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 are still lacking metrological traceability in the relevant ranges and matrix gases. The project will fill the knowledge gap regarding metrological traceability - by developing traceable and improved measurement methods at challenging amount fractions between 5 ppm and 5 ppb for use in the production of pure process gases - and will demonstrate its applicability in the gas industry.

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 presents great challenges for both gas producers and analytical instrument makers aiming to improve trace water measurement methods at the part per billion.

This would require a metrological infrastructure and measurement technology to provide robust traceability to trace water measurements with a provision of suitable primary standards, improved optically based methods and improved knowledge of the thermophysical properties of moist gases.

Objectives

The overall objective of PROMETH2O is 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 this project are:

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 is going beyond the current 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).

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 is going 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·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 will go beyond state of the art by designing new experiments to provide new data at temperatures between -90 °C and -30 °C and at selected pressures up to 1 MPa.

The uptake of measurement technology by the industry requires proven solutions with a high degree of adaptability in diverse scenarios. The project will go beyond state of the art by delivering a toolkit of metrological solutions such as improved standards and range-extended measurement capabilities to provide robust measurement traceability to process gases manufacturing and use.

Results

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

The project is developing new and improved trace water optically-based measurement methods. Several improvements such as compactness and lowest detection limit (LDL) have been implemented on a comb-calibrated frequency-stabilised cavity ring-down spectrometer (CC-FS-CRDS). A complete metrological characterisation of a system (as shown in Figure 1) has been carried out. Trace amounts of water have been measured in a nitrogen gas flow with a combined relative uncertainty estimated to be within 0.7 %. These improved results were reported at an international conference and in two peer-reviewed papers. A further refinement of the experimental set up is under way, replacing the ceramic spacer with an electro-polished stainless steel cavity and then performing a comparison against a cavity ring-down spectroscopy analyser traceable to INRIM humidity standards. Such a CRDS transfer standard has been in turn calibrated in the amount

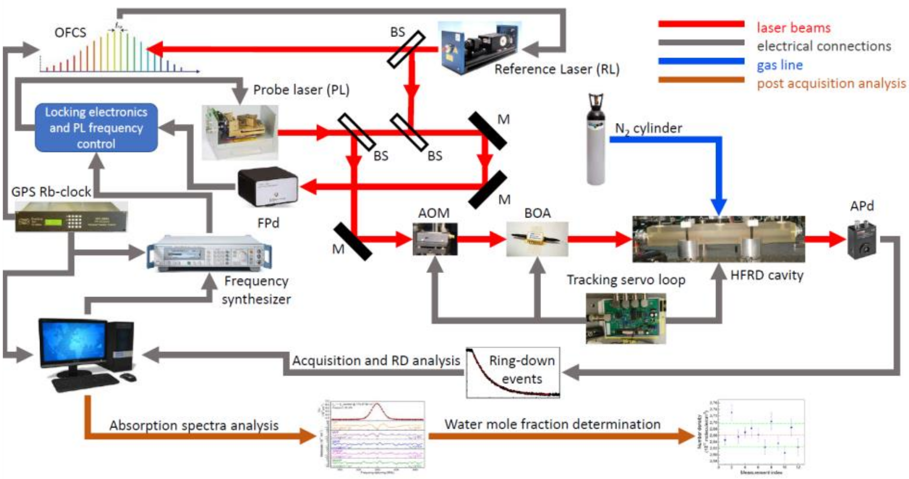

Figure 1. Experimental set up of the NIR CC-FS-CRDS for ultra-sensitive traceable measurements of water vapour in UHP gases.

fraction of water range between 20 ppb and 1 ppm at pressures from 200 hPa to 1100 hPa. A far-UV system suitable for trace water measurements in Ar and N_2 has been developed; the system includes a far-UV light source, a compact far-UV spectrometer and a gas cell. It can operate both in static and dynamic conditions at pressures up to 10 MPa. The far-UV analyser enables multi-component gas analysis of impurities in pure gases; e.g., it has been demonstrated that water and O_2 are the major contaminants in pure Ar and H_2. An upgrade of a high-resolution FTIR spectrometer has been implemented, with a new multi-pass gas cell, a new MCT detector with higher sensitivity and a new pump system 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. The geometry and the laser wavelength of a NIR cavity-enhanced frequency modulated (CE-FM) spectroscopy hygrometer have been optimised. The conceptual design and operation of the CE-FM system were demonstrated, and several lessons were learned.

