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Metrological characterisation of optical isotope analysers for carbon dioxide in the framework of EMPIR SIRS project

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The increase of carbon dioxide (CO_2) concentration in the atmosphere due to anthropogenic emission is the main cause of global warming. The isotopic composition of atmospheric CO_2 provides a powerful tracer for sources and sinks of this potent greenhouse gas applicable at various spatial and temporal scales. The ongoing EMPIR[1] project "Metrology for Stable Isotope Reference Standards (SIRS)"[2] is dedicated to providing metrological support on gaseous CO_2 reference materials, and development of spectroscopic methods for isotope ratio measurements of CO_2. The uncertainty target is 0.1‰ for δ^{13}C and 0.5‰ for δ^{18}O. Technological advances in mid-IR optical sensors provide paths for high sensitivity isotope ratio determination near 4.5μm, where isotopologues of carbon dioxide have strong ro-vibrational absorption lines and, thus, can be detected at ambient concentrations. Optical isotope ratio spectrometry (OIRS) has substantially increased popularity in atmospheric and biogeochemical research. However, a metrological characterisation of OIRS instruments is required in order to ensure traceability and improved comparability in isotopic signatures, which is of great importance for the scientific community.

We present the SIRS protocol for metrological characterisation of the OIRS which also includes recent GAW recommendations [4] and employs the methods reported in the literature [5, and references therein]. Development of the protocol has been done alongside the characterisation of two commercial instruments for CO_2 isotope analysis based on DFG source and QCL direct absorption spectroscopy, which have been characterised at PTB and the University of Groningen, respectively. The performance of both instruments demonstrates the precision on the level of 0.01‰ for δ^{18}O and δ^{13}C at atmospheric CO_2 concentrations. The ongoing research implies a comparison of the calibration strategies, quantification of matrix gas effects and estimation of the full uncertainty budget.

[1] https://www.euramet.org/research-innovation/research-empir/

[2] https://www.vtt.fi/sites/SIRS

[3] B. Kühnreich, S. Wagner, J. C. Habig, O. Möhler, H. Saathoff, V. Ebert, *Appl. Phys. B* 119:177–187, **2015**

[4] GAW report, 242. 19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2017) (27-31 August 2017; Dübendorf, Dübendorf, Switzerland)

[5] David W. T. Griffith, *Atmos. Meas. Tech.* 11, 6189–6201, **2018**

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