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TABLE OF CONTENTS

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1 Overview

Trace water is the single largest matrix contaminant in ultra-high purity (UHP) process gases (e.g., Ar, N_2 and H_2), and its presence affects the quality of products where UHP gases are used. Even though the production of UHP gases serves many key technology areas, such as high-value semiconductor manufacturing, the trace water measurements was still lacking metrological traceability in the relevant ranges and matrix gases. The project addressed these issues and filled the knowledge gap regarding metrological traceability - by developing traceable and improved measurement methods and standards at challenging amount fractions between 5 ppb and 5 ppm for use in the production of UHP process gases with state-of-the-art measurement uncertainty - and demonstrated the technology in key applications relevant to process instrumentation and gas industries. A European-wide infrastructure capable of providing a robust metrological traceability to trace water measurements in UHP process gases, specifically nitrogen, argon, air and hydrogen was developed and is now in place to serve the industry and other relevant stakeholders and users.

2 Need

Due to its ubiquity and chemical properties, water vapour is a critical contaminant and one of the most difficult impurities to remove. Water contamination effects become relevant when taking into consideration the worldwide production of gases. The global market for industrial gas is expected to reach US$ 149 billion by 2027, with Europe sharing about 16 %, owing to rising demand from the electronics, healthcare, and pharmaceutical sectors. The semiconductor market alone is expected to reach $ 5.2 billion by 2026.

Bulk process gases with ultra-high purity grade (N6.0 or better) need to be produced with total impurities below 1 ppm in volume. According to the International Technology Roadmap for Devices and Systems, water vapour measurement techniques need to measure amounts as low as a few parts per billion at the point of use. From 2015 to 2020, these requirements have tightened for some gases (nitrogen and argon) by more than a factor of five. This presented great challenges for both gas producers and analytical instrument makers aiming to improve trace water measurement methods at the part per billion level.

A metrological infrastructure complemented by adequate measurement technologies, thus enabling robust traceability to trace water measurements, providing suitable primary standards, improved optically-based methods and improved knowledge of moist gases properties was greatly welcomed. A survey among 50 key industrial stakeholders confirmed such needs and helped steering the project efforts to maximise its impact.

3 Objectives

The overall objective of PROMETH2O was to provide new and improved trace water measurements relevant for the production of pure gases and to demonstrate their impact in improving selected industrial processes and applications.

The specific objectives of the project were:

1. To improve trace water measurement methods in the amount fraction range between 5 parts in 10^6 (5 ppm) and 5 parts in 10^9 (5 ppb) or, equivalently, between -65 °C and -105 °C frost point temperature at 0.1 MPa with a relative standard uncertainty between 3 % and 8 %, from the upper to lower range, respectively.
2. To provide robust traceability to trace water measurements by developing suitable primary standards for the amount fraction range from 5 ppm to 5 ppb (or -65 °C to -105 °C frost point temperature at 0.1 MPa) with a relative standard uncertainty less than 3 % to 8 %, in selected gas matrices of air, N_2, Ar and H_2 at pressures up to 1 MPa.
3. To improve the present knowledge of thermophysical data of real humid gas mixtures, in particular the water vapour enhancement in N_2 and Ar in the temperature range from -30 °C to -90 °C and at pressures from 0.1 MPa to above 1 MPa.

4. To demonstrate improved trace water measurement methods between 5 ppm and 5 ppb or, equivalently, between -65 °C and -105 °C frost point temperature at 0.1 MPa, in two industrially relevant facilities (test beds).
5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain, standards developing organisations (CIPM, IAPWS, JCS) and end users (instrument manufacturers, gas providers).

4 Results

These are the results of joint collaborative work on metrology for trace water in ultra-pure process gases.

Objective 1: Improved, metrologically-sound, methods and techniques for trace water measurements

The project developed fast-responding optically based methods, techniques, and analysers such as a new far-UV-based analyser suitable for on-line high-pressure measurements, advancing high-resolution comb-calibrated frequency-stabilised cavity ring-down spectroscopy (CC-FS-CRDS) and refining Fourier-transform infrared (FTIR) spectroscopy. Part of the project work was also focused on the characterisation and validation of a new commercial CMH for the first time below -100 °C frost point to assess suitable transfer standards for future international comparisons in the low frost-point temperature scale.

NIR comb-calibrated frequency-stabilised cavity ring down spectrometer

Cavity ring-down spectroscopy (CRDS) is a simple, highly sensitive, direct-absorption technique that provides the absorption coefficient of an intracavity absorbing medium on an absolute scale. This method exploits the enhanced light-matter interaction length that takes place inside a high-finesse optical resonator. In a continuous wave (cw) CRDS, the coherent radiation from a single mode, tuneable, cw laser is coupled to a high-finesse optical cavity up to a threshold level, and then it is quickly switched off at the cavity resonance. Transmitted light during the ring-down event is detected and the decay rate is measured. If a molecular species inside the cavity absorbs the coupled light, it increases the cavity loss rate, compared to the case in which the cavity is empty, or the incident wavelength (λ) is off resonance. From the measurement of such variation, the absolute absorption coefficient, $\alpha(\lambda)$, can be determined, according to the following equation:

$$\alpha(\lambda) = \frac{1}{c}\left[\frac{1}{\tau(\lambda)} - \frac{1}{\tau_0}\right] \tag{1}$$

where c is the vacuum speed of light, $\tau(\lambda)$ is the decay time in the presence of an absorbing medium, while τ_0 is the empty cavity decay time. To mitigate the effect of mechanical, thermal, and electric noises that may increase the frequency jitter between the probe laser and a given cavity mode, frequency-stabilised cavity ring-down spectroscopy (FS-CRDS) were introduced. SUN introduced a new concept of FS-CRDS, based on the use of a pair of phase-locked extended-cavity diode lasers (ECDL) in conjunction with an intrinsically stable high-finesse optical cavity. The method is now known as comb-calibrated frequency-stabilised cavity ring-down spectroscopy (CC-FS-CRDS) were absorption spectra can be recorded with high resolution, precision, and fidelity, with the advantage of an absolute frequency scale underneath each spectrum.

A sketch of the 2nd generation CC-FS-CRDS analyser developed under PROMETH2O is depicted in Figure 1.

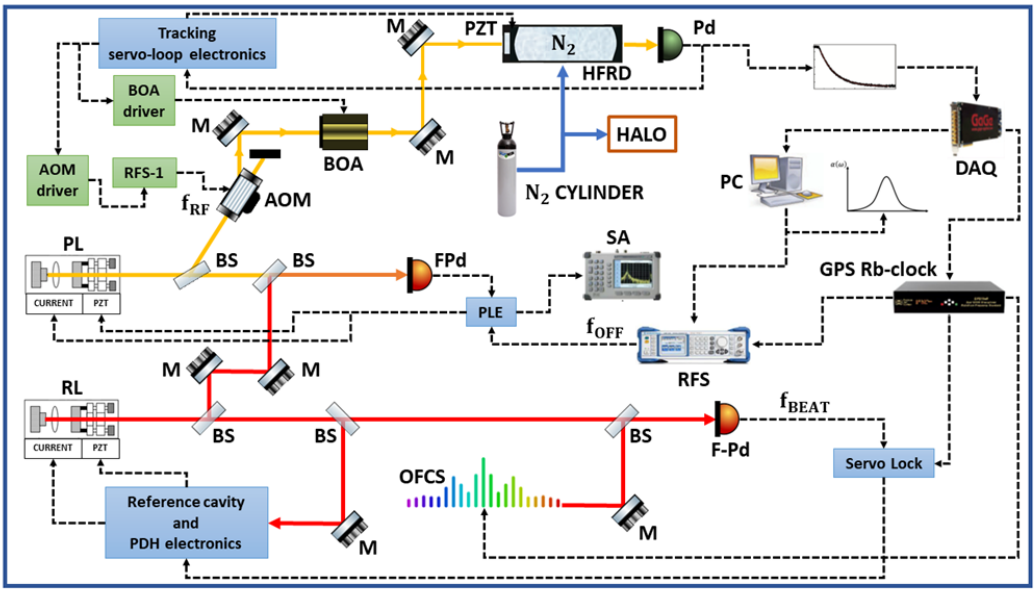


Figure 1. Experimental set up of the NIR CC-FS-CRDS for ultra-sensitive traceable measurements of water vapour in ultra-high-purity (UHP) gases.

The high-finesse ring-down (HFRD) cavity where the gas samples are interrogated by the probe laser consists of two mirrors having a nominal reflectivity exceeding 99.999%. The mirrors are mounted on a AISI 316L electro-polished spacer at a distance of about 53 cm as shown in Figure 2.

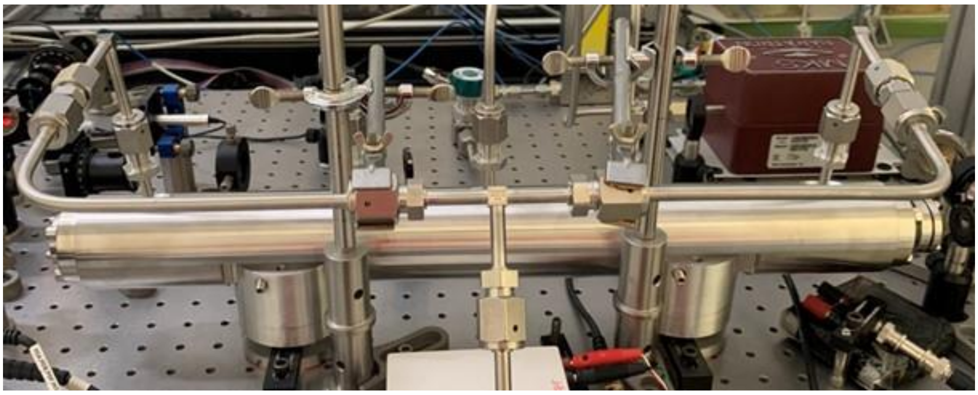


Figure 2: Picture of the AISI 316L stainless-steel cavity spacer equipped with high-reflectivity mirrors at both ends and metal-gasket (VCR®) feedthroughs developed by SUN in cooperation with INRIM.

A single ring-down event, along with a fit to a single exponential decay function, is shown in Figure 3 (left panel), while the Allan-Werle deviation analysis of 101000 consecutive decay times recorded over one hour are shown in Figure 3 (right panel). The mean value of the ring-down times and the associated standard deviation are τ_0=284.83 μs and $\sigma_{\tau 0}$=0.13 μs, respectively, leading to a relative statistical uncertainty of 0.05 %.

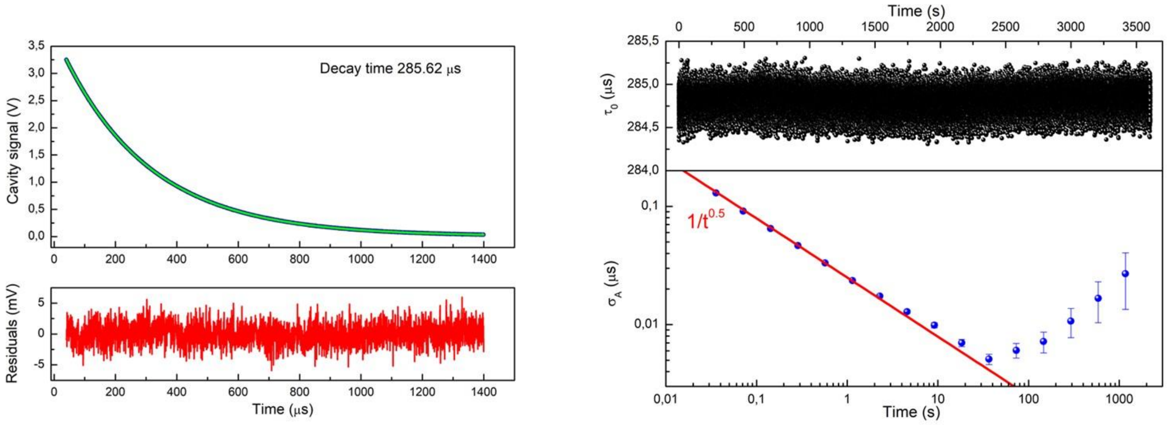


Figure 3: (left) Example of a ring-down event recorded under vacuum conditions and residuals of the fit; (right) Allan-Werle deviation (σ_A) analysis of 101000 ring-down times.

