

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

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We sincerely thank both reviewers for their efforts and also valuable comments to our work presented in the paper. Below are our responses to each of the comments and the changes we've made in the revised paper (author comment, AC). The original reviewer comments (RC) are also listed for reference.

Reviewer #1

[RC] In this manuscript, the authors develop a novel spectral method to measure atmospheric carbon dioxide with high precision and stability without using calibration tanks

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during long-term operation. By adopting their spectroscopic null method and using a permanently sealed quartz cell, the instrument stability is greatly enhanced. A long-term stability of ~ 0.1 ppm is achieved without any calibrations for more than a one month period. I am impressed.

[RC] This is a well-organized, high-quality manuscript with excellent results. However, I suggest publication with minor revisions:

[RC] (1) The introduction of the spectroscopic null method is not sufficiently clear to for non-expert. Some critical concepts should be explained in more detail, especially the meaning of normalized spectrum, residual spectrum, and spectral fitting.

[AC] The normalized spectrum (also called the ratio spectrum or residual spectrum) is the divided transmission spectrum between sample and reference. Further explanations have been added in the draft. We have also added more explanations on the spectral fitting: “The sample absorption is measured via non-linear least square Voigt fitting (Olivero and Longbothum, 1977) using simulated transition lines with known spectral parameters (line shape and position from HITRAN, and pressure and temperature from measurements) to obtain a quantitative mixing ratio.”

[RC] (2) There should also be a more detailed description and analysis of Fig. 2. The results of purging the optical compartment with dry nitrogen should also be shown in Fig. 2.

[AC] More description and analysis for Figure 2 have been added. Please refer to Section 2.4 in the revised paper. The plots in Figure 2 were measured under the purging condition. The broad spectral absorption feature shown in Figure 2(b) was due to CO₂ within the sealed sample detector can.

[RC] (3) The characteristics (LIV curve and tuning) of the DFB diode laser should be described and depicted in a figure.

[AC] More laser characteristics information has been added in the revised draft. Laser

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current-output power plot and spectrum have also been added as Figure 3.

[RC] (4) The schematic of the optical instrument should be more detailed (showing laser, mirrors, reference cell, ...).

[AC] The optical layout of the instrument has been further labeled in Figure 4a and explained in the caption.

[RC] (5) All figure captions should be more detailed even if they are explained in the text.

[AC] In the revised draft, we have added more descriptions for each figure to make them self-explanatory.

[RC] (6) Additional references that related to some of the concepts of this manuscript would make this paper easier to understand.

[AC] We have added references related to null spectrum (Nelson et al., 2008), Allan variance analysis (Werle et al., 1993), and spectral fitting (Olivero and Longbothum, 1977).

Reviewer #2

[RC] 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.

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[RC] Specific comments:

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

[AC] This has been updated in the revised paper.

[RC] 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.

[AC] The suggested reference has been added in the revised paper.

[RC] 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.

[AC] We would like to thank the reviewer for emphasizing on the importance of checking instrument accuracy through gas standards. We understand that no matter how stable or accurate an instrument is, stable gas standards are still periodically needed for quality assurance purpose. One major goal in our development of ABC is to extend this period as long as possible in order for easy operation and gas saving. To make this point clear, we have added "However, stable gas standards will be employed, at a much reduced frequency and with great care, as a practical approach for quality assurance."

[RC] 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 refer-

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ences.

[AC] We took the reviewer's advice and have changed "tedious and unregulated" to "The "tank science" required to achieve high accuracy is labor-intensive and has no generally accepted protocol, which adds another level of uncertainty to the measurements".

[RC] 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.

[AC] This additional information provided by the reviewer has been added in the revised paper.

[RC] 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: CO₂ mole fraction instead of 'CO₂ number'.

[AC] We have changed "concentration" to "dry air mole fraction" or "mixing ratio" throughout the revised paper.

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

[AC] This has been corrected in the revised paper.

[RC] 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

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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.

[AC] In the revised paper, we have updated with the 14th WMO round-robin test result in its final form published in 2009 (Zhou et al., 2009). As mentioned in the draft, we are currently developing a field-deployable ABC instrument. Challenging this instrument under different lab and field measurement conditions are underway.

