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 have been implemented on a comb-calibrated frequency-stabilised cavity ring-down spectrometer (CC-FS-CRDS), especially in terms of compactness and limit of detection (LoD). A complete characterisation of a new setup has been carried out, trace amounts of water have been measured in nitrogen gas flow, and a combined relative uncertainty of 0.7 % has been estimated for a water mole fraction of about 400 ppb in nitrogen. A comparison with a commercial calibrated cavity ring-down spectroscopy analyser used as transfer standard in the amount fraction range between 20 ppb and 1 ppm at pressures from 200 hPa to 1100 hPa is on-going. A far-UV system suitable for trace water measurements in Ar and N_2 has been developed (Fig. 1). The system can operate both in static and dynamic conditions at pressures up to 10 MPa; it includes a far-UV light source, a compact far-UV spectrometer, and a gas cell. The far-UV analyser enables multi-component gas analysis of impurities in pure gases as, e.g., it has been shown that water and O_2 are the major contaminants in pure Ar and H_2. An upgrade of a high-resolution FTIR spectrometer has largely 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

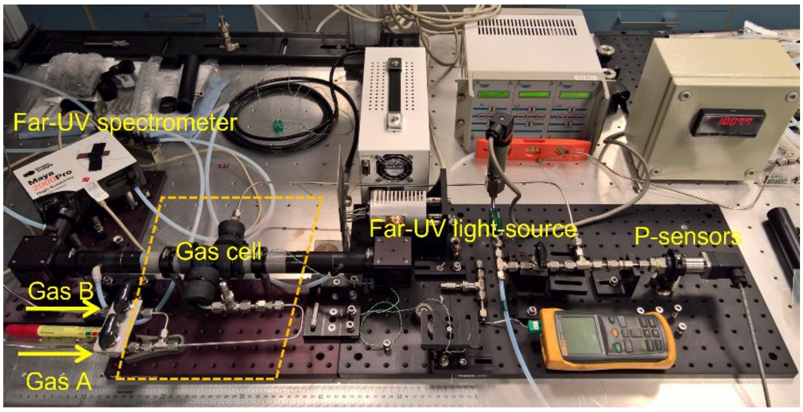

Figure 1. A far-UV system for trace water measurements in Ar and N_2.

ppb and operation at pressure up to 1 MPa. Measurements have been carried out with 0.5 ppm H_2O in air to find out the optimum measurement conditions. The geometry and the laser wavelength of a NIR cavity-enhanced frequency modulated (CE-FM) spectroscopy hygrometer have been optimised. Currently, the CE-FM system is under test at frost-point temperatures between -40°C and -80°C.

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

In the framework of the project, primary humidity standards for trace water based on a variety of principles are being developed. The realisation of a saturation-based trace water generator able to work down to -105 °C frost-point temperature (5 ppb amount fraction) at pressures up to 0.65 MPa in nitrogen and argon has been completed, and the system is in operation (Fig. 2). The generator meets and exceeds the expected performance targets. The capability is the first in Europe and among the few in the world. A thorough characterisation is underway aiming to estimate the combined uncertainty. The extension of the operating range of a second humidity generator based on the saturation principle in nitrogen and air down to -100 °C at 0.11 MPa has been completed. The generator is currently being characterised and a preliminary uncertainty budget has been established. The downward range extension of a coulometric–based generator is also in progress; the development of the overall concept, the hardware acquisition and the test of the catalyst are completed, and the final catalyst design is underway. A mixed-flow humidity generator with traceability to SI of its reference instruments has been completed. The validation is on-going and a preliminary uncertainty budget has been already estimated.

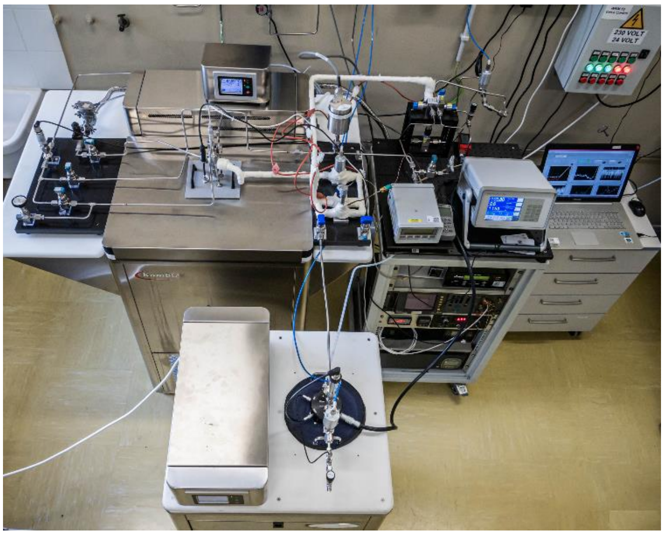

Figure 2. Primary humidity standard for trace water working down to -105 °C.

