

CALIBRATION AND PROPAGATION OF THE WMO MOLE FRACTION SCALE FOR CARBON DIOXIDE IN AIR

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ABSTRACT

The current WMO 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 Climate Monitoring and Diagnostics Laboratory (CMDL) in 1995, the fifteen WMO primary standards have been calibrated at regular interval, between one and two years, by the CMDL manometric system. From mid-1996 to 2001, the assigned CO₂ values of the WMO Primaries have been 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 micromol/mol in the one-sigma absolute scale. Manometric calibration results indicated that there is 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 NDIR analyzers. 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 micromol/mol 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 micromol/mol when the Primaries are used as the reference gases via NDIR transfer calibrations.