

Interactive comment on "Gas adsorption and desorption effects on cylinders and their importance for long-term gas records" by M. C. Leuenberger et al.

Anonymous Referee #3

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The manuscript by Leuenberger et al. presents results from a study of the effects of adsorption onto the inner wall of steel and aluminum cylinders, and the effect of cylinder pressure on the adsorption. This effect has been suspected for many years, and seen by National Metrology Institutes when attempting to create high precision gas primary standards for carbon dioxide. The practice of filling cylinders with dried air and letting them sit to equilibrate is also brought into question, as the subsequent lowering of the cylinder pressure through removal of gas for analysis, brings into play the pressure effects investigated by this paper. Thus while the methods and scope of this paper are limited, it is important to bring these issues to the forefront so users are aware of

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the risks when using cylinder standards in their work. As this paper just scratches the surface of this problem, it does open the discussion for more work to be done and published to properly define this potential bias, and the uncertainty of the bias, so it may be properly accounted for in the data collected, and in the preparation of gravimetric primary standards. The two previous referee comments make very valid points, and I support their comments as well. However I recommend publishing this paper after the authors have considered all the specific comments. Specific Comments: This is a very limited study, only three cylinders composed of aluminum and steel. In our experience this effect is very cylinder dependent, and can very guiet a bit due to cylinder treatment. Cylinder treatment is not considered in this report, and the treatment of cylinders investigated was not listed in the method section. The water measurements are below the lower bounds published in the Picarro literature. Are these values reliable? From our own Picarro instruments, water values in the ppm range <200 ppm are questionable. The conclusions are overstated, as these results are applicable to the cylinders tested only, and may not be extended to all cylinder treatments for all specialty gas sources. The larger concern is when using aluminum cylinders to prepare gravimetric standards, as this bias is very large and must be evaluated fully to prepare SI traceable gravimetric primary standards. There the source of the cylinder can largely dictate the amount of bias possible. In our experiments the bias can be as high as 0.8 ppm and as low as 0.1 ppm depending on the cylinder treatment of 30 L aluminum cylinders. The choice of Scott Marin cylinders is relevant only as the WMO community has standardized on that source, a dangerous practice, as it relies on a commercial company continuing in business. The temperature dependence may also be cylinder dependent, however this has not been rigorously tested

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