

Interactive comment on “Validation of spectroscopic gas analyzer accuracy using gravimetric standard gas mixtures: Impact of background gas composition on CO₂ quantitation by cavity ring-down spectroscopy” by Jeong Sik Lim et al.

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This is a nice, succinct paper characterizing the effect of the background gas composition on CO₂ measurement via cavity ringdown spectroscopy. This work should be useful to the atmospheric trace gas community as the number of atmospheric CO₂ measurements (particularly via cavity ringdown spectroscopy (CRDS)) are likely to rise in the near term, potentially being made by non-experts. This paper is accessible and

C1

clear and highlights a trap that many users of CRDS may fall into, by using industrially prepared calibration standards.

General Comments:

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

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 composition), this is worth mentioning (and handling) explicitly (preferably with the delta¹³C-CO₂ 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.

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Specific technical comments:

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

P3 L20, gases to become 'gas'

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