Title: Metrology for trace water in ultra-pure process gases

Abstract

Water vapour is the single largest contaminant in high-purity processing of products such as microelectronics, organic light-emitting diode (OLED) and micro-electromechanical system (MEMS) devices. Avoidance of defects requires control of water vapour to few or tens of parts in 10^9 in pure gases. Trace humidity measuring techniques for relevant matrix gases and pressures currently lack measurement traceability in respective range. This project aims to develop improved methods for trace water measurement by providing metrological infrastructure to underpin the measurement traceability as well as the relevant metrology practices for the supply chain of gases, instruments, and gas delivery systems.

Keywords

Ultra-pure gases, industrial gas production, trace water measurement, gas contamination by water vapour, laser-based humidity analyser, chilled-mirror hygrometer, electrolytic sensor, humid gas mixtures, and enhancement factors.

Background to the Metrological Challenges

Water vapour is unique among process contaminants. Its polar molecule adheres to practically all surfaces and coats all materials. At surfaces or deep within materials it influences electrical, chemical and mechanical properties, affecting surface adhesion and electrical conductivity and leading to, e.g., corrosion and degradation. It is a critical contaminant in vacuum systems and in high purity gases. Even in trace amounts, water is chemically active. Due to the many-faceted effects of water vapour contamination, solutions to its measurement and control are correspondingly diverse.

The demand for ultra-pure bulk and package gases (such as N_2, H_2, Ar, He, NH_3, CO_2) by the semiconductor and optoelectronics manufacturing industries presents great challenges to both the gas manufacturers and analytical instrument makers. Ultra-pure bulk process gases (grade N6.0 or better, i.e. with total impurities below 1 ppm) are increasingly used for blanketing and purging to prepare and protect processing zones. Furthermore, 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. Being the single largest contaminant in ultra-pure process gases, the water vapour traceable measurement is in great demand, where the lowest water vapour amount fraction (1 ppb) corresponds to a frost-point temperature of approximately -110 °C. In this range, the accuracy of current measurement methods and techniques for trace water significantly depends on influence effects which need to be thoroughly characterised.

In utility power generation, dry hydrogen (below 5 ppm of water vapour amount fraction) is used to cool large stationary generators because of its high heat capacity (2.7 times that of ambient air) and its low viscosity. High-purity H_2 plays an important role in gas chromatography (GC) and mass spectrometry, growingly used as a He-substitute as a primary tracer gas and in leak detection. In terms of GC carrier gas, H_2 offers an equivalent level of sensitivity to helium but allows for faster speed of analysis. The replacement of He with H_2 affects humidity analyser measurements, where new correlations have to be investigated in order to assure measurement traceability.

Sensor performance - in different gas species, pressures and over time - remains a challenge. Optically-based methods can have fast response and are strongly suited to some gas matrices but are prone to interferences from other gases. Although it is a rapidly developing technology, calibration facilities are not yet available for the required low trace ranges and matrix gases. Electrolytic-based methods, although improved to cover the required range and scope, still lack of measurement traceability. The key sensing techniques in use measure different quantities. Some intrinsically measure water vapour in terms of condensation temperature, and others as amount fraction. Interconversions between these quantities require compensation for gas non-ideality, which is significant at the level of one, several or tens of percent, depending on gas pressure and species. These equations are also essential for converting or comparing water vapour data for different pressures such as in high-pressure cylinders, gas supply systems and processes which might be at atmospheric or vacuum pressures. This correlation (so-called enhancement factor) is known for air down to -50 °C and up to 2 MPa with an uncertainty of 0.7 %. Values are extrapolated down to -100 °C and up to 5 MPa with several percent uncertainty, but this extrapolation and its uncertainty are questionable. For other industry-relevant gases (such as H_2, N_2, Ar and CH_4), the water vapour enhancement factor is simply unknown and requires a careful determination down to -90 °C.

Existing trace humidity standards are based on principles of evaporation, diffusion, permeation and coulometry. Many of these facilities operate down to 1 ppm (frost-point temperature near -75 °C) with uncertainty of order 2 %. A small minority operate down to near 10 ppb (frost-point temperature near -100 °C) with uncertainty around 10 % where the uncertainties dramatically increase due to the challenges of stray water. These approaches are usable in principle at any pressure, but no humidity standard is yet established to operate at variable pressure in the trace range. Thus, improved design and range extension are required to provide metrological traceability to the full extent of industrial applications.

Objectives

Proposers should address the objectives stated below, which are based on the PRT submissions. Proposers may identify amendments to the objectives or choose to address a subset of them in order to maximise the overall impact, or address budgetary or scientific / technical constraints, but the reasons for this should be clearly stated in the protocol.

The JRP shall focus on the trace water measurement relevant to the production of ultra-pure gases and their industrial process applications.

The specific objectives are

1. To improve trace water measurement methods and techniques 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 -100 °C frost point temperature, with amount fraction relative uncertainty between 3 % and 8 %, from 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 the equivalent frost-point temperatures - with relative uncertainty less than 3 % to 8 %, respectively, operating with ultra-pure gases such as N_2, Ar and H_2 at pressures between 0.1 MPa to 1 MPa.
3. To improve the present knowledge of thermophysical data of real humid gas mixtures, in particular the water vapour enhancement in the frost-point temperature range from -30 °C to -90 °C, at pressures from 0.1 MPa to above 1 MPa, focusing on selected ultra-pure gases such as N_2 and Ar.
4. To demonstrate improved trace water measurement methods between 5 ppm and 5 ppb or, equivalently, between -65 °C and -100 °C frost-point temperature in an industrially relevant facility.
5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (NMIs, DIs), standards developing organisations (CIPM, IAPWS, JCS) and end users (semiconductor industry, instrument manufacturers, gas providers).

Proposers shall give priority to work that meets documented industrial needs and include measures to support transfer into industry by cooperation and by standardisation. An active involvement of industrial stakeholders is expected in order to align the project with their needs – both through project steering boards and participation in the research activities.

Proposers should establish the current state of the art, and explain how their proposed project goes beyond this.

EURAMET expects the average EU Contribution for the selected JRPs in this TP to be 1.5 M€, and has defined an upper limit of 1.8 M€ for this project.

EURAMET also expects the EU Contribution to the external funded partners to not exceed 30 % of the total EU Contribution across all selected projects in this TP.

Any industrial partners that will receive significant benefit from the results of the proposed project are expected to be unfunded partners.

Potential Impact

Proposals must demonstrate adequate and appropriate participation/links to the “end user” community, describing how the project partners will engage with relevant communities during the project to facilitate knowledge transfer and accelerate the uptake of project outputs. Evidence of support from the “end user” community (e.g. letters of support) is also encouraged.

You should detail how your JRP results are going to:

- Address the SRT objectives and deliver solutions to the documented needs,
- Feed into the development of urgent documentary standards through appropriate standards bodies,
- Transfer knowledge to the industrial gas sector.

You should detail other impacts of your proposed JRP as specified in the document “Guide 4: Writing Joint Research Projects (JRPs)”.

You should also detail how your approach to realising the objectives will further the aim of EMPIR to develop a coherent approach at the European level in the field of metrology and include the best available contributions from across the metrology community. Specifically, the opportunities for:

- improvement of the efficiency of use of available resources to better meet metrological needs and to assure the traceability of national standards
- the metrology capacity of EURAMET Member States whose metrology programmes are at an early stage of development to be increased
- organisations other than NMIs and DIs to be involved in the work.

Time-scale

The project should be of up to 3 years duration.