Tracing Isotope Fingerprints in Crude Oil for Petroleum Exploration Assessment by Using GC-IRMS

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ABSTRACT

Compound-specific isotope analysis (CSIA) by online conversion of organic compounds separated by gas chromatography and subsequent isotope ratio mass spectrometry (GC-IRMS) is a well-established analytical approach to a variety of samples from routine and research areas, such as environmental forensics and energy exploration. Isotope Ratio Mass Spectrometry (IRMS) can visualize isotope fingerprints of hydrocarbons and their precursors involved in the process of fossil fuel production.

INTRODUCTION

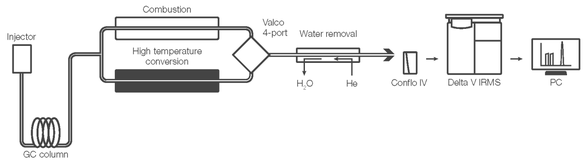
The isotope ratio analysis of hydrocarbons and their precursors (e.g. porphyrins) in ancient depositional environments provides insight into specific conditions of diagenesis. Such kinds of samples typically are very complex mixtures (e.g. crude oil), requiring highly efficient separation and background 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 nC17 and phytane from nC18 is mandatory for precise isotope ratio determination of these compounds.

Figure 1. Thermo Scientific GC-IRMS System.

INSTRUMENTATION

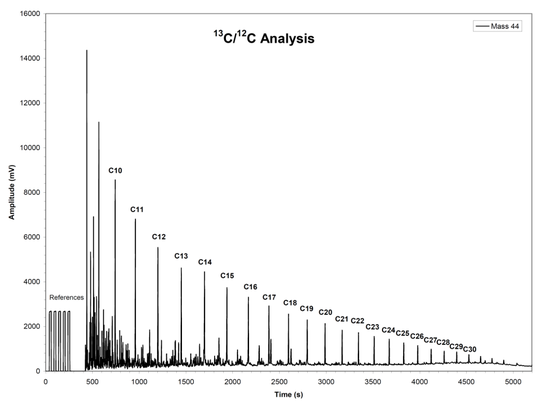
All measurements can be performed using a Thermo Scientific™ TRACE™ 1310 GC coupled with a GC-IRMS system consisting of a Thermo Scientific™ GC IsoLink II™ IRMS System, Thermo Scientific™ ConFlo IV™ Universal Interface and a Thermo Scientific™ DELTA V™ Isotope Ratio Mass Spectrometer (Figure 1).

Figure 2. GC-IRMS system schematics.



The GC IsoLink II IRMS System Conversion Unit incorporates a capillary design system built on high temperature combustion and high temperature conversion technology (Figure 2). This ensures complete conversion of compounds to simple gases. CO_2 provided by combustion imprints ^{13}C signature, where as H_2 provided by conversion imprints ^{2}H signature of compounds. Effluent from the GC passes through a micro channel device coupling GC with reactors and a temperature-controlled backflush system. True capillary design approach attains sharper peak shape and higher sensitivity (Figure 3). The GC IsoLink II IRMS System in combination with the TRACE 1300 Series GC, an extremely fast and easy to use GC, provides fully automated solution to meet the analytical challenges of isotope analysis.

Figure 3. Chromatogram of carbon isotope analysis of crude oil by GC-IRMS combustion. High separation efficiency of GC is preserved by GC IsoLink conversion unit.



METHOD

GC / GC IsoLInk setup for the measurements of crude oil was as follows:

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

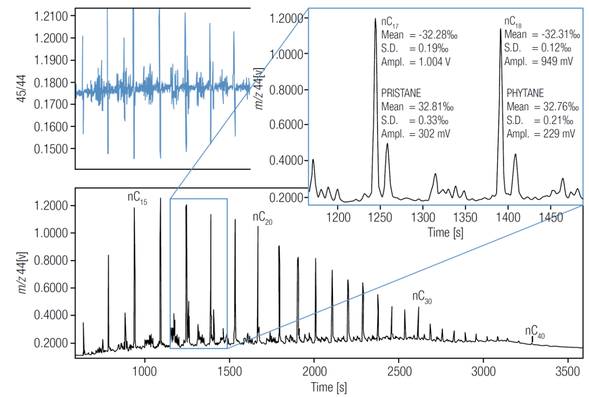
RESULTS

The chromatogram in Figure 4 shows the m/z 44 trace (lower) and the isotope ratio trace (upper) of a n-paraffin distribution. The range from nC15 to nC40 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 in Figure 4 and the Table 1. All peaks show excellent reproducibility in fully automated analysis, using the individual background algorithm. The separation of pristane (17 pmol on column) from nC17 and phytane (12 pmol on column) from nC18 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 nC18 peak.

Table 1. The mean $\delta^{13}C$-values (‰ vs. PDB) of the most prominent n-alkanes in crude oil sample.

	δ-$^{13}C_{PDB}$ [‰]	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 4. m/z 44 chromatogram and 45/44 isotope ratio trace of acyclic biomarkers.



CONCLUSIONS

Isotope fingerprints are used in analysis of crude oil by GC coupled with IRMS. By getting the unique information contained in isotope fingerprints, the source and formation of crude oil can be assessed. Here presented pristane and phytane isotope analysis in crude oil require highly efficient GC separation and are well known biomarkers providing biogeochemical information. With the GC IsoLink IRMS System, laboratories gain an effective analytical solution based on the identification of the isotope fingerprint within the sample.

INVESTIGATE MORE

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TRADEMARKS/LICENSING

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