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

Anonymous Referee #2

Summary of the manuscript

This paper presents laboratory setups and experiments for CRDS measurements of trace gases (CO2, CH4 and CO) in sample air filled in flasks. The authors showed response of the CRDS signal to the introducing pressure and examined possible effects that could adversely affect precise measurements.

General comments

This paper highlights one of interesting achievements that sample air in flasks can be analyzed even at low inner pressure as long as the pressure exceeds 175 Torr. This is not easily done using conventional NDIR or GC techniques with which sample air is introduced at pressure above ambient level in most cases. The authors also showed test results for their sub-systems to guarantee their measurement performance. The measurement precisions are reasonable for atmospheric monitoring. However, I point out some shortcomings of important information and publication of this paper should be reconsidered after the following points are satisfied.

Reply:

We thank the referee for the valuable comments to improve our manuscript. Indeed, the major merits of flask/CRDS presented in the study for flask analysis are in three ways: 1. Flask samples can be collected in low-pressure environments (e.g., high-altitude locations); 2. Flask samples can be first analyzed for other trace gases with the remaining low-pressure sample used for CRDS analysis of CO_2, CH_4 and CO; and 3. Flask samples can be archived and re-analyzed for validation. To accommodate the suggestions make by the referee, the manuscript has gone through an overhaul. We hope that these changes in the revised manuscript will further strengthen the manuscript and make the technique clearer to the viewers. Our responses to the referee are as follows.

Motivation of the study – I wonder what kinds of purpose authors established their measurement system for. Scientific interests based on the flask-CRDS measurements are not clearly described in the text. One should decide necessary level of precisions according to his/her scientific interests, being independent from the WMO/GAW suggestion. For instance, precision and accuracy required are different depending on magnitude of variability of the target (e.g. seasonal cycles, atmospheric trend, shorter-timescale pollution events). I suggest the authors to present what they are planning to observe and what types of variations they address. I personally think that this point is very important for this manuscript to meet the scope of the journal.

Reply: We hope that the viewers can feel strongly about the potential scientific interests and motivation that this paper is trying to convey. In the **Introduction section**, we mentioned multiple advantages of the CRDS technique such as: 1. Drying of sample air prior to analysis may not be necessary...; 2. Its response to concentrations is highly linear…; and 3. It is highly stable, requires fewer calibration checks, etc. We also point out the advantages when coupling flask sampling with the CRDS measurements, as stated in lines 8-12, page 7635: "Thus, CRDS is suitable for flask analysis in three ways: 1. Flask samples can be collected in low-pressure environments (e.g., high-altitude locations); 2. Flask samples can be first analyzed for other trace gases with the remaining low-pressure sample used for CRDS analysis of CO_2, CH_4 and CO; and 3. Flask samples can be archived and re-analyzed for validation." We also made a great effort to validate the proposed method by evaluating stability, wall-effects, intra-flask and inter-flask reproducibility, carry-over, etc.

We started with the intention to point out the potential advantages of the flask-CRDS method, followed by assessing the aspects of quality assurance that we think are important for the method. With the results of quality assurance and validation clearly demonstrated, we think the viewers can then decide how they can take advantage of the method.

Citation – Considering that this is a technical paper for measurements of atmospheric CO2, CH4 and CO, more papers that have devoted lots of efforts to achieving relevant measurements should be cited. The authors could mention difference between AGAGE and NOAA/GMD networks, which are two biggest atmospheric monitoring programs for in-situ and flask-based measurements. I also suggest to cite literatures focusing on CO2, CH4 and CO, not for other NMHCs and halocarbons. Original papers that studied evolution of CO2 and CH4 could be cited instead of referring the IPCC report. Please see references attached at the end of this comment.

Reply:

The suggestion is well taken. We have included the references of AGAGE and NOAA/GMD to acknowledge their original work, as kindly provided by the referee. The citation of literatures on NMHCs and halocarbons has been discarded.