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

Primary humidity standards for trace water based on a variety of principles are being developed in the project. Development, commissioning and characterisation of saturation-based trace water generators has been completed and they are able to cover the frost-point temperature from approximately -20 °C down to -105 °C (corresponding to an amount fraction equal to 5 ppb at 0.1 MPa) and operating at pressures up to 1 MPa in N_2 and Ar. These generators meet and exceed the expected performance targets. Those capabilities are the first in Europe and among the few in the world. An example of system performance is depicted in Figure 2, where the calibration of a state-of-the-art chilled-mirror hygrometer (CMH) is carried out, showing a temperature stability and repeatability of better than 25 mK at -105 °C frost point. The downward range extension of a coulometric–based trace water generator (CTWG) is progressed well; the development of the overall concept, the construction and testing of the final catalyst design were completed, and the construction of the whole system is underway. At the same time, different designs of the electrolytic cell were explored. The cell comprises platinum (Pt) electrodes with an aqueous acidic electrolyte. Figure 3 shows the schematic and a picture of the electrolytic cell. A mixed-flow humidity generator with SI-traceability of its reference instruments has been completed and partially characterised. The final metrological validation is on-going with the support of a commercial state-of-the-art CRDS made available by an industrial project partner.

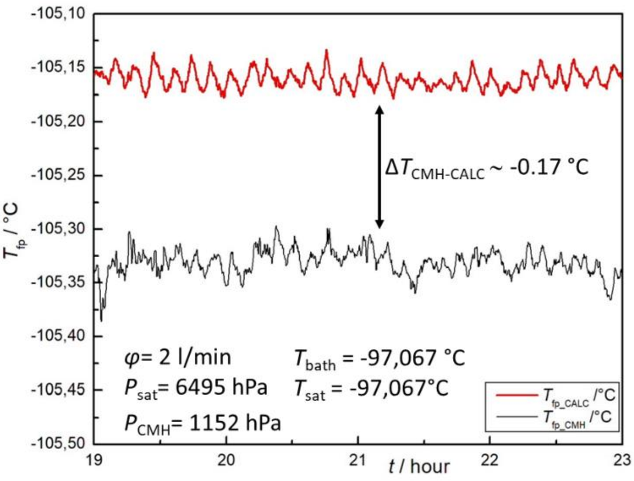

Figure 1. Calibration of a CMH at approximately -105 °C against a PROMETH2O trace water standard generator.

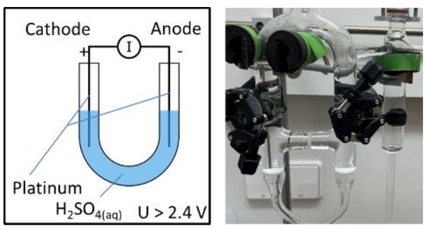

Figure 3. Electrolytic cell of the CTWG.

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 has not been studied in the trace water measurement range, the project is undertaking 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. Preparatory activity to set up concurrent experiments for the measurement of the enhancement factor in N_2, Ar and H_2 at selected temperatures and pressures has progressed succesfully. 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. Three primary humidity generators were either range-extended or improved to encompass the whole measurement conditions in selected gas matrices. One of them is being upgraded to cover the whole pressure range up to 1 MPa, while two others, already affording high-pressure operation, were retrofitted to work with different gas matrices. Two microwave-based trace water analysers operating up to 1 MPa were designed and commissioned. The characterisation of one of them is in progress at pressures up to 0.2 MPa and saturator temperatures between -30 °C and -60 °C with air and argon as matrix gases. A standard high-pressure dew-point generator is being used for confirming the measurements of the enhancement factor. A second, gold-plated, quasi-spherical microwave resonator (QSMWR) hygrometer, depicted in Figure 4, has been designed, constructed, and tested. The consortium is working on measurements of water amount fraction in air and argon using a calibrated dew-point hygrometer and the QSMWR. Once completed, the measurement of the enhancement of water vapour pressure in hydrogen will be attempted.

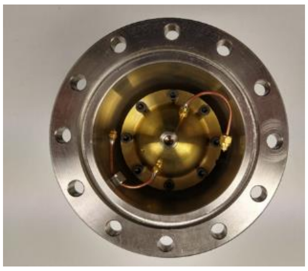

Figure 4. QSMWR used for measuring the enhancement of water vapour in various matrix gases.

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

Improved trace water measurement methods and techniques are going to be demonstrated at selected industrial facilities. The facilities were selected to validate the measurement of good practices and maximise the impact of the developed technology. Test bed preparation involved a careful review of the technical and safety aspects with the test-bed hosts to ensure smooth operations and successful field experiments carried out in a potentially harsh environment (i.e. industrial manufacturing premises with uncontrolled ambient temperature and EMI level). Traceable measurements in the calibration laboratory of a production facility manufacturing a portable frost point generator have already been planned and are ready to be demonstrated. Traceable optical and thermodynamic water vapour measurement methods in the amount fraction range from 5 ppm to 5 ppb will be soon demonstrated, compared and contrasted in the production facility for bulk and specialty gases of a worldwide industrial gas company. Further, at a green hydrogen production facility, field calibration of industrial process sensors will be demonstrated by exploiting a portable frost point generator already validated during the project in the frost point temperature range down to -90 °C.

