Application Note 30084

Quantifying $^{13}C/^{12}C$ Values in Acyclic Biomarkers by GC-IRMS

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Key Words
Compound Specific Isotope Analysis, Alkanes, GC Combustion, Isotope Ratio MS

Introduction

The isotope ratio analysis of hydrocarbons and their precursors (e.g. porphyrins) in ancient depositional environments provides insight into specific conditions of diagenesis.[1] Such kinds of samples typically are very complex mixtures (e.g. crude oil), requiring highly efficient separation and background correction prior to isotope ratio measurement.

Pristane and phytane, usually degradation products from the phytyl side chain in chlorophyll, are well known biomarkers and can provide biogeochemical information. Baseline separation of pristane from nC_{17} and phytane from nC_{18} is mandatory for precise isotope ratio determination of these compounds.

GC-IRMS is the method of choice for complex mixtures that can be separated on a GC. In GC-IRMS, all compounds eluting from the GC are converted on-line into CO_2 and/or N_2 in a combustion interface. These simple gases are transferred into a mass spectrometer for ^{13}C and ^{15}N determination, preserving GC resolution. Chromatographic fidelity, sensitivity and long term stability are indispensable instrumental prerequisites and are routinely provided by our GC/C II IRMS combination and its successors like the Thermo Scientific™ GC IsoLink™ II with Thermo Scientific DELTA™ V IRMS. Fully automated background determination and correction using flexible algorithms, together with the possibility of interactive data evaluation for complicated GC cases are powerful features of the Thermo Scientific ISODAT™ data system.

Method

Injector	on column
Cap. column	Ultra 1, 25 m, 0.32 mm i.d., film thickness 0.17 µm
GC program	1 min. at 30°C; 20°C/min to 90°C/min; 4°C/min to 180°C/min; 5°C/min to 305°C/min; 15 min. at 305°C; constant flow
GC/C interface	High temperature combustion mode

Table 1. GC-IRMS parameters.

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Results

The chromatogram in Figure 1 shows the *m/z* 44 trace (lower) and the isotope ratio trace (upper) of a n-paraffin distribution. The range from nC_{15} to nC_{40} demonstrates the excellent chromatographic performance of the whole instrumental setup. The mean $\delta^{13}C$-values (‰ vs. PDB) of the most prominent n-alkanes, as well as from phytane and pristane, are reported in the chromatographic blow-up and the list on the right. All peaks show excellent reproducibility in fully automated analysis, using the individual background algorithm. The separation of pristane (17 pmol on column) from nC_{17} and phytane (12 pmol on column) from nC_{18} is to baseline.

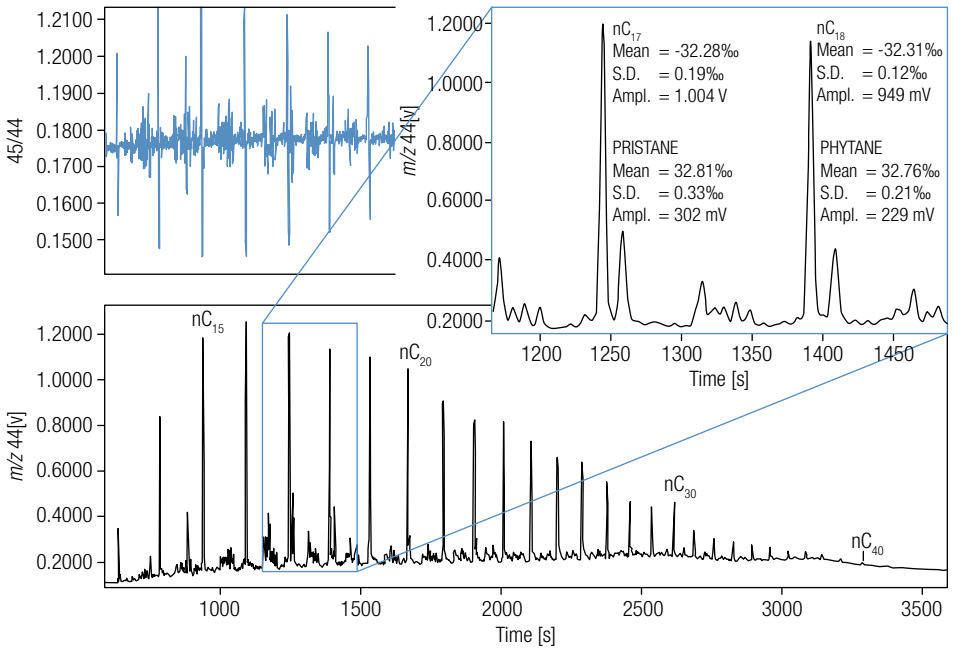
Pristane can be determined with a standard deviation of ± 0.33‰ (n = 3), which is close to the expected theoretical value of 4 times shot noise limit for peaks of this intensity. Although smaller, phytane shows a standard deviation of ± 0.21‰ (n = 3) that is the result of the quantitative GC separation from the preceding nC_{18} peak.

Minor unresolved compounds can form a varying background. For example, the nC_{19} peak is affected by partial coelution of a minor compound, which causes significant background changes. The use of the automated dynamic background correction during post-acquisition data review improves the $\delta^{13}C$-determination from -32.07‰
± 0.42‰ to -32.14‰ ± 0.11‰ (see*).

Similar results can be expected from a DELTA V IRMS or a Thermo Scientific MAT™ 253 IRMS coupled with the GC Isolink II unit via the Thermo Scientific ConFlo™ IV interface.

Reference

1 J. M. Hayes et al., Org. Geochem., Vol. 16, Nos 4-6, pp. 1115-1128, 1990



	$\delta^{-13}C_{PDB}$ [‰]	S.D. [‰]
nC_{15}	- 32.13	0.10
nC_{16}	- 32.51	0.26
nC_{17}	- 32.28	0.19
Pr	- 32.81	0.33
nC_{18}	- 32.31	0.12
Ph	- 32.76	0.21
nC_{19}	- 32.07	0.11*)
nC_{20}	- 32.23	0.07
nC_{21}	- 32.86	0.23
nC_{22}	- 32.45	0.07
nC_{23}	- 32.65	0.07
nC_{24}	- 32.44	0.17
nC_{25}	- 32.34	0.22
nC_{26}	- 32.52	0.16

Figure 1. *m/z* 44 chromatogram and 45/44 isotope ratio trace of acyclic biomarkers.

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