



# High Resolving Power Assessment for High Resolution Time-of-Flight Mass Spectrometry

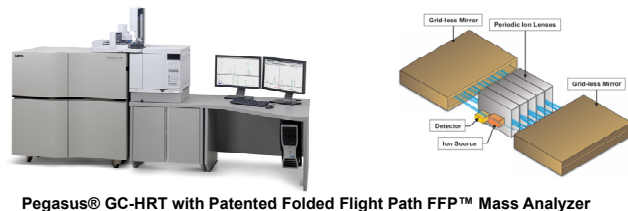
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## Introduction

Mass spectrometry has played an indispensable role in the characterization of complex petroleum and other fossil fuel resources at molecular level, especially the determination of elemental composition of components. The coupling of chromatography enhances its capabilities of detailed compositional analysis. The frequent absence of a molecular ion or novel fragment ion among hydrocarbons makes separation desirable. Gas chromatography (GC) provides high chromatographic resolving power to separate individual, even isomeric, species to facilitate extraction of informative mass spectral information. LECO Corporation's recent development of high resolution time of flight mass spectrometers capable of up to 100,000 resolving power, sub ppm mass accuracy and acquisition rates up to 200 spectra per second have opened the door for pairing high resolution chromatography methods (UHPLC, GC, and GCxGC) with high resolution mass analysis. The work contained in this poster will focus on the use of gas chromatography separations paired with high resolution time of flight mass spectrometry on the LECO Pegasus® GC-HRT.

The analysis of petroleum biomarkers, such as hopanes and steranes, can provide insights into the quality of the crude oil as well as its source. Much information can be gleaned about a crude oil sample from its hopane and sterane content. Information such as source, age, maturity, and alteration. This information can also be a useful tool for oil to oil correlation as well as oil to source rock correlation. The ability to sufficiently resolve (mass spectrometrically and chromatographically) the key masses typical of hopane and sterane compounds present in Macondo Crude oil will be evaluated.

The objective of the current study is to compare and evaluate the utility of accurate mass and resolving power in the selective extraction of qualitative information on hopane and sterane content of a representative oil sample. In this instance a sample of Macondo crude is used. In addition, GCxGC data are also shown as a complementary form of selectivity.

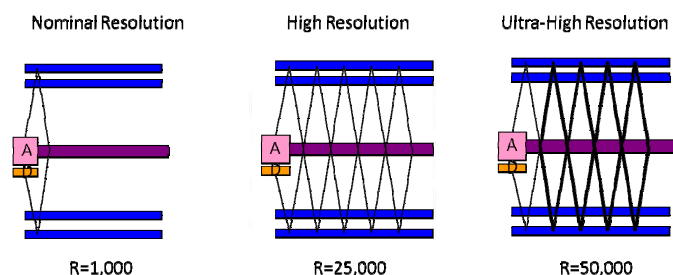


Pegasus® GC-HRT with Patented Folded Flight Path FFP™ Mass Analyzer

## Experimental

### Sample

A sample of crude oil from the Macondo well was prepared in pentane prior to analysis. This sample was analyzed in each of the three modes. Three different analysis modes are available on the Pegasus GC-HRT: Nominal Resolution (R = 1,000), High Resolution (R = 25,000), and Ultra High Resolution (R = 50,000). The mass resolution is achieved by a mass analyzer with variable flight path length. The figure below illustrates the flight paths representative of each analysis mode.



The following GC-HRT Conditions Were Utilized:

### GC Parameters

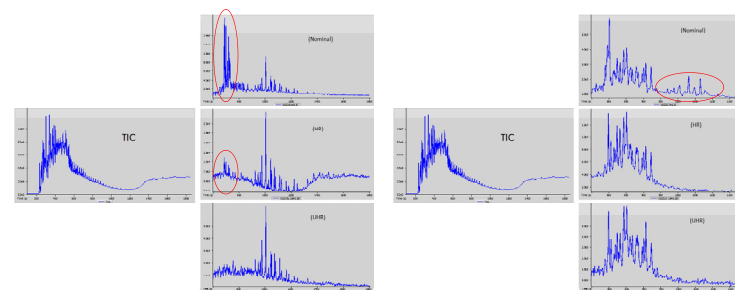
GC: Agilent 7890  
 Column Type: Rxi-5Sil MS (30m x0.25mm ID x 0.25 mm *df*)  
 Injection: 1µL, Split 20:1 at 300°C  
 Oven: 60 °C (1 min.) to 300 °C at 30 °C /min, to 350 °C at 10 °C /min  
 Carrier Gas: He, Constant Flow (1.00 mL/min.)

