

Reply to the review of P.P. Tans

The authors would like to thank P.P. Tans for his valuable comments. In the following, referee's comments are given in bold and author's responses in plain text. Suggested new text is quoted in italics together with page and line numbers.

General comments: The authors performed a series of experiments to learn more about wall effects in aluminum and steel high pressure gas cylinders at different pressures and temperatures. The trace gases considered are CO₂, CH₄, CO and low amounts of water vapor in air. In order to increase wall effects they chose to make special small cylinders with a higher wall to volume ratio. Additional advantages are that one has easy access to the interior surface and it is also easier to control the temperature of the small cylinders in a small oven. However, it is a significant disadvantage that their internal surface may not be the same as in the larger Luxfer cylinders that are almost universally used to distribute calibration mixtures for high precision greenhouse gas measurements. Luxfer claims that it has a proprietary version of the 6061 alloy, its manufacturing process is very different, and the surface treatment of the author's cylinders is also different from Luxfer's. The smallest high pressure Luxfer cylinder has a volume of only~700 cc; It is a pity that they did not include it in their experiments. The author's steel cylinder offers a comparison because its wall effects are different from aluminum. Stainless steel is often used for trace gases other than the main greenhouse gases.

We appreciate our reviewer's valuable comments and ideas. Unfortunately, we were not aware of the availability of the small size Luxfer cylinders. The small cylinder from Luxfer would indeed be a very valuable addition to these measurements, unfortunately we won't be able to conduct more measurements within the presented study. However, in our study, we put a strong focus on being able to open and close the cylinders because these measurement chambers were constructed primarily for material studies (Satar et al., 2019).

The smaller volume enables to fill and measure the cylinders easily. The surface of the small cylinder $A_{\text{cyl}} = 0.18 \text{ m}^2$ which results in a surface to volume ratio of 35.7. Therefore, we estimate the small cylinders to be more susceptible to adsorption by about 40 % than the 29.5 L Luxfer cylinders. It is also crucial to note that the real surface is expected to be significantly larger than the geometric surface area depending on the surface roughness.

We will add the following to the discussion:

"In order to understand the differences between the constructed cylinders and the Luxfer aluminum cylinder, measurements with a Luxfer cylinder of a similar size (5 L) and pressure ranges (up to 30 bar) would be very useful."

Specific comments: page 3 line 32 I wonder why the experiments did not go to 130 bar, at which pressure calibration gas mixtures are often distributed. The highest pressure was only 30 bar, not far above the recommended low pressure use limit of 20 bar.

The reviewer is right we should have conducted the measurements at higher pressures than 30 bar. However, the current equipment of our system would allow only pressures up to 68.9 bar (limited by the Swagelok valve). The selection of the valve was related to the condition that it does not include

any polymer parts (i.e. full metal valve). It would indeed be useful within further experiments to fill these cylinders higher than 30 bar. Our aim in this study was to establish a measurement and filling procedure and do the first characterization of this newly made cylinders. From these measurements we obtain a slope of $0.01 \mu\text{mol mol}^{-1} \text{bar}^{-1}$, which would lead to a $1.5 \mu\text{mol mol}^{-1}$ enrichment for a cylinder filled to a pressure of 150 bars and decanted to a final absolute cylinder pressure of 400 mbar. This is significantly higher than observed by Schibig et al. (2018) for instance. Therefore, we argue that at 30 bars filling pressure we are close to the maximal adsorption conditions (i.e. close to the measurable CO_2 amount fraction), as the Langmuir model says. Moreover, it is worthwhile to conduct experiments at lower pressure ranges (working pressure of analyzers) and increasing fill pressures step by step in order to understand fill pressure dependency.

For clarity we include this information in the manuscript on page 3 after line 27:

“Although the cylinders were constructed to withhold pressures up to 130 bar, the current setup would enable filling the small cylinders up to 68.9 bar which is limited by the valves (SS-4H from Swagelok). Since this study focused on the first characterization and the establishment of measurement and filling procedures of this newly made cylinders, we present experiments up to 30 bar only.”

p.4 line 12 This paragraph needs more detail, about the polishing material, what’s in the ultrasonic cleaning solution, and then later the “organic agent”, and “mild detergent”.

The commercial ultrasonic cleaning solution used in the first ultrasonic-bath is Deconex HT1201 (pH~9.4). The solution is used to remove oil, grease and residues of polishing compounds. However, we believe that either the cleaning agent or the oil residues which were still on the surface resulted in contamination during the temperature experiments. Therefore, we decided to do a second cleaning procedure. In the second ultrasonic bath a relatively neutral detergent (pH~7-8) was used since the alkaline solution (Deconex HT1201) was thought to be too aggressive. The organic agent is a chemical polishing material which was suited for aluminum surfaces.

On page 3, line 7, the following will be added:

“... a mildly alkaline commercial cleaning agent (Deconex HT1211, pH~9.4)”

On page 4, line 14, the following will be rephrased:

“Firstly, the aluminum cylinder was opened and placed in an ultrasonic-bath with a relatively neutral detergent (pH~7-8) and tap water, however the ultrasonic bath cycles at 60 °C ended with further contamination and visible stains (Fig. A1.b). To eliminate this, the two caps were polished with a chemical polishing material which was suited for aluminum surfaces...”

