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Towards SI-traceable Isotope Ratios of Greenhouse Gases

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The emission of greenhouse gases and the resulting global warming is one of the most important and challenging issues of the 21st century. Carbon dioxide is one of the major contributors to the greenhouse effect and its atmospheric abundance has growing constantly since the beginning of the industrialization. The isotope ratios n(^{13}C)/n(^{12}C) and n(^{18}O)/n(^{16}O) are important tools for studying the impact of anthropogenic CO_2. Usually, isotopic compositions of CO_2 are reported as δ-values, that express isotope ratios relative to an artifact based on a fossil calcite called VPDB. This relative VPDB scale was necessary, since absolute and SI-traceable isotope ratios of CO_2 are currently not available, neither by isotope ratio mass spectrometry (IRMS) nor by optical isotope ratio spectroscopy (OIRS). In this study we present a potential way of deriving absolute carbon and oxygen isotope ratios of carbon dioxide via IRMS based on the gravimetric mixture approach. Besides practical improvements like an air buoyancy correction scheme for masses of gases, we show first results applying our method which demonstrate its feasibility, limitations, and achievable uncertainties. Also, we show the mathematics behind our approach and discuss further improvements and applications. Furthermore, we show how these absolute ratios can be used in field applications by OIRS methods including a new approach on OIRS uncertainty assessments according to the GUM. For this contribution we report on our recent results within in the European metrology research projects SIRS (16ENV06). and STELLAR (19ENV05).