Atmos. Meas. Tech. Discuss., 5, C2396–C2398, 2012
www.atmos-meas-tech-discuss.net/5/C2396/2012/

Atmospheric Measurement Techniques Discussions

Interactive comment on "Design and performance of a Nafion dryer for continuous operation at CO_2 and CH_4 air monitoring sites" *by* L. R. Welp et al.

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Received and published: 2 October 2012

The paper is presenting a nice Nafion dryer setup. I like many of the thoroughly thought ideas, but still like to commend on some parts that might become critical for a measurement network.

The maximum error in CO2 of 0.05 ppm is worrisome. This number is a negative bias to the network, introducing artificial carbon sinks (in comparison to non-biased stations). For the southern hemisphere this is already not compliant with the WMO recommendations, especially because random errors, calibration errors and the remaining water correction introduce further (random) uncertainties. In contrast, the wet measurement with a full H2O correction would mainly result in random errors.

It is mentioned in the paper, that parts of this error are compensated by sending the calibration gases through the Nafion dryer as well. Unfortunately, the dryer will react quite differently for dry air; [Ma et al., 2005] report a strong preference of CO2 diffusion compared to O2 with increasing water content (almost exponential dependence). Thus, the presented setup will probably compensate the negative bias only very little (as it is also written on p. 5453, line 19ff).

Moreover, [Leckrone et al., 1997] report quite strong temperature dependency of Nafion membranes: with increasing temperature a higher storage of H2O in the membrane results in higher H2O concentration (in contrast to p. 5455 line 18f). At 45 degC the Nafion may lose some drying capabilities.

My largest concern is caused by the observations described on page 5456 line 11ff. The long stabilization time and the observed temporal drift (within the first 30 min) after wet/dry switching implies a strong sponge effect of the Nafion membrane also for changing ambient conditions, which are not yet taken into account. In my eyes, it would be helpful to run an analyzer with your suggested setup in parallel to another analyzer with a cryotrap or with a fully verified water correction. Another possibility without additional experiment might be a purely mathematical estimate: A response function of the Nafion dryer might be calculated from the data shown in Fig. 4 to convolve it with a typical ambient signal. This might give a first estimate of the magnitude of the Nafion sponge effect on the observations.

Some more specific comments: p. 5452, line 8ff: The CO2-H2O interaction is still true in the rest of the inlet line.

p. 5453, line 7f: "conserves sample and reference gas" is not really true, as you show in the following paragraph.

p. 5454 line 12 ff: Is it possible to quantify the additional measurement uncertainty due to the application of the same water correction parameters for different analyzers for H2O < 0.15% ?

References: Leckrone, K. J., and Hayes, J. M.: Efficiency and Temperature Dependence of Water Removal by Membrane Dryers, Analytical chemistry, 69(5), 911-918, 1997.

Ma, S., Odgaard, M., and Skou, E.: Carbon dioxide permeability of proton exchange membranes for fuel cells, Solid State Ionics, 176(39-40), 2923-2927, 2005.

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 5449, 2012.