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Review of the submitted article:

Experiments with CO2 -in-air reference gases in high-pressure aluminum cylinders

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General comments:

This paper describes a series of experiments performed to better understand previously observed drifts in the CO_2 mole fraction measured during the lifetime of reference gases in high pressure cylinders. The subject is of interest for worldwide measurements of atmospheric CO_2 mole fractions, which make use of such reference gases for their calibration. The authors have planned a consistent number of experiments to study the impact of various conditions. The measurements themselves appear robust, and all plots clearly summarise the observations. There is however some issue with the overall presentation, the organisation of the results, the link with the equations developed to fit the measurement results, and the relevance of some of the experiments. I therefore recommend a major revision before the paper can be published in AMT.

Although the general aim of the study appears to be a better understanding of already observed effects when using CO_2 in air standards, it is not so clear which particular questions are answered. For example, it is already recommended to leave not less than 20 bars in those cylinders, and this recommendation is again confirmed here. If that was the goal, it should be stated. The study also looked at the influence of the flow rate at which the gas is used, but the conclusions are never actually linked with some recommendation. Does this have any impact on their usage? Similarly, a big part of the paper is devoted to the analysis of thermal convections inside the cylinders. What is the impact here? Should this be followed by any recommendation, or was it only performed to better understand the process?
The organisation, terminology and wording of the paper can be improved. The description of the experiment is not very well structured and information on a same aspect is sometimes separated in different sections. At several occasions, words have been omitted, resulting in sentences which can still be understood but belong to oral language rather than a written paper. Authors also chose to sometimes use their own terminology, not following recommendations from international bodies such as IUPAC. It would be easier to follow with a more common terminology. It is also suggested to write all symbols for quantities in italic.
Finally, a recent paper dealing with the same subject was published earlier in 2018. It should be mentioned in the introduction and results compared in the discussion: Brewer, P. J., R. J. C. Brown, K. V. Resner, R. E. Hill-Pearce, D. R. Worton, N. D. C. Allen, K. C. Blakley, D. Benucci and M. R. Ellison (2018). "Influence of Pressure on the Composition of Gaseous Reference Materials." Analytical Chemistry 90(5): 3490-3495.

Specific comments by section:

1. Introduction: the end of that section needs to be revised to state more clearly which questions are being answered, which experiments were performed to do so, and which theory was applied. It is suggested to replace the assumptions with questions, such as i) is the effect cylinder−dependent? ii) in which conditions is the Langmuir model sufficient, and when does this need to be completed with the other effects already mentioned earlier in the section? iii) are SGS cylinders any better?
   In addition, other questions may be added if there are parts of the goal of the study, such as the influence of the flow rate at which the gas is sampled from cylinders, or the influence of the cylinder position.
   Finally, it is recommended to add a summary of the following sections, to clarify for the reader which information is provided in each section.
2. Section 2:
   a. The title ("methods") appears unclear. It actually contains information on the cylinders and analytical equipment, the measurement protocol, but also some theory to describe all processes at work.

b. It is suggested to modify the organisation, starting with a section only devoted to the description of the theory, then the equipment (cylinders plus gas lines plus instruments), and finally the measurement protocol. Within the protocol, the description of the measurement sequence can come first, followed by the explanation of the different conditions chosen to test the various assumptions.

c. The description of the protocol needs to be revised. Table 1 and figure 1 are clear and almost describe it completely, but the text brings more confusion. Specific words need to be chosen for each series of measurement (block, cycle, run), defined and further used with always the same meaning.

d. First part of the section 2 describes the measurement sequence, also displayed in Figure 1. Sequences were apparently setup to obtain both calibrated and a drift corrected values. This could be stated first, before providing the details of how this goal was achieved.

3. Section 2.4: is it relevant to show the equation used to determine the temperature? This cannot be checked and the only interesting value in that case seems to be the temperature.

4. Section 2.6: it is indicated that the filling was done at Niwot Ridge Station. Was this the case every time a cylinder was emptied? Was it sent back and refilled there? Please clarify.

