



Creation and Propagation of the WMO Mole Fraction Scale for Carbon Dioxide in Air

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The atmospheric burden of CO₂ has been monitored at the Mauna Loa observatory on Hawaii for half a century, and since then the observing system has been expanded to many sites worldwide. At present, non-dispersive infrared (NDIR) analyzers offer the most robust and precise method of CO₂ quantification. However, this technique requires very accurately calibrated standard reference gases. The current WMO (World Meteorological Organization) CO₂ Mole Fraction Scale consists of a set of fifteen CO₂-in-air primary standard calibration gases ranging in CO₂ mole fraction from 250 to 520 micromol/mol. Since the WMO CO₂ Expert Group transferred responsibility for maintaining the WMO Scale from the Scripps Institute of Oceanography (SIO) to the Earth System Research Laboratory (ESRL) in 1995, the fifteen WMO primary standards have been calibrated, first at SIO and then at regular intervals, between one and two years, by the ESRL manometric system. The uncertainty of the 15 primary standards was estimated to be 0.069 micromol/mol in the absolute sense. Manometric calibrations results indicate that there is no evidence of overall drift of the Primaries from 1996 to 2008. In order to lengthen the useful life of the Primary standards, ESRL has always transferred the scale via NDIR analyzers to the secondary standards. The uncertainties arising from the analyzer random error and the propagation error due to the uncertainty of the reference gas mole fraction are discussed. Precision of NDIR transfer calibrations was about 0.013 micromol/mol from 1979 to present. Propagation of the uncertainty was calculated theoretically. In the case of interpolation the propagation error was estimated to be between 0.06 and 0.07 micromol/mol when the Primaries were used as the reference gases via NDIR transfer calibrations. The ESRL secondary standard calibrations are transferred via NDIR analyzers to the working standards, which are used routinely for measuring atmospheric CO₂ mole fraction in the WMO Global Atmosphere Watch monitoring program. The uncertainty of the working standards was estimated to be 0.071 micromol/mol in the one-sigma absolute scale. For comparison with an independent absolute scale, the five gravimetric standards from the National Institute for the Environmental Studies (NIES) in Tsukuba of Japan ranging in CO₂ mole fraction from 350 to 390 micromol/mol have been calibrated relative to the ESRL secondary standards. The average and standard deviation of the differences between the NIES gravimetric and ESRL analyzed CO₂ mole fraction are 0.004±0.03 micromol/mol.