Water and pressure correction – From the results shown in this paper, I speculate that water contained in air samples is gradually liberated from the inner surface of the sampling flask, resulting in increasing water level during measurements. The authors corrected this effect by employing the water correction function offered by the manufacturer. This seems to be also the case for the pressure correction.

Reply:

We thank the reviewer for the valuable comment. The slight increase of water is likely caused by the water gradually liberated from the inner surface of the sampling flask. The equilibrium was never reached for water, because it was gradually liberated from the inner surface of the flask during the pumping process. To make this sentence clearer, we revised the sentence as follows: *"This increasing trend of water can be also clearly seen in Table 1 during the measurement period from 60 to 1012 s when the other three gases showed rather stable measured mole fractions. The possible cause for the slight increase could be that the equilibrium was never reached for the water vapor which was gradually liberated from the inner surface of the flask during the measurements."*

Experiment design – The authors described five experiments (section 2). Among them, only the first one is specific to the CRDS technique, and the others are general for all types of measurements employing sample air filled in flasks. In other words, the latter does not give new information to readers who make conventional measurement methods, and previous researchers have made more thorough inspections (see NOAA/GMD's flask measurement papers for instance). Then, together with the aforementioned water correction issues, I cannot say that the author's own achievements for the high-precision measurements were clearly written. This point should be highlighted in the manuscript.

Reply:

With respect to the validation of the sampling, storage and analysis of flask, a lot of efforts have been made by many groups based on conventional methods (e.g., Conway et al., 1988; Nakazawa et al., 1991; Dlugokencky et al., 1994; Dlugokencky et al., 2005; Novelli et al., 1992; Yashiro et al., 2009; Tsuboi et al., 2013) and these references suggested by the referee are very useful to complement our validation work. However, since connecting flask-manifold to CRDS is not entirely conventional, we feel compelled to validate the proposed method by going through some of the similar experiments of quality-assurance. Without these proofs, the proposed flask-CRDS would not hold its ground and stand the challenges from the science community. We highly appreciate the reviewer for the comment, and we have complemented and emphasized many noteworthy references in relation to the aspects of sampling, storage and analysis of the flasks in the revised manuscript.

Comparison with flask and in-situ CRDS measurements – This test gave stability of air samples in the flasks, since the authors used the same CRDS analyzer (G1301). Namely, it was a storing test in the flasks for up to one month, which could be made even only by in-lab works (filling flasks and storing for a certain period). If the authors intended to verify robustness of the system as they say, they should have analyzed the flasks by the independent CRDS system (G2401) described in most part of the manuscript. For better verification, the authors should also make comparison with conventional and totally independent measurement systems (NDIR and GC) in collaboration with other laboratories. Keep in mind that NOAA/GMD has established their scales based on such conventional measurement techniques, meaning that transferring concentration values by the different methods might cause biases when being examined for wide concentration ranges. Unfortunately I am not very clear on details about how CRDS measurements have been inspected from this viewpoint.

Reply:

The comparison experiment is aimed at assessing and validating the performance and practicability of the method of flask-manifold presented in the study by comparing with an in-service in-situ CRDS system at a high-altitude mountain site, which has been operated for more than two years. The main purpose here is to validate the apparatus of flask-manifold while keeping the CRDS measurements the same. The point is that if there is a noticeable difference arising from the comparison, we will know it is due to the apparatus and not due to, say, calibration bias resulting from a different CRDS analyzer. To avoid confusion and also to make our point clearer, we have rephrased the sentence in page 14 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."

We agree with the referee that, in essence, it is not a true inter-comparison work, but a validation study. To make this point clear, and we have revised this part of the manuscript.

Specific comments

P7635 L1: I suggest to cite original papers that studied historical evolution of atmospheric trace gases of interest over industrial era e.g. Etheridge et al. (1996, 1998).

Reply: We have complemented the original papers as suggested. Thanks for the suggestion.

P7635 L5: I would mention the two well-known atmospheric observation programs: NOAA/GMD and AGAGE. The former mainly employs a flask-based methods and the latter more focuses on in-situ temporally high-resolution measurements.

