**Atmospheric
Measurement
Techniques
Discussions**

Interactive comment on "Evaluation of a cavity ring-down spectrometer for in-situ observations of $^{13}CO_2$" *by* F. R. Vogel et al.

F. R. Vogel et al.

felix.vogel@ec.gc.ca

Received and published: 20 November 2012

Anonymous Referee #2 Received and published: 23 October 2012

This paper by Vogel et al. evaluates and characterizes a cavity ring-down spectrometer for in situ d13C measurements in different aspects: 1) assessing the short-term and long-term performance of the spectrometer; 2) characterizing the dependence ofd13C measurements on CO2 and CH4 concentrations; 3) estimating the uncertainty for ambient measurements. This contributes to the technical expertise for atmospheric measurements of in situ d13C. I recommend the publication of the paper after addressingmy concerns below.

***Reply to comment: Thank you for your thoughtful comments. We have expanded and corrected the manuscript accordingly and you will find our response to your general and specific comments below.

General comments 1) This paper has somehow a narrow view, which only mentions the cavity ring-down spectrometer. An immediate question would be that how does the cavity ring-down spectrometer compare with other available techniques, such as a quantum cascade laser based absorption spectrometer (QCLAS) by Tuzson et al. 2011 in ACP, an analyzer based on off-axis integrated cavity output spectroscopy (ICOS) by McAlexander et al. 2011 in analytical chemistry, and a FTIR trace gas analyzer by Griffith et al. 2012in AMT. Note that all these alternatives provide similar or significantly higher precision for d13C measurements at shorter time scales. With the current precision of the cavity ring-down spectrometer of 0.15‰ at 20 minutes scale or even improved precision in a later version, the statement in the abstract "emergence of widespread application of cavity ring-down spectrometers to monitor d13C in atmospheric CO2" is not justified.

***Reply to comment: Our paper is indeed focused on discussing the CRDS technique as publications for other instruments are available and even included in the WMO special issue of AMTD. We have added a brief discussion and references to the other instruments in the discussion as it definitely gives a better overview over the current "state-of-the art". It is hard to predict which technology will be the most popular in future, as precision is not the only relevant factor for a monitoring instrument. Currently 17 peer-review publications are listed that have used a CRDS in carbon isotope studies (http://www.picarro.com/resources/references?type=literature&tid=217) and according to a personal communication from Aaron v. Pelt (Picarro Inc.): "hundreds of isotope analyzers are currently in use in a wide range of applications" (Nov. 16th, 2012). We would therefore argue that "emergence of wide-spread application" seems justifiable.

2) I do not see a significant value of the 10 minutes measurements of a target gas every 30 minutes. The validation of the calibration frequency can be fully determined by the

every 7 h calibrations. If the purpose was to identify situations of unusual instrument behavior changes within the 7h calibration interval, the authors should be able to figure out whether this is necessary based on the results from the one-year operation.

***Reply to comment: For our strategy we can show that our calibration is consistent with the IRMS data over the course of one year. We find the deviation to be 0.002±0.025‰ and that the standard deviation of the measurement precision slightly changes over time. There furthermore is no drift in the calibrated data over the course of one year as shown in Figure 6. In our opinion this data is sufficient to support that this strategy works. This analysis however is only possible, because of the frequent target measurements, as the (weekly) long-term target measurements are too sparse. The short-term target was furthermore most valuable in quickly identifying episodes where the instrument failed or performed badly (missing Episodes in Figure 6, e.g. July 2011, February 2012). Identifying such episodes and quickly responding to it, is crucial to achieve the best possible data coverage (we achieved 95% raw data, 91% QA valid data). As Environment Canada is a government agency with a mandate to perform, observations data coverage and quality is of utmost importance, which might be different for campaign-based or process studies. We therefore (only) recommended the use of a second target gas cylinder ("a thorough QA routine using at least two target cylinders should be implemented"). Unfortunately, we do not fully grasp your suggestion, how we could have validated our calibration frequency solely relying on our 7h calibration data. It seems indispensable to use at least a third (independent) target gas to verify this.

