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.

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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 and results

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

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 such as far-UV spectrometers. Commercially available and novel optical measurement methods (e.g. CRDS and CE-FM spectrometers) will be validated in matrix gases other than N_2 down to 5 ppb; while a primary method based on a frequency-referenced CRDS will be introduced to measure amount fractions down to 50 ppb. Commercially available chilled-mirror hygrometers (CMHs) will be validated down to -105 °C frost point. This project will also provide input to preparing the design of a CIPM measurement comparison in the trace water regime.

Development of primary standards for trace water in selected gas matrices

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 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, whilst those generating 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 %. By obtaining these primary standards, the humidity calibration capabilities in N_2, air, Ar and H_2 will be significantly improved in Europe.

Improvement of thermophysical data knowledge of non-ideal humid gas mixtures

The conversion from frost-point temperature to water vapour amount fraction and vice versa requires knowledge of the water vapour-gas non-ideality, which is empirically expressed by 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 is extrapolated down to -100 °C without metrologically-sound data and due to that untraceable. For other gases (such as H_2 and Ar), the enhancement factor has not been studied in the trace water measurement range. The project will go beyond the current state of the art by providing new data at temperatures between -90 °C and -30 °C at selected pressures from 0.1 MPa to above 1 MPa.

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

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. 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, a major specialty gas company with a production facility for bulk and specialty gases, traceable optical and thermodynamic measurement methods – for the amount fraction range from 5 ppm to 5 ppb - will be demonstrated, compared and contrasted.

Impact

Impact on industrial and other user communities

The analysis of water vapour impurity is important in a number of speciality gas applications. Ultra-pure process gases are increasingly used for blanketing and purging to prepare and protect processing zones. 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. Trace water contamination of a few parts per billion can result in catastrophic failure in microelectronic circuits. Contamination-related failure is a key issue in OLEDs for next-generation flexible displays – a booming market which was valued at US$ 3.1 billion in 2020 and is expected to reach US$ 60 billion by 2026. The results from the project regarding novel sensors and development of suitable primary standards will provide better traceability to the industry community.

It is well known that water vapour is the single largest contaminant in pure process gases and its traceable measurement is a global challenge for instrument makers and end-users. The results from the project regarding improved, traceable, analysers for trace water in UHP gases will enhance the competitiveness of European equipment and services for pure gases through traceable methods and techniques to better serve the advanced industrial sectors of microelectronics, optoelectronics, PV and service for these. Also, results from the project regarding improved knowledge of real humid gas mixtures will enable better comparability of measurement methods based on different principles (e.g. frost-point temperature and water vapour amount fraction), in different matrices (e.g. N_2, Ar, air, H_2) and at different pressures (e.g. 0.1 MPa to 1 MPa), and will benefit users who need to relate and convert trace water measurements made in different units.

The development of improved methods and techniques from this project for traceable trace water measurement will 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. This will be also facilitated due to the strong industrial engagement, with four global players in the gas industry and ten world leading instrumentation makers supporting the project as members of the Steering Board.

Impact on the metrology and scientific communities

The project will provide a point of contact for European NMIs bringing strong co-operation for the humidity field and other RMOs to provide channels for global dissemination. Also, leading NMIs outside Europe (e.g. AIST NMIJ, KRISS) and international organisations (e.g. IAPWS, JCS, CIPM CCT) will be invited to join the Steering Board. The project outputs, partner interaction with the metrology community, and the fruitful discussion with the scientific community will enhance the integration of the metrology infrastructure in Europe in the field of trace water measurements. 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.

Formal CIPM key comparisons have only reached -50 °C in frost point, not yet covering the trace water regime, due to many NMI capabilities still developing in this range. A former EURAMET pilot study down to 10 nmol/mol indicated good comparability between some NMIs with inconclusive results in one case. This project will provide suitable elements, such as recommendation of suitable transfer standards, to CIPM CCT to develop a CIPM key comparison protocol in the trace water range.

The expected scientific and technical advancements will provide an improved underpinning for the metrology of trace water measurement in pure process gases as well as a better knowledge of measurement techniques and water vapour-gas mixture non-ideality in this low-end range which will impact a wider scientific community.

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 will enable testing and calibration laboratory activities in the field to conform to ISO/IEC 17025 (Clause 6.5) and ISO 17034 (Clause 7.9) and therefore contribute to grant EA/ILAC accreditation.

Impact will be achieved through partners involved on relevant working groups such as ISO/TC 158, DIN NA 062-05-73 AA and SEMI Gases Global Technical Committee that would be interested in results from the project such as traceable measurements of water contamination in UHP process gases. These committees are responsible for published national and international standards serving a wide variety of sectors that cover high-purity gases. To enhance the impact of the project’s results national accreditation bodies, reference material producers and the Chairman of ISO/TC 158 will be invited to join 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 expand at a compound annual growth rate (CAGR) of 6.0 % from 2021 to 2028. 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 measurement techniques in pure gases are likely to affect this important industrial sector and a very large number of their customers globally (e.g. semiconductor and energy gases industry).

Providing new and improved trace water measurements relevant to the production of pure gases after the end of the project, will be a step forward regarding quality assurance of energy gases - such as hydrogen and biogas. This new information will be vital to ensure their consistent performance 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 2030 Climate and Energy Framework. Besides, 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, an industrial sector which is witnessing a double-digit growth in the European market, and to protect and increase the operating efficiency of H_2 cooled stationary electric generators in hydroelectric power plant.

Improved trace water measurements will support 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. Such industry provides key enabling technologies for the society in the fields of energy efficiency, mobility, health care, security and Information and Communication Technology, including a more efficient use of energy. Improved water contamination control will enable enhanced efficiency in fabrication processes and will allow reduced use of toxic chemicals, reduced waste of (sometimes-scarce) raw materials, reduced need for re-work, recovery and re-processing, and higher efficiency (of energy use and facility utilisation), which are steps towards EU targets for energy reduction and carbon emissions, and the associated environmental and health risk.

<table>
<tr><td colspan="2">Project start date and duration:</td><td>1st of June 2021, 36 months</td></tr>
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<tr><td>Internal Funded Partners:
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