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A new solution to a standard problem: creating atmosphere-like isotope reference gases with precisely referenced δ^{13}C - CH_4

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Studying the isotopic composition of δ^{13}C from atmospheric CH_4 is an important tool to understand the biogeochemical mechanisms that drive atmospheric CH_4 concentrations. Analytical systems commonly measure isotope ratios of atmospheric CH_4 according to the identical treatment principle for the highest accuracy possible. This requires an atmosphere-like isotope reference gas, which serves as an anchor point to the VPDB isotope scale. The δ^{13}C - CH_4 of the applied isotope reference gas should be known as precisely and accurately as possible. Despite of its crucial importance for analyzing isotopes of atmospheric CH_4, international standards for CH_4 isotopes are not available. Also, a standardized procedure on how to reference CH_4 isotopes is not yet defined, as it is done for other gases by the World Meteorological Organization.

We present a method to overcome this referencing problem for δ^{13}C - CH_4 measurements. First, we quantitatively combust pure CH_4 and measure the δ^{13}C isotope ratios of the produced CO_2. Two pure CH_4 gases from fossil and biogenic sources are analyzed to -39.56 ‰ and -56.42 ‰ for δ^{13}C. From these two parental CH_4 gases we mix two filial CH_4 gases with δ13C of -42.21 ‰ and -47.25 ‰ similar to glacial and present atmospheric values, respectively. Next, we mix aliquots of these filial CH4 gases with ultrapure N_2/O_2 ($CH_4 \leq 2$ ppbv) and produce two synthetic isotope reference gases with CH_4 mixing ratios near atmospheric values. We measure the synthetic isotope reference gases for δ^{13}C - CH_4 on another setup, which is currently being developed for measurements of δ^{13}C - CH_4 in atmospheric and ice core samples and verify the isotope values of δ^{13}C - CH_4. Our method is suitable to produce large quantities of synthetic isotope reference gases with precisely referenced δ^{13}C - CH_4 isotope ratios. The δ^{13}C - CH_4 of the produced isotope reference gases can be adjusted to any desired composition between those of the parental CH_4 gases.