

## **A Nafion-based air sample dryer for atmospheric flask sampling allowing accurate measurements of CO<sub>2</sub> and its stable isotopes in humid air**

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Atmospheric flask samples are either collected at atmospheric pressure by simply opening a valve of a pre-evacuated flask or pressurized up to a few bar above ambient providing more air for analysis. Under humid conditions, there is a risk that water vapor in the sample leads to condensation on the walls of the flask notably at higher than ambient sampling pressures. Liquid water in sample flasks is known to affect CO<sub>2</sub> mixing ratios and more importantly, alters the isotopic composition of oxygen (<sup>17</sup>O and <sup>18</sup>O) in CO<sub>2</sub> (referred to as isotopic fractionation). Hence, to be able to accurately detect CO<sub>2</sub> and its stable isotopes it is vital to dry the air samples before they are pressurized in the flasks to a sufficiently low dew point, thus avoiding condensation (dew point < 5 °C at 2.8 Bar (40 psi)). Here we present a simple air sample dryer to provide dry air samples to be collected over the Amazon up to about 6 km altitude as part of the “Airborne Stable Isotopes of Carbon from the Amazon” (ASICA) project. A major objective of the ASICA project is to provide high-precision measurements of <sup>13</sup>C, <sup>17</sup>O, and <sup>18</sup>O in CO<sub>2</sub> from more than 5000 flasks to be collected over the Amazon at 4 different sites over a period of 5 years to improve our understanding of the carbon balance of the Amazon rain forest (<http://www.asica.eu>).

The air sampling system onboard the aircrafts used for the ASICA project consists of a “Programmable Compressor Package” (PCP) and a “Programmable Flask Package” (PFP) containing twelve 700cc flasks both designed by NOAA’s Carbon Cycle Group. The design of the “ASICA air dryer” presented here consists of 2 Perma Pure PD-Series gas dryers containing 200 Nafion strains in a stainless steel tube shell (PD-200T-24MSS) placed in series. A dry purge gas within the shell that flows countercurrent to the feed removes moisture from the sample air stream permeating the tubing. The dry purge air is provided by feeding the exhaust flow of the PFP through a 350 g of dry Molecular sieve (type 3A) cartridge.

Here we present first results of extensive experiments to test the stability and potential interference of the dryer on CO<sub>2</sub> and its stable isotopes. Our results indicate that the dryer is effectively drying a humid air stream up to ~12 L/min at 80% RH and 32 °C without any impact on the CO<sub>2</sub> mixing ratios. Isotopic measurements of a sample air stream fed through the drier was performed using a new Tunable Infrared Laser Direct Absorption Spectrometer (TILDAS, Aerodyne Research, Inc.), specially designed for the measurements of δ<sup>13</sup>C, δ<sup>17</sup>O, and δ<sup>18</sup>O. Under moderate ambient conditions (60% RH at 22 °C), the TILDAS measurements show that the Nafion based drying system has negligible impact on the CO<sub>2</sub> isotope measurements. The resulting measurement precisions obtained with the TILDAS are as specified by the manufacturer (<0.02‰ for δ<sup>17</sup>O and δ<sup>18</sup>O). Finally, we present first results of tests with a prototype ASICA dryer set up with a PCP and PFP done at NOAA-ESRL and the University of Colorado.