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Atmospheric Measurement Techniques Discussions

Interactive comment on "Gravimetrically-Prepared Carbon Dioxide Standards in Support of Atmospheric Research" *by* Bradley D. Hall et al.

Bradley D. Hall et al.

bradley.hall@noaa.gov

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Response to Reviewer 1 (also included as supplement, pdf form)

We thank the reviewer for comments and helpful suggestions.

The second paragraph of the introduction refers to a requirement for a relative standard uncertainty of áĹij0.01 % to assess the drift in CO2 amount fraction in cylinders over many years. How is this uncertainty target determined? This assessment is based on the WMO network compatibility goal for 0.1 ppm.

Response: To resolve a drift of 0.1 ppm over several years, new standards would have to be reproducible at approx. $\frac{1}{4}$ this level, or 0.006%. We have updated this sentence as follows.

"Determining the absolute amount of CO2 in air is a challenge for both gravimetric and manometric methods, particularly since the relative uncertainties must be very small (∼0.006% 1-sigma, or about a factor of 4 lower than the WMO network compatibility goal of 0.1 ppm), in order to assess changes (drift) in cylinders over many years."

The experimental methods section describes the transfer of an aliquot of CO2 to a cylinder from a 5 ml stainless steel container. Considerable experimental effort is employed (heating and re-pressurising the transfer vessel) to ensure that the CO2 is transferred with negligible losses. Would it be possible to simplify the experimental procedure by weighing the transfer vessel before and after to determine the mass transferred?

Response: We briefly experimented using the method you suggest, and found that without the additional flushing we were unable to achieve sufficient transfer using our manifold. Those standards appeared to be ∼0.6 ppm too low. Perhaps this technique could be perfected in order to achieve higher transfer efficiencies, but we decided to use the multiple flush method instead, since we have more experience with that technique.

Equation (1) defines the transfer efficiency (f), although a value is not provided. In the results and discussion section, a statement is made that the transfer efficiency is assumed to be 100 %. Further text is required to accompany equation (1).

Response: We added "f=1.00" to the paragraph following eq. (1).

The paragraph which precedes equation (1) and the first sentence after refers to the unit when the quantity is implied (e.g. "number of moles" and "moles of"). In each case this should be replaced with the quantity "amount".

Response: updated as suggested

In equation (1), in order to accurately determine the amount fraction of the mixture, XCO2,ad and XCO2,dil should be changed to amount of CO2 adsorbed and amount of CO2 in the dilution gas and be added to the numerator and denominator in the first

term of the equation (rather than added as separate terms). Also nair should be split up into its components (nAr, nN2 and nO2).

Response: Since these terms are small (order 0.01 to 0.02 ppm), we feel that expressing them as mole fraction corrections is adequate. We prefer to keep nair as is because this is how we do the calcultation: nair = massair/MWair

On page 7, amount is missing from the sentence “The amount of CO2 adsorbed to the walls, expressed as a fraction of total amount of CO2 in the cylinder”.

Response: updated as suggested

Please also note the supplement to this comment:
https://www.atmos-meas-tech-discuss.net/amt-2018-273/amt-2018-273-AC1-supplement.pdf

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