

Determination of intramolecular ^{13}C isotopic composition of *i*- and *n*-butane from natural gas samples

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We recently developed a method for the position-specific isotope analysis (PSIA) of propane from natural gas samples (Gilbert *et al.* 2016, *GCA*; Suda *et al.* 2017, *GCA*). This technic consists in the on-line pyrolysis of propane and the determination of $\delta^{13}\text{C}$ values of each generated fragment (Brenna *et al.* 1997, *Mass Spectrom. Rev.*). Promising results were obtained using propane PSIA (Gilbert *et al.*, in prep) and more information can still be obtained from other gases.

In this context, further improvements of the PSIA method have been undertaken, in particular the measurement of *n*-butane and *i*-butane. The elucidation of pyrolytic fragmentation process is necessary to calculate $\delta^{13}\text{C}$ of each carbon position of the molecule. This is so far conducted through the use of spiked samples with ^{13}C -enriched counterparts at specific positions (for instance *n*-butane ^{13}C enriched on terminal position is used: Julien *et al.*, in prep). Unfortunately, *i*-butane standard ^{13}C enriched in one position are not commercially available.

In order to study *i*-butane pyrolysis, the recently developped "Reaction Mechanism Generator" (RMG; Gao *et al.* 2016, *Comput. Phys. Commun.*) has been employed. This prediction model shows excellent fit with experimental data, so we used it to generate pyrolytic profile of *i*-butane and applied it to measured its fragments in natural gas samples.

We now can perform PSIA of propane, *n*-butane and *i*-butane from natural gas in a single run. Data obtained from natural gas samples show that PSIA of hydrocarbons differs between abiotic and thermogenic samples, and that the preference of ^{13}C for a given position is consistent with previous models of thermogenic and abiotic formation.