Publishable Summary for 20IND06 PROMETH2O
Metrology for trace water in ultra-pure process gases

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.

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.

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).

Progress beyond the state of the art

The advancement of measurement methods and techniques for trace water vapour is crucial to provide the industry with robust, validated and traceable tools. Sensor performance for different gas species at various pressures and over time remains challenging for many applications. To overcome these issues, the project went beyond the state of the art by developing and improving fast-responding optically based methods in the amount fraction range between 5 parts in 10^6 (5 ppm) and 5 parts in 10^9 (5 ppb) and reaching a world-record water vapour detection sensitivity of 9 ppt.

Primary standards for trace water vapour in pure gases, utilising a variety of generation techniques, are required to extend the lower limit for humidity traceability in Europe and to better serve the key traceability needs of the gas industry. The project went beyond state of the art by developing - first in Europe and among the few in the world - primary standards to generate frost-point temperatures down to -105 °C and amount fraction of water vapour down to 5 $nmol \cdot mol^{-1}$ (ppb).

The conversion from frost-point temperature to water vapour amount fraction and vice versa requires knowledge of the water vapour enhancement factors. The enhancement factor is known for air down to -50 °C and 2 MPa with uncertainty up to 0.7 %, but often extrapolated down to -100 °C without metrologically-sound data and thus not traceable to SI. The project went beyond state of the art by designing new experiments, achieving new data at temperatures between -90 °C and -30 °C and at selected pressures up to 1 MPa and developing a novel, validated, functional equation for the water vapour enhancement factor.

The uptake of measurement technology by the industry requires proven solutions with a high degree of adaptability in diverse scenarios. The project went beyond state of the art by delivering a toolkit of metrological solutions such as improved standards, range-extended measurement capabilities and validated portable reference systems to provide robust measurement traceability to process gases producers and end-users.

Results

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, advanced high-resolution comb-calibrated frequency-stabilised cavity ring-down spectroscopy (CC-FS-CRDS) and refined Fourier-transform infrared (FTIR) spectroscopy. Part of the work was focused on the characterisation and validation of a novel chilled-mirror hygrometers for the first time down to -100 °C frost point to assess their suitability as transfer standards for future international comparisons in the low frost-point temperature scale.

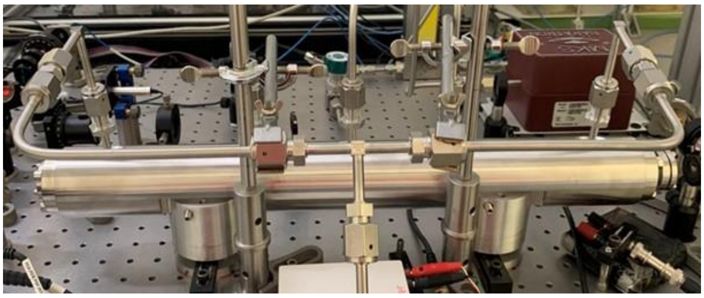

Figure 1. Ring-down cavity with high-reflectivity mirrors and metal-gasket feedthroughs developed by SUN in cooperation with INRIM.

Several improvements such as compactness and lowest detection limit were implemented on a 2nd generation CC-FS-CRDS. A complete metrological characterisation of the system demonstrated a measurement uncertainty between 0.5 % and 2.8 % in the range from 10 ppb to 10 ppm and a world-record sensitivity for water vapour detection: a limit of detection for H_2O in N_2 of nine parts per trillion (9 ppt) was achieved. The high-finesse ring-down cavity and spacer are depicted in Figure 1. A far-UV system suitable for trace water measurements in Ar and N_2 was developed. The system, that included a far-UV light source, a compact far-UV spectrometer and a gas cell, was able to operate as on-line analyser both in static and dynamic conditions at pressures up to 10 MPa. The far-UV approach allowed multi-gas component measurements; that is, in addition to H_2O, other impurities such as O_2, N_2, and VOC were measured at the time. The project addressed Fourier Transform Infrared spectroscopy (FTIR) for trace moisture analysis in nitrogen. An upgrade of a high-resolution FTIR spectrometer has been implemented, 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. PROMETH2O also investigated the performance of novel high-quality chilled-mirror hygrometers with an unprecedented accuracy in the frost-point temperature range from -100 °C to -65 °C. 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 (approximately 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.

Development, commissioning and validation of saturation-based trace water generators were finalised and they are able to cover a frost-point temperature range from approximately -20 °C down to -105 °C (the latter is equivalent to an amount fraction of 4 ppb at 0.11 MPa) and operating at pressures up to 15 MPa in N_2 and Ar. These standard humidity generators meet and exceed the expected project target. For example, in one case, the combined standard uncertainty of the frost-point temperature varied 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 ranged from 0.4 % at 5 ppm to 2.3 % at 4 ppb. The downward range extension of a coulometric–based trace water generator (CTWG) was successfully achieved. Operating on the coulometric principle, the system precisely generates amount fractions of water traceable to the SI calculated according to Faraday's law. The CTWG has the capacity to provide amount fractions of water vapour in the range of 5 nmol/mol to 600 µmol/mol in nitrogen and potentially argon. A mixed-flow humidity generator with SI-traceability was developed and characterised. The system can 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 permeation-based humidity generator based on a magnetic suspension balance was developed. The system can operate in a pressure range from 1 bar to 1.3 bar with a glass chamber and from 1 bar to 3 bar with a metal chamber with various gases such as air, nitrogen, but also energy gases such as hydrogen or methane. Permeation-based generators rely on the fundamental process of diffusion, which is the movement of molecules from higher concentration to lower concentration sites according to the Fick's law of diffusions. Example of water permeation rates determined by continuously monitoring the weight loss of the permeation tube over a period of 16 hours is shown in Figure 2.

