METROLOGY for
HYDROGEN VEHICLES

GOOD PRACTICE GUIDE:

Calibration and use of humidity sensors for hydrogen refuelling station applications

EMPIR

EURAMET

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www.metrohyve.eu

Foreword

This guide provides good practice recommendations for the calibration and use of hygrometers for the measurement of the humidity of hydrogen fuel at hydrogen refuelling stations (HRSs).

HRS operators using hygrometers for monitoring the quality of hydrogen in their stations will find the guidance within helpful to consider when understanding the potential errors and measurement uncertainty of online water content measurement. Guidance includes recommended methods of calibration for the common hygrometer types used, including comparison against standards that can replicate the industrial conditions of use, such as the Multi-Gas, Multi-Pressure Humidity Generator at NPL [1].

The information contained within can also be of use to those involved in hydrogen storage and transfer of hydrogen to the grid where online monitoring of water content is required to ensure quality requirements are met. Hygrometer manufacturers may also find this guide useful.

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1. Introduction

Background

Increasing use of hydrogen fuel-cell vehicles is contributing to emission reductions and towards meeting Europe's target to be carbon-neutral by 2050. A large hydrogen fuel infrastructure for vehicles is currently in development across Europe.

The hydrogen refuelling station (HRS) industry must meet certain measurement requirements set by European legislation (DIRECTIVE 2014/94/EU [2]) that cannot currently be achieved due to the lack of available methods and standards.

Measurement of the contaminant levels in the hydrogen produced from a HRS is required by regulators to ensure the fuel delivered to vehicles is of an acceptable quality. The ISO 14687-2 [3] standard specifies the limit for maximum water vapour content in hydrogen for fuel-cell vehicle use, together with concentration limits of other contaminants.

Water vapour content level importance for hydrogen vehicle fuel

Hydrogen produced by electrolysis and other methods can contain a large amount of water vapour which is removed during drying processes in HRSs.

The level of water vapour in hydrogen as supplied to the vehicle is not critical for the fuel cell itself, where high operating relative humidity is controlled locally in-vehicle. There is, however, a need for any water present in the refuelling station hydrogen to remain in the gas phase at -40 ^{o}C (which is the general pre-cooling temperature prior to dispensing) and at pressures in excess of tank pressures of 70 MPa (700 bar). Water is an issue for hydrogen dispensing systems, the onboard vehicle tank system and fuel cell components, due to the possible formation of ice. Excess water in the liquid state can also cause corrosion of metallic components.

When water is present as an aerosol it also provides a transport mechanism for water-soluble impurities, especially as a solvent for cations such as Na^+, K^+, Ca^{2+}, Cs^+ and NH^{4+}.

Water vapour regulation for hydrogen vehicle fuel

Reliable measurement of water vapour content is needed by the hydrogen vehicle refuelling industry to ensure that the fuel being delivered meets the specified regulatory limits for contminants.

The maximum water vapour content limit set by the ISO 14687-2 regulation is for the hydrogen used for fuel-cell vehicles to contain less than 5 μmol mol^{-1} of water vapour at the dispenser nozzle.

The water vapour content limit is expressed as an amount fraction – the ratio of the number of moles of a water vapour in a humid gas to the total number of moles of humid gas present.

At the low water content levels usually encountered in HRS applications, values are often expressed as micromoles of water vapour per mole of humid gas (μmol mol^{-1}). This unit is informally referred to as parts per million per unit volume (ppm$_v$) for gas mixtures where volume fraction is approximately the same as amount fraction.

Table 1 shows the limits for contaminants at the HRS dispenser nozzle regulated by the ISO 14687-2 hydrogen fuel quality standard.

Table 1: ISO 14687-2 contaminant limits for hydrogen fuel quality at HRS dispenser nozzle

Impurity	**Maximum concentration of indivdual contaminants / µmol mol^{-1}**
Helium	300
Nitrogen + argon	100
Water	5
Oxygen	5
Carbon dioxide	2
Total hydrocarbons	2
Carbon monoxide	0.2
Formic acid	0.2
Ammonia	0.1
Total halogenated compounds	0.05
Formaldehyde	0.01
Total sulphur compounds	0.004

Online water vapour content measurement of hydrogen at HRSs

Hydrogen from the HRS dispenser nozzle must be periodically sampled into vessels and sent for offline analysis of the concentration of the regulated contaminants at independent laboratories. It is, however, standard practice for operators to also support quality control according to ISO 19880-8 [4] by monitoring the water content of the hydrogen fuel they produce continuously in real time through online humidity measurements made using hygrometers.

Although the ISO 14687-2 standard states that measurements of water vapour content should be made from the dispenser nozzle, this is not practical for continuous online measurement due to the extremely high pressure at this point in the process, in excess of 70 MPa (700 bar).

