

On the calibration of isotopologue-specific optical trace gas analysers

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In recent years optical spectroscopic analysers have approached the precision and accuracy of established IRMS methods. Laser and FTIR-based analysers usually analyse whole air directly and quantify the concentrations or mole fractions of specific individual isotopologues, while whole-air calibration gases provided by central calibration laboratories are generally specified by their total target gas mole fractions and isotopic δ -values relative to a reference isotopic scale. The conversion between these equivalent descriptions of the trace gas and its isotopic composition is non-trivial, but with the precision and accuracy available from current optical analysers and required for atmospheric research (for example 0.05 ppm for CO₂ total mole fraction and 0.01‰ for $\delta^{13}\text{C}$) it is essential that the calculations be made accurately and precisely without systematic errors or approximations.

Several papers in the last few years have addressed these requirements, with increasing rigour (e.g. [Griffith et al., 2012](#); [Wen et al., 2013](#); [Flores et al., 2017](#); [Tans et al., 2017](#)). In this paper I review the requirements for isotopologue-specific calibration of optical analysers and describe a calculation scheme which is rigorously correct to the required accuracy, accounts for all possible isotopologues in the total sample, and is straightforward to apply. It sets out the conversions between isotopologue mole fractions, total mole fraction and δ scales, including the adjustments required to convert between the different isotope reference scales used in the GAW network and the Hitran database commonly used to analyse infrared spectra in optical analysers.

References

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