

Interactive comment on “Revision of the WMO/GAW CO₂ Calibration Scale” by Bradley D. Hall et al.

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The Central Calibration Laboratory’s role in maintaining and propagating the WMO CO₂ scale is fundamental to the international atmospheric CO₂ measurement effort. NOAA/GML have managed this responsibility over many years with skill and diligence. As a user of their services, I take this opportunity to thank them for their contribution.

This paper describes the latest revision of the scale. It builds on previous papers describing the calibration systems and earlier versions of the WMO scale. It gives a thorough account of the issues that necessitated this scale revision, evaluation of the growing body of historical data from the CCL’s reference standards, comparison of X2007 and X2019 scales, uncertainty analysis etc. It is important that this informa-

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tion be made available to the CO₂ measurement community. Open acknowledgement of problems (occasional past mistakes, missing records, methodological limitations) adds to the value of the paper. This transparency is appreciated. The paper is very appropriate for AMT and can be published with only minor revisions.

Specific comments

1) Lines 69, 80, 81 – It would be more accurate to use the term “reference gases” instead of “reference materials”, as the latter is commonly used for isotopically labelled materials including solids and liquids.

2) Line 86 – The brief description of the manometric procedure would be clearer by also stating that the larger volume is pre-evacuated, and its vacuum pressure.

3) Section 3.2 - The largest difference from the X2007 scale is allowance for loss of CO₂ in the manometer o-rings. Direct tests of the manometric method suggest this process still leaves uncertainty of as much as 0.2 ppm in defining the absolute CO₂ scale. It is sobering that uncertainties of this magnitude remain, when other metrics (e.g. network compatibility, scale propagation) can have much smaller uncertainty. The authors address this problem by comparing their manometric data with independent information, such as from gravimetrically derived scales (which have their own uncertainties), to arrive at a preferred definition of the manometric scale. I agree with their approach, though some questions remain over quantification of the uncertainty.

A key point that should be made in the paper is the distinction between total uncertainty in linking the scale to SI units and the component of uncertainty that pertains to maintaining a consistent scale and propagating it to other laboratories. The latter is more important for the CCL's main purpose of aligning CO₂ data between laboratories. This concept has been recognised in earlier CCL papers but is not mentioned in this manuscript. Absolute accuracy of the scale is not critical for most applications, and can be revisited in future if the manometer o-ring effect becomes better quantified.

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The brief description of the loss correction uncertainty in supplementary section 2.4 is not clear on whether it includes allowance for possible systematic error (elsewhere given an upper limit of 0.2 ppm) or random error only. This should be clarified.

A further minor point with the o-ring loss correction is the formulation in section 3.2. If “adsorption of CO₂ begins about 1 minute after the liquid nitrogen is removed” and “there was a delay of about 2 minutes between the time the liquid nitrogen was removed and the first data record”, why isn’t the correction applied for an elapsed time of $t_{\text{max_CO}_2} + 1$ minute?

4) Section 6, p 16/17 - Primary standards were analysed on the laser-spectroscopy (LS) system 6 times over 3 years. Linear fits to these measurements against their manometric assignments yield residuals for individual standards that are highly consistent across the 6 episodes, and lie in a significantly large range of ± 0.1 ppm with a standard deviation of 0.05 ppm (Figure 9). It is correctly stated that “variability seen in the residuals relates to the manometer average values”. The residuals are then partly attributed to shorter manometric measurement histories for higher mixing ratio standards. Other sources of variance are implied but not specified.

An assumption of the calibration system (manometric + LS harmonization) is that these residuals represent random error in manometric average values. However, the standard deviation is about double that expected based on a 0.1 ppm (1-sigma) manometric uncertainty and the number of measurements listed in Table 1. This suggests some systematic bias between the techniques. Do the authors have any insight into possible causes?

My thoughts would be - firstly, can an isotopic bias be ruled out? Data in Table 2 suggest an isotopic bias is unlikely. Could there be sensitivity in either technique to other components of the gas matrix? If so, it is hard to see an unexplained sensitivity in the manometer given the documented evaluation of that technique. Maybe some gas handling bias? Depending on the cause(s) of the bias, has the uncertainty been

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adequately captured?

5) There is no mention in the manuscript of gas handling effects or uncertainties, in particular regarding regulators. Are the author satisfied that the techniques referred to here are not subject to any significant gas handling effects, and/or can uncertainties be quantified? It was noted by Tans et al., 2017 that “Although there may be a component due to gas handling issues on the NDIR system that cannot be resolved. This is still under investigation and will be addressed in a forthcoming paper discussing the scale revision.” Some comment on the current understanding of gas handling uncertainty is desirable.

Technical comments

75 – replace viral with virial

106 – fix inconsistent cold trap temperatures shown in the caption and figure legend

178 – replace were with where

377 – What is the basis of the NIST CO₂ scale - gravimetric?

393, SM 193 – should read “Zhao and Tans (2006)”

394 – “JCGM, 2008” needs a reference or link

405 – should read “N₂O is sufficient”

444 – “function of XCO₂”

504 – “one analysis record”

521 – “due to the use”

681 – The Guenther and Keeling reference needs more information to be accessible. It does not appear to have further traceability details other than being a “technical report” but can be accessed online at https://scrippsco2.ucsd.edu/assets/publications/guenther_manometric_analysis_cdiac_report_2000.pdf

688 – Keeling, C.D., Guenther, P.R. and Moss, D.J., Scripps Reference Gas Calibration System for Carbon Dioxide-in-Air Standards: Revision of 1985. Environmental Pollution Monitoring and Research Programme No. 42, Technical Document WMO/TD-No. 125, 1986. https://scrippsco2.ucsd.edu/assets/publications/keeling_scripps_ref_gas_calibration_system_revision_1986.pdf

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707 – Tans, P. P., Zhao, C. L., and Kitzis, D.: The WMO Mole Fraction Scales for CO₂ and other greenhouse gases, and uncertainty of the atmospheric measurements, Report of the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, other Greenhouse Gases, and Related Measurement Techniques, 7–10 September 2009, GAW Report No. 194, WMO TD No. 1553, 152–159, 2011.

SM 51 – “as a way”

SM 209, 219, 228 – replace s8 with s6

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