An example of a practice used is for an electrolysis HRS operators to make online measurements of the water content of the hydrogen fuel using a metal oxide dew-point probe at elevated pressure, typically 2 MPa (20 bar), at a stage in the process after drying and prior to compression of the gas to the nozzle delivery pressure.

Common hygrometer types used for online water vapour content measurement in HRSs include:

- Metal oxide dew-point probes
- Electrolytic principle hygrometers (P_2O_5 based sensor)

ISO 14687-2 laboratory-based methods for analysing water content of hydrogen sampled into vessels include:

- Chilled-mirror hygrometers
- Water vapour spectrometers
- Gas chromatography mass spectrometry (GC-MS)
- Fourier-transform infrared spectroscopy (FTIR)
- Quartz crystal microbalance

Hygrometer calibration

It is important for the HRS operator to make as accurate a humidity measurement as possible to ensure that they are producing hydrogen with a water content within the ISO 14687-2 quality limit.

The measurement error of a hygrometer can be evaluated through calibration. Calibration of a hygrometer can be made by comparison directly against a standard humidity generator or against a calibrated reference hygrometer traceable directly, or in multiple steps, back to an authoritative standard. Hygrometer measurement error found through calibration should be corrected for and the measurement uncertainty applicable to corrected humidity values should be carefully considered.

Table 2 shows the effect dew-point hygrometer measurement error of different magnitudes could have on the calculated amount fraction of water vapour in the test gas.

Table 2: Significance of hygrometer measurement error or drift of 5 °C or 10 °C at 2 MPa

	Dew (frost) point at 2 MPa / °C	Amount fraction / μmol mol^{-1}		
	-33	15		
	-38	9		
Limit →	**-43**	**5**	±5 °C	±10 °C
	-48	3		
	-53	1.5		

If corrections are not applied to a hygrometer that over-reads in error, then the humidity measurements may imply that the hydrogen being produced requires further drying before it can be compressed for delivery to vehicles when this is not actually the case. This could lead to reduced efficiency of the HRS system due to extra processing of the gas that is not required.

If corrections are not applied to a hygrometer that under-reads in error, then the measurements may imply that the hydrogen being produced meets the quality requirements when this is not actually the case. This could lead to problems with the HRS system and potentially the vehicles the fuel is delivered to due to the issues mentioned earlier.

The uncertainty applicable to corrected hygrometer measurements should also be taken into account when determining whether the humidity value measured can be considered to represent gas of an acceptable water vapour content with respect to quality limits. The result of the corrected measured value in summation with the uncertainty should be below the quality limit for compliance with regulation to be shown.

Manufacturer's factory calibrations of hygrometers

It is common for HRS operators to use metal oxide dew-point probes supplied with a factory calibration certificate from the manufacturer. Measurement errors reported in manufacturer's factory calibration certificates tend to be very low as the response of the instrument can be adjusted to read close to the reference value during this process.

It is therefore a widespread practice to use the measured humidity values with no correction and to apply the "accuracy" from the manufacturer's specification as a blanket measurement uncertainty throughout the service period of the hygrometer. Typical accuracy claims from metal oxide dew-point probe manufacturer's specifications for dew-point temperature are of the order of ±2 °C. For some instruments of this type it is claimed that this accuracy is applicable to dew-point temperature measurements across the range -100 °C to +20 °C at pressures ranging from atmospheric pressure to 35 MPa (350 bar).

The factory calibrations are completed with nitrogen or air as the background gas at close to atmospheric pressure.

MetroHyVe hygrometer study

In Activity 3.2.1 of the EMPIR Metrology for Hydrogen Vehicles (MetroHyVe) project six commercially available metal oxide dew-point probes from five different manufacturers were calibrated against the NPL Multi-Gas, Multi-Pressure Humidity Generator [1]. Tests of the response of the hygrometer to changes in background gas species from nitrogen to hydrogen and changes in pressure from close to atmospheric pressure to 2 MPa (20 bar) were performed.

Testing of the hygrometers included conditions representative of their use in HRS applications (background gas hydrogen, pressure of 2 MPa) over a range of dew-point temperatures (-65 °C to -20 °C) that correspond to water vapour amount fractions from 0.5 μmol mol^{-1} to 50 μmol mol^{-1} at 2 MPa, spanning the ISO 14687-2 quality limit of 5 μmol mol^{-1}.

Repeated testing of the hygrometers at six and twelve months after the initial calibrations enabled evaluation of the long-term drift behaviour of instruments of this type.

The findings of this study are described in Section 5 and provide the basis for some of the calibration good practice recommendations in this guide which are summarised in Section 7.

2. Humidity theory

An introduction to some relevant background humidity theory is required to understand some of the recommendations made in this guide.

