A Re-examination of the WMO X2007 CO_2 Calibration Scale

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The NOAA ESRL/GMD serves as the Central Calibration Laboratory for the World Meteorological Organization (WMO) Global Atmospheric Watch program for carbon dioxide (and other greenhouse gases). The WMO carbon dioxide (CO_2) scale is defined and maintained using an absolute manometric method. Certified reference materials are provided to WMO partners, with values assigned relative to a well-defined reference scale, known as WMO-CO2-X2007. In 2016 we will participate in a comparison among National Metrology Institutes (NMI) to compare different mole fraction scales, or primary reference standards. In preparation for that comparison, we have started to re-examine our methods and associated uncertainties. We have recently discovered that CO_2 appears to be diffusing across an o-ring seal during measurement of the pressure and temperature of the extracted CO_2 sample, a critical step in the manometric process. While we believe that current measurements are consistent with the X2007 scale, the loss of CO_2 may indicate a small bias in the scale. Based on the example shown in the Figure, the correction to the WMO scale at 380 ppm would be about +0.08 ppm. However, the correction will be mole fraction dependent because the loss rate is mole fraction dependent, and may have changed with time. We first need to establish a consistent method for reprocessing historical data, and apply that method to data going back to the mid-1990s. We will present preliminary results from a re-evaluation of our methods and uncertainties, and possibly propose a X2016 scale revision. Any scale revision would likely be minor (~0.1 ppm) but could be important with respect to comparison with NMIs.

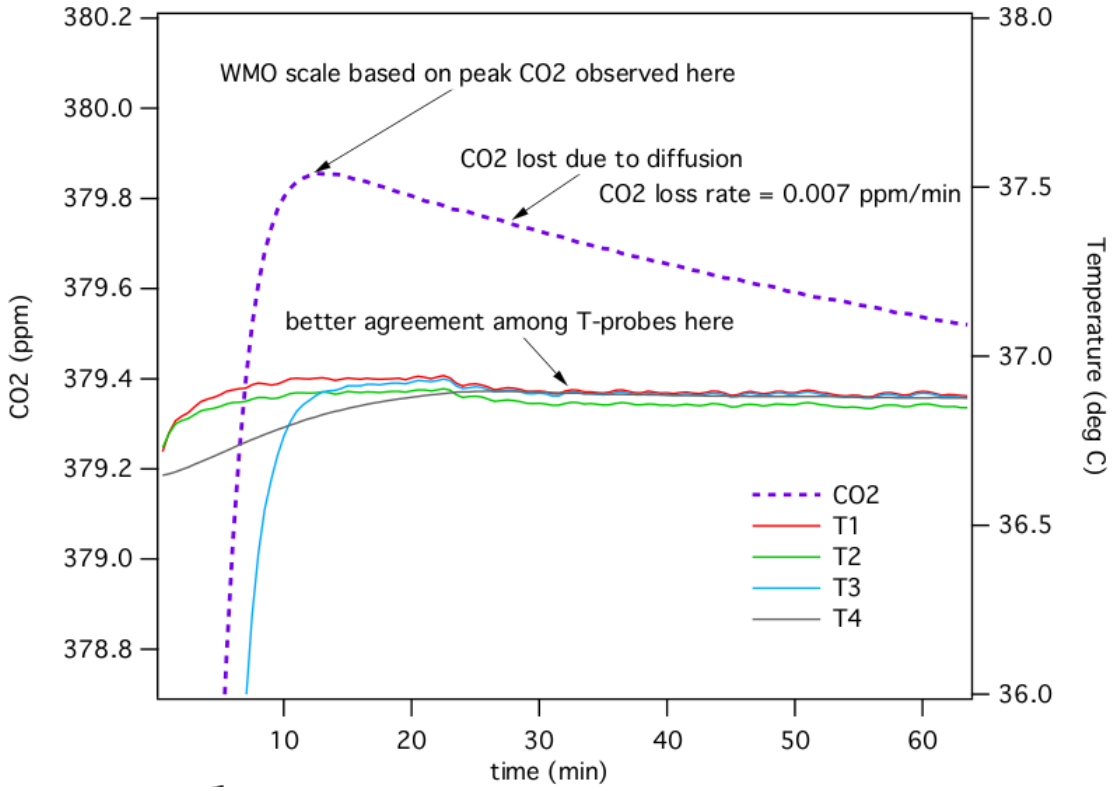

Figure 1. Calculated CO_2 and observed temperature during the final step in the determination of the mole fraction of CO_2 in air using the NOAA manometer. A small amount of CO_2 is likely lost prior to the "peak" CO_2, which forms the basis for the WMO CO_2 scale. A minor scale update may be necessary.