Petroleum Biomarkers Around the World: Fingerprinting Crude Oils

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SUMMARY

Petroleum forensics is the art of tracing the geochemistry of crude oil using petroleum biomarkers. Ratios of chemical structures such as hopanes and steranes that are resistant to weathering and other forms of degradation, often called "molecular fossils", are crucial for differentiating various sources of crude oil. Depending on thermal maturity and geographic location, the type and concentration of different hopane and sterane structures can provide unique identifiers for specific sources of oil. In this presentation, ratios of various biomarkers from samples collected in different geographic regions of the world are compared and contrasted. Analysis using a comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry system (GCxGC-TOFMS) equipped with a new, robust, and easy-to-use flow-based modulator is performed on crude oil samples from various continents. The second dimension of chromatographic separation provides the necessary chromatographic resolution to separate the multi-ringed hopanes and steranes from the straight-chained and branched alkanes that would coelute in most one-dimensional GC separations. Using a TOFMS with better-than-nominal mass resolution allows for more confident differentiation of each biomarker on the detector side, providing the option for matching full scan spectra not only to commercially available, but also user-generated spectral libraries.

FLUX Modulator

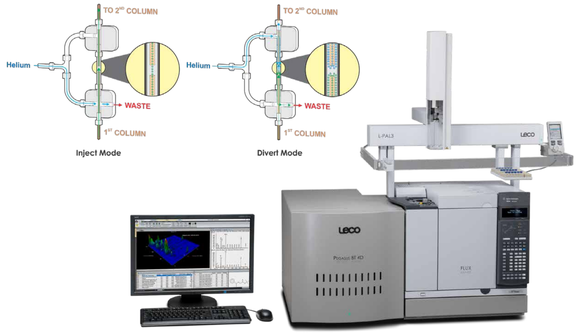

Figure 1: The Pegasus® BT 4D equipped with FLUX™ modulator used for these analyses is shown above, with a small diagram illustrating the functional states of the diverting flow modulator.

Table 1: Analytical parameters used for data acquisition of oil samples.

Gas Chromatograph	LECO FLUX GCxGC
Injection	2 µL liquid injection, splitless @ 310 °C
Carrier Gas	He @ 1.0 mL/min, Constant Flow
Primary Column	Rxi-1ms, 60 m x 0.25 mm i.d. x 0.25 µm coating (Restek, Bellefonte, PA, USA)
Secondary Column	BPX-50, 1.91* m x 0.10 mm x 0.10 µm coating *1.6 m coiled in 2nd oven and 0.31 m in transferline
Temperature Program	15 min at 80 °C, ramped 1.5 °C/min to 335 °C, hold for 10 min
	Secondary oven maintained +40 °C relative to primary oven
Modulation	3.5 s
Transfer Line	320 °C
Mass Spectrometer	**LECO Pegasus BT**
Ion Source Temperature	250 °C
Mass Range	40-600 m/z
Acquisition Rate	200 spectra/s

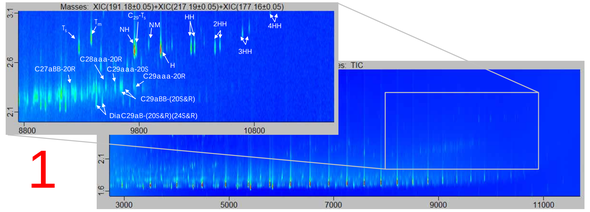

Figure 2: The Exxon Valdez oil spill occurred near Prince William Sound, Alaska on March 24, 1989, releasing 10.8 million US gallons of fuel from the Prudhoe Bay oil field in Alaska. A contour plot generated from a sample of this spill is shown above, with a zoomed-in view of the biomarkers section with characteristic masses for common hopane and sterane fragments displayed.

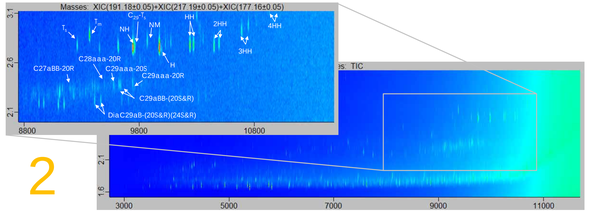

Figure 3: On July 25, 2010, a pipeline running diluted bitumen from Alberta ruptured in the Kalamazoo River in Michigan. A contour plot generated from a sample collected near the burst pipeline is shown above, with a zoomed-in view of the biomarkers section with characteristic masses for common hopane and sterane fragments displayed.