Reply: We have cited literatures made by the two well-known atmospheric observation programs, NOAA/GMD and AGAGE, in the revised manuscript.

P7635 L24: Since this paper focuses on CO2, CH4 and CO measurements, I suggest not to mention to papers on other compounds but concentrate on flask-based measurements of gases of interest by using NDIR and GC techniques. For instance, Conway et al. (1988), Nakazawa et al. (1991), Dlugockenky et al. (1994) and Novelli et al. (1992).

Reply: This point is well taken. We have cited the suggested references accordingly.

P7636 L5: "infrared absorption" – I would write non-dispersive infrared analyzer (NDIR) to clearly specify the method.

Reply: Correction has been made.

P7636 L9: "to report dry base data" to "to report on dry-air based scales"

Reply: Correction has been made.

P7636 L16: drying "of sample air" prior to analysis…measured simultaneously with gases of interest "for water vapor correction".

Reply: Corrections have been made.

P7636 L21: I would point out additional costs necessary for GC measurements. They require special carrier gases such as synthetic air and pure nitrogen as well as hydrogen gas for the FID detector. CRDS measurements are not suffered from maintaining bottles of these gases.

Reply: It is a very good point. We have added that in the revised manuscript.

P7636 L26: "must" to "should". As I mentioned earlier, it is not necessary to mention the WMO recommendation depending on your observation purpose.

Reply: Correction has been made.

P7637 L1: "are" to "has been"

Reply: Correction has been made.

P7637 L4: "the aim of this study…" – this sounds smaller than what the authors made. You have presented the other topics as well: response of CRDS to the flask inner pressure and total performance of the system.

Reply: Thanks for the comment. This sentence has been changed as follows: "the aim of this study is to present and validate a sample method of measuring flasks with CRDS to allow many advantages associated with the flask sampling to be fully exploited with optimal data quality.

P7638 L4: Clarify which part you call the "manifold" in Fig. 1. Is it the one surrounded by the square? It is important to mention the material of the manifold as you suspect adsorption of target gases. Stainless-steel?

Reply: Yes. The manifold is the one surrounded by the square. The manifold consists of stainless steel tubing (coated with fused silica, 1/8 inch, Restek) and switching valves (stainless steel, SS-41GS2 and SS-41GXS2, Swagelok). We have made it clear in the revised manuscript.

P7638 L8: …with a shut-off valve "(#1)"…

Reply: Correction has been made.

P7638 L11: A 3-way "switching" valve … was used to select air being introduced into the CRDS analyzer between the flask and the reference cylinder air.

Reply: Correction has been made.

P7638 L14: How large is the regular flow to the analyzer?

Reply: The flow is regulated by a flow-restricting orifice (65ml/min, A-9-NY, Picarro). We have added this information in the revised manuscript.

P7638 L19: A 2-L electropolished stainless-steel canister flask "filled with sample air" (or reference air) is connected to the flask-CRDS system. – Be consistent with terms "reference" and "standard" at every place in the manuscript. I would call only the NOAA certified gases "standard" and other own compressed gases "reference".

Reply: We agree that we should be more careful with these terms. Corrections have been made in the revised manuscript.

P7638 L22: "The bellow valve" – I would call this valve "inlet valve".

Reply: We have corrected it.

P7638 L24: "balance" to "equilibrium"

Reply: We have corrected it.

P7638 L24: "direct" to "introduce"

Reply: We have corrected it.

P7638 L25: "Once the measurements end,…" Please elaborate more here. How you define the end of measurement? How long does it take?

Reply: The measurement of flask sample usually takes 180 s to obtain relatively stable data for CO_2, CH_4 and CO. We have added it in the revised manuscript.

"The measurement of flask sample usually takes 180 s to obtain relatively stable data for CO_2*,* CH_4 *and CO (discussed in depth in the next section). Once the measurement ends, the 3-way valve (#2) is switched to the reference cylinder."*

P7639 L1: "was" to "is"

Reply: We have corrected it.