5. Section 2.7: the entire section is difficult to follow, partly due to some considerations on unsuccessful attempt to fit the data. Even if some choices were justified by the observations, it would be easier to read if the different models were presented independently. The section could be divided in three parts, each of them presenting the assumptions, which part of the information comes from previous work (seems to be all in model 1 for example), which is the equation used during the fits, which parameters were assumed and which were fitted.
The presentation of the maths could be better balanced: while some common knowledge is sometimes detailed (such as the definition of the Avogadro number), some more expert information is not fully described (such as the Rayleigh distillation function).

a. Model 1: Langmuir. Equation (2) comes from Leuenberger 2015 where it was derived from the Langmuir model. This should be stated clearly. In addition, the Langmuir model normally uses partial pressure, not total pressure. Some consideration on the choice of using total pressure and its impact should be provided.
The explanation on the difficult fitting may be moved to the results, to limit this section to the theory. The quantity K was fixed at the same value than in the Leuenberger paper. Is that a coincidence? This should be better explained, but again not in this section, which should only state that K was fixed to find $CO_{2,ad}$.

b. Model 2: in this approach, it is stated that the fraction of occupied sites does not depend on the total pressure. Note that the CO_2 mole fraction varies with the total pressure, as demonstrated by the paper. It is certainly negligible but this should be explained.
This section introduces the symbol Na for a number of moles. This symbol being commonly chosen for the Avogadro number, it is recommended to replace with n_a.
The derivation of Equation (9) from (8) is not straightforward, compared to equation (5) for example which is very straightforward. It is suggested to provide the steps in annex, limiting this section to the model description and the equation used later on to fit the data.
The formalism could also be improved, avoiding a sentence such as "total trace gas" to replace a quantity. Why not defining $n_{tot} = n_{ad}+n_{gas}$.
Finally, like for the first model, considerations on results of the fit should be kept for the results analysis.

c. Model 3: in the third part, a Rayleigh distillation function is introduced. Some more explanation would be needed here, describing in one sentence the process and its expected impact on the CO_2 mole fraction.
The formalism may also be improved here: equation (12) introduces a mole fraction with the symbol X, where equation (13) uses $CO_{2,\ meas}$. It is suggested to always use x for mole fractions.

6. Section 3:

   a. This section is quite long and it is not always easy to distinguish the conclusions that are derived from each particular experiment. It is suggested to revise the structure, splitting in sub−sections to clearly identify what is the tested assumption, what were the observations, and the preliminary conclusion.

7. Section 3.1: there are many details in this section which may not be relevant for the understanding of the measurements. If the change of the analyser was not an issue, this should not be highlighted so strongly. The term accuracy does not seem appropriate, as the analyser was regularly calibrated. In addition it is noted at the end of the section that only relative measurements were performed. Then why not starting with this statement, and explaining that the repeatability (expressed with the standard deviation) of the measurements was evaluated, as this is the quantity which matters.
8. Section 3.2: it is mentioned here that the values $CO_{2,ini}$ and $CO_{2,ad}$ had a fix value. This was not so clear in the section on methods. It was also not clear how their values were actually chosen.
9. Section 3.3: it is suggested to separate this section in two, to treat vertical and horizontal cylinders separately. Also the reference to figure 9 appears too early, as this figure contains results with both positions of the cylinders. The clear distinction between them helps the understanding of the analysis, but maybe this could come after. Some effort to reduce the text, summarising each observation and drawing conclusions by step would be very much appreciated as well.
10. Section 3.4: please indicate which assumption was tested here and also when the cylinders were put upside−down. Certainly the idea of moving cylinders came from the observations during previous measurements, but this is not very clear.
11. Section 3.5: Some effort to reduce the text, summarising each observation and drawing conclusions by step would be very much appreciated as well here.
12. Section 4: it is suggested to also reshape this section, starting from each conclusion drawn during section 3, and summarising. At the end, some consideration on the impact should be given. For example, a possible small bias in the calibration of CO_2 measurement is mentioned. What is the conclusion? Will it be followed by further recommendation?
    At the end of page 15, it seems that some inconsistency is noted between the observations made when sampling the gas with low and high flow rates, as they would lead to two different values of the amount of CO_2 adsorbed on the wall. This appears quite serious. What is the conclusion? Does this question the entire model?
13. Section 5: the first conclusion from the low flow experiment appears to diminish the importance of the study. Indeed, if it is already recommended to stop using calibration gases when the pressure is below 20 bar, what was the purpose of this study?
    The second part would need to be strengthened; bringing more sounds conclusions and consideration on the implication (if any) on the usage of calibration gases.

<u>Line-by-line comments:</u>

Page 1

Line 20**:** "…In this study we found that during low flow conditions". As this is the first mention of low flow rates, it should be stated more clearly that this is the flow rate used to sample the gas inside the standard.