From the Allan-Werle deviation (σ_A) behaviour as a function of the integration time, the sensitivity of the spectrometer can be inferred in terms of minimum detectable absorption coefficient, α_{min}, and in terms of noise equivalent absorption (NEA) coefficient. The α_{min} and NEA turned out to be 2.1x10^{-12} cm^{-1} and 1.4x10^{-11} cm^{-1}/Hz$^{1/2}$, respectively.

In order to test the capabilities of the CC-FS-CRDS analyser, in terms of reproducibility, the water mole fraction was determined from the acquisition of several repeated absorption spectra from a high-purity N_2 cylinder having a nominal purity of 99.9999 %. All measurements were carried out and compared with a calibrated commercial CRDS traceable to INRIM humidity standards in the range from 10 ppb to 10 ppm. A 1-σ reproducibility of 1.4 ppb, which translates into 0.25 %, was found by averaging over 90 determinations 90 ring-down measurements. Conversely, the limit of detection (LOD), which depends on the integration time of each spectral point of the acquired spectra, can be easily improved by averaging over about 1000 ring-down events to get a LOD of about 50 ppt. In a further refinement, SUN demonstrated a record sensitivity for water vapour detection with its CC-FS-CRDS analyser, achieving a minimum detectable absorption coefficient as low as 3.7×10^{-13} cm^{-1}, which corresponds to a limit of detection for H_2O in N_2 of nine parts per trillion (9 ppt) and a H_2O partial pressure of 2×10^{-8} Pa (or 2×10^{-10} mbar).

Far-UV spectroscopy-based system

A far-UV system suitable for trace water measurements in Ar and N_2 has been developed. A far-UV approach for H_2O measurements was chosen because of low-cost spectrometers can be used as sensitive detectors and in its spectral range (140-200) nm it also allowed multi-gas component measurements; that is, in addition to H_2O, other impurities such as O_2, N_2, and VOC can be measured at the time. At present, the inventors are looking at a patent application.

New enhancements in FTIR-based system

The project also addressed a Fourier Transform Infrared spectroscopy (FTIR) approach for trace moisture analysis in nitrogen. An upgrade of a high-resolution FTIR spectrometer has been implemented by TUBITAK, with a new multi-pass gas cell, a new HgCdTe detector with higher sensitivity and a new pump system to enable water vapour measurements in N_2 and Ar down to 50 ppb and operation at pressure up to 1 MPa.

To perform quantitative analysis with the FTIR, the absorbance of moisture bands in sample spectra is compared to calibration spectra produced from known standards under the same conditions. Comparison measurements against a calibrated chilled-mirror hygrometer have been carried out in air in the sub-ppm H_2O range to find the optimum measurement conditions for the upgraded FTIR.

As a substitute to the traditional calibration method that relies on reference gas mixtures, a calibration process for the FTIR spectrometer was also attempted by utilising synthetic spectra generated through a radiative transfer calculation code (MALT, Multiple Atmospheric Layer Transmission). The process entails calculating the monochromatic transmittance spectrum, then convolved with the FTIR instrument line-shape function, incorporating factors such as resolution, apodisation, and finite field of view. The resultant calculated spectrum simulated the measured spectrum and underwent iterative recalibration until the best fit, minimising the sum of squared residuals between the measured and calculated spectra was achieved.

TUBITAK demonstrated that both approaches were viable and able to provide accurate measurement in the trace water range. The instrumentation layout used to validate the FTIR trace water measurement system is shown in Figure 4.

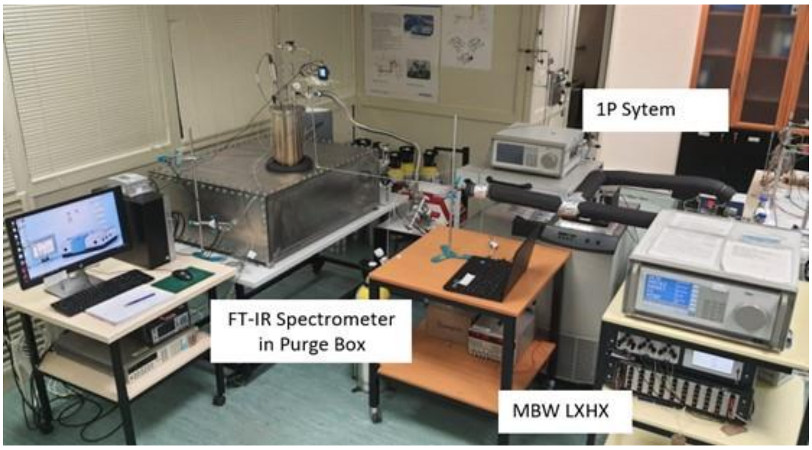


Figure 4: TUBITAK FT-IR trace water measurement system.

Assessment of state-of-the-art frost-point chilled-mirror hygrometer and CRDS trace water analysers

PROMETH2O investigated the performance of both commercially-available and novel optical measurement methods. Commercially-available systems included high-quality chilled-mirror hygrometers (CMHs) and optically-based cavity ring-down spectroscopy (CRDS) analysers.

In trace and ultra-trace humidity measurements, low frost-point CMHs feature a wide dynamic temperature range within the measuring head. Cooling a mirror to -100 °C requires significant heat dissipation, and counter-heating is necessary to avoid condensation within the measuring head assembly. Temperature flux within the measuring head increases equilibrium times and can be a significant contribution to uncertainty. To overcome this, a recent conceptual development of the CMH is based on a dew/frost point measuring head which can be submersed into a controlled temperature fluid. Submersion at low temperatures extends the cooling capability of the mirror temperature control system (thermoelectric cooler) and offers other benefits such as reducing thermal gradients in the measuring head and precooling of the sample gas to limit thermal flux within the mirror assembly.

Two commercial CMH manufactured by InsightSwiss were available within the PROMETH2O consortium and were fully characterised to understand their performance and limitations in trace water measurement of ultra-high-purity gases. Both instruments were characterised by comparison calibration against the INRIM 03 Mk 2 standard humidity generator developed and validated in PROMETH2O. The calibration was carried out by comparing the frost-point temperature of a nitrogen stream of gas as measured by the unit under calibration against the reference frost-point temperature provided by the standard humidity generator in the frost-point temperature range between -100 °C and -20 °C. Figure 5 summarises the calibration results of both CMHs (models SLX #1 and SLX #2).

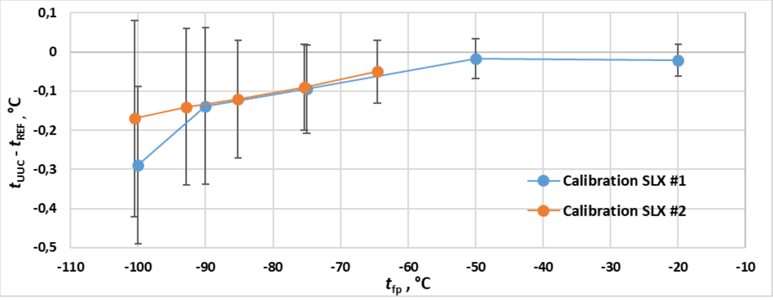


Figure 5: Calibration results of low frost-point CMHs model SLX #1 and SLX #2.

At frost-point temperatures below -75 °C, the CMHs performance slightly deviate from the preliminary manufacturer's specifications but they are still acceptable at the challenging frost-point temperatures of -90 °C and -100 °C (equivalent to an amount of water fraction of 97 ppb and 14 ppb, respectively, at atmospheric pressure). Based on the extensive performance characterisation work carried out in PROMETH2O, results, such low frost-point CMH technology is recommended for use as a transfer standard for measurements in the range from -20 °C down to -100 °C. However, NMIs and industrial users must be aware that before carrying out any meaningful measurements at any low frost-point temperatures, an extremely long stabilisation time is needed (e.g., more than 100 hours at -100 °C frost point).

Two commercial, off-the-shelf, CRDS trace water analysers were also metrologically characterised by comparison against a standard humidity generator in the amount of water fraction ranging from approximately 5 nmol/mol to 0.1 mmol/mol and pressure range from 0.2 MPa to 0.65 MPa. The investigation involved a Tiger Optics/Process Insights analyser mod. SPARK H2O M7700 specified for the measurement range 0-to-2000 ppm and a Photonics Technologies Inc. trace water analyser mod. Pure^{n}-T H2O specified for the measurement range 0-to-5 ppm in nitrogen. The assessment of the metrological performance of both CRDS analysers was carried out via a traceable calibration against the standard humidity generator INRIM 03 Mk 2. As an example of the investigation, Figure 6 shows the calibration results of the Photonics Technologies Inc. trace water analyser.

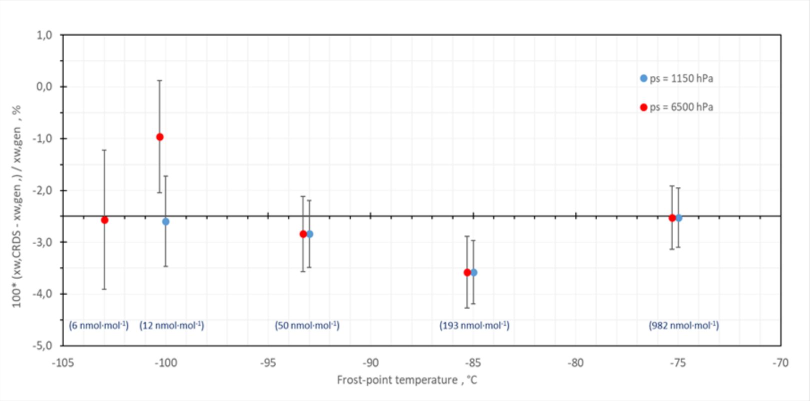


Figure 6: Percent difference between the water vapour amount fraction as measured by the Pure^{n}-T H2O CRDS analyser and the reference value in the range between 4 nmol/mol and 1000 nmol/mol in N_2 at two saturation pressures.

Based on PROMETH2O investigations, a CRDS with performance similar to the Tiger Optics SPARK H2O could be recommended as a transfer standard for trace water measurements above 1 ppm, while a CRDS with performance similar to the Photonics Technologies Inc. could be suitable as a transfer standard for trace water measurements between 5 ppb and 5 ppm in moist nitrogen.

Summary of key results

Several spectroscopy-based analysers have been developed, improved, and further upgraded to cover the challenging trace water vapour amount fraction between 5 ppb and 5 ppm. Two new high-quality commercial CMH systems were metrologically characterised and validated as suitable transfer standards for the frost-point temperature range between -100 °C and -20 °C.

