

Laboratory Evaluation of the Effect of Nitric Acid on Chilled Mirror Hygrometer Measurements in the Upper Troposphere (UT)/Lower Stratosphere (LS)

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Chilled mirror hygrometers (CMH) are widely used to measure water vapor in the UT/LS from balloon-borne sondes. CMH instruments operate by determining the temperature required to maintain a condensate layer with constant optical scattering on a chilled mirror in contact with ambient air. The dependence of the scattering on condensation and evaporation of water from the mirror surface allows the mirror temperature to be used to calculate the partial pressure of water vapor in the ambient air from a formulation of the Clausius-Clapeyron relation. Systematic discrepancies among *in situ* water vapor instruments have been observed at low water vapor mixing ratios (< 5 ppm) in the UT/LS, and understanding these measurement discrepancies is important for accurate determination of water vapor values and trends in this region. We have conducted a laboratory study to investigate the potential interference of gas-phase nitric acid (HNO_3) with the measurement of frost point temperature, and consequently the water vapor mixing ratio, by CMH. The CMH instruments used in these experiments are a reconfiguration of the Cryogenic Frostpoint Hygrometer (CFH) to include a hermetically sealed flow path and a modified optical arrangement allowing direct imaging of the mirror surface as an additional measurement diagnostic. A HNO_3 permeation source and a reactive nitrogen (NO_y) instrument were used to add and measure HNO_3 to the flow system. A water vapor permeation source was used to produce stable H_2O mixing ratios of a few ppm in the flow system at pressures of 90-140 hPa and flows of 2-4 slpm, representative of conditions for CFH operation in the UT/LS. No detectable change in the measured frost point temperature was found for HNO_3 mixing ratios up to 4 ppb for exposure times up to 150 minutes. HNO_3 was observed to co-condense on the mirror frost layer with the mass increasing linearly with time at constant exposure levels. During a typical CFH ascent period (90-120 min), the maximum condensed HNO_3 amounts were comparable to monolayer coverage of the geometric mirror surface area.

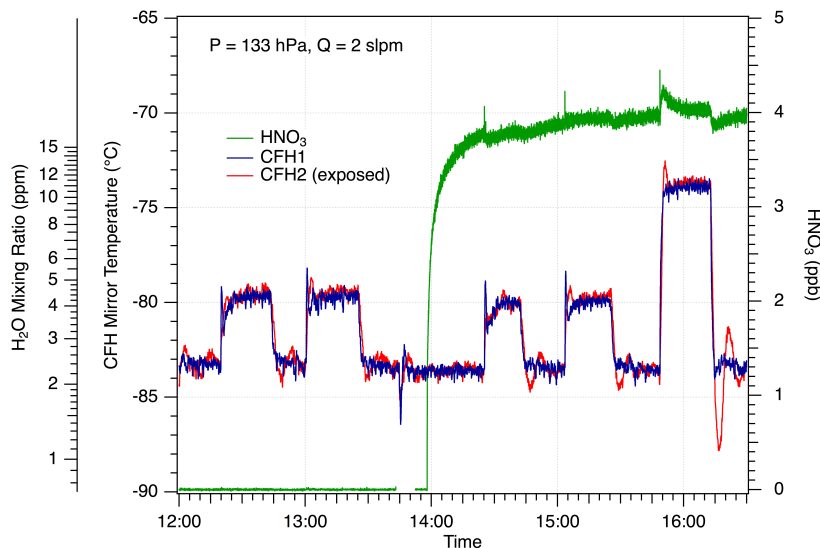


Figure 1. Time series showing the measured frost point temperatures from exposed and unexposed CFH instruments prior and subsequent to the addition of HNO_3 to the sample flow and the HNO_3 abundance in the flow system as measured with the NO_y instrument. Increases in observed frost point temperature were due to addition of small flows of room air to the sample flow.