[RC] 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 CO₂-free purge gas. Please add a few words about the additional uncertainty due to this effect.

[AC] The external CO₂ difference introduced from small external beam path bias can be fitted separately and won't affect the measurement as long as it's stable. We plan to address this with hermetic sealing and active mixing of the air inside the optical box. These features have already been employed on the current field-deployable ABC instrument. Another approach to avoiding purge gas would be circulation through a CO₂ chemical scrubber inside the optical box (Andersen et al., 2010). These steps have been added in the revised paper: "We plan to improve the hermetic sealing of the optical box, chemically scrub and homogenize external-path CO₂, and further balance the external beam paths in the next development step."

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

[AC] As mentioned in the paper, the extra CO₂ in the sealed sample detector can was found relatively stable over years. It's less likely that this interference will cause variation on the CO₂ measurement and we have already got rid of this possibility by using two new CO₂ free detectors in the current ABC platform.

[RC] Section 3.2: It would be interesting to see the smoothing results for 1h values in

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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 CO₂ can occur within a few hours, which clearly is larger than the current data quality goal for CO₂ 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?

[AC] As the reviewer suggested, we have changed Figure 6 (now Figure 7 in the revised paper) by replacing the daily median running filter with the hourly and daily average values. The one-sigma standard deviation for the hourly mean is 0.059 ppm, and for the daily mean is 0.031 ppm. This is quite good for the purpose of long-term measurements which report at 1 hr resolution to the data center.

[AC] We are aware that additional testing using calibration standards will be necessary. Our development work on the prototype instrument of ABC mainly focused on improving the stability, which serves as the basis for long-term absolute CO₂ measurement.

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

[AC] This has been corrected in the revised paper.

[RC] 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).

[AC] As stated above, the one-sigma standard deviation for the hourly mean data is

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0.059 ppm, and 0.031 ppm for the daily mean. This is quite good for the purpose of long-term measurements which report at 1 hr resolution to the data center. We have added these numbers to the revised paper.

[RC] 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.

[AC] We agree that "if the isotopic composition is known", then the main contribution to the uncertainty is the uncertainty of the primary standard.

[RC] General remark: As pointed out in the conclusions, the major disadvantage of the instrument is the lack of concurrent measurement of H₂O. 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 commercially available (e.g. Rella et al, 2012).

[AC] Agreed. The manuscript already states that this is a disadvantage and that we have plans to address it by measuring water vapor. See below for one potential spectral region.

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

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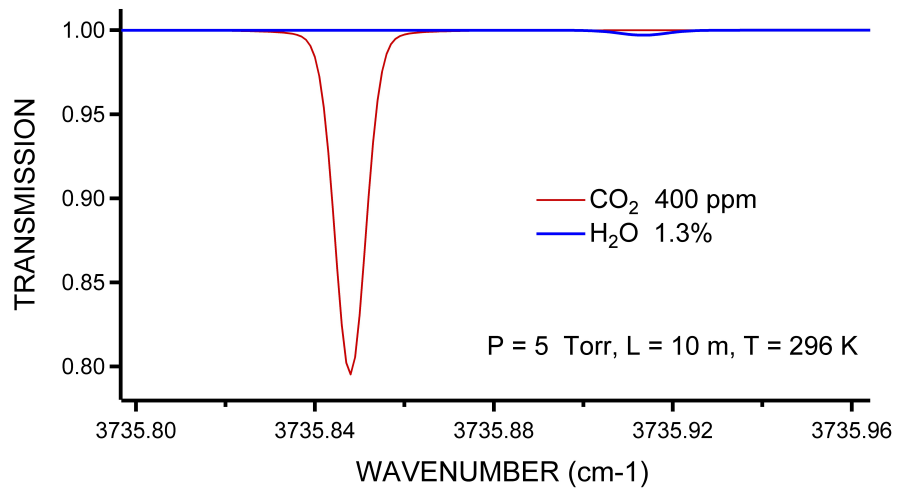


Fig. 1. Potential spectral region for cocurrent water measurement

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