Interactive comment on "Flask sample measurements for CO2, CH4 and CO using cavity ring-down spectrometry" by J.-L. Wang et al.

Anonymous Referee #1

Wang et al. present a method to take air samples in stainless steel flasks and analyze it subsequently with a CRDS instrument for CO2, CH4, and CO. The manuscript gives a clearly structured overview of several tests to characterize a flask setup, and the CRDS analyzer performance.The topic of the manuscript matches the scope of the journal. Indeed, it presents some interesting new facts:

• CRDS can measure with changing inlet pressure (even though this seems to be expected, because of a constant cell pressure).

• Dry air from tank and dry air from a tank stored for a short time in the flask have the same concentration (within the noise of the analyzer).

• Storage over one month gains a 0.1 ppm CO2 offset, measured with the same instrument on the same calibration scale with the same air inlet.

However, there are serious shortcomings that suggest not publishing the manuscript in its current form. The presented work does not yet add together to a convincing package.

There are still serious open questions to the presented tests. The manuscript points out that the stainless steel flasks and the manifold can be used to get reproducible data points. To prove that the proposed stainless-steel flasks are a suitable sampling method, the filling effect and associated artifacts have to be excluded for wet air as well. In the current version, it remains unclear, whether this has been tested in Sect. 3.2 (does the manifold include the flask?). As the measurement of wet air flasks is the main motivation for the newly proposed technique, it should be much more convincing.

Furthermore, there is more investigation needed on the storage effect (several storage times, . . .). Other questions arise about the water correction. Which correction is used? Is the water correction valid over the wide range of inlet pressure presented here?

The overall manuscript does not yet present an overall verified setup. There are flask measurement methods already known that have proven their stability over time in international intercomparison programs. The paper poorly motivates the need for a new flask sampling system. Some suggestions for further reading about current flask sampling might be [NOAS ESRL], [Tsuboi et al., 2013], [Sturm et al., 2004], [Neubert et al., 2004],

[Rothe et al., 2005], and [van der Laan-Luijkx et al., 2013]. In case the focus lies on the usage of the CRDS technique, it is already known that this system can stand WMO criteria (see various references in the discussion paper). However, this authors miss the final prove that they can reliably link the presented data to an absolute scale. The presented repeatability tests do not give the number required by WMO. A comparison to an independent measurement technique is required to rule out systematic biases (e.g. spectral features depending on water vapor, gas composition, inlet pressure, adsorption, ...). When explaining all missing points, ideally in combination with a first prove of its practicality of the flask sampling for a longer time series, the manuscript could finally go to AMT.

Reply:

We thank the referee for the valuable comments. Some significant references in relation to atmospheric observation network and flask sampling have been added into the revised manuscript. In this study, all the tested samples are ambient air, and therefore water was not deliberately removed. The water correction equation and coefficients are as follows:

$$C_{wet}/C_{dry} = 1 + aH_{rep} + bH_{rep}^2$$

where C is the mole fraction of CO_2 or CH_4, and H_{rep} is the measured water vapor concentration (in %). $a = -1.55\times10^{-2}$, $b = 5\times10^{-5}$ for CO_2 and $a = -1.27\times10^{-2}$, $b = 1\times10^{-5}$ for CH_4. The measurements of CO_2 (dry), CH_4 (dry) after the transition period (0-60 s) were stable (shown in Fig. 2, Fig. 3 and Table 1) when the remaining pressure in the flask was above 175 Torr.

The purpose of comparing the flask-manifold method with the in-situ method is to validate the flask method by minimizing the uncertainty in the CRDS measurements. The point is that if there is a noticeable difference arises from the comparison between the flask-manifold apparatus and the in-situ method, we will know it is due to the apparatus or storage, and not due to, say, calibration bias resulting from different analyzers. Whether or not the CRDS analyzer is accurate or linked to an absolute scale is irrelevant for this particular purpose. However, we do admit that, in essence, it is not a true inter-comparison work, but only a validation work. To avoid confusion and also to make our point clearer, we have rephrased the sentence in page 7645 lines 1-2 as follows: *"The*

systematic bias ***due to the uncertainty in the calibration scale*** *was minimized because the same CRDS and calibration scale were used for the measurements."* and revised the Section 3.5 as follows:

*"**3.5 Validation experiment between flask and in-situ measurements***

To assess the performance of the flask method presented in the study and to validate its practicability for low-pressure field samples, a validation experiment between the in-situ method and the flask method was performed using the same CRDS analyzer at a mountain station of 3000 m in elevation (Lulin Atmospheric Background Station)….."

