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 process yield in UHP gas applications. Even though the manufacturing 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 the 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 eliminate. Water contamination effects becomes relevant when taking in 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 manufactured 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 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 to both gas producers and analytical instrument makers which aim 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 to 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

Advancing measurement methods and techniques for trace water vapour is crucial to provide industry with robust, validated and traceable tools. Sensor performance for different gas species, at various pressures and over time remains a challenge for many applications. To overcome these, the project will go 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 key traceability needs of the gas industry. The project will go beyond the state of the art by developing 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 factor. The enhancement factor is known for air down to -50 °C and 2 MPa with an uncertainty up to 0.7 %, but often extrapolated down to -100 °C without metrologically-sound data and thus not traceable to SI. The project effort will go beyond the 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 the 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 development of new and the improvement of existing trace water optically based measurements methods have begun. Several improvements were implemented to the existing comb-calibrated frequency-stabilized cavity ring-down spectrometer (CC-FS-CRDS). A complete characterization of the new setup has been carried out, trace amounts of water have been measured in nitrogen gas flows, and a preliminary uncertainty budget has been made. A new gas cell being capable to keep up to work at 10 bar has been developed for a commercial compact far-UV spectrometer. The far-UV system with the new cell and sampling line should meet the requested dynamic measurement of trace water. The upgrade of the existing high-resolution FTIR spectrometer has been started, with a new multi-pass gas cell, a new MCT detector with the highest sensitivity and a new pump system, in order to enable water vapor measurements in N_2 and Ar down to 50 ppb and operation pressure up to 1 MPa. New and improved measurement methods will be validated in different humid gases down to 5 ppb in addition to the validation of a commercially-available chilled-mirror hygrometer (CMH).

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

The development of primary standards for trace water has started. The initial steps were undertaken, i.e. i) to extend downwards the operation of current frost point generators based on thermodynamic saturation with the ability to generate frost-point temperatures down to -105 °C with a target standard uncertainty of better than 0.35 °C and ii) to retrofit a permeation trace water generator to produce reference amount fraction of water vapour to reach a lower limit of 5 $nmol \cdot mol^{-1}$ (ppb) with a relative standard uncertainty of better than 8 %. The extension of the lower limit of a coulometric–based generator is also in progress, and the development of the overall concept, the hardware acquisition and the test of catalyst have begun.

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

As the enhancement factor for gases such as H_2 and Ar has not been studied in the trace water measurement range, the project is undertaking this effort by designing new experiments to provide new data at temperatures between -90 °C and -30 °C at selected pressures from 0.1 MPa to above 1 MPa. The preparatory activities for the measurement of the enhancement factor have started. The design of two microwave-based trace water analysers operating up to 1 MPa has been completed. For one of them, the manufacturing procedure is in progress and the standard high-pressure dew point generator, to be used for confirming measurement of enhancement factor at -80 °C at selected pressure values, has been tested at pressures up to 0.6 MPa, and at a saturator temperature of -30 °C, with air as a carrier gas. The second microwave-based trace water analyser has been constructed and tested, while the construction of its new thermostat is almost completed.

Objective 4: Demonstration of improved methods for trace water measurement in industrially relevant facilities (test beds)

Improved trace water measurement methods and techniques will be demonstrated at two selected industrial test beds. In one of the facilities, a hydrogen production facility, novel portable calibrators will be made available to cover the frost point temperature down to -90 °C and field calibration will be demonstrated. The other facility is of a major specialty gas company with a production facility for bulk and specialty gases. There, traceable optical and thermodynamic measurement methods, for the amount fraction range from 5 ppm to 5 ppb, will be demonstrated, compared and contrasted.

Impact

Since its beginning, the project pursued a strong stakeholder engagement. In order to facilitate technology transfer and effectively create impact, representatives from the industry and international and standards organisations were invited to join the project Steering Board. At present, 21 organisations have joined the Steering Board and 17 have attended the first progress meeting at month 9.

To help steering the project objectives and match the industry needs, an informal consultation process with the industrial members of the Steering Board was initiated, confirming the expectation from the project regarding novel sensors and the development of suitable primary standards to provide better traceability to the industry community.

Moreover, to make the scientific community and to the general public aware of the project, several initiatives were undertaken. A YouTube interview was released at the beginning of the project and posts on social media (Facebook and LinkedIn) by the coordinating NMI were published. A project website was established and project LinkedIn and Research Gate accounts were established. Consortium members presented the project at the EURAMET Technical Committee –Thermometry (TC-T) annual meeting and at the European Metrology Network for Energy Gases community during a virtual brainstorm event.

Initial project achievements are being presented at the forthcoming Gas Analysis 2022 Conference where the metrology of trace water measurement in pure process gases as well as the improved measurement techniques in the low-end range may impact the wider industrial and technical community.

