

Estimating Uncertainty of the WMO Mole Fraction Scale for Carbon Dioxide in Air

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A fundamental requirement for CO₂ source and sink determination is to link the worldwide CO₂ measurements to a common calibration scale. The current World Meteorological Organization (WMO) CO₂ mole fraction scale consists of a set of 15 CO₂-in-air primary standard calibration gases ranging in CO₂ mole fraction from 250 to 520 $\mu\text{mol mol}^{-1}$. Since the WMO CO₂ Experts Group transferred responsibility for maintaining the WMO scale from the Scripps Institution of Oceanography (SIO) to CMDL in 1995, the 15 WMO primary standards have been calibrated at regular intervals, between 1 and 2 years using the CMDL manometric system (Figure 1). From mid-1996 to 2001, the assigned CO₂ values of the WMO primaries were jointly based on the SIO and CMDL manometric measurements and completely on the CMDL manometric measurements alone from 2001 to present. The uncertainty of the 15 primary standards is estimated to be 0.07 $\mu\text{mol mol}^{-1}$ in the 1 σ absolute scale. Manometric calibration results indicated no evidence of overall drift of the primaries from 1996 to 2004. In order to lengthen the useful life of the primary standards, CMDL has always transferred the WMO scale to the secondaries via non-dispersive infrared analyzers (NDIR). The uncertainties arising from the analyzer random error and the propagation error due to the uncertainty of the reference gas concentration are discussed. Precision of NDIR transfer calibrations is about 0.01 $\mu\text{mol mol}^{-1}$ from 1979 to present. Propagation of the uncertainty is calculated theoretically. In the case of interpolation, the propagation error is estimated to be between 0.05 and 0.07 $\mu\text{mol mol}^{-1}$ when the primaries are used as the reference gases via NDIR transfer calibrations.

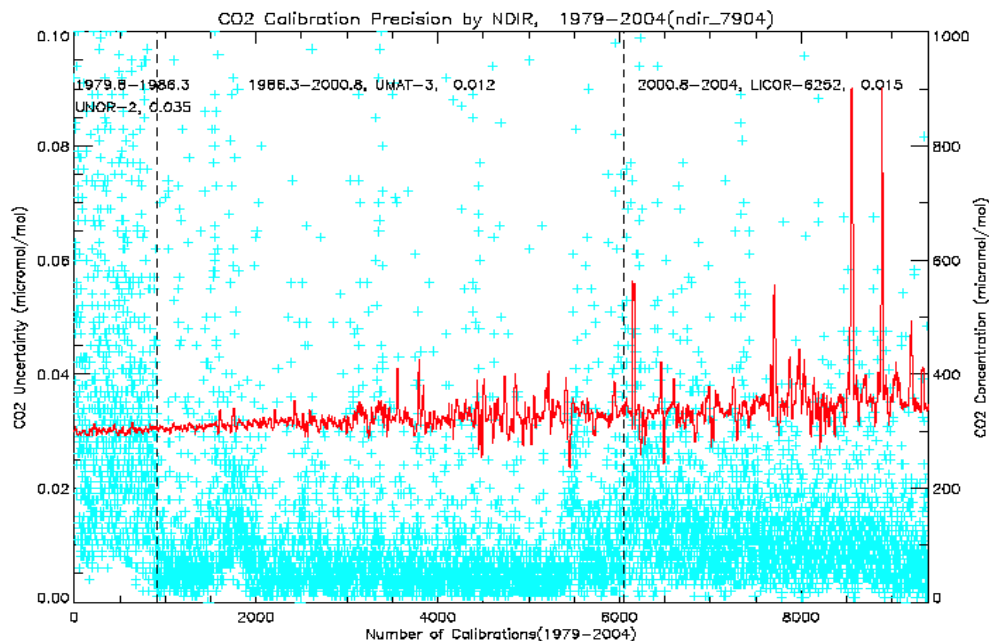


Figure 1. The uncertainty of all CMDL standard transfer calibrations from 1979 to present. A plus indicates the 1 σ standard deviation of each unknown determination. The red line indicates the CO₂ concentrations of the unknown gases to be calibrated. The vertical dashed lines indicate the place where the NDIR analyzers were changed.