4. Standards for Low Concentrations of Water Vapor in Gases

***J. T. Hodges**, G. E. Scace, P. H. Huang, W.W. Miller, and D.C. Hovde (Southwest Sciences)*

Objective: To provide absolute standards for water vapor generation and measurement in the concentration range 1 to 1000 nmol H_2O/(mol of carrier gas).

Problem: Strict monitoring and control of trace quantities of water vapor are required in numerous industrial processes related to the fabrication of microelectronics, photonics and semiconductors. Regrettably, metrology-grade standards are not well established in this range, and existing hygrometers are inadequate as they often suffer from hysteresis, irreproducibility and relatively slow response. Further, measurements of low levels of water vapor are complicated by poorly understood interactions between the water vapor, carrier gases and transfer lines, as well as uncertainty in thermodynamic properties of as water vapor and carrier gas mixtures.

Approach: The strategy of this program is to develop standard sources of humidity and complementary methods of humidity measurement spanning the same range. Both the generation and measurement schemes are optimized for stability, and both are based on processes that can be modeled from first-principles so that the respective uncertainties can be estimated with confidence.

Results and Future Plans: A thermodynamically based standard humidity source, known as the Low Frost-Point Generator (LFPG), was developed. Its output is linked primarily to the vapor pressure of ice and therefore is governed by the system temperature and pressure, two quantities that can be precisely controlled and accurately measured. The LFPG delivers water-vapor concentrations as low as 3 nmol/mol, with a long-term stability of better than ±0.2 % in water vapor concentration and a relative uncertainty (coverage factor = 2) of better than 1 %. Comparison of the new generator with another long-established NIST standard generator indicates that in the region of overlap of the two systems, the two agree to within the stated uncertainty of the reference generator. The LFPG is now available to provide special test services for clients desiring direct traceability to national humidity standards. Commercial sensors being characterized include chilled-mirror devices, optical absorption spectrometers, electrolytic and capacitive devices, and vibrating crystal transducers. Also, using a stable hygrometer as a nulling device, the LFPG provides a reference to which other precision humidity generators may be compared. This approach enables the measurement of water vapor concentrations differing by less than 1 nmol/mol. At present, a comparison of several standard generators (based on permeation tube/flow dilution schemes) is underway, spanning the water vapor amount fraction range 10 to 100 nmol/mol.

Two techniques based upon absorption spectroscopy are being developed for absolute measurement of water vapor concentration. With the first approach, called wavelength modulation spectroscopy (WMS), we demonstrated relatively fast time response, linearity over two decades of water vapor amount fraction in the range 3 to 3000 nmol/mol, and precision of better than 1 nmol/mol. The other laser absorption technique being developed is cavity-ring-down spectroscopy (CRDS). It is expected to be more accurate than WMS, as it provides a fundamental measure of water vapor concentration linked to measurements of time and frequency and referenced to the triple point of water.