Comb-calibrated frequency-stabilised cavity ring-down spectroscopy (CC-FS-CRDS) was demonstrated as a potential primary method for water vapour density measurements, showing the highest metrological qualities. Its measurement uncertainty between 0.5 % and 2.8 % was mainly limited by the reproducibility of decay time determinations and by the uncertainty of the line intensity factor of the selected H_2O line. A record sensitivity for water vapour detection with the CC-FS-CRDS analyser was demonstrated, achieving a limit of detection of nine parts per trillion (9 ppt).

A far-UV system suitable for trace water measurements in Ar and N_2 has been developed. The system allowed multi-gas component measurements; in addition to water, other impurities such as O_2, N_2, and VOC can be measured at the time. All such features were the basis for an on-line analyser able to operate both in static and dynamic conditions at pressures up to 10 MPa. A patent application case is in progress for this system.

A Fourier Transform Infrared spectroscopy (FTIR) approach for trace moisture analysis of nitrogen was developed. An upgrade of a high-resolution FTIR spectrometer has been implemented to enable water vapor measurements in N_2 and Ar down to 50 ppb and operation at pressure up to 1 MPa. Comparison measurements against a calibrated chilled-mirror hygrometer have been carried out in air - in the sub-ppm H_2O range to find the optimum measurement conditions for the upgraded FTIR - and further demonstrated in N_2 and Ar.

To provide useful elements for recommending suitable travelling standards to design a future international comparison in the trace water range, PROMETH2O investigated the performance of commercially-available systems (CMH and CRDS) in a wide humidity interval, corresponding to a frost-point temperature range from -100 °C to -20 °C or, equivalently, a water vapour amount fraction range from 5 ppb to 100 ppm at atmospheric pressure in N_2. Based on the PROMETH2O findings, several recommendations were given to help designing such future international comparisons in the trace water regime. The objective was successfully achieved.

Objective 2: Development of primary humidity standards for trace water in selected gas matrices

Another objective was to provide robust traceability to trace water measurements in the challenging amount fraction range from 5 ppb to 5 ppm (or equivalently from -105 °C to -65 °C frost point temperature at 0.1 MPa) with a relative standard uncertainty of less than 3 % to 8 % in several gas matrices (air, N_2, Ar and H_2) at pressures up to 1 MPa.

Primary standards for ultra-trace water vapour based on a variety of complementary principles and generation techniques - such as saturation, diffusion, permeation, mixing flow and coulometry – were developed and/or improved. Given the breadth and width of the work carried out in the project, only a brief account of each humidity realisation will be reported here. However, the overall picture shows that a European infrastructure on trace water measurements is now in place to support industry and other relevant stakeholders and such capabilities are the first in Europe and among the few in the world.

Dilution-type Humid Air Generator

CETIAT upgraded its Humid Air Generator (HAG) based on the dilution principle to operate in a pressure range from 0.1 MPa to 1 MPa with various gases such as air, nitrogen, and argon at frost-point temperatures down to -80 °C. A detailed schematic of the generator is shown in Figure 7 together with a picture of the cabinet interior.

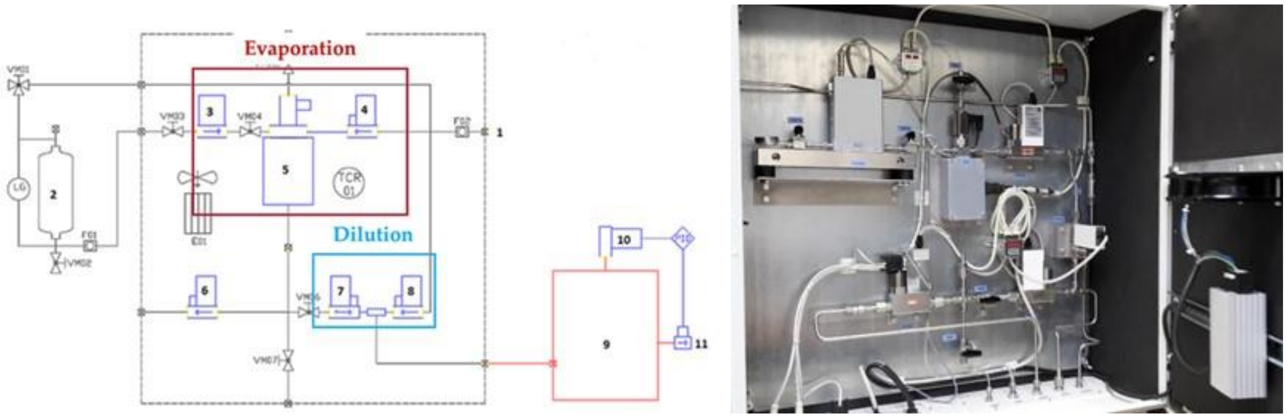


Figure 7: Technical drawing and picture of the CETIAT HAG.

The system produces a known mixing ratio, $r_{\mathrm{evaporation}}$, resulting from the evaporation of the liquid flow mixed with the dry gas flow according to:

$$r_{\mathrm{evaporation}} = \frac{m_{\mathrm{water}}}{m_{\mathrm{dry\ gas,MFC1}}} = \frac{\dot{m}_{\mathrm{water}}}{\dot{m}_{\mathrm{dry\ gas,MFC1}}}$$

where $\dot{m}_{\mathrm{water}}$ is the flow of liquid water and $\dot{m}_{\mathrm{dry\ gas,MFC1}}$ the flow of dry air. After dilution, the mixing ratio, r_{dilution}, resulting from the combination of a fraction of the flow from the evaporation stage, $\dot{m}_{\mathrm{MFC\ fraction}}$, with a flow of dry gas, $\dot{m}_{\mathrm{dry\ gas,MFC2}}$, leads to:

$$r_{\mathrm{dilution}} = \frac{\dot{m}_{\mathrm{MFC\ fraction}} \cdot r_{\mathrm{evaporation}}}{\dot{m}_{\mathrm{MFC\ fraction}} + \dot{m}_{\mathrm{dry\ gas,MFC2}}}.$$

The upgraded HAG is capable of operating across a pressure range from 0.1 MPa to 1 MPa with various gases, including air, nitrogen, and argon. Uncertainty estimation for the HAG has been effectively performed down to -80 °C frost point where the overall expanded uncertainty has been estimated at $U(k=2) = 0.35$ °C.

Saturation-based Generators

INRiM, VTT, CMI and UL, while developing their own saturation-based primary humidity generators, in a coordinated approach shared key information and data about their operation, characterisation and validation. Such standard humidity generators were designed to work in either single-pressure (1-P) or two-pressure (2-P) modes to cover an envelope of frost-point temperature between -105 °C and -20 °C and saturation pressure from 0.1 MPa to 1 MPa in N_2 and Ar.

In such systems, after passing a water saturator/condenser, the gas emerges fully saturated resulting in a water vapour amount fraction x_{w} equal to:

$$x_{\mathrm{w}} = \frac{e'_{\mathrm{w}}}{p} = \frac{f(p_{\mathrm{s}}, T_{\mathrm{s}}) \cdot e_{\mathrm{s}}(T_{\mathrm{s}})}{p_{\mathrm{s}}}$$

where $e_{\mathrm{s}}(T_{\mathrm{s}})$ is the saturation water vapour pressure of the pure phase at temperature T_{s}, $f(p_{\mathrm{s}}, T_{\mathrm{s}})$ is the water vapour enhancement factor that takes into account the non-ideality of the moist gas and p_{s} is the total pressure of the moist gas. In two-pressure mode, after the expansion to p_{o}, the frost-point temperature T_{fp} is then calculated by solving the following equation:

$$\frac{f(p_{\mathrm{s}}, T_{\mathrm{s}}) \cdot e_{\mathrm{s}}(T_{\mathrm{s}})}{p_{\mathrm{s}}} = \frac{f(p_{\mathrm{o}}, T_{\mathrm{fp}}) \cdot e_{\mathrm{s}}(T_{\mathrm{fp}})}{p_{\mathrm{o}}}$$

The generators can flexibly choose the most suitable operating mode to optimise the speed of operation and/or the measurement uncertainty. The generators met and exceeded the expected performance targets.

INRIM has improved its thermodynamic saturation-based primary humidity generator, extending its operating principle to a single-temperature, two-pressure, mode. The INRIM 03 Mark 2 can generate a humid gas (such as N_2 and Ar) with a frost-point temperature from -20 °C down to -105 °C, corresponding to a water vapour mole fraction from 1 mmol·mol^{-1} to 5 nmol·mol^{-1} at atmospheric pressure. The combined standard uncertainty of the frost-point temperature varies from 0.03 °C above -95 °C to 0.07 °C at -105 °C, while the combined standard relative uncertainty of water vapour mole fraction ranges from 0.4 % at 5 µmol·mol^{-1} to 2.3 % at 4 nmol·mol^{-1}. The system can saturate the carrier gas at any temperature above -100 °C and at any pressures up to 0.65 MPa (in single-pressure mode) before being expanded to a lower pressure (two-pressure mode) resulting in a minimum frost-point temperature of -105 °C.

Figure 8 shows the experimental set-up of the trace water generator during the calibration run and a diagram of the gas manifold and expansion system.

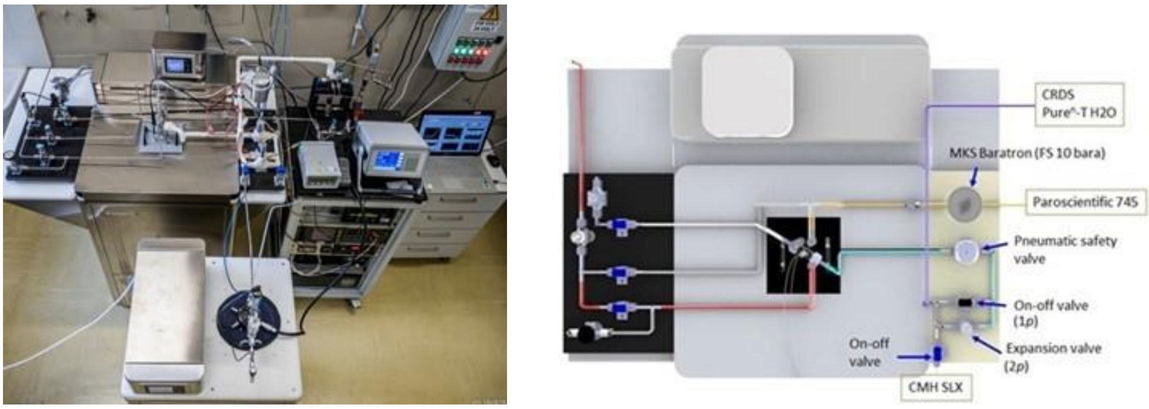


Figure 8: (Left) Calibration set-up of INRIM 03 Mk2 connected to a CMH and a CRDS analyser; (Right) Top view of the trace water generator manifold for 1-P and 2-P operation.

Figure 9 shows an example of performance validation of the trace humidity generator with a series of measurements carried out in the frost-point temperature range from -105 °C to -75 °C (mole fraction from 5 nmol·mol^{-1} to 1 µmol·mol^{-1}) at two different saturation pressures. The relative percent difference between the water vapour mole fraction x_w as measured by the CRDS analyser and the reference (theoretical) value is plotted as a function of the nominal frost-point temperature/water vapour mole fraction of the gas. The carrier gases are nitrogen in panel a) and argon in panel b).

