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Metrology of carbon dioxide gas isotope ratio for the development of gas isotope reference materials

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Realization of reliable and accurate isotope ratio measurement of carbon dioxide (CO_2) calls for the development of accurate SI-traceable gas isotopic reference materials (iRMs) and establishment of the relationship between the VPDB (Vienna Peedee belemnite) isotope scale and SI traceable measurements. This formalism guides our development of atmospheric gas isotope reference material and data.

In this study, we have investigated instrumental correction factors, data treatment, scale traceability and comparability of isotope ratio measurements for a series of isotopically distinct pure CO_2 samples and their derivative gravimetric, manometric mixture in dry synthetic air (at ambient abundance concentration levels). Both dual-inlet isotope ratio mass spectrometry (IRMS) and gas chromatographic (GC) IRMS methods were used to measure the isotopic composition.

For this series of pure CO_2 gas samples, we made VPDB value assignments of $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ with values spanning -42‰ to +2‰ and -23‰ to +10‰ respectively using dual inlet-IRMS. To establish traceability to the VPDB scale, all assigned values were referenced to the pure CO_2 NIST iRMs RM 8562, RM 8563 and RM 8564. The GC-IRMS measurements were conducted on CO_2-Air gas mixtures (400 μmol mol^{-1} nominal atmospheric abundance). These included mixtures of isotopically assigned pure CO_2 sample in dry synthetic air prepared in high pressure cylinders as well as the NIST Standard Reference Material SRM 1720 (Northern Continental Air with x_{CO2}= 393.97± 0.13($u_{95\%}$) μmol mol^{-1}, $\delta^{13}C_{VPDB}$= -8.6‰ , $\delta^{18}O_{VPDB}$= -1.1‰ .

Overall, the $\delta^{13}C_{VPDB}$values agree within ±0.2‰ across methods, measured samples and known isotope ratio values. Finally, ongoing comparisons of δ^{13}C values obtained from a recently developed laser-based FS-CRDS (frequency stabilized cavity ringdown spectroscopy) isotope ratio technique will also be discussed.