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Spectroscopic metrology for isotope composition measurements and transfer standards

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The World Meteorological Organization (WMO) has identified greenhouse gases such as CO_2, CH4 and N2O as critical for global climate monitoring. Other molecules such as CO that has an indirect effect of enhancing global warming are also monitored. WMO has stated compatibility goals for atmospheric concentration and isotope ratio measurements of these gases, e.g. 0.1 ppm for CO_2 concentration measurements in the northern hemisphere and 0.01 ‰ for δ13C-CO_2.
For measurements of the concentration of greenhouse gases, gas analysers are typically calibrated with static gas standards e.g. traceable to the WMO scale or to the International System of Units (SI) through a national metrology institute. However, concentrations of target components, e.g. CO, in static gas standards have been observed to drift, and typically the gas matrix as well as the isotopic composition of the target component does not always reflect field gas composition, leading to deviations of the analyser response, even after calibration. The deviations are dependent on the measurement technique. To address this issue, part of the HIGHGAS (Metrology for high-impact greenhouse gases) project [1] focused on the development of optical transfer standards (OTSs) for greenhouse gases, e.g. CO_2 and CO, potentially complementing gas standards.
Isotope ratio mass spectrometry (IRMS) [2] is currently used to provide state-of-the-art high precision (in the 0.01 ‰ range) measurements for the isotopic composition of greenhouse gases. However, there is a need for field-deployable techniques such as optical isotope ratio spectroscopy (OIRS) that can be combined with metrological measurement methods. Within the HIGHGAS project, OIRS methods and procedures based on e.g. cavity enhanced spectroscopy (CES) and tunable diode laser absorption spectroscopy (TDLAS), matched to metrological principles have been established for the measurement of 13C/12C and 18O/16O ratios in CO_2, 15N/14N ratios in N2O, and 13C/12C and 2H/1H ratios in CH4.
Here, based on HIGHGAS project results, we present OTSs for atmospheric CO_2 and CO measurements. The results delivered by the OTSs are in excellent agreement with gravimetric values of metrological "primary" static gas standards. The repeatabilities of the OTS results are matching the compatibility goals stated by WMO for atmospheric CO_2 and CO measurements. In addition, we present OIRS measurement methods and procedures to demonstrate their applicability and validation. The requirements on, e.g. absorption line data quality and temperature sensitivity of isotope ratio, are discussed. Uncertainty budgets are presented and the traceability of the results is addressed. The current limitations in our measurements are discussed and steps taken to address these limitations are presented.

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References

[1] EMRP project ENV52-HIGHGAS, available at: http://www.euramet.org/
[2] Prosenjit Ghosh, Willi A. Brand, International Journal of Mass Spectrometry 228, 1–33 (2003).