Definitions

Dew-point / Frost-point temperature T_{dp} / T_{fp}: temperature at which the vapour pressure of the vapour in a humid gas is equal to the saturation vapour pressure over pure liquid and at which condensate forms as liquid on cooling the gas. This value is defined as a frost-point temperature below 0 °C when the condensate formed is ice. However, water can exist as a liquid at temperatures below 0 °C and when referring to supercooled liquid dew point it is normal to state this explicitly.

Saturation vapour pressure of water e_s : maximum pressure of water vapour that can exist at a given temperature. Expressed in units of pressure (e.g. pascals (Pa)).

Vapour pressure e : the partial pressure of a gas contributed by the water vapour. Expressed in units of pressure (e.g. pascals (Pa)).

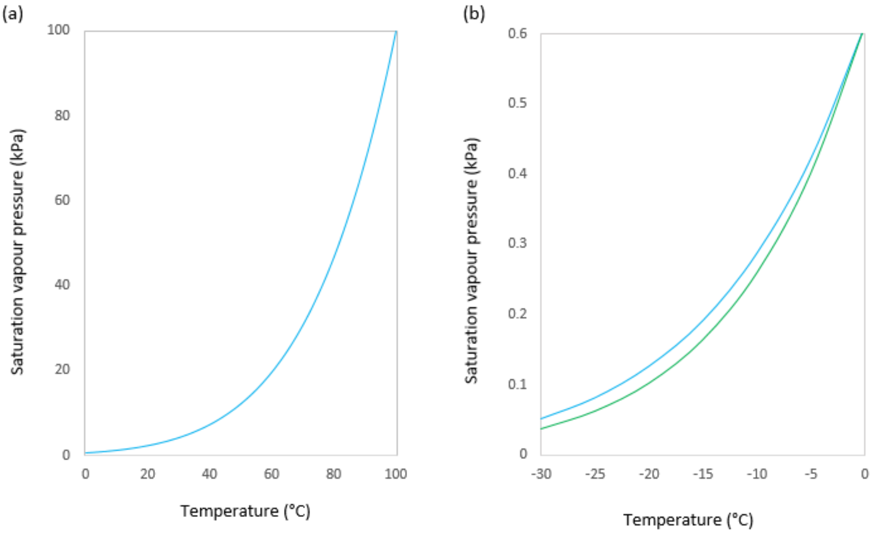

Figure 1 *Saturation vapour pressure curves for (a) water and (b) supercooled water (blue, upper curve) and ice (green, lower curve)*

It can be seen from Figure 1 that below 0 °C **t**he same saturation vapour pressure exists for different values of frost-point temperature (ice) and dew-point temperature (supercooled water).

Relative humidity $\varPsi$ **:** Relative humidity describes how saturated a gas (or a space) is with water vapour. This is the most commonly used measure of humidity and is usually expressed as a percentage, with the symbol '%rh'. Relative humidity ($\varPsi$) is calculated using the following formula:

$$\varPsi = \frac{e}{e_s} \times 100 \qquad \text{(\% rh)} \qquad (1)$$

where:

- e is the actual water vapour pressure
- e_s is the saturation vapour pressure at the temperature of the gas

Pressure P : Overall pressure exerted by all components of the humid gas. Absolute pressure values should be used in humidity calculations and expressed in units of pressure (e.g. pascals (Pa)).

Water vapour enhancement factor f : factor by which a value of pure saturation vapour pressure is multiplied by to obtain the actual saturation vapour pressure which takes into account the effect of the presence and overall pressure of air or other background gases.

Mole fraction of water vapour x : ratio of the number of moles of a water vapour in a humid gas to the total number of moles of humid gas present where:

$$\boldsymbol{x = \frac{ef}{P}} \quad (\text{ mol mol}^{-1}) \tag{2}$$

At the low water content levels expected in HRS applications values are often expressed as micromoles of water vapour per mole of total gas (µmol mol^{-1}), often informally referred to as parts per million per unit volume (ppm$_v$) for gas mixtures where volume fraction is approximately the same as amount fraction.

Introduction to humidity calculations

There are methods for calculating and converting between humidity values in terms of dew point, amount fraction of water vapour, relative humidity, vapour pressure and other parameters. However, most humidity calculations involve several steps.

Some hygrometer companies provide software for making humidity conversions. This is often a good alternative to struggling with pen, paper and a calculator. Either way, humidity calculations need to be made carefully, with some understanding. In this section some of the more commonly made humidity calculations and any considerations for applying these to measurements of the water content of hydrogen are discussed.

Accepted formulae for calculating vapour pressure and water vapour enhancement factor from measurements of dew-point temperature and overall pressure in air and nitrogen can be found in papers by Sonntag [5] (also available in *A Guide to the Measurement of Humidity* [6]) and Hardy [7].

