

## Effect of analytical conditions on position-specific $\delta^{13}\text{C}$ of propane measured by a GC-pyrolysis-GC-IRMS method

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Recent studies of position-specific isotope analysis of gaseous hydrocarbons provide us new and important constraints on origin and generation/degradation mechanism of natural gases. Several methods have been developed to measure position-specific carbon and hydrogen isotopes of propane in natural gases such as GC-pyrolysis-GC-IRMS (Gilbert et al., 2016), high-resolution IRMS (Piasecki et al., 2016), chemical degradation method followed by GC-IRMS (Gao et al., 2016) and quantitative NMR spectrometry (Liu et al., 2018).

The GC-pyrolysis-GC-IRMS technique requires small sample size (~0.1  $\mu\text{mol}$  of propane) and uses a GC for the initial separation of propane from other hydrocarbons, which is followed by fragmentation by online pyrolysis. The fragments are subsequently separated in a 2nd GC and analyzed for their  $\delta^{13}\text{C}$  values. The position-specific  $\delta^{13}\text{C}$  value is defined as the difference of  $\delta^{13}\text{C}$  values between terminal and central carbon atom positions of propane. It has been suggested that isotopic fractionation associated with the GC-pyrolysis-GC-IRMS method depends on detailed analytical conditions and/or specific instruments (Liu et al., 2023), which makes comparison of analytical results between devices or laboratories difficult.

We measured the position-specific  $\delta^{13}\text{C}$  value of a standard propane sample by the GC-pyrolysis-GC-IRMS method with changing analytical conditions such as pyrolysis temperature, flow rate and injection volume of the sample. The results revealed that the position-specific  $\delta^{13}\text{C}$  value increased with injection volume of the sample but decreased with flow rate. No significant impact on the position-specific  $\delta^{13}\text{C}$  value was observed with pyrolysis temperature between 760 to 840 °C. Our study suggests that analytical conditions including flow rate and propane volume injected should be constant to reproduce same isotope fractionation during fragmentation in the pyrolysis furnace when comparing analytical results between samples or devices. We applied an improved GC-pyrolysis-GC-IRMS method to natural gas samples from the Norwegian Continental Shelf for the first time to study the effective source rock and generation and degradation processes of the gas.