

Atmos. Meas. Tech. Discuss., author comment AC2
<https://doi.org/10.5194/amt-2021-10-AC2>, 2021
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Reply on RC1

Marvin Glowania et al.

Author comment on "Comparison of formaldehyde measurements by Hantzsch, CRDS and DOAS in the SAPHIR chamber" by Marvin Glowania et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-10-AC2>, 2021

We thank the reviewer for the helpful comments.

Comment: L112: There are also applications in the 10s and 100's of ppt range, where there are different challenges.

Response: We added in L112: "...for atmospheric concentrations in the low and sub-ppbv range."

Comment: L186-189: Is this proprietary information? This "rod-shaped material" sounds like Hopcalite or a similar catalyst. Would this material be recommended as a zero-method for the CRDS?

Response: Unfortunately, the manufacturer did not provide which exact material is used, though we asked for this information. Therefore, we cannot give more information than currently done. To make this point clear, we added: "However, the exact scavenging material is not specified by the manufacturer."

Comment: L254: This implies that the DOAS is not "calibration-free" as stated in the abstract. It was calibrated against a Hantzsch. Rather it does not need to be continuously calibrated. Recommend clarifying language.

Response: We replaced the "cross-calibration" in line 247/248 by "comparison" and cancelled "calibration-free" in the abstract.

Comment: L263: Does this accuracy also propagate the uncertainty in the Hantzsch method used to calibrate the differential cross section? Also, does this match current recommendations by, e.g., the JPL handbook? HCHO UV cross sections changed by 8% between JPL 2011 and 2016, and these are based on Meller and Moortgat (2000).

Response: The rotational-vibrational absorption lines of HCHO around 308 nm are very narrow (in the low picometer range) and consequently the experimentally observed cross section is strongly dependent on the spectral resolution of the instrument. Meller and Moortgat used a resolution of 0.025 nm while our DOAS instrument has a resolution of 0.0025 nm and therefore the cross sections are different. We changed the text L263: "The accuracy of the DOAS formaldehyde data is estimated to be 7%. It is mainly determined by the accuracy of the calibration procedure of the former Hantzsch instrument which was

used for the comparison with the DOAS. It also takes into account the uncertainty in the absorption cross section from the regression between the DOAS and Hantzsch data which was 0.16%. The derived high-resolution absorption cross section is valid for the given spectral resolution of 0.0027 nm. Under ambient conditions the pressure and temperature dependence of the cross section is very small (Cantrell et al., 1990) and does not affect the accuracy of the DOAS measurements.”

Comment: Figure 1: A plot comparing the mixing ratios calculated using either method might be more informative.

Response: In our opinion, plotting calculated mixing ratios of a zero signal does not illustrate exactly what we intend to show. The point we would like to make is that there is a changing zero signal that needs to be adequately monitored. Plotting mixing ratio would require subtracting the changing zero signal from the measurements and the information, how much the zero signal changes over time is lost. Therefore, we prefer keeping the plot as it is. The information how the signal converts to an equivalent HCHO concentration is given in the caption.

Comment: L283: Is the timing of calibration measurements random?

Response: Yes, calibration was performed, when there was no experiment performed in the chamber. Breaks were not done on a regular basis but were done according to the schedule of experiments.

Comment: L287: While this empirical correction method may work for this particular set of experiments, it does not provide a recipe that is easily generalized for other CRDS users. How rapidly does this offset change over a day? Is there a dependence on ambient or instrument temperatures? Such questions could be answered with lab experiments under controlled conditions (sampling the same concentration and systematically varying H₂O or temperature), and it is somewhat surprising that such experiments were not done in this case to provide robust empirical correction algorithms.

Response: This work focusses on the results of the application of the instrument in ambient conditions. In our opinion the type of experiments does not play a role for the observed effects. The instrument was placed in an air-conditioned sea container. This type of deployment is very typical, so that the performance of the instrument can be expected to be similar in many cases. In addition, the ring-down cavity is pressure and temperature stabilized, so that the variability of the offset cannot be explained by effects from the specific deployment. Recommendations for the required characterization of the instrument are given in the text. The instrument's offset needs to be measured at least once a day and the dependence on water needs to be characterized on a regular basis. From the drifts of parameters we observe, we do not expect that there a correction with fixed numbers can be provided, but parameters need be determined for each individual instrument and deployment.

Comment: L335: would these “time-dependent systematic errors” be less evident if the test were done at higher HCHO (well above the instrument detection limit)?

Response: The Allan deviation is calculated for baseline measurements without HCHO. The relative impact of the baseline noise would be small for high HCHO concentrations, but the purpose of the Allan deviation is to estimate the limit of detection of instruments.

Comment: General comment: do the authors recommend implementing an automated zero system (background determination) for the CRDS? If so, how frequent should zeros be to achieve good accuracy? Should the method of zeroing retain ambient water vapor concentrations (e.g. using a catalyst) or can one get away with drierite or zero air? This is

considering uses like routine monitoring for air quality.

Response: The need for an automated zero system depends on the accuracy that the user needs. Our observations demonstrate drifts are within the specification of the manufacturer, but that there is need for regular zero measurements, if the user wants to achieve a higher accuracy. From what we see, zeroing once a day would be sufficient and characterization of the humidity dependence on a regular basis. Our dataset does not allow to specify how often this needs to be done. We added L425: "Observations in this work suggest that zero measurements should be done once a day and that the water dependence of the zero point of the CRDS instruments does likely not significantly change at least for a month-long deployment."

Comment: L63: maybe worth noting that this detection limit is with a data frequency of 1 Hz. Also, maybe worth also citing Cazorla et al. (2015, AMT).

Response: Done.

Comment: L77: delete "the sensitivity is not satisfying and"

Response: Done.