A Low-Maintenance Drying System for Ambient Air Greenhouse Gas Monitoring

L.R. Welp¹, W. Paplawsky¹, R.F. Keeling¹, R.F. Weiss¹ and S. Heckman²

¹Scripps Institution of Oceanography (SIO), University of California at San Diego, La Jolla, CA 92093; 858-822-1642, E-mail: lwelp@ucsd.edu ²Earth Networks, Inc., Germantown, MD 20876

In preparation for the routine deployment of the Earth Networks greenhouse gas monitoring network, we have designed and tested a simple method for drying ambient air to below 0.1% mole fraction H_2O using a Nafion model MD-050-72S-1 dryer. We tested the prototype inlet drying system on a Picarro model G2301 Cavity Ring-Down Spectroscoy $CO_2/CH_4/H_2O$ analyzer. The analyzer measures water vapor mixing ratio at the same frequency as CO_2 and CH_4 and then corrects for the dilution and peak broadening effects on the CO_2 and CH_4 mixing ratios. This analyzer is remarkably stable and performs well on water vapor correction tests, but we believe there is an added benefit of reducing the dependence on the H_2O correction for long-term field measurement programs. Unlike CO_2 and CH_4 measurements, which can be calibrated in the field with compressed gas standards, the H_2O correction is not easily calibrated in the field. Substantially lowering the amount of H_2O in the sample can reduce uncertainties in the applied H_2O corrections by an order of magnitude or more, and reduce the need to verify the H_2O correction algorithm stability.

Our Nafion drying inlet system takes advantage of the extra capacity of the external Picarro analyzer pump to redirect 30% of the dry gas exiting the Nafion to the outer shell side of the dryer. This method has no consumables and does not appear to alter the CO₂ and CH₄ concentrations of the sample gas within measurement precision. We restrict sample flow through the G2301 analyzer to 70 cc/min to conserve calibration gases during routine deployment. It is difficult to humidify air without changing its dry-gas CO₂ mixing ratio slightly because of the propensity of CO₂ to interact with water adsorbed on tubing walls. For this reason, we compared our Nafion dryer system with a proven cold trap at -95°C. Dry air from a standard tank was passed through a humidifier in the wet-gas test (or bypassed in the dry-gas test) and then alternately directed through the Nafion or cold trap at 15-min intervals. Differences between the Nafion dryer and cold trap in the dry-gas and wet-gas tests were less than the targeted precision of the measurements. Systematic differences between the drying methods were at the level of 0.01 ppm in CO₂ and 0.007 ppb in CH₄ for the wet-gas test (Fig 1) and 0.01 ppm in CO₂ and 0.04 ppb in CH₄ for the drygas test.

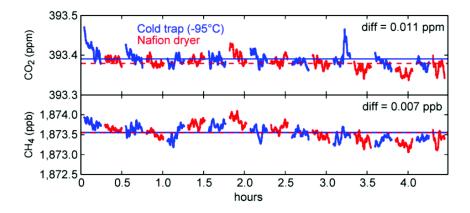


Figure 1. Time series of wet-gas experiment showing 1-min running means of the analyzer's 1-sec sampling. Tank air was humidified to 2.2% H_2O (mole fraction) and either passed through the cold trap (blue) or Nafion (red) in 15- min switching intervals. The first 2 min and last 1 min of each 15-min interval were excluded from the analysis because of transient artifacts. The moisture content of the Nafion-dried stream increased from 0.004% to 0.016% over the course of the experiment. CO_2 and CH_4 have been corrected for water vapor using factory default settings on the analyzer. Blue and red horizontal lines are means of cold trap intervals and Nafion intervals respectively over the entire experiment. The cause of the small drift in CH_4 is unknown, but is subtracted in these tests.