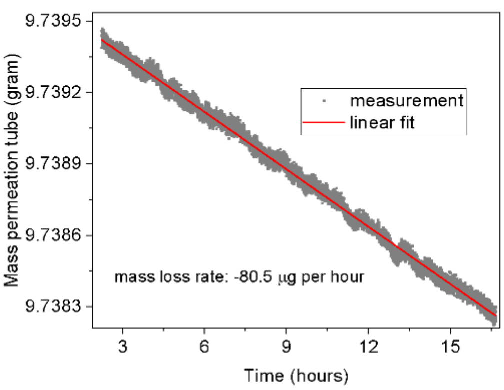

Figure 2. Example of a mass loss rate measurement from a H_2O permeation tube in a glass chamber.

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 and the available capabilities are the first in Europe and among the few in the world. The objective was successfully achieved.

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

Enhancement factor for gases such as N_2, H_2 and Ar were not available in the literature in the trace water measurement range. To fill the gap, the project designed 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. A literature review of water vapour enhancement factor measurements in selected gases has been completed for temperature measurements below -30 °C and the pressures up 1 MPa. The experimental work set up concurrent experiments for the measurement of the enhancement factor at selected temperatures and pressures. Three primary humidity generators were either range-extended or improved to encompass the whole measurement conditions. Two microwave-based hygrometer operating up to 1 MPa were developed for such measurements in air, argon and nitrogen. The theoretical studies were initially based on thermodynamic equations and *ab initio* calculations to estimate the water vapour enhancement factor. Building upon these theoretical foundations, the work harnessed large datasets to derive optimal functional equations, unveiling a novel approach to formulate the water vapour enhancement factor. The extensive experimental efforts under the PROMETH2O project, and beyond, 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. The web-app tool for computer (see Figure 3) is freely available to industrial users and can be easily accessed via the PROMETH2O web site (www.prometh2o.eu). The objective was successfully achieved.

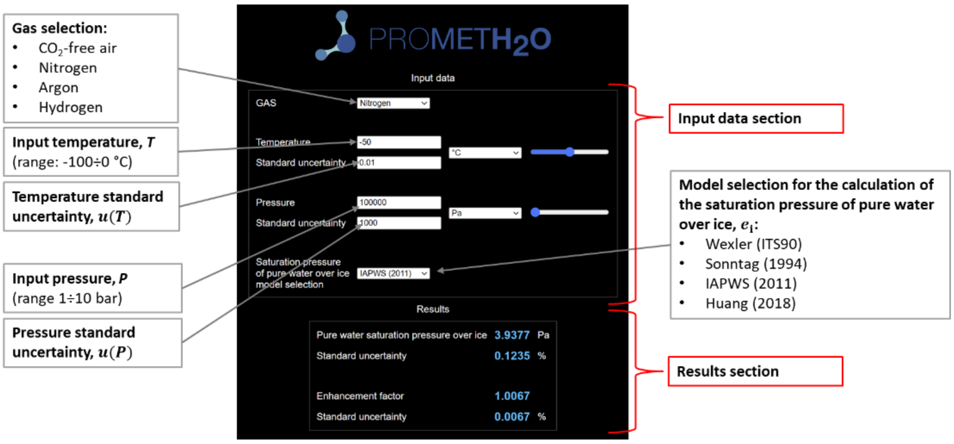

Figure 3. Graphical user interface of the PROMETH2O web application.

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

Improved trace water measurement methods and techniques were demonstrated at two 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 a smooth operation and successful field experiments in potentially harsh industrial environments. Test Bed 1 successfully demonstrated traceable measurements in a calibration laboratory associated with the production facility that was manufacturing the world's first portable frost point generator (FPG). The FPG is a new conceptually innovative product, that can generate precisely controlled dew/frost point conditions to be used for calibrating dew point sensors and most types of hygrometers, from ambient dew point to frost point temperatures as low as -100 °C. Test Bed 2 successfully demonstrated traceable optical and thermodynamic water vapour measurements in the amount fraction range from 5 ppm to 5 ppb at the production facility of a global industrial gas company that is producing cryogenic, technical, medical, refrigerant, pure and specialty gases. As the gas plant was under the Seveso Directive (Directive 2012/18/EU), safety was a primary concern during all experiments. The demonstration involved on-line traceable optical and thermodynamic measurements of the water vapour concentration in high-purity nitrogen and argon (< 0.5 ppm of water) both from gas cylinders up to 20 MPa and from quality control sampling lines up to 0.6 MPa, respectively. The demonstration outcomes and lesson learned helped improving and refining the measurement good practices at industrial laboratory and plant levels. The objective was successfully achieved.

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.

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/

<table>
<tr><td colspan="2">Project start date and duration:</td><td>1st of June 2021, 36 months</td></tr>
<tr><td colspan="3">Coordinator: Vito C. Fernicola, INRIM Tel:+39 011 3919737 E-mail: v.fernicola@inrim.it
Project website address: http://www.prometh2o.eu</td></tr>
<tr><td>Internal Funded Partners:
1. INRIM, Italy
2. CEM, Spain
3. CETIAT, France
4. CMI, Czech Republic
5. CNAM, France
6. INTA, Spain
7. PTB, Germany
8. TUBITAK, Türkiye
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14. Qrometric, United Kingdom
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18. InsightSwiss, Switzerland
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