Humidity calculation applicability to HRS water content measurements

A common practice is for operators to make online humidity measurements of the hydrogen fuel in the HRS system at elevated pressure with a hygrometer measuring in units of dew-point temperature.

As the ISO 14687-2 standard water vapour limit is specified in terms of amount fraction, x this requires the results of measurements of dew-point temperature and overall pressure to be used to calculate values for e and f in equation 2 such that a value of x can then be realised.

Care should be taken that an absolute pressure value is used for the overall value of pressure, P, as the use of gauge pressure values could lead to significant errors in the calculations of amount fraction, x. For example, x calculated as 4 µmol mol^{-1} with an absolute value of pressure of 0.5 MPa (5 bar) would result in an amount fraction of 5 µmol mol^{-1} if a gauge pressure 0.4 MPa gauge (4 bar) was used in the calculation.

As there is limited accepted data for water vapour enhancement factor in mixtures with hydrogen then any value of f approximated using formulae for air and nitrogen [5,6,7] should have a suitable estimation of uncertainty applied. If this uncertainty is expressed in terms of percent of value of f then this will transfer directly as a percentage uncertainty in the calculated value of amount fraction from equation 2.

The dew-point temperature measurements made at HRSs in practice tend to be relatively low leading to calculated values of x much lower than the quality limit. In such cases the relatively large resultant amount fraction uncertainties can therefore be accommodated and the measurements made would still demonstrate hydrogen of acceptable quality.

Amount fraction of water vapour is unaffected by changes in temperature and pressure of the gas. Therefore, hydrogen can be monitored at pressures lower than that of the nozzle delivery pressure at stages in the system prior to the final compressor and the water content value can be assumed to be the same at the point of delivery. However, this supposes there is no stray water influence or absorption of water during the compression stage which is why the periodic sampling of hydrogen for quality analysis must be made from the nozzle.

Dew-point temperature measurements are not pressure independent. Variations in the total pressure of a gas lead to changes in the water vapour partial pressure resulting in a change in dew-point temperature.

3. HRS humidity measurement best practice

Sampling

In general, correct sampling is required to ensure that the humidity of the gas reaching the hygrometer is representative of gas at the test location. In this regard, it is important to avoid water being spuriously added to the measured gas, and to avoid unintended removal of water from the sample.

For measuring very dry gases (frost points around -40 °C, -50 °C, or below; water vapour fraction around 100 µmol mol^{-1}, or less), sample tubing and all materials in the gas flow path are critical. In this range, even tiny amounts of stray water released from surfaces can significantly add to the gas moisture content, and can give badly misleading results. A plot of the dew point measured after the same dry gas has passed through a variety of tubing materials as a function of time is shown in Figure 2. To avoid moisture permeation through tubing walls and minimise desorption effects, clean internally electropolised stainless steel; the smallest possible volume of pipework; and long flushing times should be used when sampling gas to be measured by hygrometers.

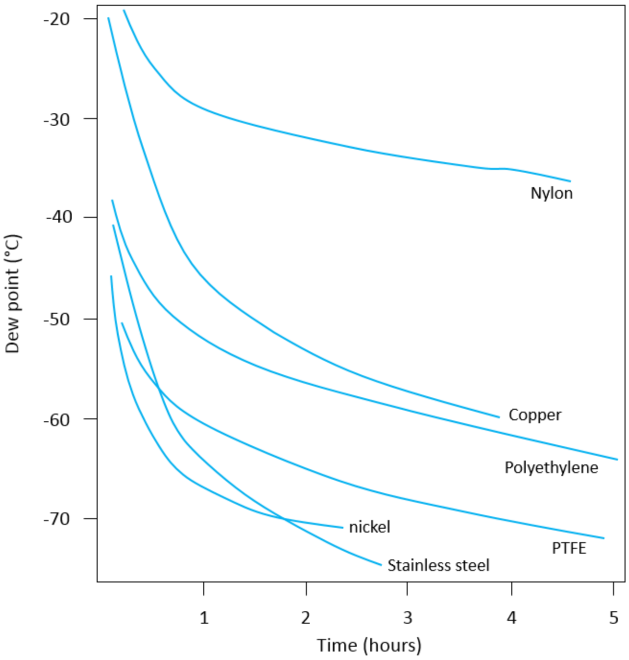

Figure 2. *Dew-point measurements of the same dry gas after passing through a variety of tubing materials*

Measurement of dry gases using metal oxide dew-point probes

In the majority of HRS conditions measured, the dew-point temperature will be -40 °C or below. The response time of metal oxide dew-point probes is much slower than some laboratory based instruments such as water vapour spectrometers or chilled-mirror hygrometers. As well as use of the correct pipework and vessel materials as described above to ensure accurate sampling of test gas, enough time must be left for sample tubing equilibration and for the instrument to stabilise, ensuring a representative measurement is made. In practice this can take many hours at trace moisture levels and hysteresis (metal oxide hygrometers can measure different values at the same humidity depending on whether the current condition has been reached following a rise or fall in humidity) can lead to further errors in the measured value.

