SPARC Water Vapor Assessment: Measurement of water vapor at low-ppm mixing ratios using chemical ionization mass spectrometry

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Over the past several decades there has been considerable disagreement among in situ water vapor measurements by different instruments at the low part per million (ppm) mixing ratios found in the upper troposphere and lower stratosphere (UT/LS). These discrepancies contribute to uncertainty in our understanding of the microphysics related to dehydration and cirrus cloud particle nucleation and growth and affect our ability to estimate the influence of climate change on the radiatively important UT/LS water vapor distribution. To address the discrepancies observed in the measurement of UT/LS water vapor, a new chemical ionization mass spectrometer (CIMS) instrument has been developed for the fast, precise, and accurate measurement of water vapor at low mixing ratios. The instrument utilizes a radioactive alpha particle source to ionize a flow of sample air drawn into the instrument. A cascade of ion-molecule reactions results in the production of protonated water ions proportional to the water vapor mixing ratio that are then detected by the mass spectrometer. The multi-step nature of the ionization mechanism results in a non-linear sensitivity to water vapor, requiring calibration across the full range of values to be measured. To accomplish this calibration, we have developed a novel calibration scheme using catalytic oxidation of hydrogen to produce well-defined water vapor mixing ratios that are introduced into the instrument inlet. The CIMS instrument was deployed for the first time aboard the NASA WB-57 high altitude research aircraft during the Mid-latitude Airborne Cirrus Properties Experiment (MACPEX) mission in March and April 2011. For operation in the unheated, unpressurized environment of the aircraft, instrument temperatures, pressures, and flows are controlled in order to maintain constant operating conditions. The sensitivity of the instrument was calibrated every 45 minutes in flight from < 1 to 150 ppm. Analysis of in-flight data demonstrates a typical sensitivity of 1800 Hz/ppm at 4.5 ppm with a signal to noise ratio (3 sigma) > 24 for a 1 second measurement. The instrument and its calibration system performed successfully in 7 flights during the MACPEX mission, sampling water vapor mixing ratios as low as 4 ppm in stratospheric air. A comparison of this new measurement with other measurements on board the aircraft is expected to help resolve the long-standing differences in low water measurements in the stratosphere.