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 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 in N_2, Ar and H_2 in selected temperature and pressure ranges are on-going. 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 a standard high-pressure dew point generator, to be used for confirming measurement of enhancement factor, has been tested at pressures up to 0.6 MPa and at a saturator temperature of -30 °C, with air as a carrier gas. A second gold-plated quasi-spherical microwave resonator (QSMWR) has been designed, constructed, and tested. Measurements of water amount fraction in air using a calibrated dew point hygrometer and the microwave resonator have been started. A literature review of water vapour enhancement factor measurements in selected gases has been completed. The review covers the measurements below -30 °C at pressures up 1 MPa.

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

Improved trace water measurement methods and techniques will be demonstrated at two industrial test beds. Technical and safety aspects are under review with the test bed hosts, and a necessary preparation is in progress. The former is a hydrogen production facility where a portable frost point generator will be made demonstrated to cover the frost point temperature down to -90 °C in field calibrations. The latter is a world-wide industrial gas company with a production facility for bulk and specialty gases. There, traceable optical and thermodynamic water vapour measurement methods in the amount fraction range from 5 ppm to 5 ppb will be performed, compared and contrasted.

Impact

Since its beginning, the project has pursued strong stakeholder engagement. In order to facilitate knowledge and technology transfer and effectively create impact, a large stakeholder Steering Board (SB) has been established with 21 members from international organisations, instrument makers and gas providers. Thanks

to a fruitful cooperation, the SB helped to survey the needs and priorities of the stakeholders' community concerning the water contamination of ultra-pure process gases and its measurement. A questionnaire was shared among 50 organisations receiving responses from 30 of them, a remarkable 60 % response rate. The main respondents were instrument makers (20 %), gas producers, industrial users and NMIs (17 % each), and conformity assessment bodies (13 %). Key findings were an excellent match of the project objectives with the stakeholder needs and a strong requirement of moisture (trace water) measurements in hydrogen.
To make the scientific community and the public aware of the project, several initiatives were undertaken. A project website, as well as LinkedIn and Research Gate accounts, were open. A YouTube interview was released, and several posts on social media (Facebook and LinkedIn) were published.
The project developments resulted in one open access article published in an international journal, while another one is accepted and awaiting publication. The project results and the consortium activities were presented at 13 international and national conferences. Thirteen 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. The project achievements will be presented at the upcoming 21st International Metrology Congress to be held in Lyon (France) in March 2023.

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 and control sector for precision humidity measurements are involved both as 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 the FPG among its industrial customers. Furthermore, the results from the project regarding improved, traceable optical analysers for trace water in pure gases are encouraging. Testing and validation of the above systems are now possible thanks to the concurrent improvement of primary humidity standards that provide the measurement traceability down to 5 ppb (or -105 °C frost point) in different gas matrices and pressure regimes. On 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 H_2 and biomethane quality control.

Impact on the metrology and scientific communities

The project has become a hub 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 is facilitating the integration of the metrology infrastructure in Europe in the challenging field of trace water measurements. 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 Chairperson of the CIPM CCT/WG Humidity.

Impact on relevant standards

The project outputs regarding the provision of traceability to measuring instruments in the trace water range will 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 in relevant working groups such as ISO/TC 158 and DIN NA 062-05-73 AA that disseminate the results from the project, with reference to traceable measurements of water contamination in UHP process gases. The IAPWS Annual Meeting 2022 highlighted PROMETH2O in the final Press Release. The IAPWS Executive Committee established a Task Group (TG) to study the second virial coefficients $B_{12}(T)$ and the enhancement factor of water-gas mixtures inviting a PROMETH2O representative to join the TG that will work toward preparing an IAPWS Guideline and recommended values based on PROMETH2O 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. Sustainability has become the biggest concern of semiconductor fabrication because of the many toxic compounds involved in manufacturing. Improved water contamination control in UHP process gases enhances the fabrication process efficiency 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's climate goals and 'Fit for 55' package implementation.

List of publications

1. 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

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

Project start date and duration:	1st June 2021, 36 months	
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