### MS Parameters

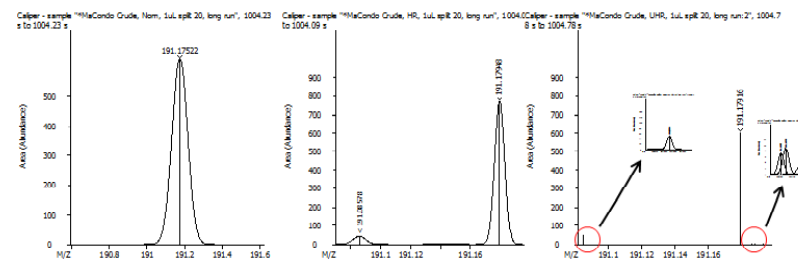
Spectrometer: LECO PEGASUS GC-HRT®  
 Ion Source: EI  
 Polarity: Positive  
 Flight Path: Nominal, HR and UHR, and UHR  
 Spectral Acquisition: 6 spectra / second  
 m/z Range: 60 – 510 (N and HR); 90 – 340 (UHR)  
 m/z Calibration: PFTBA

## Results

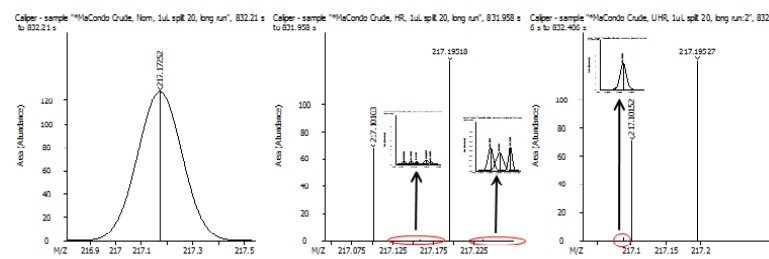
The GC-HRT results for the Macondo crude oil are displayed in the figures that follow.



Total and Extracted Ion Chromatograms for diagnostic m/z fragments from Hopanes (191) and Steranes (217). It is apparent that with increasing resolving power, interferences with similar m/z values are removed. The interferences are circled in the chromatograms above.

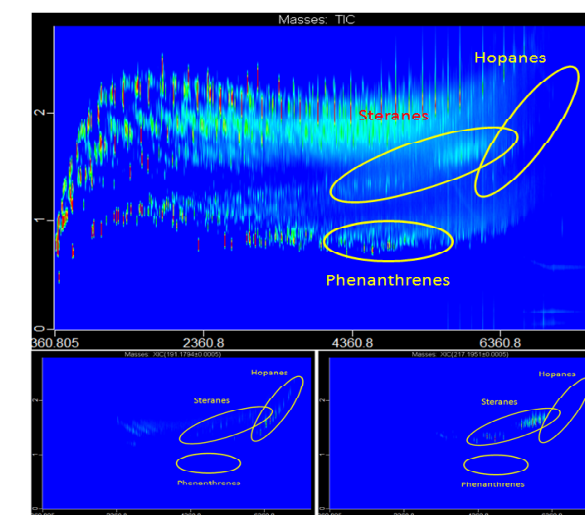


m/z 191 (hopane fragment) above is observed in 3 different operation modes. It is apparent that in nominal mode (left), interfering masses are not resolved. In the center and right examples (HR and UHR modes, respectively), additional interfering masses have been resolved.



m/z 217 (sterane fragment) above is observed in 3 different operation modes. It is apparent that in nominal mode (left), interfering masses are not resolved. In the center and right examples (HR and UHR modes, respectively), additional interfering masses have been resolved.

## Results



Preliminary GCxGC-HRT data above shows great promise as a tool to further unravel the complexity of petroleum products.

### Conclusion:

- HRT is needed for resolving overlapping components and cleanly defining the appropriate analyte signal. Nominal mass resolution does not distinguish the chromatographically unresolved nominal isobars.
- Coupling with chromatography is necessary for resolving components of different compound classes with identical formula, i.e., same accurate mass.
- Coupling of comprehensive two-dimensional gas chromatography (GCxGC) with HRT shows promise and the potential to resolve additional isomers and provide mass resolution to distinguish components not sufficiently resolved.

### References:

- Beynon, J. H.; Williams, A. E. *Mass and Abundance Tables for Use in Mass Spectrometry*; Elsevier: Amsterdam, 1986.
- Nikolaev, E. N.; Boldin, I. A.; Jert, R.; Baykut, G. *J. Am. Soc. Mass Spectrom.*, 2011, 22, 1125-1133.
- Hsu, C. S. *Energy Fuels*, 2012, 26, 1169-1177.
- Song C.; Hsu, C. S.; Mochida, I. (eds.) *Chemistry of Diesel Fuels*, Philadelphia: Taylor & Francis, 2000.
- Hsu, C. S. (ed.) *Analytical Advances for Hydrocarbon Research*, New York: Kluwer Academic/Plenum Publishers, 2003 (ISBN 0-306-47476-X)