Summary

My research work during the Ph.D. thesis concerned the advancement of reference-grade humidity generators to be used in a broad range of applications, where traceability of trace water measurements is of paramount importance for environmental issues, technological advancement, and the low-carbon energy transition.

Water vapor, the most abundant greenhouse gas, was identified as an Essential Climate Variable (ECV), and plays a central thermodynamic role in the climate system. Accurate and traceable water vapor measurements improve climate model predictions, support emission monitoring, increase energy efficiency, and enable clean energy technologies. Water vapor is also a critical contaminant in ultra-high purity (UHP) process gases such as N_2, Ar, and H_2, especially in semiconductor fabrication, where trace amounts can significantly impact product quality.

This research thesis presents the INRiM low frost-point humidity generator (INRIM 03 -Mark 1), designed to meet the above needs and support the achievement of these goals. This primary system is a saturation-type humidity generator operating in a single-temperature, single-pressure (1T-1P) mode, designed to produce gas mixtures with a frost-point temperature ranging from -100 °C to -20 °C, in a pressure range from 200 hPa to 1100 hPa. This work builds upon previous work that demonstrates its operation between -20 °C and -75 °C, and through a comprehensive series of tests, extended the frost-point temperature range from -75 °C to -100 °C, under sub-atmospheric and atmospheric pressure conditions. The corresponding water vapor amount fractions generated by the system range between 6.5×10^{-6} mol·mol^{-1} and 12×10^{-9} mol·mol^{-1}. This study includes a detailed uncertainty analysis, validating all sources of the uncertainty budget for the frost point temperature and water vapor amount fraction. The expanded uncertainty ($k = 2$) of frost-

point temperature measurements was found to be 0.07 °C between -75 °C and -95 °C, and 0.26 °C at -100 °C. For the water vapor amount fraction, the relative expanded uncertainty ($k = 2$) was estimated to be 1.2 % or better in the range from 35×10^{-9} mol·mol^{-1} to 6.1×10^{-3} mol·mol^{-1}, increasing to 6.5 % at 13×10^{-9} mol·mol^{-1}.

To support the international decarbonization efforts, such as the Paris Agreement and the European Green Deal, with the use of hydrogen as a sustainable energy vector for the transition to clean, low-carbon systems, this work contributed to improving the gas quality measurements in the hydrogen supply chain. To meet the above needs, a transportable Precision Humidity Generator (t-PHG) was designed, constructed, and characterized at INRiM humidity standard lab. The t-PHG is a saturation-based humidity generator designed to operate within a frost-point temperature range between -55 °C and -10 °C and at pressures between 0.3 MPa and 5.5 MPa. This corresponds to water vapor amount fractions between 0.5×10^{-6} mol·mol^{-1} and 50×10^{-6} mol·mol^{-1}. The system was designed to operate in both single-temperature, single-pressure (1T-1P) mode and single-temperature, two-pressure mode (1T-2P). The amount fraction and pressure working ranges were selected to cover the operating conditions of humidity sensors/analyzers typical of applications of hydrogen production, storage, and refueling fuel cell vehicles. The expected relative uncertainty of the water vapor amount fraction spans from 3 % to 5 %, depending on the operating conditions. This research presents the t-PHG design, along with a preliminary uncertainty assessment of the generated frost-point temperature and amount fraction in both hydrogen and nitrogen gas carriers.

Finally, to address trace humidity calibration needs in industrial gases, VTT-MIKES developed a low frost-point humidity generator (LFPHG), a condensation-based system designed to operate in 1T-1P or 1T-2P mode, generating humid gas streams with frost points as low as -100 °C at pressures up to 0.5 MPa—equivalent to water vapor fractions approximately 10×10^{-9} mol·mol^{-1}. Thanks to a mobility grant, I contributed to finalizing the LFPHG's development, conducting performance tests, and carrying out a comprehensive uncertainty evaluation. Uncertainty components across the frost-point and water vapor amount fraction ranges were analyzed and reported, particularly at the lowest operating temperatures.