For the reviewer's information, the in-situ CRDS is linked to the NOAA flasks via participating in the round-robin program which will be discussed and possibly published in the future. With respect to the storing test, we acknowledge that many significant efforts have been made in the past, which are worth citation in our study, e.g., Nakazawa et al. (1991), Tsuboi et al. (2013), Chen et al.(2012), Tanaka et al. (1983), Dlugokencky et al. (1994), Novelli et al.(1992), Yashiro et al. (2009) etc. As a result, we have added these references in the revised manuscript.

Specific comments (page/line):

7634/13ff: You use ppm/ppt in the text and ppmv/pptv in the figures and tables, please keep consistent to one unit.

Reply: We have corrected it.

7640/20: Where does this formula coming from? Are all reported values pressure corrected?

7640/25: May you quantify the trend in the data shown in Fig. 3? What is the improvement for the slope when using the pressure correction?

Reply: The formula is derived experimentally with an algorithm to correct for the dilution and broadening effects. Only the data in Table 1 are corrected for the cavity pressure. As shown in Fig. 3b (original manuscript), only slight improvement in CO_2 and CH_4 is seen after the cavity-pressure correction. Since the correction for the cavity pressure has only a very minor influence on the data, after a long deliberation, we decide

to remove the text of cavity-pressure correction from the manuscript to make the revised manuscript more concise.

7641/5ff: Which period is exactly used? 60-120 s, or 60-1012 s, or some different?

Reply: The period of 60-120 s is used to represent the measured data.

7641/29: What are the water correction factors used? Which function (linear, quadratic)? What does "notably stable" mean?

Reply:

The water correction equation (quadratic) and coefficients for the Picarro G2401 used in the study are as follows:

$$C_{wet}/C_{dry} = 1 + aH_{rep} + bH_{rep}^2$$

where C is the mole fraction of CO_2 or CH_4, and H_{rep} is the measured water vapor concentration (in %). $a=-1.55\times10^{-2}$, $b=5\times10^{-5}$ for CO_2 and $a=-1.27\times10^{-2}$, $b=1\times10^{-5}$ for CH_4.

We have complemented the water vapor correction equation and coefficients in the revised manuscript and revised "notably stable" to "stable (as shown in Fig.3 and Table 1)" in page 12 (revised manuscript).

7642/11: "through the manifold". It is not clear, whether the flask volume is attached or not. Does the test and Table 2 prove that a reference air volume gives the same measurement result by 1) directly attaching it to the CRDS analyzer, and 2) filling it to a flask and then analyzing it with the CRDS instrument? Or does your test only state that the air directly attached to the analyzer gives the same results as when it goes through the additional tubing and valves?

Reply: Thank for the comment. We have rephrased this paragraph to make it clearer.

"A pressurized sample in a 15-L canister (29-11521G, SILONITE Coated, Entech) containing CO_2, CH_4 and CO was analyzed using two procedures. In one procedure, the canister with pressurized sample was directly connected to the 3-way valve in Fig. 1 for analysis, thus bypassing the manifold to minimize the exposed surface area. In the other procedure, the pressurized canister was connected to the manifold (the flask adapter of

the manifold in Fig. 1) to analyze the sample in accordance with the procedure described in Section 2.2."

7642/25: Isn't it inconsistent with the result shown in Fig. 3? When you measure repeatedly the same flask (this sect. 3.3), you do not get the same time series as a continuous data stream (see sect 3.1)? How do you know, which period is the correct one to measure (60-120 s, and not e.g. 180-240 s)?

