Investigation of adsorption / desorption behavior of high pressure small volume cylinders and its relevance to atmospheric trace gas analysis

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A critical issue for the long term monitoring of atmospheric trace gases is precision and accuracy of the measurement systems employed. In order to achieve a globally integrated and well established greenhouse gas observation network, the World Meteorological Organization (WMO) has recommended compatibility goals for measurements of trace gases within its Global Atmosphere Watch (GAW) programme [1]. These challenging limits can only be achieved by regular calibration with standard gases of known composition. However, standard gases may not be stable throughout a measurement period due to diffusion, leakage, regulator effects, gravimetric fractionation and surface processes [2, 3]. The latter, which encompasses adsorption / desorption, is also dependent on temperature, pressure and surface processes [4, 5].

For this study, high pressure small volume measurement chambers were produced which enable to investigate trace gases and their affinity for adsorption / desorption on various surfaces over a set of temperature and pressure ranges. The presented experiments are designed to investigate the filling pressure dependency up until 40 bars, and temperature dependency up until 50°C for these prototype cylinders of steel and aluminum. Here, we focus on measurements of CO₂, CH₄, CO and H₂O using a cavity ring down spectroscopy analyzer. Moreover, a theoretical adsorption isotherm is used to explain the changes in the measured concentrations for both pressure and temperature variations.

References

[1] World Meteorological Organization (WMO), Global Atmosphere Watch(GAW): Report No. 229, 18th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2015), 2016.

[2] Keeling, R. F., Manning, A. C., Paplawsky, W. J., and Cox, A. C.: On the long-term stability of reference gases for atmospheric O_2 / N_2 and CO_2 measurements, Tellus B, 59, 10.3402/tellusb.v59i1.16964, 2007.

[3] Langenfelds, R. L., van der Schoot, M. V., Francey, R. J., Steele, L. P., Schmidt, M., and Mukai, H.: Modification of air standard composition by diffusive and surface processes, Journal of Geophysical Research: Atmospheres, 110, n/a-n/a, 10.1029/2004JD005482, 2005.

[4] Leuenberger, M. C., Schibig, M. F., and Nyfeler, P.: Gas adsorption and desorption effects on cylinders and their importance for long-term gas records, Atmos. Meas. Tech., 8, 5289-5299, 10.5194/amt-8-5289-2015, 2015

[5] Miller, W. R., Rhoderick, G. C., and Guenther, F. R.: Investigating Adsorption/Desorption of Carbon Dioxide in Aluminum Compressed Gas Cylinders, Analytical Chemistry, 87, 1957-1962, 10.1021/ac504351b, 2015.