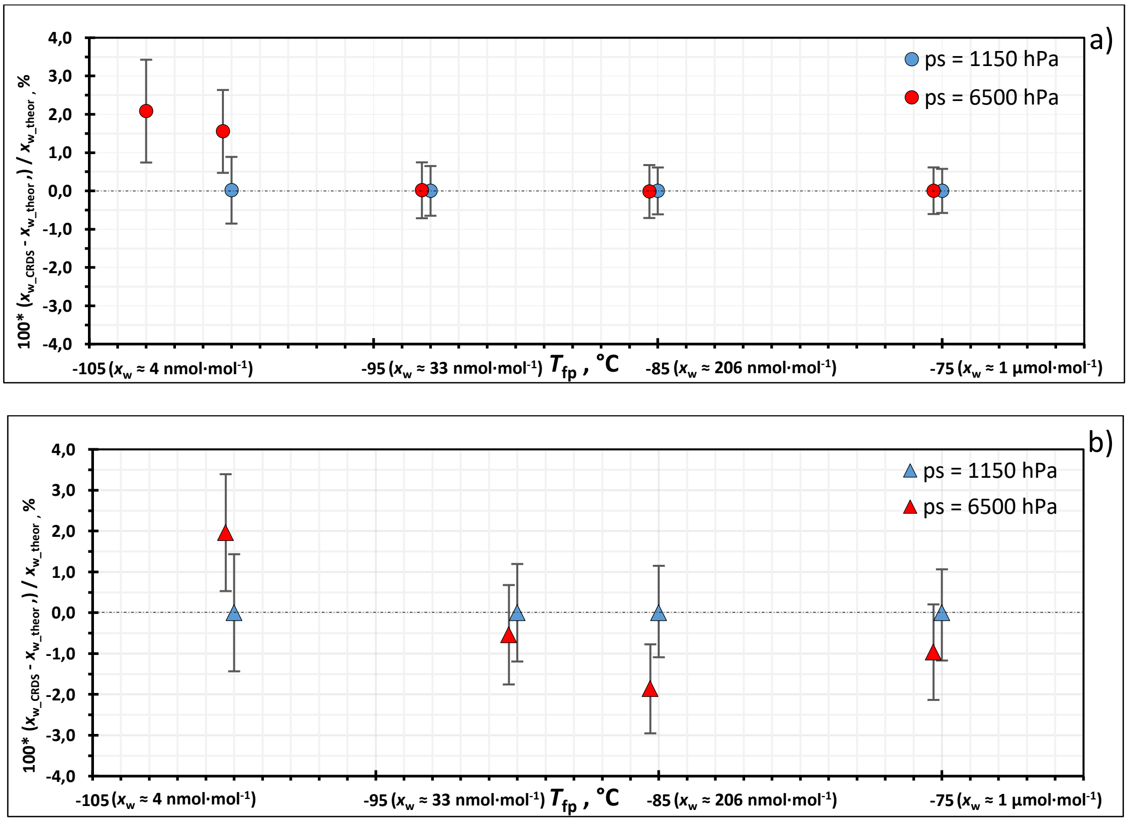


Figure 9: Relative percentage difference between the water vapour mole fraction measured by the CRDS analyser and its reference (theoretical) value, at two pressures (the lowest saturation pressure and 0.65 MPa) at the given nominal frost-point temperatures. The gas mixtures are N_2-H_2O in panel a) and Ar-H_2O in panel b).

VTT has extended the working range of its Low Frost Point Humidity Generator (LFPHG) down to -100 °C in terms of frost point temperature and up to 0.7 MPa in pressure. The system operates as a 1T-2P condensed base humidity generator (the previous version operated in 1T-1P mode) and generates humid gases like Air, Ar, and N_2. The combined standard uncertainty of the generated frost point temperature at -100 °C, atmospheric pressure, is 0.04 °C.

The working principle of the generator is described in the schematic diagram presented in Figure 10 (left panel) while the actual instrument is illustrated in Figure 10 (right panel). Figure 11 shows some examples of recorded data at -94 °C.

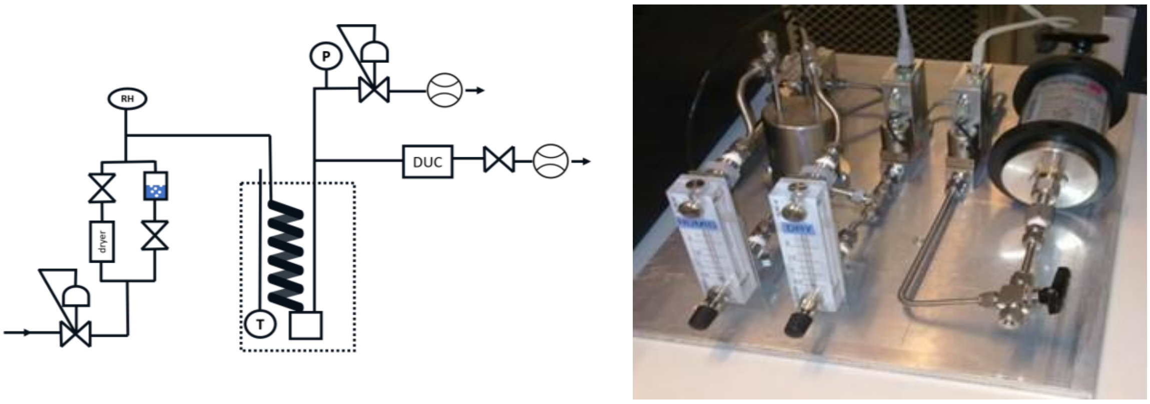


Figure 10: Schematic of the VTT two-pressure low-temperature frost point generator (left panel), where T is the SPRT, P the pressure gauge, and DUC the device under calibration. Picture of the 2-flow mixing pre-saturator (right panel).

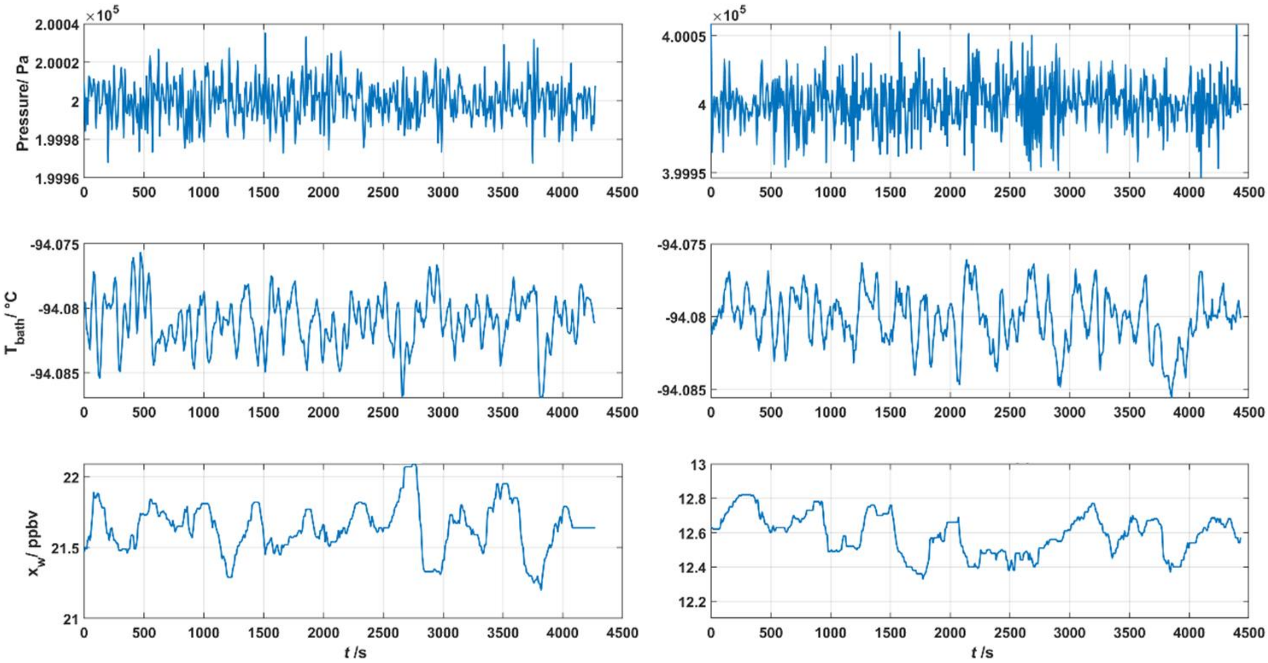


Figure 11: Example of recorded data at saturation pressure at T_{fp} = -94 °C, P_{sat} = 0.2 MPa, and P_{sat} = 0.4 MPa.

CMI has developed a saturated-based humidity generator able to work at temperature down to -90 °C at different pressure values up to 15 MPa with different carrier gas (Air, Ar, and N_2). The system can be operated in four different configurations: 1P-1T mode (working mode of the primary humidity generator), 1P-2T, 2P-1T and 2P-2T mode when used as a secondary generator. The combined standard uncertainty of the generated frost point temperature at -60 °C, 200 kPa, in N_2 is 0.08 °C.

A demonstration of the generator operation and connections during the measurement is shown in Figure 12.

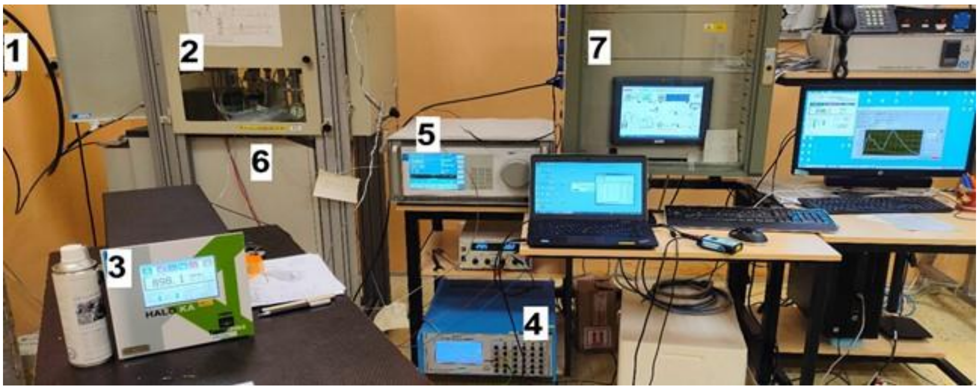


Figure 12: Set of instruments used in the operation of the CMI humidity generator.

UL has upgraded its ultra-low frost-point generator from a 1T-1P to a 1T-2P system. The new saturator withstands pressures above 1 MPa and achieves temperature down to -95 °C when operated as 1T-1P system, while a frost-point temperature below -100 °C is reached when used as a two-pressure system. Different humid gases like N_2 and Ar can be generated. The frost point temperature at -30 °C and -90 °C is generated with a combined standard uncertainty of about 0.02 °C and 0.10 °C, respectively.

Figure 13 (right panel) shows the upgraded UL-FE/LMK low frost-point generator that withstands pressures up to 1 MPa, while Figure 13 (left panel) shows the schematic diagram of the generator.