Impact on industrial and other user communities

The analysis of water vapour impurity is important in a number of speciality gas applications. It is known that water vapour is the single largest contaminant in pure process gases and its traceable measurement is a global challenge for gas producers, instrument manufactures and end-users. In challenging applications, such as in the semiconductor industry, total impurities below 10 ppb and selectively below 1 ppb at the point of use are required.

Initial results from the project regarding improved, traceable analysers for trace water in UHP gases are encouraging. The comb-calibrated frequency-stabilized cavity ring-down spectrometer (CC-FS-CRDS) and the compact far-UV spectrometer prototypes which are targeted to serve the pure and ultra-pure gas producers are in an advanced development phase. Their testing and validation is underpin by the concurrent improvement and range-extension of several trace water primary standards that ultimately will provide the measurement traceability to such methods and techniques and will enable better comparability of measurement methods in the measurement range between 5 ppb and 5 ppm based on different principles, in different matrices (e.g. N_2, Ar, air, H_2), and at different pressure regimes (e.g. 0.1 MPa to 1 MPa).

The development of improved methods and techniques for traceable trace water measurement is expected to lead to more robust process control in ultra-pure gas production and supplies, facilitating industrial sectors that rely on them, from the semiconductor industry to optoelectronics, as well as industrial gas production and distribution. Thanks to a strong industrial engagement, with five global players in the gas industry and seven world leading instrumentation makers being members of the Steering Board, the path from R&D to innovation will be as short as possible.

Impact on the metrology and scientific communities

The project is becoming a hub and a point of contact for European NMIs and other RMOs in the humidity field facilitating a stronger co-operation and providing channels for global dissemination. The interaction with the metrology community and the broader scientific community will spur the integration of the metrology infrastructure in Europe in the field of trace water measurements. In addition, leading NMIs outside Europe (e.g. AIST NMIJ, KRISS) and international organisations (e.g. IAPWS, JCS, CIPM CCT) has joined the Steering Board and attended the first progress meeting, actively contributing to the discussion. These interactions are the baseline for the further development of a joint and coordinated European landscape of the inherent metrology capabilities to advanced applications, calibration and measurement capabilities and metrology services for trace water measurements.

To further align the project goals with and its impact on the global humidity community perspective, the Chairperson of the CIPM CCT/WG Humidity was appointed to chair the project Steering Board. This will provide a unique opportunity to present the project results and provide key elements, such as a recommendation of suitable transfer standards, to CIPM CCT which has the mandate to develop a key comparison protocol in the trace water range.

Impact on relevant standards

The project outputs regarding traceable calibrations available for instruments measuring water vapour in the trace range, such as CMH and CRDS, against primary standards in the relevant gases are expected to enable testing and calibration laboratories (i.e. conformity assessment bodies) in the field to conform to ISO/IEC 17025 (Clause 6.5) and ISO 17034 (Clause 7.9) to grant EA/ILAC accreditation.

Further impact is expected through partners involved on relevant working groups such as ISO/TC 158 and, DIN NA 062-05-73 AA that disseminate the results from the project, in particular the traceable measurements of water contamination in UHP process gases. To enhance the impact of the project's results, three national accreditation bodies, reference material producers and the ISO/TC 158 Chairperson has joined the project's Steering Board.

Longer-term economic, social and environmental impacts

The global industrial gases market size was valued at US$ 92 billion (2020) and is expected to further expand in the years to come. Within Europe, the industry employs 45.000 people, with 4-million customers, 4.5-million delivery points, and a gas production of approximately 220.000 tons per day. Improved, traceable, trace water measurements in pure gases are expected to affect this important industrial sector and a very large number of their customers globally (e.g. semiconductor and energy gases industry).

Providing and demonstrating new and improved trace water measurements relevant to the production of pure gases is a step forward regarding quality assurance of energy gases - such as hydrogen and H2-blended mixtures - in relevant applications, such as in sustainable transports where H_2 fuelled vehicles contribute to the reduction of CO_2 and other emissions to the atmosphere as set by COP21 and EU's "Fit for 55" goals. Moisture contamination control plays a major role in preventing pipeline corrosion and infrastructure failure during CO_2 transport. Quality assurance of blanketing gases is paramount to improve the process efficiency of PV manufacturing and to increase the efficiency of H_2 cooled stationary electric generators in hydroelectric power plant.

Improved trace water measurements supports the sustainability and waste reduction of many industries such as semiconductors. Sustainability has become the biggest concern of the semiconductor industry because of the many toxic compounds involved in manufacturing. Improved water contamination control enables enhanced efficiency in fabrication processes and allows for reduced use of toxic chemicals, reduced waste of raw materials, reduced need for re-work and re-processing and higher efficiency, all steps towards the EU targets for energy reduction and decarbonisation.

List of publications

R. F. Berg, N. Chiodo, and E. Georgin, Silicone tube humidity generator, Atmos. Meas. Tech., 15, 819–832, 2022. https://doi.org/10.5194/amt-15-819-2022

This 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	
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