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Atmospheric Measurement Techniques Discussions

Interactive comment on "Validation of spectroscopic gas analyzer accuracy using gravimetric standard gas mixtures: Impact of background gas composition on CO_2 quantitation by cavity ring-down spectroscopy" *by* Jeong Sik Lim et al.

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The authors appreciate Dr. Loh's kind consideration of this manuscript. Please find our replies to the referee comments below.

General Comments

1. The authors present a set of total pressure broadening coefficients (TPBCs) that

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substantially improve agreement between CRDS determined CO2 mixing ratios and the mixing ratios assigned to each tank during gravimetric or manometric preparation. However, the use of TPBCs does not reduce the discrepancy to within the World Meteorological Organization's CO2 inter-laboratory compatibility goal of +/- 0.1 umol/mol (in the Northern Hemisphere, and 0.05 umol/mol in the Southern Hemisphere). As such, I would urge the authors to consider appending something similar to the following to the end of their abstract.

P1, L20: "... instrument calibration, or better still, use standards prepared with ambient air."

Additionally, I would like the authors to consider adding a sentence or two to this effect in their discussion section.

- Thank you for the suggestion. Authors will add sentence as follow.

- P1, L20: ". . .. Instrument calibration or use standards prepared in same background composition of ambient air.

- The authors conjecture that major error sources arose from the mole fraction uncertainties of major components, e.g. N2, O2, Ar and CO2, and uncertainty of pressure broadening coefficients. According to this opinion, the authors will add sentences at the end of discussion section as follow.

- "It is worth noting that the quality of the TPBC correction can be improved further by using quality standards with lower composition uncertainties, including 13CO2 isotopologues and precisely measured broadening coefficients that are deduced from advanced line-shape functions such as Galatry and Rautian profiles."

- With regard to the isotopes ratio, please see the reply for general comment 2.

2. A further comment is that the authors do not mention the isotopic composition of the CO2 used to prepare their synthetic standards. While I assume all eight standards were prepared with the same batch of CO2 (and thus having the same CO2 isotopic compo-

sition), this is worth mentioning (and handling) explicitly (preferably with the δ13CCO2 of the pure CO2 used). As CRDS is a single line spectroscopic technique, it is inherently isotopologue specific. Therefore, using a pure CO2 source with a significantly different isotopic composition from the background atmosphere will induce a systematic bias in CRDS determinations of mixing ratio unless this effect is accounted for. The authors already cite Lee et al. (2006), which deals with this question (though for NDIR rather than CRDS (for which the problem is at its most extreme)), so I assume they are familiar with the issue.

- The authors understand this comment is very similar to first specific comment of RC1. The 12/13 ratio of CO2 raw gas for gravimetric standards was similar to the atmospheric level approximately -11‰.The volumetric standards with prepared with the dry air and high purity N2 (>99.999%). This suggests similar isotope ratios would occur across the prepared cylinders. For verification (calibration) of prepared gravimetric (volumetric) standards, the CO2 mole fractions in them were verified by GC-FID, which measured total carbon isotopes. Therefore, the isotope effect were hardly discernable in this study. However, it might be the case that the isotope ratios of CO2 in the "dry air" can vary or deviate from the CO2 raw gas to cause some extent of discrepancy in the CRDS response. The authors will add sentences at the end of the section 2.1 as follow.

- The 12C/13C ratio of CO2 raw gas for the gravimetric standards was similar to the atmospheric level of approximately -11‰ which suggests similar isotope ratios would occur across the prepared cylinders as determined by gravimetry and volumetry. Nevertheless, isotope effects biasing the CRDS response seemed to be hardly discernable in this study because verification (calibration) of the CO2 mole fractions in the prepared gravimetric (volumetric) standards was carried out by GC-FID, which measured the total carbon isotopes."

Specific Comments

1. P1 L28, consider inserting ’all’ between quantify and its, and remove "considerably"

- It will be corrected as suggested.

2. P3 L20, gases to become ’gas’

- It will be corrected as pointed out

Please also note the supplement to this comment:
https://www.atmos-meas-tech-discuss.net/amt-2017-54/amt-2017-54-AC1-supplement.pdf

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