Measurement of trace water content of hydrogen at elevated pressure

As amount fraction, *x*, of water vapour remains the same independent of the total pressure of the test gas, water vapour in hydrogen can be measured at pressures lower than that of the nozzle delivery pressure at a stage in the system prior to final compression and the result assumed to be the same at the point of delivery.

The applicability of using this measured value as a water content quality check for the nozzle delivery gas assumes that no further water is spuriously added to or unintentionally removed from the measured gas during compression.

Pressure regulator devices [8,9,10] exist that are used at the nozzle to reduce the supply pressure to an acceptable level for sampling hydrogen into vessels for offline purity analysis. Spot checks of the water content of the hydrogen fuel from the nozzle after the compressor stage could be performed using a hygrometer if it could be connected to such a device. The instrument response time and the time taken for the test gas to stabilise may be prohibitive for this to be a practical approach.

Analogue output scaling

Measurement results from industrial dew-point hygrometers are usually logged from DC current outputs scaled for example from 4 mA to 20 mA for the full scale range of the instrument (e.g. -100 °C to +20 °C). Depending on the specific hygrometer type this current range could be equivalent to dew-point temperature ranges of -110 °C to +20 °C, -100 °C to +20 °C or -80 °C to 0 °C. It is therefore important to read the manufacturer’s instructions to ensure the correct conversion of the current output to dew-point temperature.

Temperature compensation of metal oxide dew-point probe measurements

Some older dew-point probes might exhibit some error due to sensitivity to ambient temperature, and the specification from when they were purchased will give a temperature coefficient that should be used to compensate for this.

Most manufacturers now include an internal temperature sensor within the dew-point probe and temperature compensation is applied from the measured ambient temperature (over a specified range) to improve the accuracy of the humidity measurement. If the ambient temperature the hygrometer at the HRS is exposed to is likely to differ significantly from the laboratory conditions at which its calibration was performed then it is recommended to request calibration of the hygrometer at a range of ambient temperatures representing the conditions of use. (e.g if measuring in ambient conditions of 0 °C in the field, a different hygrometer measurement error to that found during calibration in the laboratory at +20 °C may result).

4. Hygrometer calibration

Like all measuring instruments, hygrometers don’t always read exactly true. They can suffer from bias and long-term drift. Therefore calibration is essential for accurate humidity measurement.

Calibration is the comparison of an instrument against a reference value. For a hygrometer, this comparison might be against a calibrated reference hygrometer, using an environmental chamber or other stable source of humid gas. The reference hygrometer should itself have a calibration traceable directly, or in multiple steps, back to an authoritative standard. This is known as measurement traceability.

Some users assume that calibration will leave an instrument ‘reading correctly’. However, this is not necessarily true because calibration is not the same as adjustment. A calibration certificate reports any instrument errors, and gives the uncertainty in these. Calibration corrections then need to be applied to instrument readings (or else taken into account as a source of uncertainty). With any measurement, the practical uncertainty in using the instrument is always more than that stated on the calibration certificate.

Calibrations against reference hygrometers, using humidity generators, can be performed in laboratories. A calibration laboratory may have ISO 17025 [11] accreditation (through UKAS in the UK) giving assurance that calibrations are traceable and competently performed.

Calibration methods

The calibration of hygrometers is typically carried out by comparing their indication, in a stable environment, against a humidity reference. Several methods that can be used to generate reference humidities to calibrate hygrometers used in HRSs are described in the sections that follow.

Single-pressure dew-point generator

Dew-point generators are capable of producing test gas streams with a well-defined dew-point temperature. This is typically achieved by passing the gas through, or flowing it over, water or ice at a defined temperature in a device called a saturator. The result of this process is the production of a gas with a dew point that is equal to the temperature of the saturator used, assuming saturation of the gas is efficient. The test gas used is usually air or nitrogen and is applied to test hygrometers at close to atmospheric pressure. Recent developments at national measurement institutes such as NPL [1] have led to facilities where humidified hydrogen can be used as the test gas and can be supplied at elevated pressures reflecting industrial conditions of use.

Two-pressure generators

The operating principle of a two-pressure generator is for a gas to be humidified at high pressure and then expanded to a lower pressure whilst maintaining a non-condensing temperature. In accordance with Dalton’s law, as the total pressure falls, so does the partial pressure of water vapour and, assuming that the initial value of the humidity is known, the dew point after the expansion process can be determined. Different values of dew point or amount fraction can be obtained using a two-pressure generator through variation of the initial pressure and saturation temperature.