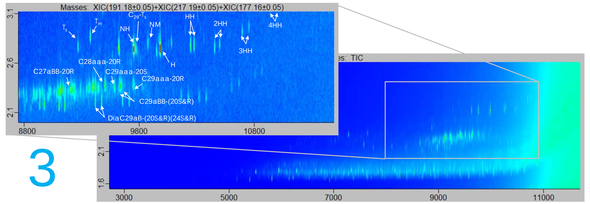

Figure 4: A contour plot generated from a sample of a natural oil seep near Coal Oil Point, California is shown above, with a zoomed-in view of the biomarkers section with characteristic masses for common hopane and sterane fragments displayed.

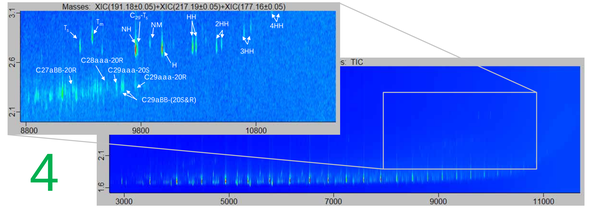

Figure 5: Ixtoc I, an exploratory oil well in the gulf of Mexico, suffered a blowout on June 3, 1989, releasing over 30,000 barrels per day in the initial stages. A contour plot generated from a sample of this spill is shown above, with a zoomed-in view of the biomarkers section with characteristic masses for common hopane and sterane fragments displayed.

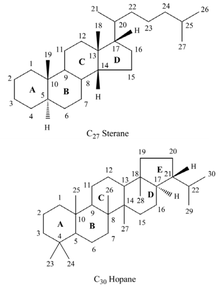

Figure 6: The base structures for hopanes and steranes with the labelling system for the C27 sterane and C30 hopane are shown above.

Table 2: Biomarkers labelled in contour plots.

Abbreviation	Compound Name
T_s	18α(H)-22,29,30-trinorneohopane
T_m	17α(H)-22,29,30-trinorhopane
NH	17α(H),21β(H)-30-norhopane
C_{29}-T_s	18α(H),21β(H)-30-norneohopane
NM	17β(H),21α(H)-30-norhopane
H	17α(H),21β(H)-30-hopane
M	17β(H),21α(H)-30-hopane
HH	17α(H),21β(H)-22-homohopane
2HH	17α(H),21β(H)-22-bishomohopane
3HH	17α(H),21β(H)-22-trishomohopane
4HH	17α(H),21β(H)-22-tekatrishomohopane
C27aBB-20R	5α(H),14β(H),17β(H)-20R-cholestane
C28aaa-20R	24-methyl-5α(H),14α(H),17α(H)-20R-cholestane
C29aaa-20S	24-ethyl-5α(H),14α(H),17α(H)-20S-cholestane
C29aaa-20R	24-ethyl-5α(H),14α(H),17α(H)-20R-cholestane
C29aBB-(20S&R)	24-ethyl-5α(H),14β(H),17β(H)-20S&R-cholestane
DiaC29aB-(20S&R)(24S&R)	24S&R-ethyl-13α(H),17β(H)-20S&R-diacholestane

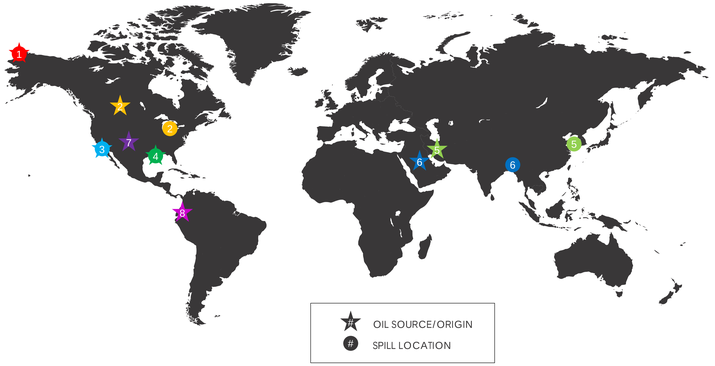

Figure 7: A world map indicates where each sample was collected and the putative location of the source oil.