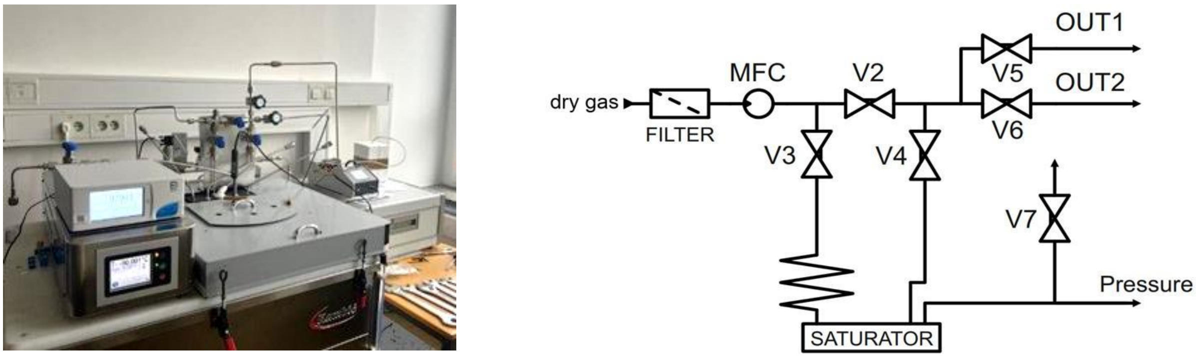


Figure 13: The new generator that withstands pressures up to 1 MPa (left panel) and the schematic diagram of the UL-FE/LMK low frost-point generator (right panel).

Coulometric–based trace water generator

PTB progressed with the downward range extension of a Coulometric trace water generator (CTWG). Operating on the coulometric principle, it precisely generates amount fractions of water traceable to the SI by current. The generator provides amount fractions of water vapour in the range of 5 nmol/mol to 600 µmol/mol in nitrogen and potentially argon at 1000 – 1400 hPa. With a flow between 1 – 5 L/min, it can provide reference gas to multiple devices, rendering it optimal for the project.

In general, the CTWG produces a known amount of humidity in a side stream (2) and mixes it with a matrix stream (1) in an additive process (Figure 14). The matrix gas nitrogen was dried by a combination of absorption cartridges and a getter device to dry the zero gas to a level below 1 nmol/mol. A combination of two critical orifices ensures constant split into a matrix gas stream (1) and a side stream (2). The humidification of the side stream is achieved by the dissociation of water to hydrogen and oxygen by an aqueous electrolyser and the catalytic recombination. The cooling trap ensures the condensation of extent water which was taken up in the aqueous electrolyser.

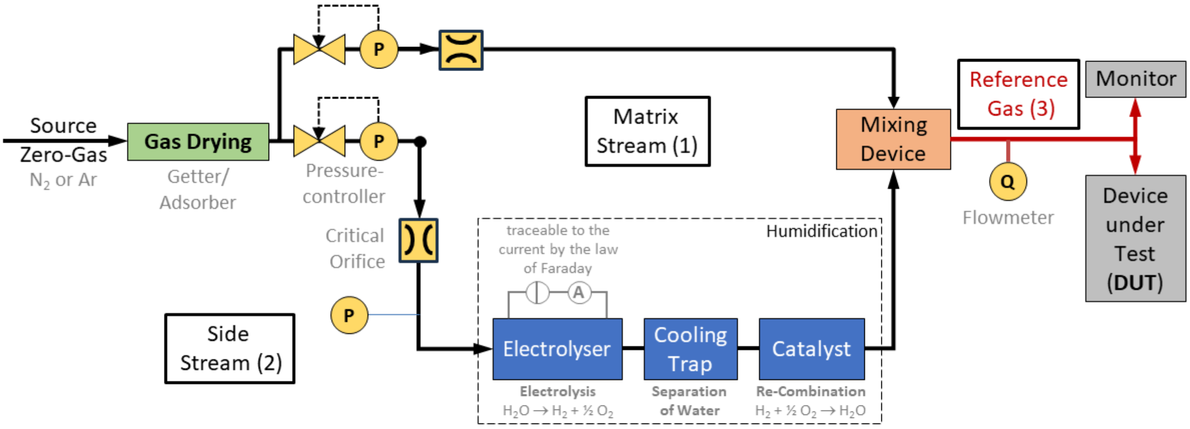


Figure 14: Schematic of the PTB Coulometric Trace Water Generator (CTWG).

The final trace water concentration is obtained by recombination of the streams (1), (2) in a mixing device. The mixing ratio r of the reference gas is calculated according to Faraday's law:

$$r = \frac{m_{\mathrm{V}}}{m_{\mathrm{N_2}}} = \frac{M_{\mathrm{V}}}{M_{\mathrm{N_2}}} \frac{V_0}{z\,F} \frac{I}{\dot{V}} \eta_{\mathrm{all}}$$

Herein, m_{V} and $m_{\mathrm{N_2}}$ are the masses of the water and nitrogen, I is the current of the electrolysis cell, $\dot{V}$ is the flow rate of the reference gas at 0 °C and 1013.25 hPa, F is the Faraday's constant, $z = 2$ is the amount of transferred charges, M_{V} and $M_{\mathrm{N_2}}$ are the molar masses of water and nitrogen, and V_0 represents the molar volume of the ideal gas. The efficiency of the main steps is summarised in the factor η_{all} which is given as a product of the efficiencies of the single steps: electrolyser η_{EC}, cooling trap η_{CT} and catalyser η_{Cat} as follows:

$$\eta_{\mathrm{all}} = \eta_{\mathrm{EC}} \cdot \eta_{\mathrm{CT}} \cdot \eta_{\mathrm{Cat}}$$

The flow rate of the reference gas is determined by a calibrated mass flow meter. The amount fraction of water x_{w} is then calculated by:

$$x_{\mathrm{w}} = \frac{r}{\frac{M_{\mathrm{V}}}{M_{\mathrm{N_2}}} + r} + blank\ value$$

Permeation-based humidity generator

VSL upgraded its permeation-based humidity generator based on a magnetic suspension balance. The system can operate in a pressure range from 1 $\mathrm{bar_a}$ to 1.3 $\mathrm{bar_a}$ (glass chamber) and 1 $\mathrm{bar_a}$ to 3 $\mathrm{bar_a}$ (metal chamber) with various gases such as air, nitrogen, but also energy gases such as hydrogen or methane. The permeation method is based on the constant transfer of a specific substance from a permeation device, often referred to as a *permeator*, to the surrounding environment or a downstream collection system. This transfer results in a continuous loss of mass, which is constantly monitored.

Permeation-based generators rely on the fundamental process of diffusion, which is the movement of molecules from an area of higher concentration to an area of lower concentration. Fick's First Law of diffusion describes the rate of diffusion (*J*) across a surface area (*A*) through a material with a given concentration gradient ($\Delta C/\Delta x$) and diffusion coefficient (*D*). It can be expressed as:

$$J = -D \cdot \frac{\Delta C}{\Delta x} \cdot A$$

This law essentially tells that the diffusion flux is directly proportional to the concentration gradient and the diffusion coefficient. It describes how quickly a substance diffuses through a material. Fick's Second Law describes how the concentration of a diffusing substance changes over time ($\partial C/\partial t$) in a material. It can be expressed as:

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2}$$

This law tells us that the rate of change in concentration at a point is proportional to the second derivative of the concentration profile with respect to distance. It describes how the concentration of a substance spreads out over time in a given medium. For each substance k, the amount fraction y_k, can be calculated as:

$$y_k = \frac{\frac{m_1}{M_1} \times x_{1k}}{\frac{m_1}{M_1} + \frac{m_2}{M_2}}$$

where
m_1 , representing the mass flow rate from the permeation tube;
m_2, signifying the mass flow rate measured by the thermal mass flow controller;
M_1 and M_2 stand for the molar masses of the parent gases
x_{1k}, denotes the amount fraction of the calibration component in parent gas 1 (originating from the permeation tube).

Permeation devices are positioned within a permeation chamber, which maintains precise control over temperature and pressure, and is continually flushed with a carrier gas stream. To determine mass loss, the permeator is placed within the magnetic suspension balance (MSB). The experimental setup used in this work is shown schematically in Figure 15. The VSL permeation system consists of a metal magnetic suspension coupling and a glass permeation chamber from TA Instruments, Germany, paired with a Sartorius Balance with 10 µg balance resolution and a 60 g measuring load.

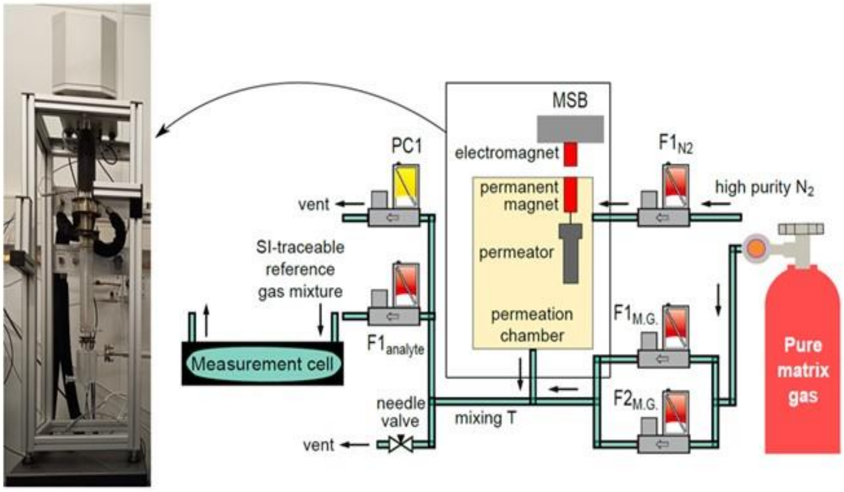


Figure 15: Diagram of the permeation system of VSL. For the pure matrix gas, gases like CH_4 or H_2 from cylinders have been used with this facility but here only purified nitrogen was used (from evaporated liquid nitrogen).

An example of water permeation rates determined by continuously monitoring the weight loss of the tube over a period of approximately 16 hours is shown in Figure 16 (left panel), while an example of comparison of the amount fraction of H_2O as determined by the magnetic suspension balance measurements and a CRDS analyser is shown in Figure 16 (right panel). A satisfactory agreement was found between the measurements.

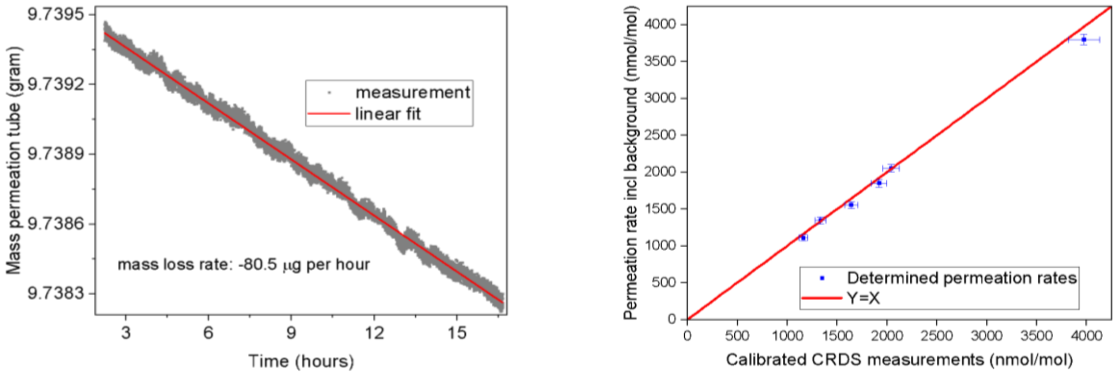


Figure 16: Example of a mass loss rate measurement from a H_2O permeation tube in a glass chamber (left panel). Comparison between the water vapour amount fractions determined by the MSB and by a CRDS analyser (right panel).

