**Quantifying Nafion cross-membrane $CO_2$ and $CH_4$ gas leakage and it's dependence on sample mole fraction and water content**

Ann Stavert[1], Simon O'Doherty[1], Kieran Stanley[1] and Dickon Young[1]

[1] Atmospheric Chemistry Research Group, University of Bristol, Cantock's Close, Bristol, UK. ann.stavert@bristol.ac.uk

The UK DECC (Deriving Emissions linked to Climate Change) tall tower sites were established in 2012 with the aim of quantifying key greenhouse gases including halocarbons, sulphur hexafluoride, nitrous oxide, methane and carbon dioxide. As Nafion water-permeable membranes have a history of successful use in drying air samples of halocarbons, $N_2O$ and $SF_6$ (e.g. Foulger and Simmonds (1979)) the approach was implemented at DECC and later GAUGE (Greenhouse gAs Uk and Global Emissions) tall tower sites coupled with Picarro Cavity Ring-Down Spectrometers (CRDS). Unfortunately, this drying method is not suitable for $CO_2$ and $CH_4$ as these gases can pass across the Nafion membrane (Chiou and Paul 1988). Once the issue was identified, the drying systems were removed; however, a quantity of possibly contaminated data remained.

Welp et al. (2013) have previously considered the issue of gases passing through the Nafion membrane. However, the drying approach they used was not directly comparable to that of the DECC/GAUGE sites. Also, that study was limited to only two sample $H_2O$ saturations, dry (0% $H_2O$) or wet (2% $H_2O$), and did not conduct wet experiments with samples of above ambient (~393 ppm $CO_2$ & ~1874 ppb $CH_4$) mole fractions. Considering the importance of water in gas transport across the membrane (Naudy et al. 2014) and the elevated range of water content (>3% $H_2O$), and $CO_2$ and $CH_4$ mole fractions (>500 ppm $CO_2$ & >2500 ppb $CH_4$) observed in the DECC/GAUGE network, further investigation of this issue was required.

As such, a series of laboratory experiments were designed to investigate the effect of sample water content (0 to 3.5%v) and sample mole fraction (370 to 510 ppm $CO_2$ and 1780 to 2600 ppb $CH_4$) on Nafion cross-membrane leakage, with the aim of deriving an empirical correction that could be applied to the effected tall tower data. These experiments showed $CO_2$ and $CH_4$ leakage, with losses greater than 0.2 ppm $CO_2$ and 5 ppb $CH_4$ observed at high sample mole fractions and elevated water content. Interestingly $CH_4$ leakage was found to increase linearly with water content while $CO_2$ leakage peaked at ~2%v $H_2O$ and then decreased. The exact mechanism driving these results and the possible impact of the CRDS water correction is not yet clear.

References

Chiou, J. S. and D. R. Paul (1988). "Gas permeation in a dry Nafion membrane." Industrial & Engineering Chemistry Research **27**(11): 2161-2164.

Foulger, B. E. and P. G. Simmonds (1979). "Drier for field use in the determination of trace atmospheric gases." Analytical Chemistry **51**(7): 1089-1090.

Naudy, S., F. Collette, F. Thominette, G. Gebel and E. Espuche (2014). "Influence of hygrothermal aging on the gas and water transport properties of Nafion® membranes." Journal of Membrane Science **451**: 293-304.

Welp, L. R., R. F. Keeling, R. F. Weiss, W. Paplawsky and S. Heckman (2013). "Design and performance of a Nafion dryer for continuous operation at $CO_2$ and $CH_4$ air monitoring sites." Atmos. Meas. Tech. **6**(5): 1217-1226.