The stains mentioned have deposited something on the surface, but the elimination of the stains may have deposited something else later.

We agree with the reviewer that the elimination of the stains might have deposited something else on the surface of the cylinder. However, our experience was that the aluminum cylinder showed better performance after the elimination of stains without any visible changes in the surface.

p.7 section 2.3 What is the purpose of going to these low pressures, other than the small size of ice core samples? The section seems to be somewhat out of place with the rest of the experiments. Section 3.1.1 The CRDS analyzer has been used outside of its recommended range, where it cannot regulate its flow and pressure any more. There is a long description, incl. Fig. 3, of how to push a little below the factory-recommended lowest pressure. But is that relevant? Does the adsorption/desorption effect show up between the (absolute) pressures of ~1.4 and ~1.2 bar? Does any calibration gas user insist on going that low? My recommendation is to just stop at 1.4 bar, and shorten this section. It also would make the paper easier to read.

We highly appreciate our reviewer's comments on this section. However, in our opinion it is useful to include the measurements from the QCLAS analyzer, since an independent measurement device is a valuable addition for the interpretation of our current results. Moreover, presenting the lower pressure ranges is also useful for other gas applications including development of measurement systems. Although calibration gases are not used at such low limits, the aim of this study is to understand adsorption / desorption processes in its full extent including low pressures where adsorption effects should follow an exponential path.

Regarding the CRDS analyzer, our observations highlight possible systematic errors related to pressure and flow. Reporting such observations are valuable for the understanding of the measurement devices.

Section 3.1.2 I would like to thank the authors for their honest reporting, I wish more people would do that. However, also the one retained filling is a bit worrisome. Why is the response non-linear, both above and below the standard target pressure of 5 mb? Is the absorption line partially saturated?

We are confident that after our trials with the aluminum cylinder, we have established a successful procedure and used this setup for further measurements. Since these measurements were conducted after loading material blocks to the aluminum cylinder, they are not presented within this study. The runs with steel loading were reproducible, therefore, we think that presenting the one retained filling for the empty cylinder is non-problematic.

The non-linear response might indeed be related to the relatively high absorbance of the target lines (we observed this issue on two $^{12}\text{CO}_2$ lines, one of which was close to saturation which led to a significant offset in the carbon isotope ratio $^{13}\text{C}/^{12}\text{C}$). Therefore, we have selected the one which was further away from saturation, hence a saturation influence is less probable. A mismatch between the fitting model and the effective profile, crosstalk from the background or a combination of these might explain the response. It should as well be taken into consideration that the set pressure differences were large, corresponding to an order of magnitude change in the lower end (0.5 mbar).

Also, in the correction formula the fitted coefficient "c" (which corresponds to a constant offset between samples and standard) has been omitted.

The pressure correction was done relative to the cell pressure. Therefore, in Eqn. 2 (page 11, line 14) the constants (c) cancel each other.

p. 12 line 12 Note that Schibig found that even at 150 bar pressure only a relatively small fraction of available adsorption sites was occupied.

We rephrase the sentences in page 12 line 12 for clarity:

“The aluminum cylinder was in a pressure range (up to 30 bars) where most of its available sites for adsorption were unsaturated. This is in line with the observations of Schibig et al. (2018), which states that even at 150 bar pressure only a relatively small fraction of available adsorption sites was occupied. Changes between 30 and 150 bars seem to be minimal due to the shape of the adsorption isotherm.”

p.19 line 17 There is an important typo here. The “>” symbol should be changed to “<” (less than) in both cases.

We thank our reviewer for his attention. The signs are changed accordingly.

p. 19 last paragraph needs re-formulation. It now suggests that the authors have lost sight of Schibig’s observation that the Langmuir adsorption effect is only ~0.01 ppm at 75 bar, ~0.02 ppm at 45 bar, and 0.03 ppm for the 20 bar suggested cutoff. If one’s starting pressure is 30 bar, significant effects are not expected above ~4 bar, and still lower for lower starting pressures. Also the word “problematic” is an overstatement: The high reproducibility of Schibig’s results suggest that one could correct for adsorption effects. Finally, the second cleaning may have done some good, but I am not sure that is practical for the large cylinders that are mostly used.

We thank our reviewer for his insights. However, the results presented in this study have not followed the shape of the observations of Schibig et al. (2018). This difference is highly likely due to different cylinder properties used in these studies. Please see the replies to anonymous referee #2 for the discussion on K values. It would be worthwhile to investigate the adsorption using the flow-through approach. This would indicate whether the adsorption occurs already at very low pressure or not.

On page 19 line 24, we will change the word “problematic” to “not recommended”.

On page 20 after line, the following sentence will be added:

“Additionally, the reverse process of desorption will be investigated by using the flow through approach. Such experiments would be valuable to understand whether adsorption already occurs at very low pressures.”