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Atmospheric Measurement Techniques Discussions

Interactive comment on "Investigation of adsorption/desorption behavior of small volume cylinders and its relevance for atmospheric trace gas analysis" *by* Ece Satar et al.

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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

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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.

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. 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 stains mentioned have deposited something on the surface, but the elimination of the stains may have deposited something else later. 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. 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? Also, in the correction formula the fitted coefficient "c" (which corresponds to a constant offset between samples and standard) has been omitted. 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. p.19 line 17 There is an important typo here. The “>” symbol should be changed to “<” (less than) in both cases. 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 $\sim$0.01 ppm at 75 bar, $\sim$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 $\sim$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.

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