Revision of the WMO CO_2 calibration scale

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The NOAA Global Monitoring Division serves as the Central Calibration Laboratory for the WMO Global Atmospheric Watch program for carbon dioxide (along with CH_4, CO, N_2O, and SF_6). The WMO CO_2 scale, identified as WMO-CO_2-X2007, is defined, maintained, and linked to the SI using a manometric method. Since the last scale revision in 2007, we have identified two issues that impact the accuracy of the CO_2 scale: 1) we discovered a minor calculation error in the 2nd Virial coefficient for CO_2, and 2) apparent loss of CO_2 during the measurement process. While our primary objectives are consistency and reproducibility, we should also correct for bias when possible. In addition to these issues which affect accuracy, operational changes such as implementing a new laser spectroscopic methods for CO_2 analysis (Tans et al., 2017) and expansion of the core mole fraction range from 250-520 μmol mol^{-1} to 250-600 μmol mol^{-1} also justify a scale update.

We recalculated the CO_2 mole fractions derived from NOAA's manometric measurements (1996-2015) for the 15 WMO primary standards, making corrections for the 2nd Virial coefficient and apparent CO_2 loss. We then harmonized the manometric values by correcting for the residuals following analysis by the laser spectroscopic method. Since the applied corrections are mole fraction dependent, the scale update is also mole fraction dependent. The net change in scale is approximately equal to 0.0008179*X – 0.153, where X is the X2007 scale. Hence, at 400 μmol mol^{-1}, the net change is +0.17 μmol mol^{-1}. We have also re-examined uncertainties and find that the total, expanded (~2-sigma), uncertainty is ~0.22 μmol mol^{-1} (0.056%) at 400 μmol mol^{-1} (previous estimate was 0.14 μmol mol^{-1}). We will present our proposed scale revision, including updated mole fraction assignments for the primary standards as well as propagation to secondary and tertiary standards.

References

Tans, P. P., A. M. Crotwell, and K. W. Thoning (2017), Abundances of isotopologues and calibration of CO_2 greenhouse gas measurements, *Atmos. Meas. Tech. Discuss.*