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Atmospheric Measurement Techniques Discussions

Interactive comment on "Flask sample measurements for CO_2, CH_4 and CO using cavity ring-down spectrometry" *by* J.-L. Wang et al.

Anonymous Referee #1

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Wang et al. present a method to take air samples in stainless steel flasks and analyze it subsequently with a CRDS instrument for CO_2, CH_4, 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 CO_2 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 does 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.

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.
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?
7641/5ff: Which period is exactly used? 60-120 s, or 60-1012 s, or some different?
7641/29: What are the water correction factors used? Which function (linear, quadratic)? What does "notably stable" mean?
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?
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)?
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?
7644/1f: Do you always evacuate the manifold, or only during this test?
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 CO_2 when doubling the storage time between sampling and analysis?
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?

Minor corrections (page/line):
7634/4: Instead of "propose" it might be better to use "present" here? Otherwise, the sentence seems inconsistent.
7643/12: add serial comma two times: ", and" instead of "and"

References:
NOAA ESRL http://www.esrl.noaa.gov/gmd/outreach/behind_the_scenes/measurementlab.html
K. Tsuboi, et al.: Evaluation of a new JMA aircraft flask sampling system and laboratory trace gas analysis system, Atmos. Meas. Tech., 6, 1257-1270, doi:10.5194/amt-6-1257-2013, 2013.
P. Sturm, et al.: Permeation of atmospheric gases through polymer O-rings used in flasks for air sampling, J. Geophys. Res.-Atmos., 109, D04309, doi:10.1029/2003JD004073, 2004
R. E. M. Neubert, et al.: A Computer-Controlled Continuous Air Drying and Flask Sampling System. J. Atmos. Oceanic Technol., 21, 651–659, 2004.
I. T.van der Laan-Luijkx, et al.: Atmospheric CO2, d(O2/N2) and d13CO2 measure-

ments at Jungfraujoch, Switzerland: results from a flask sampling intercomparison program, Atmos. Meas. Tech., 6, 1805-1815, doi:10.5194/amt-6-1805-2013, 2013.
Rothe et al., 2004 in 12th WMO/IAEA Meeting of Expert on Carbon Dioxide Concentration and Related Tracers Measurements Techniques (Toronto, Canada, 15-18 September 2003) (WMO TD No.1275), 274 pp, May 2005 ftp://ftp.wmo.int/Documents/PublicWeb/arep/gaw/gaw161_final_3jun.pdf#page=73
H. Chen, et al.: Validation of routine continuous airborne CO2 observations near the Bialystok Tall Tower, Atmos. Meas. Tech., 5, 873-889, doi:10.5194/amt-5-873-2012, 2012.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 7633, 2013.