Hygrometer field checks with reference gas mixtures certified for water content

A static reference cylinder with certified water content can be prepared by transferring pure gases, pure liquids, or gravimetrically prepared mixtures of known composition quantitatively into a cylinder in which the calibration gas will be contained. Such cylinders can be used for field checks of hygrometers at a HRS site. A check can help in assessing whether a hygrometer is functioning as expected, and whether repair or recalibration is needed.

HRS hygrometer calibration recommendations

The anticipated range of humidities that will be encountered in service should be considered when purchasing a calibration. A calibration consisting of at least three values of dew point or water vapour amount fraction including points above and below the maximum and minimum humidity in this range should be requested to understand the error characteristics of the hygrometer.

Calibrations need to be repeated, because hygrometers can drift due to conditions of use, or just due to sensor ageing. The frequency of recalibration is dependent on usage, risk of drift, and how critical the measurement is. Generally metal oxide dew-point probe manufacturers recommend a six to twelve month interval between calibrations.

It is recommended that hygrometer long-term drift is assessed following the service period in a HRS station. A common practice followed by HRS operators is to apply corrections from the factory calibration certificate (or to use the output of the hygrometer with no correction) and assume this is valid for the entire service period of the hygrometer. At the end of the service period the hygrometer is returned to the manufacturer for replacement, usually via an exchange programme. It is not common practice for users to request an "as-found" calibration of the returned hygrometer in order to assess the measurement error drift during service. Such a calibration could reveal important information about the performance of the hygrometer used and could explain trends in the HRS hydrogen water content level data which may be due to instrument drift over time rather than HRS system issues.

Recommendations when requesting calibrations of hygrometers for HRS use:

- Use a laboratory with ISO 17025 accreditation for humidity calibration in the relevant range
- Request that the calibration is in the working units of the hygrometer e.g. dew-point temperature (°C) or volume fraction (ppm_v)
- Request at least three points covering minimum and maximum expected humidity values of the process being monitored
- If possible, request that calibration is performed at the range of ambient temperatures the hygrometer would experience during service
- Request an "as-found" calibration of the hygrometer at the end of service to assess long-term drift

5. Dew-point probe behaviour observed during MetroHyVe hygrometer study

In Activity 3.2.1 of the EMPIR Metrology for Hydrogen Vehicles (MetroHyVe) project, six commercially available metal oxide dew-point probes from five different manufacturers were calibrated against the NPL Multi-Gas, Multi-Pressure Humidity Generator [1]. Conditions were applied that tested the response of the hygrometers to changes in background gas species from nitrogen to hydrogen and changes in pressure from close to atmospheric pressure to 2 MPa (20 bar). Calibrations were completed across a range of dew-point temperatures (-65 °C to -20 °C) that correspond to water vapour amount fractions from 0.5 µmol mol^{-1} to 50 µmol mol^{-1} at 2 MPa, spanning the ISO 14687-2 limit of 5 µmol mol^{-1}.

The calibrations across this dew-point temperature range completed at close to atmospheric pressure and with nitrogen as the background gas enabled testing of potential differences in instrument response between the manufacturer’s factory calibration and a calibration completed in conditions reflecting industrial use in a HRS.

One of the hygrometers tested in the study was owned by ITM Power, operators of the NPL onsite HRS. This hygrometer was calibrated alongside the other hygrometers loaned to the project before it was installed for its one year service period in the NPL onsite HRS. Subsequent calibrations of the HRS hygrometer were performed six months into the service period during an HRS maintenance shutdown and again at the end of a year of service. The five other hygrometers in the study were also re-calibrated at these times and were kept in the NPL humidity laboratory measuring dry air in the intervening periods.

Repeated calibrations of the test hygrometers at six and twelve month periods after the initial calibration enabled evaluation of the long-term drift behaviour of instruments of this type.

The findings of this study [12] and resultant calibration recommendations are summarised below and should be considered together with the measurement and calibration recommendations from Sections 3 and 4.

Background gas dependence of instrument reading

Finding:

Of the six metal oxide probes tested in the study, four showed no noticeable change in reading when the background gas carrying the water vapour was changed from nitrogen to hydrogen at a fixed humidity condition. However, one of the hygrometers showed a downward shift in reading of approximately 4 °C, whilst another showed an upwards shift of approximately 1°C, due simply to the change in background gas species.

Recommendation:

Where available, a calibration in a background gas of hydrogen for hygrometers used in HRS applications 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.