Reply: We treated all the repeated analyses as independent ones, and for each analysis only the data of 60-120 s were taken for averaging. Although the canister pressure became lower every time a new analysis was performed, the measurements were not significantly affected. Before each analysis started, the manifold was pumped and the reference gas was re-routed by the 3-way switching valve of the manifold to CRDS; thus, the manifold surface and CRDS cavity was "re-conditioned" in an identical manner every time a replicate analysis was made. As a result, the repeated procedure created a similar analytical setting for the nine replicates and, hence, highly agreeable results among them. This paragraph has been rephrased to make it clearer. Thanks for the valuable comments. The measurements during 60-120 s are close to those during 120-180 s as shown in Table 1 of the revised manuscript. The period of 60-120 s for each analysis is used for averaging to minimize data size and sample consumption.

7643/4ff: Is your reproducibility test not just a leak test? How do the samples compare to the direct measurement in the 15-L canister? Do you observe adsorption effects?

Reply: The purpose of the inter-flask test is to evaluate the possible deviation caused by different canisters. We used five different 2-L canisters filled with the same air from a 15-L flask for the test. Any significant difference observed between the five different canisters would suggest the occurrence of adsorption effects. The inter-flask precision test indicated high reproducibility with overall relative precisions (1σ) of 0.07 ppmv, 0.4 ppb, 0.5 ppb and 0.003% for CO_2, CH_4, CO and H_2O, respectively. We have revised the paragraph to make it clearer. We thank the referee for the comment.

7644/1f: Do you always evacuate the manifold, or only during this test?

Reply: Yes, we always evacuate the manifold before analysis and tests.

7645/1ff: The systematic bias is minimized indeed, when using the same instrument on the same calibration scale. For your setup the 0.1 ppm difference is actually quite large, maybe a weighting function can help, since 2L flask and in-situ do not reflect the same point in time (cmp. e.g. [Chen et al. 2012]). The difference between flask and in-situ can be assumed much larger for realistic comparison between two different inlets and analyzing systems (what the inter-laboratory-comparability of the WMO requires). Can you exclude 0.2 ppm difference for CO2 when doubling the storage time between sampling and analysis?

Reply: We thank the referee for the comment. We think that the sources for the difference of 0.1±0.09 ppm could be multiple. First, the filling of a pre-evacuated canister with ambient air took about one minute. Consequently, the concentrations were the average of not only the CRDS measurements of the canister sample, but also the air collected over the duration of one minute. As a result, the canister data points were not entirely representing the instantaneous concentrations as reported by the in-situ data. Second, we also cannot rule out the possibility that the 0.1ppm difference can be partially caused by the 1-month storage time. Third, the uncertainty of 0.09 ppm is almost as large as the mean of 0.1 ppm itself, suggesting that the difference could be mostly random in nature, rather than systematic. Whether the 0.1ppm difference is considered large or small should depend on what the flask method is used for. It could still be acceptable for many applications where 0.1ppm is considered negligible.

7655/Fig3b: What is the slope for uncorrected and corrected data? Is there any improvement through the pressure correction? Are the data points water corrected, using which formula?

Reply: The slopes for uncorrected and corrected data are $7x10^{-4}$ ppbv/s and $5x10^{-4}$ ppbv/s for CH_4 and $6x10^{-5}$ ppmv/s and $5x10^{-5}$ ppmv/s for CO_2, respectively. Only slight improvement in CO_2 and CH_4 is obtained after correction for cavity pressure.

The data points in Fig3b were corrected using the manufacturer-supplied water correction factors. As mentioned earlier, the water correction equation (quadratic) and coefficients for the Picarro G2401 used in the study are as follows:

$$C_{wet}/C_{dry} = 1 + aH_{rep} + bH_{rep}^2$$

where C is the mole fraction of CO_2 or CH_4, and H_{rep} is the measured water vapor concentration (in %). $a=-1.55\times10^{-2}$, $b=5\times10^{-5}$ for CO_2 and $a=-1.27\times10^{-2}$, $b=1\times10^{-5}$ for CH_4.

Minor corrections (page/line):

7634/4: Instead of "propose" it might be better to use "present" here? Otherwise, the sentence seems inconsistent.

Reply: We have revised it. Thanks.

7643/12: add serial comma two times: ", and" instead of "and"

Reply: We have revised it.

We highly appreciate the referee for the references listed below.

References:

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