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Atmospheric Measurement Techniques Discussions

Interactive comment on "Gravimetrically-Prepared Carbon Dioxide Standards in Support of Atmospheric Research" *by* Bradley D. Hall et al.

Anonymous Referee #3

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The manuscript describes accurately performed gravimetrical preparations of CO2 reference gases and a thorough evaluation of individual aspects that limit the accuracy of the assigned numbers. The results are very consistent and show the value of these gravimetric standards to compare them as independent primary references with the standard gases that define the WMO CO2 mole fraction scale. Therefore, it is clearly relevant information for the community of people that make global atmospheric CO2 monitoring using reference gases linked to the WMO calibration scale. The paper is generally clearly written but there are some points that have raised questions for me. I would like to ask the authors to comment on these topics before publication of the manuscript.

Page 5, line 26: A blank in the dilution gas of 0.01 ppm is quoted. This is a very low

value that appears quite challenging to be quantified also in the light of the noise visible in the data presented in Figure 3 b. How is the limit of detection of the measurement method determined?

Page 7, lines 6ff: In the last part of the "Experimental Methods" section (starting page 6, line 21) the authors begin to describe their experiments to quantify CO2 adsorption on cylinder walls where the reader is referred to experimental details of the Schibig et al 2018 paper. This is followed by a discussion (page 7, line 6 to page 8, line 9) comparing these adsorption tests with experimental findings from literature and additional decanting experiments done as part of the work submitted here. I suggest that this discussion is moved to the Results and Discussion section. In this discussion on the experimental determination of adsorbed CO2 it is stated that all of these experiments agree in similar qualitative alterations of the CO2 content throughout venting gas cylinders but that the individual experiments do not agree to a very high degree in quantitative terms. The authors conclude that this is due to experimental approaches that introduce confounding temperature fractionation that add to the observed increase of CO2 over time. This is conclusive but it is not convincing to me that the authors completely exclude the possibility that there might be a small temperature fractionation influence affecting the low flow adsorption experiments done within the Schibig et al 2018 work that they rely on in the submitted manuscript. They state that during these low flow tests no significant temperature gradients were measured on the cylinder surfaces. However, in Figure 7 of that publication the adiabatic cooling effect is clearly visible in lower pressure regulator temperatures relative to the cylinder top (0.3-0.4 K) indicating the potential of a contribution from temperature fractionation. The adsorption terms are not large (0.016 ppm) and if temperature fractionation was playing a role would be even smaller. Yet, this is one of the adjustment terms and it is specified with a very low uncertainty in Tables 1 and 3. This uncertainty quote reflects the standard deviation of the calculated adsorbed CO2 as it results from the fit functions of the data of repeated low flow decanting experiments derived from the Langmuir's adsorption/desorption model. If other effects than the Langmuir adsorption may come into play the uncertainty of the adsorption adjustment term in Table 1 will not be adequately represented by this standard deviation.

Page 8, line 24: A linear fit is applied to the data and the residuals of these data are presented. On the CCL webpage a statement can be found that their NDIR system is not linear. The residuals of the fit presented in Figure 2 and Table 5 would probably improve if a quadratic fit was applied. The authors provide a clear explanation for assuming a small bias in the 405 ppm standard and the consistency achieved already for a linear fit proves the success of their work. Still they might add a comment on the certainty they have to assume a linear response.

One minor last suggestion: Page 5, line 6: the reference to Dlugokencky et al. 2005 does not show the manifold used, a further reference to Novelli et al 2001 is made in there. If the authors could show the manifold in another figure in here would be of help to the reader.

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