

## **Review of “Flask sample measurements for CO<sub>2</sub>, CH<sub>4</sub> and CO using cavity ring-down spectrometry” by Wang et al.**

### **Summary of the manuscript**

This paper presents laboratory setups and experiments for CRDS measurements of trace gases (CO<sub>2</sub>, CH<sub>4</sub> 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.

**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.

**Citation** – Considering that this is a technical paper for measurements of atmospheric CO<sub>2</sub>, CH<sub>4</sub> 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 CO<sub>2</sub>, CH<sub>4</sub> and CO, not for other NMHCs and halocarbons. Original papers that studied

evolution of CO<sub>2</sub> and CH<sub>4</sub> could be cited instead of referring the IPCC report. Please see references attached at the end of this comment.

**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.

**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.

**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.

### **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).

**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.

**P7635 L24:** Since this paper focuses on CO<sub>2</sub>, CH<sub>4</sub> 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).

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

**P7636 L9:** “to report dry base data” to “to report on dry-air based scales”

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

**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.

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

**P7637 L1:** “are” to “has been”

**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.

**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?

**P7638 L8:** ...with a shut-off valve “(#1)”...

**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.

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

**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”.

**P7638 L22:** “The bellow valve” – I would call this valve “inlet valve”.

**P7638 L24:** “balance” to “equilibrium”

**P7638 L24:** “direct” to “introduce”

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

**P7639 L1:** “was” to “is”

**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).

**P7639 L2:** Please give concentrations of CO<sub>2</sub>, CH<sub>4</sub> and CO in the reference air here.

**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?

**P7639 L3:** “fixed concentrations” – It is known that concentrations of trace gas (particularly CO<sub>2</sub> 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.

**P7639 L8:** CO<sub>2</sub>, CH<sub>4</sub> and CO “concentrations of our reference gas” are calibrated...

**P7639 L8:** “with a series of certified standards ranging from” to “relative to standard gases whose concentrations range from...”

**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).

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

**P7639 L18:** “fed” to “introduced”

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

**P7639 L24:** Do you mean that you had no experiments to double-check the performance of the H<sub>2</sub>O correction on your own system and just rely on the system default function?

**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.

**P7640 L6:** How long is the “unstable transition period”?

**P7640 L20:** Give subscripts to each [CONC] so that readers can clearly recognize the difference. You might write “ $\Delta P$ ” instead of “P”. Please cite the source of this equation.

**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 CO<sub>2</sub> and CH<sub>4</sub> or insert 3b in 3a so that the original and corrected CO<sub>2</sub> and CH<sub>4</sub> 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”.

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

**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.

**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.

**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.

**P7642 L4:** Please clearly define first what you mean for “the wall-effect”. CO<sub>2</sub> 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.

**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.

**P7642 L26:** Again please clarify “the pathway”.

**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?

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

**P7643 L20:** “at the coast” – where? Please give the place name.

**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.

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

**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.

**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.

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

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

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

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

## References

AGAGE, <http://agage.eas.gatech.edu>

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

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