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Interactive comment on "Experiments with CO_2 -in-air reference gases in high-pressure aluminum cylinders" *by* Michael F. Schibig et al.

Anonymous Referee #1

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The manuscript "Experiments with CO2 -in-air reference gases in high-pressure aluminum cylinders" of M. Schibig et al. studies the stability of CO2 in air mixtures at ambient mole fractions. The topic is relevant, since accurate and reproducible measurements with traceability to standard scales are needed to detect changes in regional sources and sinks of CO2.

The manuscript is generally well written and concise. The chain of arguments is sound, and the topic is relevant for the scientific community. I therefore do recommend publication in AMT after addressing the following concerns.

General comments

The experiments carried out are clearly relevant for laboratory studies using large amount of standard gases within a short time period. However, this is mostly not the case for long-term monitoring of CO_2 and other research projects, where the gas of a standard cylinder is used over a much longer time period and in intervals. During period without use of standard gas, re-equilibration might take place, and the effect of changing CO_2 mole fraction during the use of a standard that was observed in this study will in many cases not happen or be much less pronounced in a normal measurements set-up for ambient CO_2.

Stability is much better for low flow conditions, but again, in reality, it might even be worse due to effects of the regulators. Especially in realistic measurement set-ups, this can be a problem, since only small aliquots of standard gases are used in longer time intervals, and the air is mostly sampled from the regulator and not directly from the cylinder. I recommend adding a few words on this issue.

The study was carried out with dry air mixtures ($H_2O < 1$ μmol mol-1). Residual water content might have a significant impact on the behavior of CO_2 absorption. Has the low water content be verified by measurements or other means? What will be the effect of residual water, even if less than 1 μmol mol-1? Could it be that differences in the residual water content explain at least partly the difference between individual cylinders or fillings?

A very recent publication studies similar effects including the influence of water on the stability of gaseous reference materials (Brewer et al., 2018). Citation of this work should be made in the final AMT version of the paper.

SGS (Superior Gas Stability) cylinders are mentioned in the introduction and methods, but no results are shown in the paper. In the conclusions, they are mentioned again, saying that they behave in the same way as untreated cylinders. This should also be shown and discussed in the results. E.g. individual fits could be shown for SGS and untreated cylinders in a separate figure similar to Fig.6.

I don't see much additional value of the experiments with heating and changing the orientation of the cylinders during venting. The results of the heating experiments were not consistent between different runs, and probably more experiments would be needed to get a clear picture. For example, the mole fraction change after the start of the heating shown in Fig. 15 is not significantly different from changes observed at higher pressures during the same run. The results of the experiments with changing orientation during the draining are also based on only one run for each experiment, and it is unsure if they can be reproduced. The paper could be shortened and would improve if only the results of the low and high flow experiments, including different cylinder orientation and treatment, are presented.

I further recommend re-writing the conclusions. Currently, they are difficult to read without the full context of the paper, and present results which are not mentioned previously (e.g. SGS cylinders). Furthermore, the statement 'This opens the possibility to use a general correction function in case a calibration cylinder on a field station runs empty' should be made in the results section because it needs more careful discussion. Most likely, corrections will be associated with high uncertainties, since the calibration sequence at stations is different from your experiments in which the cylinders were emptied with a constant flow.

Specific comments

Page 2, line 13: kilogram is a SI unit, despite the fact that it is still based on an artifact. It should be removed from the list of examples in parenthesis.

Page 3, line 21ff: Add a short description of the performance of the analytical system (repeatability, drift etc.) here. This could be done by moving paragraph 3.1 to the method section.

Page 3, line 34: According to Fig. 1, C1 is repeatedly measured, not C2.

Page 9, first lines of result section and section 3.1 would better fit in the method section.

Page 10, section 3.2.: The low flow experiments are probably the most relevant for most users of standard gases. Beside the average of all cylinders, the result of only one (representative) standard is shown, while in total 38 experiments of the same type were made. It would be valuable to see the variation between different cylinders / fillings, which could be added in either an additional figure or Fig. 6 (e.g. individual fits for all experiments). I recommend to also show and discuss the similar behavior of SGS and untreated cylinders could here.

Figures 6 and 8: The y-axis shows ΔCO_2, and not CO_2 mole fraction, which needs to be corrected. Why do the measurements at higher pressures show a negative delta? Especially in Fig. 8 all ΔCO_2 as well as the fits at higher pressures are negative. Is this correct?

Technical corrections

Page 2, line 24: the latest available GGMT report is not cited (WMO, 2016). It should be added. The format of the citations of the WMO reports needs also to be changed.

Page 2, line 28: replace 'SI values' with 'SI traceable values'.

Page 2, line 35: Cite the latest GGMT report here.

Page 3, line 36: Change to 'An additional full calibration was made at the end of each experiment'.

Page 6, line 25: Kitzis (2017) is missing in the references.

References

Brewer, P. J., Brown, R. J. C., Resner, K. V., Hill-Pearce, R. E., Worton, D. R., Allen, N. D. C., Blakley, K. C., Benucci, D., and Ellison, M. R.: Influence of Pressure on the Composition of Gaseous Reference Materials, Analytical Chemistry, 90, 3490-3495, 2018.

WMO: 18th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2015), La Jolla, CA, USA, 13-17

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Discussion paper

September 2015, GAW Report No. 229, World Meteorological Organization, Geneva, Switzerland, 2016.

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