Detailed comments

P6039/L13: correct references according to the rules of AMT, e.g. Yakir et al., 1996

***Reply to comment: We, unfortunately, cannot find the problem with the citation of (Yakir and Wang, 1996) etc. The convention with AMT is to sort multiple citations by year and the style of (Authorname et al., date) and (Author1 and Author2,

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

date) follows the AMT guidelines outlined at (http://www.atmospheric-measurement-techniques.net/submission/manuscript_preparation.html)

P6039/L24: the effective optical path length of the cavity is an estimated value, and is not an exact one. I can imagine it varies from one cavity to the other. Furthermore, the value of about 14km seems small, please double check the value. Besides these, one important parameter, the wavelength, is missing.

***Reply to comment: We have revisited the path length estimate and found that it can be up to 20km for this type of instrument (G1101+), we have also specified the wavelength (6251cm-1).

P6041/L1-3: The CRDS technique detects the ring-down time instead of the absorption strength, and therefore is not very sensitive to the performance of the detector. The laser precision is one of the limiting factors for the measurement precision, but isn't the low signal/noise ratio of d13C measurements mainly due to the weak absorption signal in the near-infrared region?

***Reply to comment: The laser precision is indeed the major factor limiting the precision of this instrument, besides the optical quality of the cavity. The weak absorption in the near-infrared is definitely an underlying problem and a laser with similar precision would perform better if the absorption was stronger. We have altered the text to reflect this.

P6042/L16-17 what does "average 4 injections" mean?

***Reply to comment: As the precision for a single target measurement is quite large (i.e. 0.177‰) we perform four 20min measurements ("injections"). If we want a higher precision for the weekly data those 4 measurements can be average, reducing the uncertainty to about 0.1‰ . We have altered the text to clarify.

P6042/"3.3 Concentration dependence" the CO2 concentration dependency of IRMS does not suggest CRDS may have a CO2 concentration dependency. I do not see a

good reason to perform such a test.

***Reply to comment: We removed the remark about the non-linearity of IRMS systems as it is unnecessary and seems distracting. Checking the linearity of the instrument, however, is a standard procedure. As the cross-sensitivity to CH4 is also dependent on the CO2 concentration this test, for example, ensures that the CH4 cross-sensitivity does not significantly change in the tested CO2 range (c.f. Section 4.1.).

P6043/4.1 Scale offset and cross-sensitivity: the calculations for Xsens are hard to follow because of the use of d13CVPDB*and d13CVPDB, and the use of d13Cres. I recommend starting with an equation that already includes the CH4 sensitivity term, and derive an equation for calculating Xsens based on d13Craw, not based on d13Cres (d13Cres is not a directly measured term).

***Reply to comment: We have changed the derivation of Xsens and now solely use 13Craw, d13CVPDB*and d13CVPDB as these are readily available quantities. This significantly facilitates this section. As we have to define the above mentioned quantities we kept the definition of d13Craw, d13CVPDB*and d13CVPDB in the manuscript. We felt it was easier to start by defining the simple d13CVPDB* before introducing the more complex equation for d13CVPDB.

P6046/L4: "the data is flagged if water levels exceed 0.1%", was the data corrected for water effects when water levels were below 0.1%? Using the default water corrections?

***Reply to comment: We meant to write 0.1‰ , we have corrected that. If the H2O level would be significantly above 0 the default correction would be used. Our samples, however, usually have water levels even below 0.001%.

P6048/L23-27 There is no point claiming them as "the fundamental approach". These are well known in the community. Especially Allan variance has been widely used to evaluate the stability of instrument measurements, and the authors should cite available publications for this.

***Reply to comment: We used "fundamental" to signify that our strategy combines known, basic methods. We have reformulated the passage. Figure 2. actually gives the standard deviation for different integration intervals. We have corrected the caption. Thank you for catching this glitch.

P6049/L3 I cannot agree with "using at least two target cylinders" until more convincing results are shown.

***Reply to comment: We assume that you imply that a single QA target would be sufficient. The need for a long lasting target (long-term target) is apparent, as it ensures the consistency of the data over the life-time of several working gases (i.e. calibration gases). For the benefit of frequent measurements of a short-term target, please see our reply to your general comment 2.).

P6053 the label on the y-axis should be "Allan deviation" instead of "Standard deviation". Note that the definitions of the two terms are different. And in the caption, should be "Allan deviation plot" instead of "Allan-variance plot".

***Reply to comment: We have corrected the wrong axis label.

―――――――――――――――――

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 6037, 2012.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper