

# PETROLEOMICS: COMPOSITION/STRUCTURE RELATION TO PROPERTIES/PERFORMANCE OF PETROLEUM AND ITS FRACTIONS

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## INTRODUCTION

Petroleum, coals, and shale oils are the most complex mixtures in nature, containing thousands of components. They require sophisticated analytical technologies for correlation and prediction of the properties/performance of the products as well as the processability of the feeds. After decades of endeavor and development, the analyses of heavy fractions of these hydrocarbon resources remain major challenges. Among a variety of analytical techniques, mass spectrometry provides unique capabilities for looking into detailed composition down to molecular-level.

In mass spectrometry, various ionization techniques, mass analyzers, detectors, and data collection systems have been developed over last 60 years for a wide range of molecular information, as shown in Figures 1 and 2.

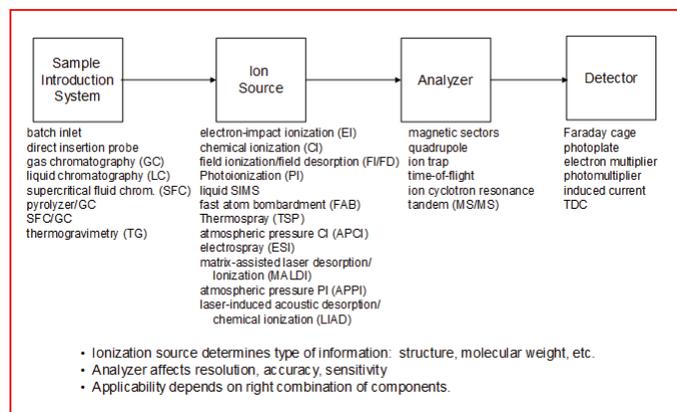


Figure 1. An array of MS techniques has been developed for petroleum mass spectrometric analysis



Figure 2. Various petroleum fractions require different mass spectroscopic techniques

The coupling of mass spectrometry with chromatography greatly enhances the separation power and specificity of components in complex mixtures. The most commonly used combined method is gas chromatography-mass spectrometry (GC-MS) with 70-eV electron ionization due to ease of operation/maintenance. In the upstream applications, use of tandem mass spectrometry in GC-MS-MS has greatly enhanced the geochemical information, such as source input, age, maturation and alteration, through the distribution of sterane isomers, as shown in Figures 3 and 4.