P7639 L2: I would take off the part "to maintain…" in that sentence, since using compressed air as a reference gas is very common way regardless of the measurement techniques employed (you would use compressed air even if you used a GC method).

Reply: We have corrected it.

P7639 L2: Please give concentrations of CO2, CH4 and CO in the reference air here.

Reply: We have stated the concentrations of CO_2, CH_4 and CO in the revised manuscript.

P7639 L2: The sentence "water vapor in the reference cylinder…" (L4) should be given just before the previous sentence ("Furthermore,…"). How did you remove water vapor in the ambient air? Cooling traps? Magnesium perchlorate? Nafion? etc. What is the dew point temperature of the gas?

Reply: We did not deliberately remove water. This reference air is a compressed air sample with certain amount of water remained in the cylinder. In fact, all samples used for testing this method were ambient air, and water vapor was not removed, since CRDS can measure water along with other GHGs simultaneously.

P7639 L3: "fixed concentrations" – It is known that concentrations of trace gas (particularly CO2 and CO in this case) could change over long-term period in a cylinder. The cylinder's material is one of important points. Please give how you confirmed stability of concentrations in the cylinder during your measurement period, which actually allow you to check the stability of the CRDS method.

Reply: We use NOAA standards to validate the stability of the trace gases in the reference cylinder over time. The reference cylinder used in this study is to keep an uninterrupted flow to the CRDS analyzer and to validate the short-term stability of the flask-CRDS method before and after measurements of every flask sample. We have rephrased the text in the revised manuscript and as follows.

"The reference cylinder is an ambient air sample pressurized to approximately 68 bar (~1000 psi) to keep an uninterrupted flow to the CRDS analyzer before and after the flask measurements occurred. Furthermore, CO_2, CH_4 and CO in the reference cylinder (395.95 ppmv for CO_2, 1970.5 ppbv for CH_4 and 189.4 ppbv for CO) can be used to validate the stability of the CRDS method before and after measurements of every flask sample."

P7639 L8: CO2, CH4 and CO "concentrations of our reference gas" are calibrated…

Reply: We have corrected it.

P7639 L8: "with a series of certified standards ranging from" to "relative to standard gases whose concentrations range from…"

Reply: We have corrected it.

P7639 L8: How many standards purchased from NOAA do you have? You should also mention that some of your measurements were done outside the range of the NOAA standards you have (extrapolated calculation).

Reply: We have 4 NOAA standards with various mole fractions for CO_2, and 3 standards for CH_4, and 3 standards for CO. We have added this information and stated that some of the measurements in the study were done outside the range of the NOAA standards.

"Some of the measurements in the study were made outside the range of the NOAA standards and, thus, were extrapolated for concentrations."

P7639 L16: Where did you collect the ambient air? The measured concentrations look like urban air.

Reply: The air sample was collected on a campus on the outskirts of Taipei. We have revised it as follows.

"To test the system's stability at sub-ambient pressures, a 2-L stainless-steel canister filled with relatively clean urban air"

P7639 L18: "fed" to "introduced"

Reply: We have corrected it.

P7639 L19: Why do you give the time resolution of the analyzer here suddenly? You might write in the previous section.

Reply: We have moved it to the previous section.

P7639 L24: Do you mean that you had no experiments to double-check the performance of the H2O correction on your own system and just rely on the system default function?

Reply: Actually we did perform the water test, but decided not to include this result in the manuscript, since many papers have discussed this issue. To test the water correction equation of the CRDS, we repeatedly added different levels of water vapor into a canister (2-L) filled with the same air from a 15-L canister (29-11521G, SILONITE Coated, Entech). After water correction the measurements of the samples with different levels of water vapor agreed highly with negligible differences in the CO_2 and CH_4 dry mole fractions (<0.1 ppmv for CO_2 and <2 ppb for CH_4).

P7640 L3: I do not think Figure 2 is needed if its data origin is same as Figure 3. If you keep the figure, you might not plot different variables on the same axes. It is not a good idea to put variables in different units on one axis.

