A Re-examination of the WMO X2007 CO_2 Calibration Scale

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Introduction

The WMO X2007 CO_2 scale is defined by 15 primary standards containing modified natural air. The amount fraction of CO_2 was determined, on an absolute basis, from 1996-2016 using the NOAA manometer. Recently, we have discovered two small bias corrections that need to be applied. While we are concerned mainly with long-term reproducibility, accuracy is also important, and since we know the current scale is biased, we will correct for this bias in the next scale revision, anticipated in 2017.

How the manometer works

After recording the pressure and temperature of a 6-L sample of air, we cryogenically extract CO_2 and N_2O into a 10 cc volume, sealed with a Viton o-ring. Then we allow the CO_2 (and N_2O) to vaporize and we measure the pressure and temperature. From the equation of state, we calculate the mole fraction of CO_2:

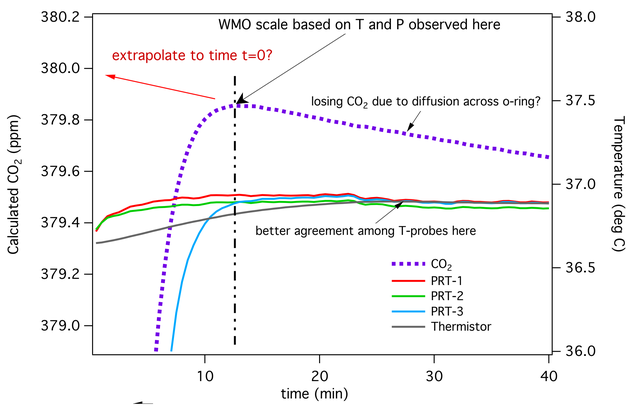
$$X_{CO2} = (VR^{-1})*[P_{CO2}*T_{air}/(P_{air}*T_{CO2})]*(1+A_1 - A_2) - X_{N2O}$$

where VR = ratio of 6 L volume to 10 cc volume, A_1 and A_2 account for non-ideal gas behavior (using 2nd Virial coefficients, β_{air}, β_{CO2}).

We have recently discovered a small bias in the X2007 data:

1) The 2nd Virial coefficient, β_{CO2}, was incorrect in code dating to 1996.
2) Some CO_2 is likely lost due to diffusion into or through the o-ring before the final T and P are recorded.

Typical result

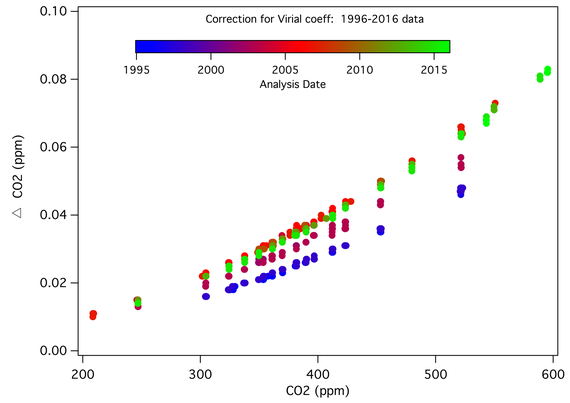


This Work

1) We reprocessed data files back to 1996 (732 data files).
2) We compared CO_2 calculated using the incorrect and corrected β_{CO2}.
   ➔ Virial correction, V_{corr}
3) We calculate the CO_2 loss rate (ppm/cycle) and extrapolated to time = 0.
   ➔ Diffusive correction, L_{corr}
4) We estimated the total correction needed: $V_{corr} + L_{corr}$

1) Correction for 2nd Virial coefficient

At 37 deg C, β_{CO2} is -112.6 cm^3/mol. Due to an error in the data processing code, β_{CO2} was incorrectly calculated as -104 cm^3/mol. This results in underestimation of the sample CO_2 mole fraction.

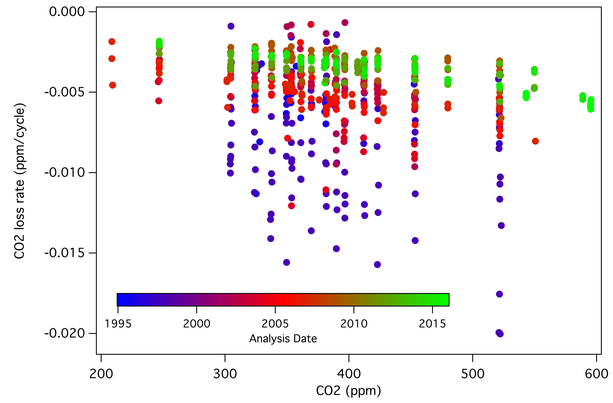


The correction, V_{corr}, varies with the amount of CO_2 present, and analysis date (oven temperature not always the same), but can be approximated by a number of well-behaved functions.

At 400 ppm, the bias correction is ~ 0.03 ppm.

2) Estimating diffusive loss

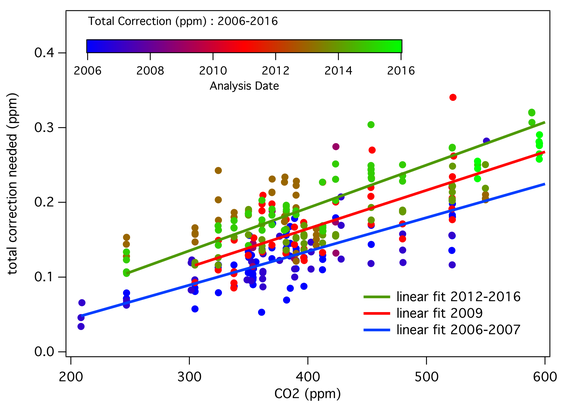
Files were reprocessed automatically. After finding the time (cycle) corresponding to maximum CO_2, we then calculated the loss rate (dc/dt).



Loss rates calculated for 2006-2009 and 2012-2015 are fairly consistent. **Loss rates calculated for earlier years show considerable scatter**. These files will likely need to be reprocessed manually.

For many data files, the loss rate is around -0.004 ppm/cycle at 400 ppm, which corresponds to a diffusive loss of 0.15 ppm, for CO_2 recorded at cycle 40 (t=20 minutes). This also results in underestimation of the sample CO_2 mole fraction.

3) Estimating the total correction



The X2007 CO_2 scale is likely biased low.

Extrapolating back to time t=0 (cycle =0) we calculate the total correction needed. The total bias correction needed is a function of mole fraction and appears to depend on analysis date. The figure above was generated by re-processing all data files, some of which may not be valid.

4) Conclusions and future work

The X2007 CO_2 scale is likely biased low.

The correction needed is small: ~0.15 ppm at 400 ppm CO_2.

However, bias correction required is a function of mole fraction, and may be important for future international comparisons.

Implementing the bias correction will increase the absolute uncertainty in the WMO scale (currently estimated to be 0.20 ppm at 400 ppm, 2σ).

Correcting for the Virial coefficient will be straight forward, but correcting for diffusive loss will require additional work.

We will continue to examine other possible sources of bias, such as impurities other than N_2O in the cryogenically-purified CO_2.

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