



## **iSAAC; a fully automated analytical system for high-accuracy $\delta^{13}\text{C}$ and $\delta^2\text{H}$ analyses of atmospheric methane**

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To resolve the temporal and spatial variability of  $\text{CH}_4$  isotope ratios ( $\delta^{13}\text{C}\text{-CH}_4$  and  $\delta^2\text{H}\text{-CH}_4$ ) in the atmosphere, the highest possible measurement precision is needed. We introduce a fully automated GC-C-IRMS and GC-P-IRMS setup to measure  $\delta^{13}\text{C}\text{-CH}_4$  and  $\delta^2\text{H}\text{-CH}_4$  with a precision of 0.07 ‰ and 1.5 ‰, respectively, by injecting a total of 160 mL per air sample into an online system for both isotopes. We introduce a new cryo-trapping technique that enables precise temperature control for quantitative trapping and pre-concentration of  $\text{CH}_4$  while making the use of liquid nitrogen redundant, thereby increasing the reproducibility of the trapping process. We show that the design and temperature stability of this cryo-trap are crucial parameters in particular for the high precision of the  $\delta^2\text{H}\text{-CH}_4$  measurements. Every sample is referenced to an accompanying isotope reference gas measurement in each measurement sequence, thereby achieving a balanced statistics for the referencing of every sample. Blocks of two isotope reference gas measurements that are injected as samples bracket a full sequence, comprising of up to twelve samples and one quality control standard where the latter is treated as an unknown sample. We show the excellent performance of our setup, which enables high precision analysis of larger quantities of samples, as it is necessary to measure high quantities of flask samples from the GAW sampling network.