Summary of key results

A European-wide infrastructure capable of providing a robust metrological traceability to trace water measurements in ultra-high purity process gases, specifically nitrogen, argon, air and hydrogen has been set up and is now in place to serve the industry and other relevant stakeholders. Primary standards based on different principles are now available to provide measurement traceability in an envelope of temperatures, mole fractions and pressures that encompasses a range of water vapour amount fraction from approximately 4 $\text{nmol}\cdot\text{mol}^{-1}$ to 1 $\text{mmol}\cdot\text{mol}^{-1}$ with measurement uncertainties between 2.3 % and 0.4 % and frost-point temperature from -105 °C to -20 °C with measurement uncertainties between 0.07 °C and 0.03 °C. These primary standards encompass an operating pressure range from 0.1 MPa to 6 MPa. These results meet and largely exceed the PROMETH2O project targets. The objective was successfully achieved.

Objective 3: Improvement of thermophysical data knowledge of non-ideal humid gas mixtures

Enhancement factor for gases such as N_2, H_2 and Ar are not available in the literature in the trace water measurement range. To fill the gap, the project undertook this effort by designing a series of experiments to gather new accurate data at temperatures between -90 °C and -30 °C and at selected pressures from 0.1 MPa to above 1 MPa and worked to develop a theoretical framework and a new class of correlation equations for the water vapour enhancement factors in the such gas matrices.

The experimental work set up concurrent experiments for the measurement of the enhancement factor in N_2, Ar and H_2 at selected temperatures and pressures. Three primary humidity generators were either range-extended or improved to encompass the whole measurement conditions in selected gas matrices. Those generators from CMI, VSL and UL were already described in previous sections. Two microwave-based trace water analysers operating up to 1 MPa were designed and commissioned by LNE-CNAM and UVa, respectively. The LNE-CNAM microwave-based trace water analyser was fully characterised and operated up to 0.2 MPa and at saturation temperatures between -30 °C and -60 °C, initially with air and argon matrix gases. The UVa gold-plated, quasi-spherical microwave resonator (QSMWR) hygrometer was designed, constructed, and tested to cover the whole project pressure range up to 2 MPa.

The theoretical studies, mainly from VTT and INRIM, included the use of the Helmholtz equations, *ab initio* calculations and integration over the Lennard-Jones potential and Stockmayer potential force fields to calculate the water vapour enhancement factor. Building upon these theoretical foundations, the work harnessed vast datasets to derive optimal functional equations, unveiling a novel approach to formulating the water vapour enhancement factor. The extensive experimental efforts under the PROMETH2O project, and beyond, have enabled the cross-validation and refinement of those models to fine-tune the equation coefficients.

Finally, to make such powerful calculation tools readily available, a web-based application for the estimation of the enhancement factor and corresponding uncertainty in the temperature and pressure ranges of interest was developed by UNICAS in cooperation with VTT. The web-app tool developed for computer is freely available to users and industrial stakeholders and can be easily accessed from the PROMETH2O web site (www.prometh2o.eu).

Theoretical foundation of novel water vapour enhancement factor equations

The water vapour enhancement factor is widely regarded as one of the most crucial properties of gaseous mixtures and is set to become vital in converting the humidity parameters. In many cases, the primary humidity generators are based on the saturation of a gas stream over the pool of liquid or solid water. In contrast, the operation of the device under calibration may rely on the water vapour partial pressure, e.g., amount-fraction and dew/frost point temperature detectors.

The water vapour enhancement factor considers the deviation of the water vapour partial pressure in the presence of a carrier gas mainly due to the force field changes and plays a crucial role in humidity metrology for its inevitable importance in converting humidity parameters. Denoting by e the saturation vapour pressure of pure water and by e' the water vapour partial pressure of saturated moist gas, the enhancement factor, f, is defined as the ratio of the saturation vapor pressure of moist gas, to that of pure water vapour, according to the following equation:

$$f = \frac{e'}{e} = \frac{x_\mathrm{w} \cdot P}{e}$$

where the quantity e' can also be expressed as the product between the water vapour mole fraction, x_w, and the gas total pressure, P.

Previous works have focused on experiments that simultaneously derive the dew point temperature and water mole fraction to single out the water vapour enhancement factor into the desired temperature and pressure range but have failed to address the theoretical basis to establish new numerical estimations. The work carried out, mainly by VTT and partly by INRIM, addressed the numerical implementation of different approaches to estimate the water vapour enhancement factor as well as a new functional equation for metrological applications. It followed two independent pathways. In the first method, the virial coefficients of the air-water vapour gas mixture equation of state was rewritten in terms of a series of sub-enhancement factors (from f_1 to f_{15}), resulting in an overall enhancement factor having the following form:

$$f = \prod_{I=1}^{15} f_i$$

In the second method, the Thermodynamic Equation of Seawater-2010 (known as TEOS-10) was used to determine the properties of the air-water equilibrium conditions. By proper use of thermodynamic functions, the water vapour enhancement factor was estimated in a two-step process: *i*) the mole fraction is converted into the specific humidity, *ii*) from the specific humidity and the total pressure, the dew-point temperature is estimated. Then, the water vapour saturation pressure was calculated by employing the water vapour pressure curves to eventually get the enhancement factor from the equation:

$$f(P, T_\mathrm{DP}) = \frac{x_\mathrm{w} \cdot P}{e_\mathrm{ws}(T_\mathrm{DP})}$$

where x_w is the water vapour mole fraction, P is the total pressure, e_ws the water vapour saturation partial pressure of the pure phase, and T_DP the dew/frost point temperature.

Although the methods, at first sight, may look complex, they proved to be very useful in deriving the enhancement factors in a wide range of temperature, pressure and gas matrices and build a large dataset useful for further data driven methodologies. An example of their application is depicted in Figures 17 where the water vapour enhancement factor for humid N_2 as a function of temperature and pressure was estimated and plotted, based on first and second method, respectively.

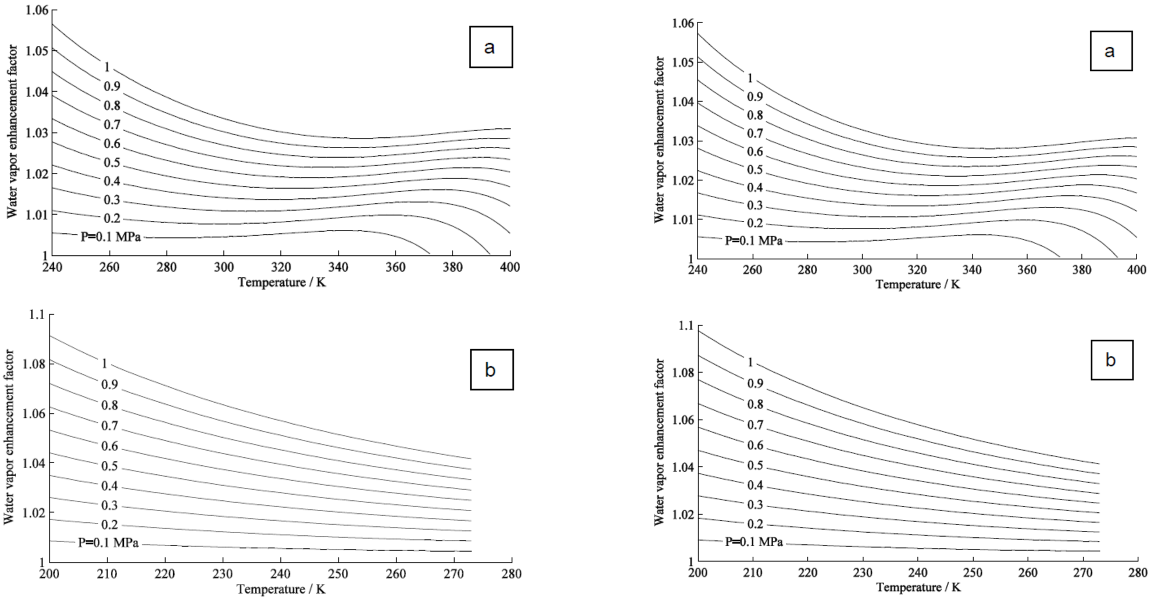


Figure 17: The water vapor enhancement factor for humid nitrogen as a function of temperature and pressure based on the first method (left panel) and the second method (right panel). a) for equilibrium over a planar pool of liquid water; b) for equilibrium over a planar ice layer.

A universal functional equation for water vapour enhancement factor

A key result of the project was the introduction of a universal functional equation based on two factors that solely depend on the water vapour mole fraction. The equation is given by:

$$f = \exp\left[(1-x)\cdot F_1(x)\cdot P^{F_P(x)}\right]$$

$F_1(x)$ is named as atmospheric factor and varies significantly by changing the carrier gas, however, $F_P(x)$ named as the pressure factor can be considered an universal value for non-polar gasses within the uncertainty of the current knowledge of the enhancement factor.

For decades, the Greenspan's equation has served as the cornerstone in both academic and industrial applications, offering the most reliable equation for predicting the behaviour of water vapour enhancement factor in humid air. However, the limitations of Greenspan's approach become evident particularly when faced with the gas matrices other than air and in the extreme cases. Building upon the meticulous calculations summarised above, the project introduced this novel methodology that diverges from traditional practices. This new approach, anchored in rigorous data-driven techniques, marked a significant departure from the past.

Novel experiments with improved measurements and extended datasets

The water vapour enhancement factor, f, empirically expresses the non-ideality of a mixture, knowledge of which is required for the conversion from frost-point temperature to water vapour amount fraction and vice versa. For that reason, f can be evaluated by means of different cross-domain experiments, such as i) the generation of a humid gas mixture with a specific frost point temperature (by saturator-based generator) and measurement of the water vapor mole fraction by an amount-of-substance fraction analyser; ii) the generation of a humid gas mixture with a specific water amount fraction (e.g. by coulometric generators) and measurement of the corresponding frost-point temperature, as measured by thermodynamic-based instruments.

To cover the wide range of temperature and pressure targeted by the project, a combination of humidity standards and analytical methods for trace humidity measurements were identified and exploited by the partners.

VSL exploited its primary humidity standard, the High Pressure Dewpoint Generator (HPDG), for the dew/frost-point temperature range of +20 °C to -80 °C up to 1 MPa both in argon and nitrogen. Briefly, a dew/frost point is realised in the saturator at a certain temperature at an elevated pressure and subsequently expanded to atmospheric pressure. UL upgraded its existing primary frost-point generator to withstand and control pressure up to 1 MPa to carry out the experiments for the enhancement factor at frost points down to -90 °C for both N_2 and Ar. INRIM performed supplementary experiments to further expand the measurement range. The saturation temperature has been varied from -97 °C to -52 °C and the saturation pressure from 1600 hPa to 6500 hPa to cover the frost-point temperature range between -105 °C and -65 °C. Figure 18 shows the VSL set up used in such experiments.

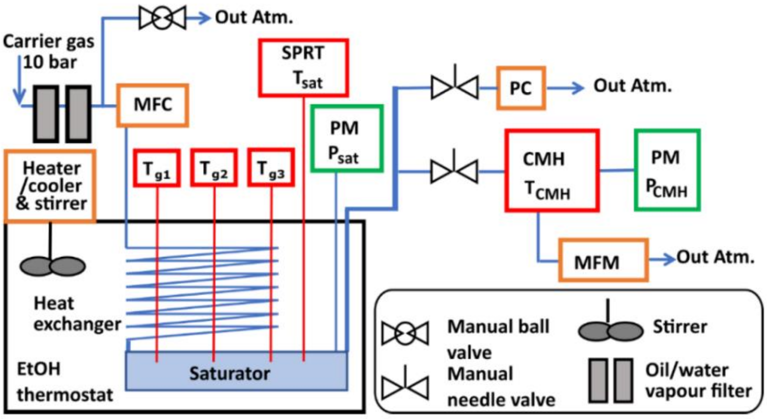


Figure 18: Schematic representation of the primary humidity standard used at VSL for the water vapour enhancement factor experiments.