Line 21: "showed similar CO_2 enrichment of 0.090 ± 0.009 μmol mol^{-1} as the cylinder was emptied from about 140 to 1 bar above atmosphere". This is misleading, because the increase happens only after a certain pressure, not gradually during the cylinder was emptied. This is quite important as users could be afraid of using the standards.

Line 28: "In case they are used in high flow experiments that involve significant cylinder temperature changes, special attention has to be paid to possible fractionation effects". This is the only statement in the entire paper about possible impacts of sampling gas from the standards at a high flow rate. Some more consideration should be provided, both in the introduction to explain the current situation, and in the conclusion to provide a recommendation.

Page 2

Line 14-17**:** the sentence about the traceability explains the situation within WMO/GAW. It may not be extended to all CO_2 measurements in the world.

Line 18:"The resulting…" this sentence describes a goal rather than an observation. In addition the word "true" should be avoided and could be replaced with "unbiased".

Line 28:" SI values". Incorrect terminology. May be replaced with "values traceable to the SI".

Line 32:"accuracy". Incorrect terminology. To be replaced with Data Quality Objective or compatibility.

Page 3

Line 17**:** "To check the third hypothesis, two SGS cylinders were added to the set…" this would mean that 8 + 2 = 10 cylinders were tested. Table 1 shows only 8 cylinders (not considering the one which was replaced).

Line 30 and 32: the term "block" seems to indicate 10 measurements recorded during 5 minutes. Later in the text, the same quantity is sometimes only referred to as "a measurement". It can be understood to define a measurement as a 5 minute average, but this should be stated and always used in the same way.

Page 4

Line 2:" continuously at 10 ml min^{-1} flowing reference cell signals". Revise the order of words in the sentence.

Line 16: C2 was measured twice? Should this be C2, C3?

Line 17: define what is "one run"

Line 19: "secondary". This term may be replaced here as it was already used previously in the traceability hierarchy.

Line 26:"before a block of C2 was measured". As the word "block" is not so appropriate to a 5 minute average, the entire sentence is difficult to understand.

Line 31:"lasts" should be "lasted".

Page 5

Line 28: "showed that they perform even slightly better." Sounds more like an opinion than an observation. Values should be provided, or the statement can simply be removed as it does not bring additional value.

Page 6

Line 15:"as soon as the cylinder reached 30 bar". Omission of the word "pressure", to be included.

Page 7

Equation (2): using the symbol of the molecule for its mole fraction is confusing when it is used in the text. It is recommended to follow IUPAC terminology.

Line 23:"amount density". This should be "amount concentration".

Line 24: "function of CO_2 only". This illustrates the problem of using the molecule's name instead of a symbol for its mole fraction.

Page 8

Line 2:"available". The term can be misleading, as it could indicate non occupied sites. May be replaced with "total number of sites".

Line 2:"amount of sites, expressed in moles". The mole is limited to an amount of molecules, atoms, ions, electrons, or other particles. This may be replaced with "maximum amount of adsorbed molecules", which also corresponds to the total number of sites.

Page 10

Line 23 to 25: revise the sentence, maybe using two distinct sentences.

Line 24:”standard error”. A better term would be “standard deviation”, as used later on in the text.

Page 11

Line 15: revise the last part of the sentence. It seems that some words are missing.

Page 12

Line 11:”errors”. To be replaced with “uncertainties”.

Page 14

Line 13: “are the virtually”. Remove “the” and consider replacing the word “virtually”, which seems more appropriate for a talk than for a paper.

Page 15

Line 15: “By using a ….the number becomes even smaller”. Consider revising the sentence, first because the fraction of occupied sites goes from 13% to 37%, secondly because the second calculation seems to be an alternative one, so that two models are compared.

Line 17: “the number of molecules…Avogadro number”. Is it really needed to state what is the Avogadro number?

Line 24:”a second conclusion”: what was the first conclusion?

Page 17

Lines 9 to 12: consider splitting the sentence. This is currently difficult to understand.

Page 18

Line 12 and 13: “to describe the CO_2 enrichment”. Consider removing one of the appearances of this part of the sentence.

Figures 6, 8, 12: the y−axis is a difference, not the CO_2 mole fraction. From the legend it seems that the first value was subtracted from the set, but then why is the first point not at zero?