Pressure dependence

Finding:

A dependence on background pressure of readings was observed for three of the six metal oxide probes tested in the study. This effect was largest at -65 °C dew-point temperature, the lowest humidity tested. The fixed humidity condition was applied at two pressures: 0.17 MPa and 2 MPa. Those hygrometers affected responded in different ways, ranging from an upward shift of 1 °C to a downward shift of 4 °C.

Recommendation:

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

Long-term drift of measurement error

Finding:

The measurement error of five of the six metal oxide hygrometers tested showed large drift towards under-reading during the one-year period of the study. Values of long-term drift ranged between -7.5 °C and -12.5 °C dew-point temperature.

The calibration results after six months of service showed that this was an approximately progressive change for three of the affected hygrometers, with more drift occurring in the second six months of the study. The two remaining hygrometers drifted during the first six months of service, but no further drift was observed at the twelve-month calibration stage. Therefore, it is not possible to predict whether hygrometer drift will occur at start of service, or towards the end, or uniformly with time.

Recommendation:

Methods could be developed for periodic field checks of hygrometers onsite at HRSs using cylinders containing reference gas mixtures of water vapour in hydrogen. A check would help in assessing whether a hygrometer has drifted significantly during service and whether recalibration or replacement is needed.

It is recommended to obtain “as-found” calibration results at the end of the hygrometer service period, in order to gain information about sensor drift. This would enable assessment of the extent of the in-service drift of the hygrometer since the initial factory calibration.

Alternatively, if it is possible to have a second port available at the HRS a new hygrometer could be installed in parallel with the hygrometer it is replacing (before this is removed). The extent of the measurement drift during use could then be evaluated in-situ before the hygrometer due for replacement is returned to the manufacturer.

6. Sources of uncertainty in humidity measurements

As we have seen throughout this guide, every humidity measurement is subject to a degree of uncertainty. The sources and magnitude of uncertainty involved in the use of a hygrometer will depend on the instrument being used and on the specific measurement being made. However, as a general guide, the following sources of uncertainty should be considered in humidity measurements of hydrogen at a HRS:

- The calibration uncertainty of the hygrometer
- Long-term drift in hygrometer error
- Pressure sensitivity of the hygrometer
- Sensitivity of hygrometer to background gas
- Equilibration (settling time, response time)
- Temperature dependence of the hygrometer (if not temperature compensated)
- Irreproducibility of the hygrometer
- Hysteresis of the hygrometer
- Non-linearity of the hygrometer
- Short-term stability (noise)
- The resolution of the display or electrical output

7. Summary of good practice recommendations

Calibration good practice:

- ✓ Ensure that the hygrometer calibration is traceable to national standards.
- ✓ Request that the calibration is in the working units of the hygrometer e.g. dew-point temperature (°C) or water vapour volume fraction (ppm$_v$).
- ✓ Request at least three calibration points covering minimum and maximum expected humidities.
- ✓ If using corrections from a hygrometer's factory calibration certificate (performed in nitrogen or air at atmospheric pressure), ensure that possible measurement errors due to use in hydrogen background gas at elevated pressure have been considered.
- ✓ Where possible obtain a calibration of the hygrometer with hydrogen as background gas at the anticipated pressure of use to replicate operating conditions.
- ✓ Ensure that the hygrometer manufacturer has provided an estimate of long-term drift (or if not available perform independent checks at regular periods during service).
- ✓ Measurements of humidity using a new hygrometer installed in parallel with the end of service hygrometer it is replacing (before this is removed) can give an in-situ check of long-term error drift.
- ✓ If an older dew-point probe type that may not have temperature compensation is being used, request that calibration is performed at a range of ambient temperatures the hygrometer would experience during service.

Measurement good practice:

- ✓ Ensure a representative humidity measurement from the hygrometer used. Avoid moisture permeation through tubing walls and minimise desorption effects by using clean internally electropolised stainless steel and the smallest possible volume of pipework when installing hygrometer.
- ✓ Leave enough time for tubing material and hygrometer to stabilise.
- ✓ Apply corrections from calibration certificates to measured humidity values.
- ✓ Measurement uncertainty factors applicable to corrected humidity values should be carefully considered.

8. References

International Standards are subject to change. Reference should be made to the current published version of the standard where applicable.

[1] Carroll PA, Bell SA, The NPL Multi-gas, Multi-pressure Humidity Generator. Paper in preparation, Metrologia.

[2] DIRECTIVE 2014/94/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 22 October 2014 on the deployment of alternative fuels infrastructure.

[3] ISO 14687-2:2012. Hydrogen fuel product specification part 2: proton exchange membranes (PEM) fuel cell applications for road vehicles.

[4] Draft BS ISO 19880-8 1, Gaseous hydrogen - Fueling stations - Part 8: Hydrogen quality control.

