant laboratory then it should be ensured that only faster responding instruments, with negligible hysteresis, be used.

The scope of the ILC should be considered at the planning stage because of the significant effort involved. In fact, if evaluating equivalences, many equivalence tables might be needed:

$$\text{No. of tables} = \text{measured quantities} \times \text{pressures} \times \text{gas species} \times \text{measured values}$$

Participants may choose their own conversions parameters (e.g. the enhancement factors) in future ILCs or this may be standardised. The participants would need to decide, bearing in mind this is relevant to ensure the measurement traceability and the uncertainty evaluation.

The inlet operating pressure of certain spectroscopy-based analysers should be considered. Not all can be operated at nominally atmospheric inlet pressure, only selected models. When operating at pressures higher than atmospheric pressure, the correction due to a non-ideal gas mixture (via the enhancement factor) is larger.

The humidity quantity that is the most meaningful for the comparison based on the capabilities of the participants should be considered and a suitable transfer standard instrument selected accordingly.

Data processing for the prototype far-UV analyser was performed after measurements had been made at the laboratories remotely by the instrument developer. Access to real-time moisture measurement data would have allowed the participants to react to any anomalous data (e.g. to look for leaks in connecting pipework).

The results demonstrate that the connections between a generator and an analyser are important for low water amount fraction measurements. As short a length as possible of internally electropolished stainless steel tubing should be used for with no dead volumes along the flow path and connections should be thoroughly leak checked before measurements commence.

This results of the intercomparison work in this report will be shared with the ISO/TC 197 in order to support further standardisation and developments in international standards.

References

[1] D Sonntag (1990) “Important new values of the physical constants of 1986, vapour pressure formulations based on the ITS-90, and psychrometer formulae” Z. Meteorol. 40(5), 340–344.

[2] R. Bosma, A. Peruzzi, *Development of a Dew-Point Generator for Gases Other than Air and Nitrogen and Pressures up to 6 Mpa,* International Journal of Thermophysics 33 (2012), 1511–1519.

[3] Metrology for the hydrogen supply chain Report number Met4H2-A3.2.3: Inter-laboratory comparison of standards for trace water in hydrogen over the nominal range -60 °C to -15 °C frost-point temperature (0.5 µmol mol^{-1} to 50 µmol mol^{-1}) Inter-laboratory comparison protocol.

[4] www.prometh2o.unicas.it

[5] Metrology for Advanced Hydrogen Storage Solutions (MefHySto) Deliverable D7 : Report on (i) the definition of underground gas storages (UGS)-relevant impurities, (ii) recommendations for measurements of hydrocarbon traces and (iii) an extension of the enhancement factor for hydrogen mixtures : https://mefhysto.eu/wp-content/uploads/2024/08/20240320_Report-D7_to_MSU.pdf