

Optical measurements of $\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$ – method development and calibration

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Concordant clumped isotope analysis of methane - $\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$ - is an important tool in today's geochemistry and atmospheric sciences. Measurements are routinely performed on ultra-high-resolution mass-spectrometers achieving sub-permil precision within ~24 h integration time. Recently, we demonstrated that mid IR spectroscopy provides similar precision within a significantly shorter measurement time of about 20 minutes. Here we present our calibration approach based on reproducible and robust preparation of reference gases covering a wide range of equilibrium temperatures and bulk isotopic compositions. To obtain reference gases, small amounts of CH_4 (10-30 ml) are re-equilibrated over an activated $\gamma\text{-Al}_2\text{O}_3$ catalyst in a custom-made reactor, which maintains sample purity and isotopic composition. We demonstrate the applicability of our method by measurements of natural samples and discuss requirements for chromatographic gas purification to eliminate unwanted spectral interferences introduced by contamination with alkanes.

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