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

Abstract

Humidity measurements are needed over a broad range of pressures and temperatures, and at water vapour amount fractions between parts per billion to unity. The manufacturing of ultra-high purity gases (i.e. impurities amount fractions below 10 ppb) where trace water is, in fact, the single largest matrix contaminant is still lacking harmonised measurement standards. Therefore proposals in response to this SRT should develop the metrological infrastructure to underpin the traceability of trace water measurements in terms of both the experimental framework and the relevant metrology practices.

Keywords

Humidity, ultra-trace water measurements, ultra-high pure gases, UHP gases, enhancement factor, humid gas mixtures.

Background to the Metrological Challenges

Bulk process gases need to be manufactured with ultra-high purity (UHP) grade (N6.0 or better) with total impurities below ppm amount fraction levels. However, in several applications, such as in the semiconductor industry, there is a demand for total impurities below 10 ppb, selectively below 1 ppb at the point of use. The demand for UHP bulk gases (N_2, H_2, Ar, He, CO_2) by the semiconductor industry presents great challenges to both the gas manufacturers and analytical instrument makers. Water vapour is one of the most difficult impurities to eliminate because of its ubiquity and chemical properties. Sensitive and traceable measurement techniques are required to detect water vapour amount fractions as low as few parts per billion, with an increasing pressure to reduce the detection level below ppb. Similarly, instrument manufacturers need traceable references to support their product development down to a -100 °C frost point.

Available trace water vapour standards are based on different principles (i.e. diffusion, permeation, coulometry, or evaporation). Depending on its operating principle, an instrument is sensitive to a specific way of expressing the water content of a gas. In order to compare diffusion-based, permeation or coulometric generators to saturation-based generators in the trace water range, the knowledge of the enhancement factor is required.

Enhancement factors are known for air down to -50 °C and 2 MPa with an uncertainty of 0.7 % and were extrapolated down to -100 °C and 5 MPa with a few percent uncertainty, though some authors questioned the uncertainty attributed to such extrapolation. For other gases (such as H_2, N_2, Ar and CH_4), the enhancement factor is simply unknown in the above trace water measurement range. Similarly, UHP gases are often employed at atmospheric or lower pressures, but they are manufactured and stored in high-pressure cylinders, thus the non-ideal mixture terms impact at both the manufacturing and the user level.

In ultra-trace water detection, several effects have a significant impact on the measurement accuracy and need to be thoroughly investigated in order to assure traceable measurements. Among others, gas non-ideality, i.e. water vapour enhancement factor and compressibility of water vapour at different pressures and temperatures, needs to be investigated and the current practice for applying enhancement factor versus compressibility need to be compared and contrasted with national realisations of water vapour standards.

A better knowledge of humid gas mixtures non-ideality will enable better comparability of water vapour standards, based on different principles and with different gas matrices, as well as comprehensive and robust uncertainty estimation and robust correlation equations for the calculation of trace humidity in different gases this will allow different industries benefit of calibrated, traceable and comparable instruments for water vapour measurements in different gases as a tool to improve the quality of their products.

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 traceable measurement of ultra-trace water in pure gases.

The specific objectives are

1. To develop ultra-trace standards of water in selected gas matrices such as air, N_2, Ar and H_2, in the amount fraction range between 5 ppm and 5 ppb, with relative uncertainty lower than 2.5 % across the range.
2. To improve the present knowledge of non-ideal humid gas mixtures, e.g. determination of the enhancement factors, in selected gas matrices such as air, N_2 and Ar in the frost-point temperature range from -30 °C to -80 °C and at pressures from 0.1 MPa to above 1 MPa.
3. To compare improved ultra-trace water in gas preparation methods (e.g. based on saturation, diffusion, coulometric generation and permeation) between 5 ppm and 5 ppb or, equivalently, between -65 °C and -100 °C frost point temperature.
4. To develop a traceable thermodynamically-based, and a traceable optically-based, ultra-trace water measurement method in the range between 5 ppm and 5 ppb or, equivalently, between -65 °C and -100 °C frost point temperature, with amount fraction relative uncertainty below 2.5 %.
5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (e.g. gas manufacturers and instrument manufacturers), standards or regulation developing organisations and end users such as the semiconductor industry and humidity sensor manufacturers.

These objectives will require large-scale approaches that are beyond the capabilities of single National Metrology Institutes and Designated Institutes. To enhance the impact of the research work, the involvement of the larger community of metrology R&D resources outside Europe is recommended. A strong industry involvement is expected in order to align the project with their needs and guarantee an efficient knowledge transfer into industry.

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 1.8 M€, and has defined an upper limit of 2.1 M€ for this project.

EURAMET also expects the EU Contribution to the external funded partners to not exceed 20 % of the total EU Contribution across all selected projects in this TP.

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 semiconductor industry and also the gas production 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.