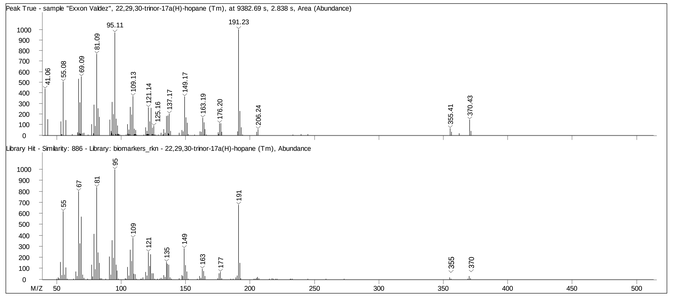

Figure 8: Automatically generated deconvoluted Peak True spectra corresponding to analytes of interest were compared to spectra from a user-generated library of common biomarkers. The result for a common hopane peak T_m in the sample from the Exxon Valdez spill is shown with an excellent similarity score of 886/1000.

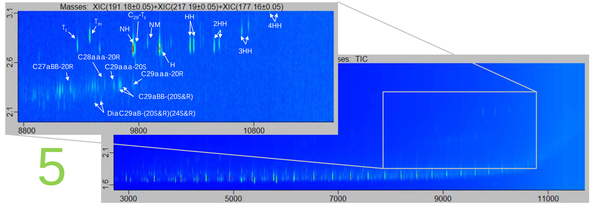

Figure 9: On December 7, 2007, a crane barge collided with an anchored crude carrier, the Hebei Spirit, on the coast of South Korea. The contour plot of the sample, which was taken from one of the carrier's tanks that contained heavy crude oil from Iran, is shown above with a zoomed-in view of the biomarkers section with characteristic masses for common hopane and sterane fragments displayed.

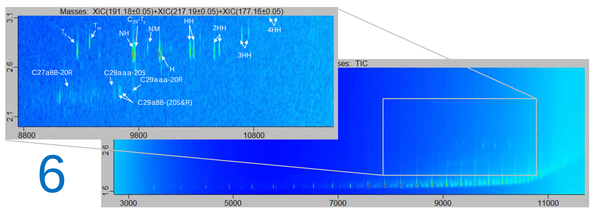

Figure 10: An oil tanker spilled 92,000 gallons of furnace oil from the Middle East in Sunderbans, Bangladesh, on December 9, 2014. A contour plot generated from the sample is shown above, with a zoomed-in view of the biomarkers section with characteristic masses for common hopane and sterane fragments displayed.

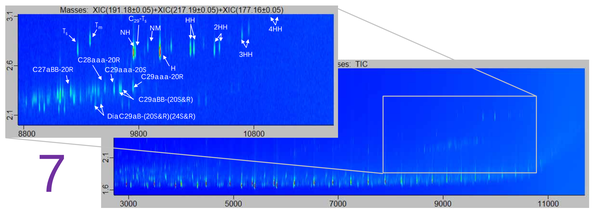

Figure 11: A contour plot generated from a sample of oil from the Permian Basin in West Texas is shown above, with a zoomed-in view of the biomarkers section with characteristic masses for common hopane and sterane fragments displayed.

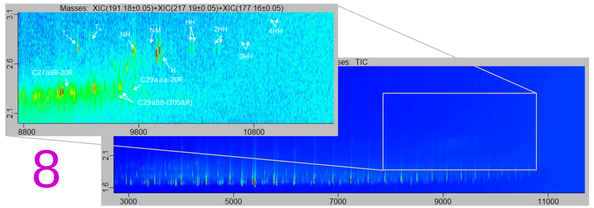

Figure 12: A contour plot generated from a sample of oil from the Peninsula de Santa Elena in Ecuador is shown above, with a zoomed-in view of the biomarkers section with characteristic masses for common hopane and sterane fragments displayed.