

## ***Interactive comment on “Evaluation of a cavity ring-down spectrometer for in-situ observations of $^{13}\text{CO}_2$ ” by F. R. Vogel et al.***

**F. R. Vogel et al.**

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Comments on manuscript amt-2012-171 by FR Vogel et al.: The manuscript by Vogel and co-authors reports on a 1-year evaluation of a commercial CRDS analyzer (Picarro G1101-i) for following the  $\delta^{13}\text{C}$  signature in atmospheric  $\text{CO}_2$  with high precision. The major results can be summarized as follows: 1. The instrument precision of 0.26 to 0.28 ‰ for 10-min time slices does not meet the WMO inter-laboratory compatibility goal of  $\pm 0.01$  ‰ due to the limited signal-to-noise ratio. 2. The authors devised a calibration scheme which essentially eliminates short- and long term drifts. After this,

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the determined offset for four target gases over the course of the measurement period is only  $0.002 \pm 0.025$  ‰. However, a long-term target with  $\delta^{13}\text{C} = -12.47$  ‰ measured weekly had a precision of 0.177 ‰ in line with all other sources of error, limiting long-term errors to  $\pm 0.18$  ‰ for 20 min time slices. 3. There is a serious interference from  $\text{CH}_4$ , amounting to  $0.42 \pm 0.024$  ‰ per ppm methane, which needs to be corrected experimentally. For a typical air sample, this introduces an uncertainty of  $\pm 0.048$  ‰. 4. The authors suggest to use their calibration scheme (or a similar one) for future measurements with improved instrumentation. The paper is well written and describes all experimental results carefully. The figures provide a clear insight into the capabilities and limitations of the investigated instrument. The authors speculate that with improved signal-to-noise and reduced cross contamination from  $\text{CH}_4$  (and other components?) the performance could be improved to values around  $\pm 0.05$  ‰. This is still a factor of 5 (!) off the inter-laboratory compatibility target, but is in accord with the requirements for local studies using optical absorption technique, as discussed for the first time at the 16th GGMT experts meeting 2011 in Wellington, NZ (see recommendations). Publication in the special GGMT issue of AMT is recommended, provided the following minor points are taken care of:

\*\*\*Reply to comment: Thank you for your thoughtful comments. We have corrected and clarified the manuscript. You will find the reply to your specific comments below.

P6039 L27: Please be more specific regarding the consumption of reference gas. Moreover: The comparison is made with FTIR, which makes the CRDS system the winner. However, when compared to MS techniques, the comparison is much less favorable.

\*\*\*Reply to comment: We have clarified the flow rates and included a comparison to other in-situ instruments as well. The reference gas consumption was added later in the text (Section 3.2.).

P6040 L16: The flushing time of 3 min translates to a 3-fold exchange of the gas in the

cavity. For flasks, a 10-fold exchange is usually employed. The 3-fold exchange might be sufficient for the current accuracy level, but will have to be increased when better instruments become available. In principle, this low figure means a scale compression for  $d^{13}C$ , when larger isotopic deviations are measured.

\*\*\*Reply to comment: In fact, the effective exchange of the gas in the cavity more than 10 fold since the pressure inside the cavity is  $\sim 140$  torr. We have added this information, but still included a comment about a possible scale contraction effect.

P6042 L28: Mass spectrometric non-linearities seem to be much smaller and can usually be easily corrected for.

\*\*\*Reply to comment: We removed the remark about the non-linearity of IRMS systems as it is unnecessary and seems distracting.

P6044 L6 ff: The raw Picarro calibration is not important at all. It will vary from instrument to instrument and over time. Therefore, the emphasis should be formulated even stronger on the frequent on-line WGH and WGL calibration, which essentially overwrites all old, non-traceable factory calibrations.

\*\*\*Reply to comment: We agree that only the calibrated data can be used and added a comment to emphasize this.

P6048 L 13: 'negligible' instead of 'neglectable' (?)

\*\*\*Reply to comment: Although, neglectable and negligible are synonymous we changed the wording to the more common negligible.

P6048 L24 ff: Please be consistent with the sentence structure in the bulleted text: e.g. "(I) Quantify the fundamental. . . (II) Determine... (III) Determine. . . (IV) Identify. . . (V) Establish. . . (VI) Develop most importantly. . ."

\*\*\*Reply to comment: We have altered the wording accordingly to be more consistent.

P6052 Fig 1: Is the MFC external to the instrument??

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\*\*\*Reply to comment: The flow controller is indeed external to the G1101+. We have added this information to the caption and the text

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

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