Pressure Dependent CO_2 Enrichment in High-pressure Aluminum Cylinders

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Introduction

The primary standards to maintain the WMO CO_2 X2007 scale as well as the secondary and the tertiary CO_2 standards to pass the scale down are stored in high pressure aluminum cylinders. To meet the WMO's accuracy goal[1] of ± 0.1 µmol mol^{-1}, it is crucial that the gas standards are stable during their whole life time. At field stations but also in laboratory experiments, some analytes showed CO_2 enrichment with decreasing pressure[2], which was most probably caused by either desorption of CO_2 molecules from the cylinder walls with decreasing pressure, as described by Langmuir[3], or by Rayleigh distillation[4]. If these enrichment effects are reproducible, a function could be applied to correct the enrichment effects of the cylinders and improve the accuracy of the CO_2 measurements calibrated with these standards.

Methods

To investigate possible CO_2 enrichment effects, a batch of eight high pressure aluminum cylinders is repeatedly filled at NOAA's Niwot Ridge station with pressurized ambient air following the same procedures as for the CO_2 standards provided by NOAA. After delivery to the laboratory and reaching thermal equilibrium, they are decanted at low flows (0.3 ml min^{-1}) and high flows (5 l min^{-1}), while the CO_2 mole fraction is measured continuously by a temperature and pressure controlled NDIR analyzer (LI-7000). A suite of four standards are measured at regular intervals to calibrate the measurements with a quadratic function, a target gas gives information about the quality of the measurements (see Figure 1). A nonlinear least square algorithm is used to determine the unknown parameters of Langmuir's adsorption/desorption function and of the Rayleigh distillation function.

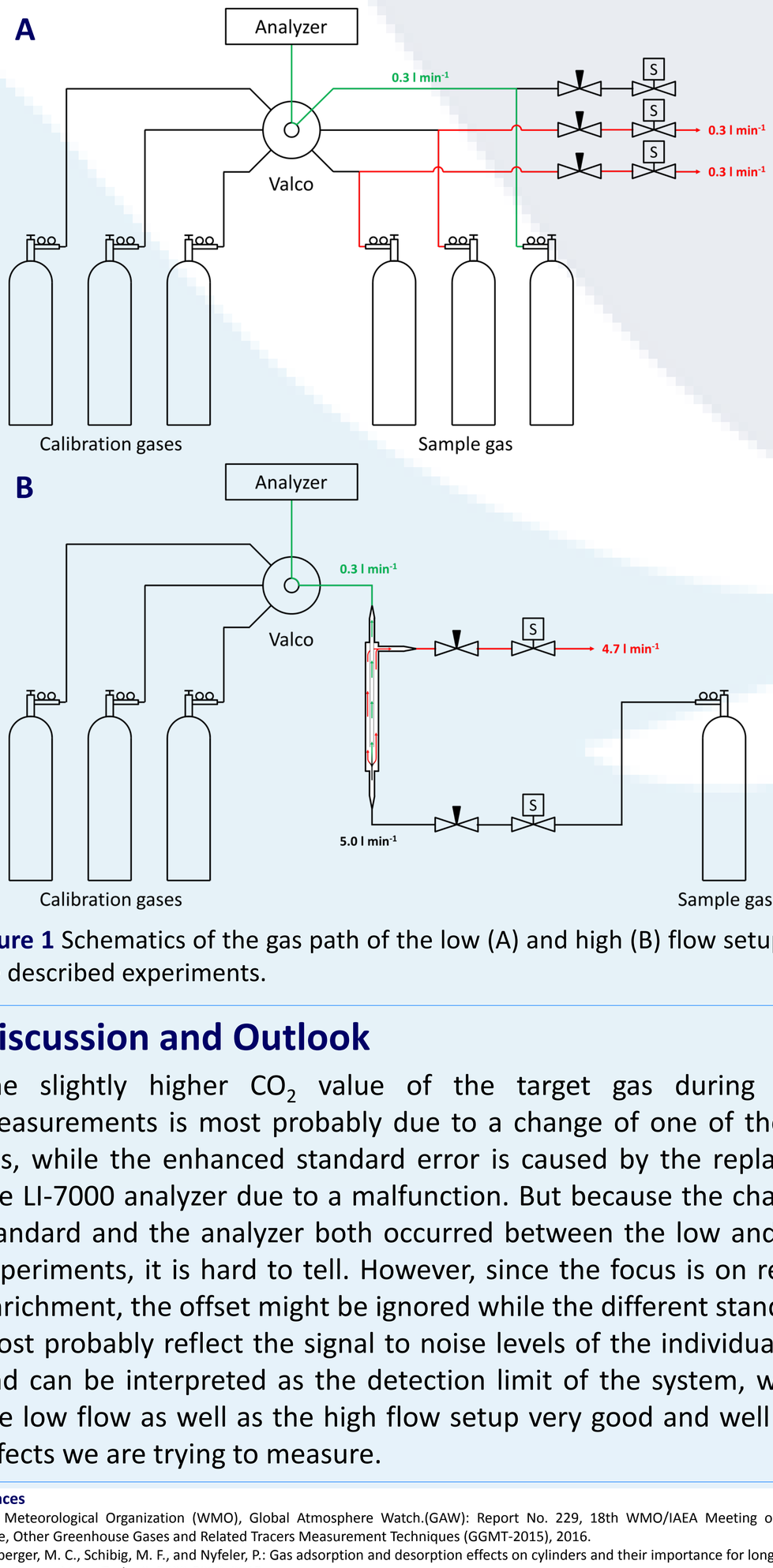

Figure 1 Schematics of the gas path of the low (A) and high (B) flow setups as used in the described experiments.

Results

During low flow decanting experiments, the eight different aluminum cylinders show all a similar CO_2 enrichment of about 0.1 µmol mol^{-1} with a small, almost negligible, linear looking CO_2 increase from the beginning down to about 30 bar and a clear accelerated, exponential looking increase from 30 bar until the cylinder is empty (see Figure 2 A). During the high flow decanting experiments the CO_2 enrichment is about 0.2 µmol mol^{-1}, the increase from the beginning down to 30 bar seems to be slightly steeper, but again from 30 bar until the cylinder is empty, the increased CO_2 enrichment can be observed (see Figure 2 C). In the low flow as well as in the high flow experiments it is possible to fit both, the Langmuir adsorption/desorption function (red lines in Figure 2 A and C) as well as the Rayleigh distillation function (green dashed lines in Figure 2 A and C) nicely to the data.

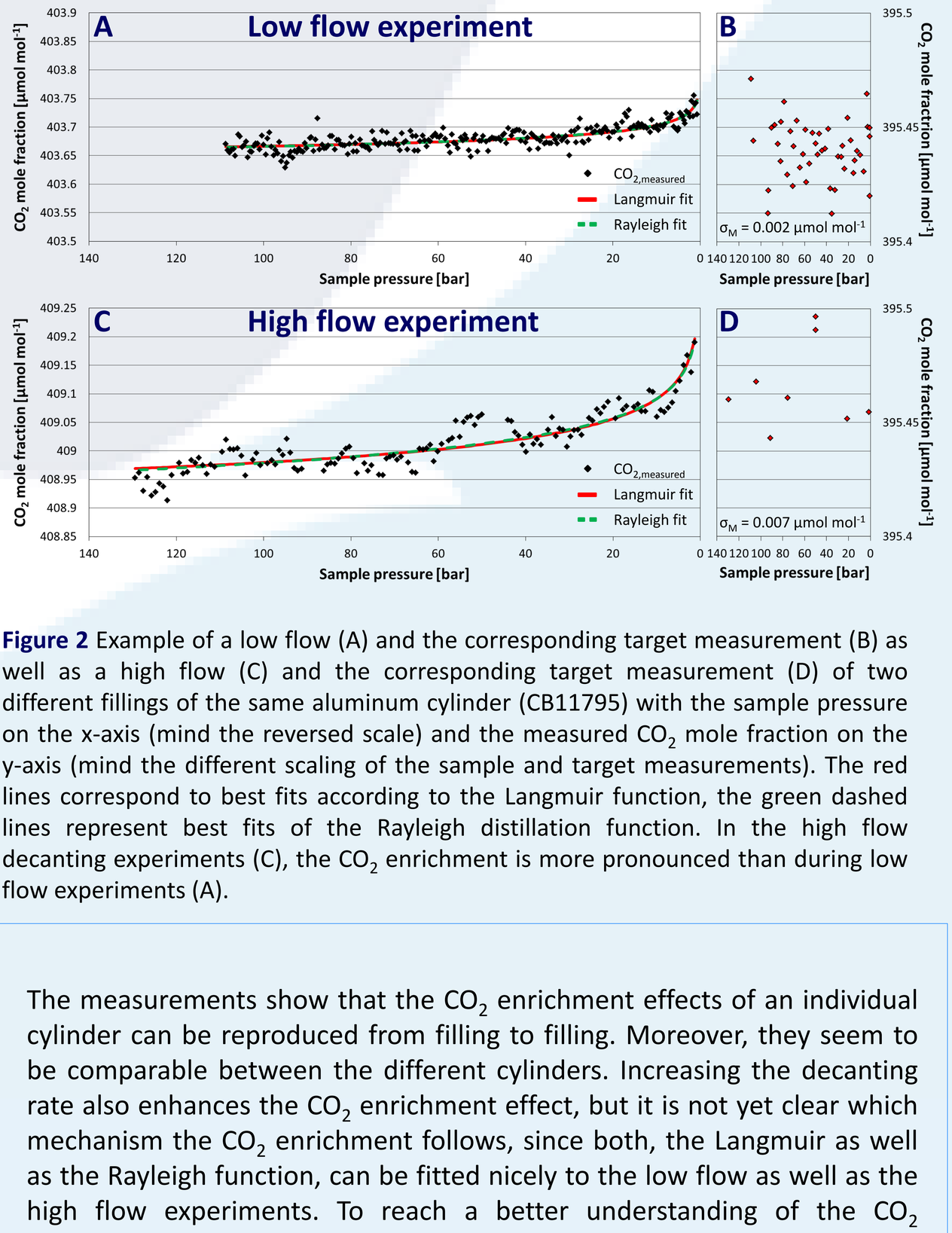

Figure 2 Example of a low flow (A) and the corresponding target measurement (B) as well as a high flow (C) and the corresponding target measurement (D) of two different fillings of the same aluminum cylinder (CB11795) with the sample pressure on the x-axis (mind the reversed scale) and the measured CO_2 mole fraction on the y-axis (mind the different scaling of the sample and target measurements). The red lines correspond to best fits according to the Langmuir function, the green dashed lines represent best fits of the Rayleigh distillation function. In the high flow decanting experiments (C), the CO_2 enrichment is more pronounced than during low flow experiments (A).

Discussion and Outlook

The slightly higher CO_2 value of the target gas during high flow measurements is most probably due to a change of one of the standard gas, while the enhanced standard error is caused by the replacement of the LI-7000 analyzer due to a malfunction. But because the change of the standard and the analyzer both occurred between the low and high flow experiments, it is hard to tell. However, since the focus is on relative CO_2 enrichment, the offset might be ignored while the different standard errors most probably reflect the signal to noise levels of the individual analyzers and can be interpreted as the detection limit of the system, which is for the low flow as well as the high flow setup very good and well below the effects we are trying to measure.

The measurements show that the CO_2 enrichment effects of an individual cylinder can be reproduced from filling to filling. Moreover, they seem to be comparable between the different cylinders. Increasing the decanting rate also enhances the CO_2 enrichment effect, but it is not yet clear which mechanism the CO_2 enrichment follows, since both, the Langmuir as well as the Rayleigh function, can be fitted nicely to the low flow as well as the high flow experiments. To reach a better understanding of the CO_2 enrichment, we plan to do additional experiments in the near future, where we will change different parameters such as flow rate and cylinder temperature. This might give a clear indication of the enrichment process at work and enables us to find a general correction function.

References

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