The dew/frost point of the humid gas at atmospheric pressure is measured using a calibrated chilled mirror hygrometer, therefore the VSL, UL and INRIM data were actually used to calculate an enhancement factor ratio as follows:

$$f^* = \frac{f\left(T_\mathrm{d}^\mathrm{sat}, p^\mathrm{sat}\right)}{f\left(T_\mathrm{d}^\mathrm{CMH}, p^\mathrm{CMH}\right)} = \frac{e_\mathrm{w}\left(T_\mathrm{d}^\mathrm{CMH}\right)}{e_\mathrm{w}\left(T_\mathrm{d}^\mathrm{sat}\right)} \cdot \frac{p^\mathrm{sat}}{p^\mathrm{CMH}}$$

CMI exploited its saturation-based humidity generator developed for the determination of f in nitrogen and argon in the dew/frost-point temperature range of -80 °C to -60 °C up to 0.8 MPa. A chilled mirror hygrometer and a CRDS analyser were both used in these experiments, enabling direct measurement of f. Further, PTB exploited its Coulometric Trace-water Generator (CTWG) to perform focused experiments at specific mixing ratios in nitrogen in order to independently confirm the experimental data.

UVa, in collaboration with INTA, carried out measurements of water vapour enhancement factors in nitrogen and hydrogen at frost point temperatures between -38 °C and -15 °C, and at pressures between 0.1 MPa and 0.5 MPa, using its quasi-spherical microwave resonator (QSR) and a calibrated dew-point hygrometer. Furthermore, CEM, in collaboration with VSL, prepared static pressurised humid gas mixtures in matrices of hydrogen in cylinders to support the development and validation of microwave-based hygrometers. The QSR is used by first determining the permittivity of a gas mixture then, once the gas polarisability is known, to determine the mole fraction as:

$$\varepsilon_\mathrm{mix}(p,T) = \varepsilon_\mathrm{dry}(p,T)\left(\frac{f_\mathrm{dry}(p,T)}{f_\mathrm{mix}(p,T)}\right)^2 \qquad x_\mathrm{w} = \frac{\left(\frac{\varepsilon_\mathrm{mix}-1}{\varepsilon_\mathrm{mix}+2}\frac{\varepsilon_\mathrm{dry}+2}{\varepsilon_\mathrm{dry}-1}\right)-1}{\frac{\wp_\mathrm{w}}{\wp_\mathrm{dry}}-1}$$

A schematic of the UVa experiment exploiting the QSR is depicted in Figure 19.

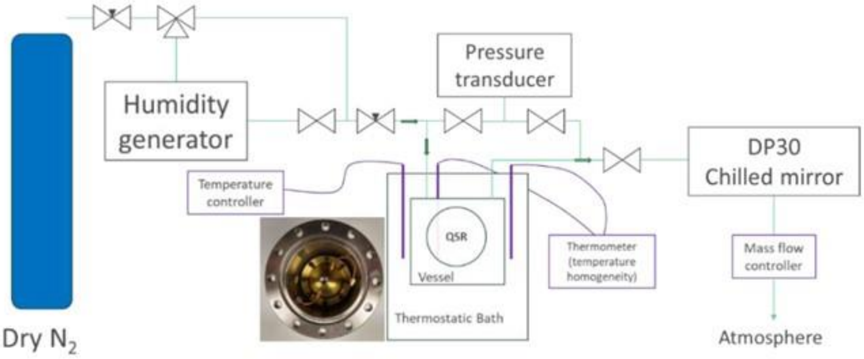


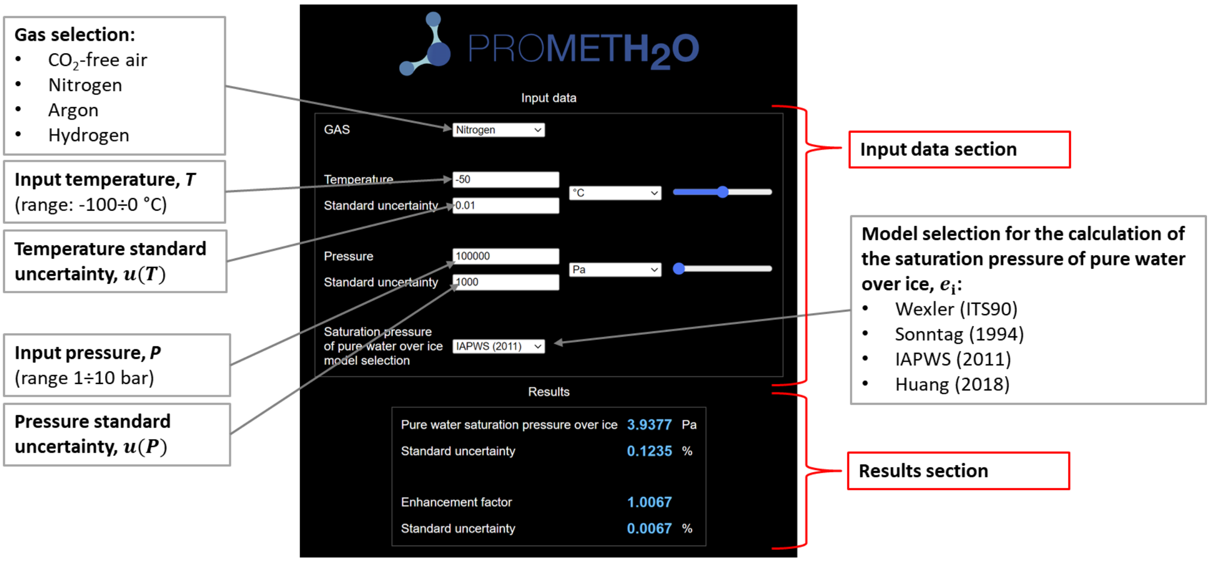
Figure 19: Experimental setup used for the measurement of the enhancement factor at UVa in cooperation with INTA and CEM.

Finally, thanks to a fruitful cooperation across different EMPIR projects, NPL made available its experimental work on moist hydrogen performed under the auspices of the 19ENG03 MefHySto project. Such data were useful to confirm the correlation equation developed for moist hydrogen at elevated pressure.

All such novel and improved experiments made available extended datasets crucial for the validation of the methodologies in a metrologically-sound manner and provided the coefficients for functional equations of the water vapour enhancement factor, highlighting the process of data fusion and cross-validation of the experiments with theoretical studies.

Web-based application tool

To make such powerful calculation tools readily available, a web-based application was developed by UNICAS in cooperation with VTT. The user interface of the web app is available in Figure 20. The tool calculates the saturation pressure of pure water vapour over ice, the enhancement factor and the corresponding uncertainties for CO2-free air, nitrogen, argon and hydrogen, as a function of temperature and pressure, in the temperature range from −100 °C to 0 °C and the pressure range from 0.1 MPa to 1 MPa.



Input data

GAS: Nitrogen
Temperature: -50 °C
Standard uncertainty: 0.01
Pressure: 100000 Pa
Standard uncertainty: 1000
Saturation pressure of pure water over ice model selection: IAPWS (2011)

Results

Pure water saturation pressure over ice: 3.9377 Pa
Standard uncertainty: 0.1235 %
Enhancement factor: 1.0067
Standard uncertainty: 0.0067 %

Figure 20: Graphical explanation of the web app user interface.

The app contains two main sections: an input data section and a results section.

In the input section, the user can insert the carrier gas pressure and temperature in different measurement units (°C or K for temperature, bar or Pa for pressure). Alongside with input temperature and pressure, user can provide input standard uncertainties $u(T)$ and $u(P)$, respectively.

In the result section, the pure water vapour saturation pressure over ice and the enhancement factor are estimated, together with their uncertainties.

The PROMETH2O web application can be reached at the address: https://www.prometh2o.unicas.it/

Summary of key results

The project achieved new accurate data of the enhancement factor in humid gases in the trace water range at temperatures between -90 °C and -30 °C and at selected pressures from 0.1 MPa to 1 MPa and above with an extensive experimental effort to provide large datasets and enable the cross-validation and refinement of theoretical models.

The project developed a theoretical framework and new class of correlation equations for the water vapour enhancement factors in gas matrices such as N_2, H_2 and Ar. Building upon theoretical foundations, the work harnessed vast datasets to derive optimal functional equations, unveiling a novel approach to formulating the water vapour enhancement factor.

Finally, to make such powerful calculation tools readily available, a web-based application for the estimation of the enhancement factor and corresponding uncertainty in the temperature and pressure ranges of interest was developed and made available to users and stakeholders via the PROMETH2O web site. The objective was successfully achieved.

Objective 4: Demonstration of improved methods for trace water measurement in industrially-relevant facilities

Improved trace water measurement methods and techniques were demonstrated at selected industrial facilities. The facilities were chosen to validate the measurement technology and standards, establish good practices and maximise the impact of the developed methodology.

Test beds preparation involved a careful review of the technical and safety aspects with the test-bed hosts to ensure smooth operations and successful field experiments in a potentially harsh environment (i.e. industrial manufacturing premises with uncontrolled ambient temperature and electromagnetic interferences).

Test Bed 1, traceable measurements in the Qrometric Ltd. calibration laboratory associated with the production facility that manufactures the world’s first portable frost point generator (FPG) were successfully demonstrated. Qrometric is a UK metrology company specialising in product and system innovation. The company focuses on the generation and measurement of temperature and humidity conditions and the calibration of associated instruments. The FPG (Figure 21) is a new conceptually innovative product, which can generate precisely controlled dew/frost point conditions that can be used for calibrating dew point sensors and most types of hygrometers, from ambient dew point conditions to frost point temperatures as low as -100°C

Figure 21: The Qrometric Frost Point Generator (FPG) and the PI/MBW SLX chilled mirror hygrometer calibrated at INRIM and used for its initial validation.

The FPG was initially validated at INRIM to demonstrate the fundamental nature of the FPG generation technique and shows that measurement traceability can be made directly via calibration of its external platinum resistance thermometer (PRT). When used with a calibrated pressure sensor, this measurement combined with the FPG saturator temperature may be employed to provide humidity reference values in terms of dew/frost point or mole fraction.

Once validated, several field demonstrations were performed. Qrometric hosted two events at their premises in Brighton, UK, in cooperation with DTU, UL, VSL and Vaisala. There were also public demonstrations at the PROMETH2O Workshop at Gas Analysis in Paris and at Nippon Gases facilities in Italy (Figure 22).

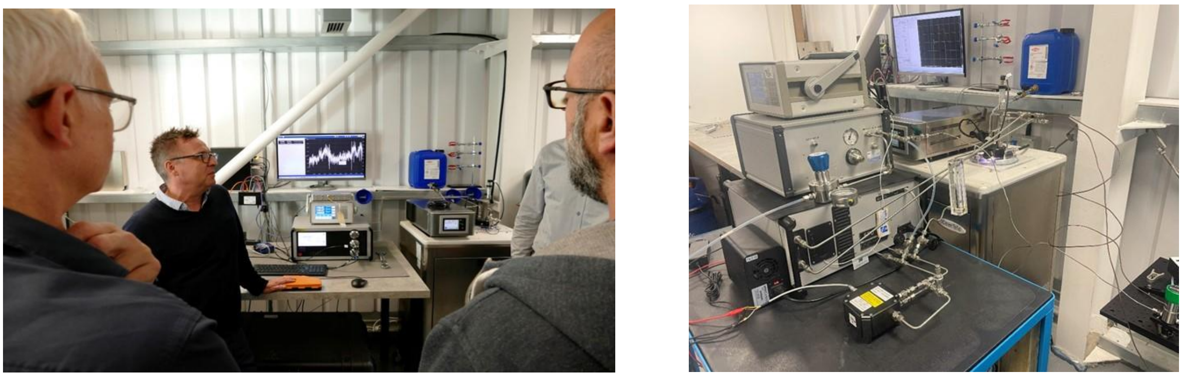


Figure 22: Discussion between the project partners Qrometric, UL and Vaisala on the running experiments (left). Experimental FPG set up at high pressure for testing with the DTU Far UV analyser (right).