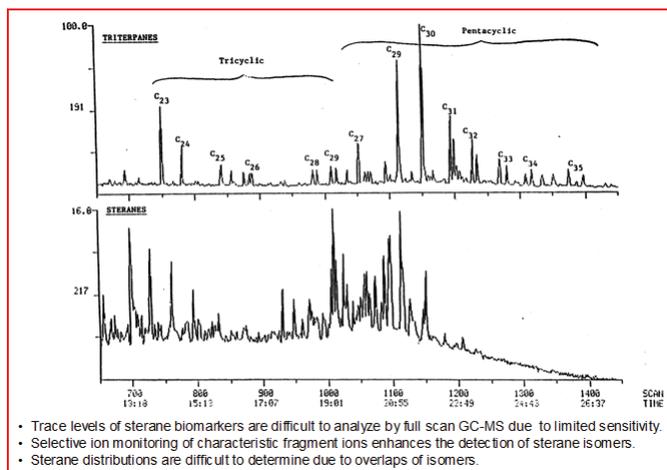


Figure 3. Selected ion monitoring enhances GC-MS detection of biomarkers

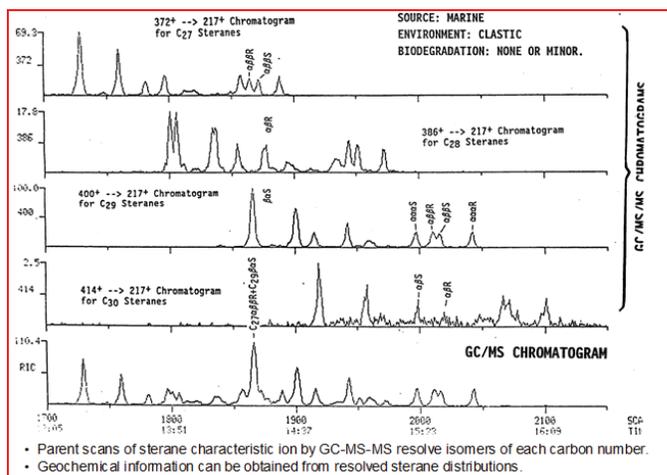
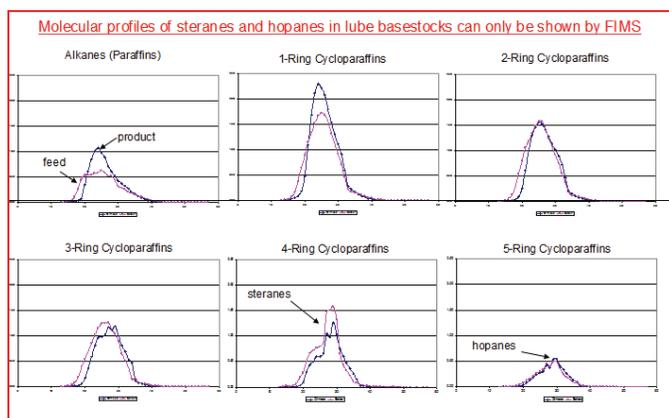


Figure 4. GC-MS-MS resolves overlapping sterane biomarkers

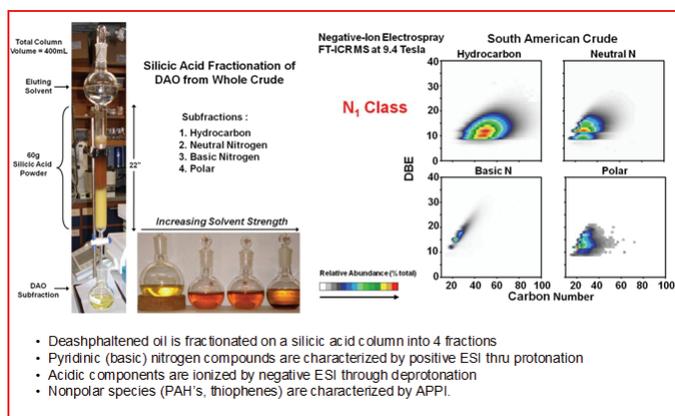
In the downstream applications, it has become common to use fragment-free field ionization and reflectron time-of-flight mass analyzer for accurate measurement of molecular species. The molecular transformations during petroleum processing can be easily discerned through molecular profiles obtained as shown in Figure 5. Detailed molecular composition is the basis of modern process kinetic models for better predictions of the process performance (process conditions, catalyst life cycles, etc.) and product quality (octane number, cetane number, etc.)



**Figure 5.** Difference in molecular profiles between feed and product can be easily discerned from molecular ion distribution

The analysis of heavy petroleum fractions that consist of > 50,000 chemical constituents, such as resids and asphaltenes, has long been a tremendous challenge. It is now achievable with ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with advanced data analysis.

Column chromatography combined with FT-ICR MS enhances speciation of complex heavy crude oil fractions containing expansive chemical functionalities. A recent example is shown in Figure 6 for the analysis of the polar and nonpolar LC fractions from deasphalted oils characterized by positive/negative electrospray ionization (ESI) for polars and atmospheric pressure photoionization (APPI) for nonpolars.



**Figure 5.** Column separation followed by FT-ICR expand compounds class/type identification

Another challenge is to interpret an overwhelming volume of analytical data for its physical and chemical significance. Chemometrics have been used as a data mining tool to identify key species that would mostly affect the overall properties of feed and products. Recent development in molecular modeling provides us with abilities for prediction of effectiveness of refining processes from the molecular composition data.

This presentation will give an overview of the analytical, particularly mass spectrometric, and modeling approaches to obtain relevant molecular data or information for further understanding of

the product quality and the prediction/assessment of petroleum process effectiveness.