Fractionation of O_2/N_2, Ar/N_2, and CO_2 at Aircraft Sampling Inlets

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For airborne measurements of high relative precision, such as those of $\delta(O_2/N_2)$ or $\delta(Ar/N_2)$, separation of gases as a result of pressure driven diffusive effects has been recognized as a potential challenge (Steinbach, 2010; Bent, 2014). We have conducted airborne in situ measurements of $\delta(O_2/N_2)$ and CO_2 since 2007 and airborne flask sampling for $\delta(O_2/N_2)$, $\delta(Ar/N_2)$, CO_2, and isotopologues of CO_2 since 1999 using a wide range of aircraft and inlet designs. We have used the $\delta(Ar/N_2)$ measurements, expected to be near constant in the troposphere, as well as differences in $\delta(O_2/N_2)$ between *in situ* and flask measurements made using differing inlets and flow rates, to characterize inlet fractionation effects.

Fortuitously, for the combination of inlets and flight envelopes we used from 1999-2015, inlet fractionation was modest at -20 per meg $\delta(Ar/N_2)$ and -5 per meg $\delta(O_2/N_2)$ over the full tropospheric column or less. For the HIPPO1-5 (2009-2011) campaigns on the NSF/NCAR GV aircraft, we used aft facing tubes inside of a cylindrical pylon with expanding diameter, designed to slow the internal air speed. The small fractionation effects we observed were consistent with pressure gradients perpendicular to the streamlines, as suggested by Steinbach (2010), which resulted in more of the lighter molecules making the turn into the inlet tube.

After switching to a new exposed aft facing inlet design for the ORCAS (2016) campaign, in order to mitigate concerns over potential cabin air contamination via the pylon, we found fractionation of up to -40 per meg $\delta(O_2/N_2)$ for our *in situ* analyser between 400 and 200 hPa. Then, moving to the NASA DC-8 aircraft for ATom I (2016) we experienced extreme fractionation effects of up to -200 per meg $\delta(O_2/N_2)$ between 400 and 200 hPa. During this campaign we experimented with 6 different inlet configurations and were successful in eliminating these effects part way through the campaign.

The most extreme fractionation we observed using these experimental configurations was with a side-facing inlet, which performed nominally up to an altitude of 350 hPa then fractionated $\delta(O_2/N_2)$ by approximately -2000 per meg and CO_2 by approximately -3 ppm. The ratio between these effects matches the ratio of O_2 and CO_2 mass differences with N_2, suggesting a pressure gradient effect such as that proposed by Steinbach (2010). This observed fractionation of CO_2 relative to air suggests that even for lower relative precision airborne measurements, careful consideration of inlet sampling artifacts should not be neglected.

References

Steinbach, J. (2010), Enhancing the Usability of Atmospheric Oxygen Measurements Through Emission Source Characterization and Airborne Measurements, PhD thesis, 145 pp, Max-Planck-Institut für Biogeochemie, Jena.

Bent, J. D. (2014), Airborne Oxygen Measurements over the Southern Ocean as an Integrated Constraint of Seasonal Biogeochemical Processes, Ph.D. thesis, 276 pp, Scripps Institution of Oceanography, Univ. of Calif., San Diego.