Reply: We have separated variables into their own axes in Figure 2.

P7640 L20: Give subscripts to each [CONC] so that readers can clearly recognize the difference. You might write "ΔP" instead of "P". Please cite the source of this equation.

P7641 L3: The concentration values are slightly different from those in Table 1.

Reply: They are typos. We have corrected them.

P7640 L24: The improvement after the correction is hard to see in Figure 3. You might explain more in the text. It might also help if you overlay Figure 3b on 3a for CO2 and

CH4 or insert 3b in 3a so that the original and corrected CO2 and CH4 values are close to each other. Use the same y-axis range for 3a and 3b.

P7640 L26: Give the standard deviations of your measurements instead of writing "can meet the WMO/GAW standards".

Reply: Thanks for the comment. The slopes for uncorrected and corrected data in Fig. 3b (original manuscript) 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. 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 and rewrite the text to make the revised manuscript more concise.

P7641 L4: Please clarify what part of the measurement get stabilized. There are some possibilities: time for replacing residual air in the line, time for pressure and temperature in the analyzer getting equilibrium…etc.

P7640 L6: How long is the "unstable transition period"?

P7641 L5: "concentration gradients" – Do you mean concentration gradients between the previous and following gas? I wonder why it affects. The system pumps sample air at same flow rate at anytime, which gives same time for replacing air in the analyzer, resulting in the same equilibrium time. I speculate that the change in output signal toward the stabilization is less visible when the following gas has concentrations similar to the previous one.

Reply: The comment is highly appreciated. We have revised the paragraph in accordance with the referee's suggestion.

"Table 1 shows the means and standard deviations of the measurements of CO_2, CH_4, CO and H_2O in the different time intervals of the measurement. As shown in Fig. 3, there was an unstable transition period when the 3-way valve was switched. The measurements of the four gases changed abruptly from the measurements of the reference air to those of the sample in the canister. The measurements of CO_2, CH_4 and CO became stabilized after approximately 60 s in this case (see Fig. 3 and Table 1). The equilibrium time mainly depends on the time needed for replacing residual air in the transfer tubing and analyzer, and for pressure and temperature to equilibrate in the analyzer."

P7641 L25: Please clarify where do you mean for “the pathway”. Inner wall of the flask? Or the manifold, other lines? I speculate that water in sample air was adsorbed on the inner wall of the flasks during storage, and when sample air being introduced to the analyzer, the water was gradually released as the pressure goes down.

Reply: The pathway is the path that the sample took from manifold to the CRDS analyzer (flask is not included). We agree that the slight increase of water is likely caused by the water gradually liberated from the inner surface of the sampling flask. In other words, during the pumping process the equilibrium was never reached for water, because it was gradually liberated from the inner surface of the flask. To make this sentence clearer, we revised the sentence as follows:

“This increasing trend of water can be also clearly seen in Table 1 during the measurement period from 60 to 1012 s when the other three gases showed rather stable measured mole fractions. The possible cause for the slight increase could be that the equilibrium was never reached for the water vapor which was gradually liberated from the inner surface of the flask during the measurements.”

P7642 L4: Please clearly define first what you mean for “the wall-effect”. CO2 adsorption on the inner wall of the manifold? It’s known that it could attach on some materials. Again you should give the material of the manifold. I suggest to examine this experiment also for wet sample air.

Reply: We have rephrased the sentence regarding the “wall-effect” as follows: “The wall-effect is a bias associated with any surface onto which the air constituents are adsorbed.”

The manifold consists of stainless steel tubing (coated with fused silica, 1/8 inch, Restek) and switching valves (stainless steel, SS-41GS2 and SS-41GXS2, Swagelok).

The pressurized sample employed for manifold adsorption test was not a dry air sample. It still had approximately 0.64% water vapor in the 15-L canister (29-11521G, SILONITE Coated, Entech). To avoid confusion and also to make our point clearer, we have rephrased the sentence as follows:

"A pressurized ambient 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, ….."