Impact

Since its beginning, the project has pursued a strong stakeholder engagement. In order to facilitate knowledge and technology transfer and effectively create impact, a stakeholder Steering Board (SB) with 21 members from international organisations, instrument makers and gas providers has been established. The SB helped to survey the needs and priorities concerning water contamination measurement and control in ultra-pure process gases. Thirty organisations out of 50 inquiries replied to the survey. The main respondents came from instrument makers (20 %), gas producers (17 %), industrial users (17 %), NMIs (17 %), and conformity assessment bodies (13 %). Key findings included an excellent match of the project objectives with the stakeholder needs and a strong requirement to improve traceability of trace water measurements in moist hydrogen.

To make the scientific community and the public aware of the project, several initiatives were undertaken over the project lifespan. 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. The project developments resulted in four articles published in peer-reviewed open-access international journals. The project achievements and the consortium activities were presented at 20 international and national conferences, the latest was the 21st International Metrology Congress (Lyon, 2023). Nineteen events at international and national standard-developing organisations, regulatory bodies and metrology committees have been promoted, including IAPWS, UNI-CIG, ACCREDIA, DKD, CIPM CCQM, EURAMET TC-T and TC-MC, and the EMN on Energy Gases.

Impact on industrial and other user communities

There is a substantial engagement of the gas industry: companies represented by project partners and stakeholder members of the SB encompass almost 80 % of the European market share. Likewise, most of the European key players in the process measurement & control sector are involved as both partners and stakeholders. Such a close-knit cooperation accelerated the development and validation of the first portable frost-point generator (FPG) with an extended range down to -90 °C. The partner SME that developed it is now promoting and demonstrating the FPG among its industrial customers. The results from the project regarding improved, traceable optical analysers for trace water in pure gases are encouraging. A sound metrological validation of such systems was possible thanks to the concurrent improvement in primary humidity standards, enabling measurement traceability at the part-per-billion level in different gas matrices and pressure regimes. In the long run, it is expected that the outcomes of the project will also be used for trace water measurements in other industrial applications, such as the gas quality control in the production of hydrogen, natural gas, biomethane and blends of them. A one-day training course is currently being organised for industrial stakeholders. The course will take place at Nippon Gases plant in Italy in March 2024. Such a two-part course comprises a theoretical part and the hand-on training.

Impact on the metrology and scientific communities

The project has become a hub in the humidity field for 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 is facilitating 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) are active members of the Steering Board, which, in turn, is chaired by the CIPM CCT/WG HU chairperson. A project workshop aimed at the scientific and technical communities has been organised and will take place at the beginning of 2024. To maximise its impact, the workshop will be held in conjunction with the Gas Analysis 2024 Symposium in Paris and it is scheduled on 30th January 2024. The workshop programme is available at https://www.gasanalysisevent.com/images/gasanalysis/docs/GAS2024-Fullprogramme.pdf

Impact on relevant standards

The project outputs regarding the provision of traceability to measuring instruments in the trace water range 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 is expected 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 of the project in the sector of traceable measurements of water contamination in UHP process gases. At the IAPWS Annual Meeting 2023, the project representatives are supporting the effort of the special Task Group (TG) 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.

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 enhances the fabrication process efficiency. Itallows 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 also move towards the EU’s climate goals and ‘Fit for 55’ implementation.

List of publications

1. Fasci E., Khan M. A, D’Agostino V., Gravina S., Fernicola V., Gianfrani L., Castrillo A., Water vapor concentration measurements in high purity gases by means of comb assisted cavity ring down spectroscopy, Sensors and Actuators A: Physical 362 (2023), 114632. https://doi.org/10.1016/j.sna.2023.114632

2. Fasci E., D’Agostino V., Khan M.A., Gravina S., Porzio G., Gianfrani L., Castrillo A., 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 (2023), 012017. https://doi.org/10.1088/1742-6596/2439/1/012017

3. Castrillo A., Fasci E., Furtenbacher T., D'Agostino V., Khan M.A., Gravina S., Gianfrani L., Császár A.G., On the 12C2H2 near-infrared spectrum: absolute transition frequencies and an improved spectroscopic network at the kHz accuracy level, Physical Chemistry, Chemical Physics 25 (2023), 23614-23625. https://doi.org/10.1039/d3cp01835k

4. Berg R.F., Chiodo N., Georgin E., Silicone tube humidity generator, Atmospheric Measurement Techniques 15 (2022), 819-832. https://doi.org/10.5194/amt-15-819-2022

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

Project start date and duration:	1st of June 2021, 36 months	
Coordinator: Vito C. Fernicola, INRIM Tel:+39 011 3919737 E-mail: v.fernicola@inrim.it Project website address: www.prometh2o.eu		
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 9. UL, Slovenia 10. VSL, Netherlands 11. VTT, Finland	External Funded Partners: 12. DTU, Denmark 13. Nippon Gases, Italy 14. Qrometric, United Kingdom 15. SUN, Italy 16. UNICAS, Italy 17. UVa, Spain	Unfunded Partners: 18. MBW, Switzerland 19. Vaisala, Finland
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