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Atmospheric Measurement Techniques Discussions

Interactive comment on "Towards a stable and absolute atmospheric carbon dioxide instrument using spectroscopic null method" *by* B. Xiang et al.

Anonymous Referee #2

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The manuscript 'Towards a stable and absolute atmospheric carbon dioxide instrument using spectroscopic null method' by B. Xiang et al. presents a new spectroscopic technique for the measurements of CO2 with high temporal resolution and without the need of calibration by standard gases. The manuscript presents a novel and interesting approach for the measurement of CO2. The new instrument is compared to other CO2 analyzers (Licor NDIR systems), and isotopic effects on the accuracy of the measurements are discussed in detail. Overall, the manuscript is well structured, and the results are scientifically sound. However, more careful estimation of the uncertainties is needed with respect to the available standard scales (e.g. NOAA). Therefore I recommend publication in AMT after the following aspects have been addressed.

Specific comments:

Rella et al. (2012) is now published in AMT, update reference.

P2057 L6: It should be considered to include a more recent publication on the FTIR technique, e.g. Griffith, D.W.T., et al., A Fourier transform infrared trace gas and isotope analyser for atmospheric applications. Atmos. Meas. Tech., 2012. 5(10): p. 2481-2498.

P2057 L9-11: The statement 'one common disadvantage in most previous instruments is that calibration tanks are employed and the majority of them cannot claim a good long-term (over months) stability without relying on these standards' is true for most but not all techniques. Recent advances in the CRDS techniques show that these instruments can achieve excellent long-term stability, which however must be verified using calibration standards. Such verification should be done even in the case of a stable analytical technique, because it is part of a good QA/QC practice.

P2057 L14: I wouldn't call the efforts made e.g. by NOAA (acting as a central calibration facility for CO2 measurements within the WMO/GAW program) as 'tedious and unregulated "tank science"'. Such a statement seems a little too 'sloppy' to me, especially without citing the relevant work. This must be revised. See below for references.

P2057 L17: WMO itself does not have standards. It should be mentioned that NOAA ESRL GMD is the WMO/GAW Central Calibration Laboratory (CCL) for CO2 and provides standards for the calibration of CO2 measurements. In this context, Zhao, C.L. and P.P. Tans, Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air. Journal of Geophysical Research-Atmospheres, 2006. 111(D8) needs to be cited.

P2057 L18: Concentration in this context is the wrong terminology. It should be 'mole fraction' instead of concentration (see e.g. http://gaw.empa.ch/glossary/glossary.html). Please carefully revise terminology throughout the whole paper.

P2057 L19/20: CO_2 mole fraction instead of 'CO_2 number'.

P2057 L21: Tanks are not from WMO (but usually from NOAA, acting as the CCL for the WMO/GAW programme). These tanks are not primary tanks. Please revise.

P2058 L9: You state that the long-term stability of your prototype instrument is 0.1 ppm in the time period of one month. This is half of what was observed by the comparison among different laboratories using different instruments about a decade ago (your reference Daube et al., 2002). I expect that the 0.1 ppm one-month stability cannot be directly compared to such an experiment, and most likely the difference would exceed 0.2 ppm if different laboratories would run your instrument at different location under different conditions.

P2065 L14: Biases caused by external beam paths are potentially a serious issue that make this instrument difficult to operate, especially if you need additional CO_2-free purge gas. Please add a few words about the additional uncertainty due to this effect.

P2066 L14/15: What is the additional uncertainty due to this interference?

Section 3.2: It would be interesting to see the smoothing results for 1h values in Figure 6, since most long-term measurement programs report 1h values to the data centers. It seems that drift of 0.2 – 0.3 ppm CO_2 can occur within a few hours, which clearly is larger than the current data quality goal for CO_2 measurements of 0.1 ppm in the northern hemisphere. Thus the current performance of the ABC instrument would not be sufficient without additional measurements of standard gases. The experiments here were made with a sealed quartz cell, and it was argued that this is better since no effects due to gas handling and consumption is observed. However, this approach potentially underestimates effects that would occur with continuous air sampling. Could you comment on this, or do you have additional data that could be shown?

P2070 L9 'which meets the WMO Data Quality Objectives' instead of 'WMO standards?

P2070 L9/10: Figure 6 shows that the 0.1 ppm Data Quality Objectives are reached

over a one month period. However, it is also obvious that the DQOs are not always met for shorter averaging times. Please provide the reader with a number of what can be expected from 1h and daily averages (1h resolution is submitted to data centers, and the DQOs should be met for this period).

P2070 section 3.3 Calibration with 'a' primary standard would of course be something that would be nice; however, I doubt that it really reduces the uncertainties. Zhao and Tans (2006) e.g. estimated the uncertainties of the NOAA primaries to be 0.069 nmol/mol (one sigma); compared to this, the propagation uncertainty using an NDIR instrument was relatively small (0.014 nmol/mol). If the isotopic composition is known, the propagation uncertainty could further be reduced using e.g. CRDS instruments instead of NDIR. From this it is obvious that the main contribution to the uncertainty is the uncertainty of the primary standard itself rather than the uncertainty of the propagation.

General remark: As pointed out in the conclusions, the major disadvantage of the instrument is the lack of concurrent measurement of H_2O. This would be a requirement for successful application in the field, since other techniques (e.g. CRDS) with proven reliability of the water vapor corrections are already are commercially available (e.g. Rella et al, 2012).

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 2055, 2013.