P7642 L21: I suggest not to use the term "readings". Instead, I would use "measured concentrations" for instance. This is for everywhere in the text.

Reply: We have changed that throughout the manuscript.

P7642 L26: Again please clarify "the pathway".

Reply: The pathway is the path that the sample took from manifold to the CRDS analyzer (flask is not included). We have rephrased it in the revised manuscript.

P7643 L9: Did you analyze these sub-samples soon after the transfer from the large canister? And did you also analyze air samples in the original 15-L canister?

Reply: We analyzed the sub-samples consecutively after 4-hour equilibrium time, but we did not analyze the original 15-L sample.

P7643 L9: I think that presenting the averages and standard deviations in the text are enough and Table 3 is not necessary.

Reply: It has been removed.

P7643 L20: "at the coast" – where? Please give the place name.

Reply: The low level sample was collected at the coast (Zhunan, northern Taiwan). We have added the location in the manuscript.

P7643 L26: I would expect that this kind of memory effect is more likely when you introduced a high-concentration sample first, followed by a low concentration sample. In this sense, I would present the opposite case in the manuscript.

Reply: We agree with the referee in that the procedure should be reversed by first introducing a high-concentration sample, followed by lower-concentration samples. We have presented the new result instead in the revised manuscript.

P7644 L1: You should give the volume of the manifold in the previous section, not here.

Reply: It has been corrected.

P7644 L12: "Mixing ratios" – Use one term everywhere ("concentrations" is used at the other places). Be careful to which matches your measurements. Also note that "mole fraction" is the term NOAA always uses.

Reply: We have taken the advice and used "mole fraction" for CO_2, CH_4 and CO throughout the text.

P7644 L8: As mentioned earlier, I am not convinced for the purpose of this section. The term "intercomparison" recalls comparison with independent systems, the other laboratory for instance. But the experiments made here is a storing test. With respect to storing tests, you might mention previous efforts. See for instance in Novelli et al. (1992), Tanaka et al. (1983), Dlugokencky et al. (1994), Yashiro et al. (2009), Tsuboi et al. (2013) etc.

Reply: We agree that the term "inter-comparison" is misused. The real intention here is to validate the method of flask-manifold while keeping other variables unchanged. As mentioned earlier, the point is that if there is a noticeable difference arising from the comparison, we will know it is due to the flask-and-manifold and not the calibration bias resulting from a different CRDS analyzer. The storing issue was not the only intention we tried to convey. We agree with the reviewer that, in essence, it is not a true inter-comparison work, but a validation study. To avoid confusion and also to make our point clearer, we have rephrased the sentence in page 14 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."*

P7644 L22: I wonder whether the room air in the connector was adequately flushed in the way described.

Reply: The shut-off valve (#1) was opened for approximately 10 minutes to allow fresh air from the glass manifold to flush the room air left in the connector (approximately 1 mL in volume) when connecting a canister. We believe that the remaining air is extremely minimal if there is any, and the data can support our argument.

P7644 L26: How long did it take to fill each sample and collect all the samples?

Reply: The bellows valve of the pre-evacuated canister was opened for one minute to fill the canister and to equilibrate the pressure with the outside ambient pressure. Twelve canisters were used to sample air every two hours, totally for 24 hours.

P7645 L2: "because the same CRDS" – This makes sense if you intended to make storing test. Otherwise I cannot understand what you mean here.

Reply: As mentioned earlier, the storing test is one of the intentions, but we also tried to convey that the method of flask-and-manifold is sufficiently sound and robust. The detailed answer to this comment can be referred to our earlier replies.

P7645 L2: Why are the results for CO not presented? If the data are not available, you should write it.

Reply: The G1301 CRDS used at the mountain station is an older model of CRDS, which only measured CO_2 and CH_4, but not CO. We have added this information in the revised manuscript.

We highly appreciate the referee for the references listed below.

References

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NOAA: http://www.esrl.noaa.gov/gmd/

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