Validation of standard-production FPGs performed by various different parties suggested that it can be used as a fast, accurate frost point reference generator down to trace conditions (10 ppb) and that can be relied upon by industry to perform both in situ and lab-based calibrations of trace water vapour instrumentation traceable to national standards.

In the demonstration at Qrometric, a large set of experimental data were gathered with both standard-production and high-pressure prototype FPGs in a relatively short period of time. Above ambient pressure, matrix gases other than air were tested in the prototype instrument. The demonstration resulted in a number of new insights. The lesson learned is that it is vital to maintain a closed loop with good pressure integrity; the FPG can compensate for small leaks, but any leaks local to test instrumentation may have an adverse effect on measurements. When using external chilled mirror test or reference instrumentation, or instruments that require long lengths of sample pipe, sufficient time must be allowed for the whole measurement system to reach equilibrium. This can be a surprisingly long time, sometimes days. Shorter timeframes need to be accounted for in any uncertainty calculation.

In Test Bed 2, traceable optical and thermodynamic water vapour measurements in the amount fraction range from 5 ppm to 5 ppb in a Nippon Gases production facility in Chivasso, Italy, of bulk and specialty gases were demonstrated, and the different measuring technologies compared and contrasted. Nippon Gases Italia Group is one of the leading companies in the industrial gas sector in Italy, and is a member of the Nippon Gases Europe and Nippon Sanso Holding Corporation. It produces, markets and distributes cryogenic, technical, medical, refrigerant, pure and specialty gases. Besides its core products, Nippon Gases Italia Group supplies services, materials, equipment and plants for gas users.

The Nippon Gases Chivasso plant is under the Seveso Directive (Directive 2012/18/EU) and, consequently, safety is the primary goal during all kinds of operation. To consider every possible risk related to the Test Bed demonstration, Nippon Gases HSE department analysed all possible interferences through a thorough analysis and shared the outcomes among the test bed participants.

Because of the restricted access to many production areas, tests were carried out on the sampling lines delivering the gas to the on-site laboratory that is performing calibration of gas mixtures according to UNI CEI EN ISO/IEC 17025; quality control and raw material acceptance analysis; purity control of pure gases (according to the specifications); and calibration of specialty gas mixtures.

This demonstration involved on line traceable measurements of the water vapour concentration in high-purity nitrogen and argon (with less than 0.5 ppm of water) both from gas cylinders up to 20 MPa and from sampling lines up to 0.6 MPa, respectively. A gamut of calibrated instruments was made available by project partners, including a commercial CRDS analyser from Nippon Gases, a set of novel capacitive humidity probes from Vaisala and the prototype far UV analyser from DTU. Figure 23 (left panel) shows a schematic of the experimental set-up with three analytical systems used to analyse the moisture content of high-purity N_2 cylinders. The flow is split, enabling parallel measurements by the three analytical systems. On Figure 23 right panel, measurement of trace water in nitrogen from the cryogenic tank (purity grade 99.9995 %) for a period of about 3 days is shown. It took about 7 hours before the analyser stabilised at around 100 nmol/mol (see inset).

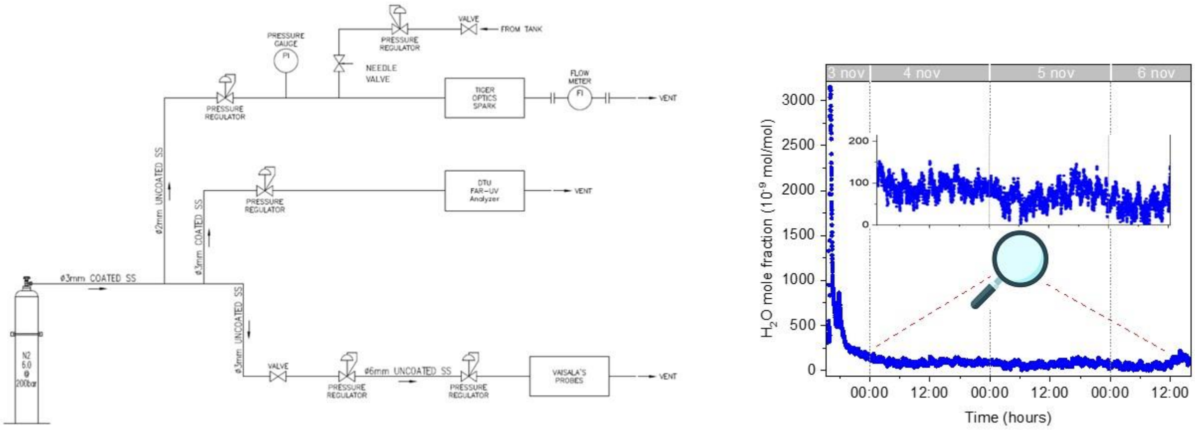


Figure 23: Schematic of the experimental set-up with three analytical systems used to analyse the moisture content of high-purity N_2 cylinders (left panel). Measurement of the moisture content of N_2 using a calibrated CRDS analyser. The inset shows a magnification of the period when the measurement stabilised (right panel).

The demonstration resulted in a number of new insights and lesson learned related to: the use of suitable material, tubing and fittings for the gas connections; the need to accurately control the gas flow and pressure; the need to continuously purge the system with dry gas while minimising any dead volume in the sampling lines; the care took to avoid potential back diffusion and Venturi effect when working at low to medium pressures; the consideration for suitable stabilisation time when measuring humidity at very low amount fractions (ppb level).

Summary of key results

The test bed demonstrations proved to be well-aligned with the stakeholder needs identified in an initial project survey. The demonstration outcomes and lesson learned helped improving and refining the measurement good practices at industrial laboratory and plant levels. The demonstrations targeted nitrogen and argon, the top-ranking priority in the stakeholder’s survey, covered the range of trace humidity levels identified by the stakeholders and, finally, met the needs for having a portable, easy to use reference system, such as the FPG, ready for use within a working day. The objective was successfully achieved.

5 Impact

At the end of the project, a stakeholder Steering Board (SB) had 21 members from international organisations, instrument makers and gas providers. A project website as well as LinkedIn and Research Gate accounts were open. A YouTube interview was released, multiple posts on social media (Facebook and LinkedIn) were published, and two e-newsletters were released (more details here www.prometh2o.eu). The project published five scientific articles and presented results in 26 international and national conferences.

Impact on industrial and other user communities

There was a substantial engagement of the gas industry in the project: companies represented by project partners and stakeholders, members of the project Steering Board, encompass almost 80 % of the European market share. Likewise, most of the European key players in the Process Measurement and Control (PMS) sector were involved both as partners and stakeholders. Such a close-knit cooperation accelerated the development and validation of the first portable FPG with an extended range down to -90 °C. The partner SME is now promoting and demonstrating it among its industrial customers and widened its accredited calibration scope. The results from the project regarding improved, traceable optical analysers for trace water in pure gases were unique at world level. A sound metrological validation of such systems was possible thanks to the concurrent improvement of top-level primary humidity standards, enabling measurement traceability at the part-per-billion level in different gas matrices and pressure regimes. The outcomes of the project were also used in trace water measurements for other industrial applications, such as the gas quality control in the production of hydrogen, natural gas, bio-methane and blends of them. Two training courses were organised for industrial stakeholders to share good measurement practices and perform hand-on training and new calibration services are now available from several NMIs.

Impact on the metrology and scientific communities

The project became a hub in the humidity field for the European and other RMOs NMIs, fostering a stronger co-operation and providing channels for global dissemination. The interaction with the metrology community and the broader scientific community facilitated the integration of the metrology infrastructure in Europe in the challenging trace water measurement sector. Leading NMIs outside Europe (e.g. AIST NMIJ, KRISS) and international organisations (e.g. IAPWS, JCS, CIPM CCT and CCQM) were active members of the Steering Board and helped steering and focusing the project in the most effective way. A project workshop aimed at the scientific and technical communities was organised in conjunction with the Gas Analysis 2024 Symposium in Paris and was quickly sold out with more than fifty attendees.

Impact on relevant standards

The project underpinned the traceability to measuring instruments in the trace water range and enabled testing and calibration laboratories (CABs) in the field to conform to ISO/IEC 17025 (Clause 6.5) and ISO 17034 (Clause 7.9) to grant EA/ILAC accreditation. A project partner granted accreditation for trace water analyser calibration traceable to the primary standards developed in this project. Further impact was made through partners involved in relevant working groups such as the ISO/TC 158 and DIN NA 062-05-73 AA to disseminate the good practice in the area of measurements of water contamination in UHP process gases. Interactions and cooperation with IAPWS supported the effort of a special Task Group set up to study the second virial coefficients $B_{12}(T)$ and the enhancement factor of water-gas mixtures toward preparing an IAPWS guideline and recommended values also based on the project results. Twenty-four events to liaise with the relevant standard developing organisations were put in place.

Longer-term economic, social and environmental impacts

Improved trace water measurements support the sustainability and waste reduction of European strategic sectors, such as the microelectronics industry. EU launched a ‘Chips for Europe’ initiative, which has the objective of supporting technological capacity building and innovation in the Union by bridging the gap between the Union’s advanced research and innovation capabilities and their industrial exploitation. In this context, sustainability is a concern in EU semiconductor fabrication because of the many toxic compounds involved in devices manufacturing. Improved water contamination control in UHP process gases are enabling the enhancement of the fabrication process efficiency, thus allowing for reduced use of toxic chemicals, reduced waste of raw materials, reduced need for re-work and re-processing and higher efficiency. All steps that move towards the EU’s climate goals and ‘Fit for 55’ implementation.

6 List of publications

1. Berg, R.F., Chiodo, N., Georgin, E. (2022) 'Silicone tube humidity generator', *Atmospheric Measurement Techniques*, 15 p. 819-832. Available at https://doi.org/10.5194/amt-15-819-2022
2. Castrillo, A. et al (2023) 'On the 12C2H2 near-infrared spectrum: absolute transition frequencies and an improved spectroscopic network at the kHz accuracy level', *Physical Chemistry Chemical Physics*, 25 p. 23614-23625. Available at https://doi.org/10.1039/D3CP01835K
3. Cuccaro, R. et al (2024) 'Assessment of the INRIM trace water generator and analysis of the uncertainty components down to −100 °C frost-point temperature', *Metrologia*, 61(4) p. 045003. Available at https://doi.org/10.1088/1681-7575/ad53cc

4. Fasci, E, et al (2023) 'Water vapor concentration measurements in high purity gases by means of comb assisted cavity ring down spectroscopy', *Sensors and Actuators A: Physical*, 362 p. 114632. Available at https://doi.org/10.1016/j.sna.2023.114632
5. Fasci, E. et al (2023) 'Comb-assisted cavity ring-down spectroscopy for ultra-sensitive traceable measurements of water vapour in ultra-high purity gases', *Journal of Physics: Conference Series*, 2439 p. 12017. Available at https://doi.org/10.1088/1742-6596/2439/1/012017

The list is also available here: https://www.euramet.org/repository/research-publications-repository-link/