[5] Sonntag D, *"Important new values of the physical constants of 1986, vapor pressure formulations based on the ITS-90, and psychrometer formulae"* Z. Meteorol. 70, 340 (1990).

[6] A Guide to the Measurement of Humidity Published by the Institute of Measurement and Control, 1996, 68 pp, ISBN 0-904457-24-9 www.npl.co.uk/publications/guide-to-the-measurement-of-humidity.

[7] Hardy B *(1998) "ITS-90 Formulations for Vapor Pressure, Frost point Temperature, Dew point Temperature, and Enhancement Factors in the range –100 °C to +100 °C",* Papers and Abstracts of the Third International Symposium on Humidity and Moisture.

[8] SAE J2600. Compressed hydrogen surface vehicle fuelling connection devices. 2012.

[9] SAE J2799. 70 MPa compressed hydrogen surface vehicle fuelling connection device and optional vehicle to station communications. 2007.

[10] ISO 17268:2012. Gaseous hydrogen land vehicle refuelling connection devices. 2012.

[11] ISO 17025 General requirements for the competence of testing and calibration laboratories. 2017.

[12] Carroll PA, Bell SA, A study of the measurement response of hygrometers typically used to measure humdiity at hydrogen refuelling stations. Paper in preparation, Int. J. Hydrogen Energy.

9. Links to other sources of useful information

International Standards are subject to change. Reference should be made to the current published version of the standard where applicable.

Further reading

DIRECTIVE 2014/94/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 22 October 2014 on the deployment of alternative fuels infrastructure.

Brown AS, Vargha GM, Downey ML, Hart NJ, Ferrier GF, Hall KL. NPL report AS 64-methods for the analysis of trace-level impurities in hydrogen for fuel cell applications. 2011.

Murugan A, Brown AS, Review of purity analysis methods for performing quality assurance of fuel cell hydrogen. Int. J. Hydrogen Energy. 2015, pp. 1–15.

Standards – Hydrogen

ISO 14687-1, Hydrogen fuel — Product specification — Part 1: All applications except proton exchange membrane (PEM) fuel cell for road vehicles.

ISO 14687-2:2012. Hydrogen fuel product specification part 2: proton exchange membranes (PEM) fuel cell applications for road vehicles.

ISO 14687-3:2014. Hydrogen fuel product specification part 3: proton exchange membrane (PEM) fuel cell applications for stationary appliances.

BS ISO 21087:2019 Gas analysis — Analytical methods for hydrogen fuel — Proton exchange membrane (PEM) fuel cell applications for road vehicles.

BS ISO 19880-1 Gaseous hydrogen - Fuelling stations. Part 1: General requirements.

BS ISO 19880-8 1, Gaseous hydrogen - Fueling stations - Part 8: Hydrogen quality control.

BS EN 17124:2018 Hydrogen fuel - Product specification and quality assurance - Proton exchange membrane (PEM) fuel cell applications for road vehicles.

SAE J2719. Hydrogen fuel quality for fuel cell vehicles. 2011.

ASTM D7649-10. Standard test method for determination of trace carbon dioxide, argon, nitrogen, oxygen and water in hydrogen fuel by jet pulse injection and gas chromatography / mass spectrometer analysis. 2010.

ISO/TR 15916 Basic considerations for the safety of hydrogen systems. 2015.

ISO/IEC 80079 (all parts), Explosive atmospheres.

Humidity

Bell, S A (2013) The beginner's guide to humidity measurement. Measurement. Good Practice Guide. 124.

A Guide to the Measurement of Humidity Published by the Institute of Measurement and Control, 1996, 68 pp, ISBN 0-904457-24-9 www.npl.co.uk/publications/guide-to-the-measurement-of-humidity.

BS1339-1 (2002) Humidity. Terms, definitions and formulae.

BS1339-2 (2009) CD-ROM. Humidity calculation functions, tables and user guide.

BS1339-3 (2004) Guide to the measurement of humidity.

General metrology

Bell, S A (2001) A beginner's guide to uncertainty of measurement. Good Practice Guide 11 (Issue 2).

JCGM 200 (2008) International vocabulary of metrology. Basic and general concepts and associated terms (VIM).

ISO/IEC GUIDE 98-3(2008) Ed 1 Uncertainty of measurement. Guide to the expression of uncertainty in measurement.

BS PD 6461-4 (2004) General metrology. Practical guide to measurement uncertainty.

Other useful links

National Physical Laboratory,
Hampton Road,
Teddington,
Middlesex
TW11 0LW
+44 (0)20 8977 3222
www.npl.co.uk/temperature-humidity
humidity_enquiries@npl.co.uk

British Standards Institute (BSI) www.bsigroup.com

International Standards Organisation (ISO) www.iso.org