Crude Oil And Asphaltene Characterization by Pyrolysis Coupled to Gas Chromatography High Resolution Time-of-flight Mass Spectrometry

Clécio F. Klitzke, David Alonso, Joe Binkley, Jeffrey Patrick | LECO Corporation, St. Joseph, MI

Background

Petroleum is the most complex matrix in nature, constituted by many thousands of compounds, and presents an analytical challenge. As the world's remaining deposits of petroleum become heavier, it's important to understand the chemical nature of heavy crude oil and its fractions. The analysis of high-boiling point constituents adds a new dimension for the complete characterization of crude oil. In this study we evaluated the use of a pyrolysis probe coupled to gas chromatography high resolution time-of-flight mass spectrometry (Py-GC-HRTOFMS) for the characterization of crude oils and asphaltene fractions.

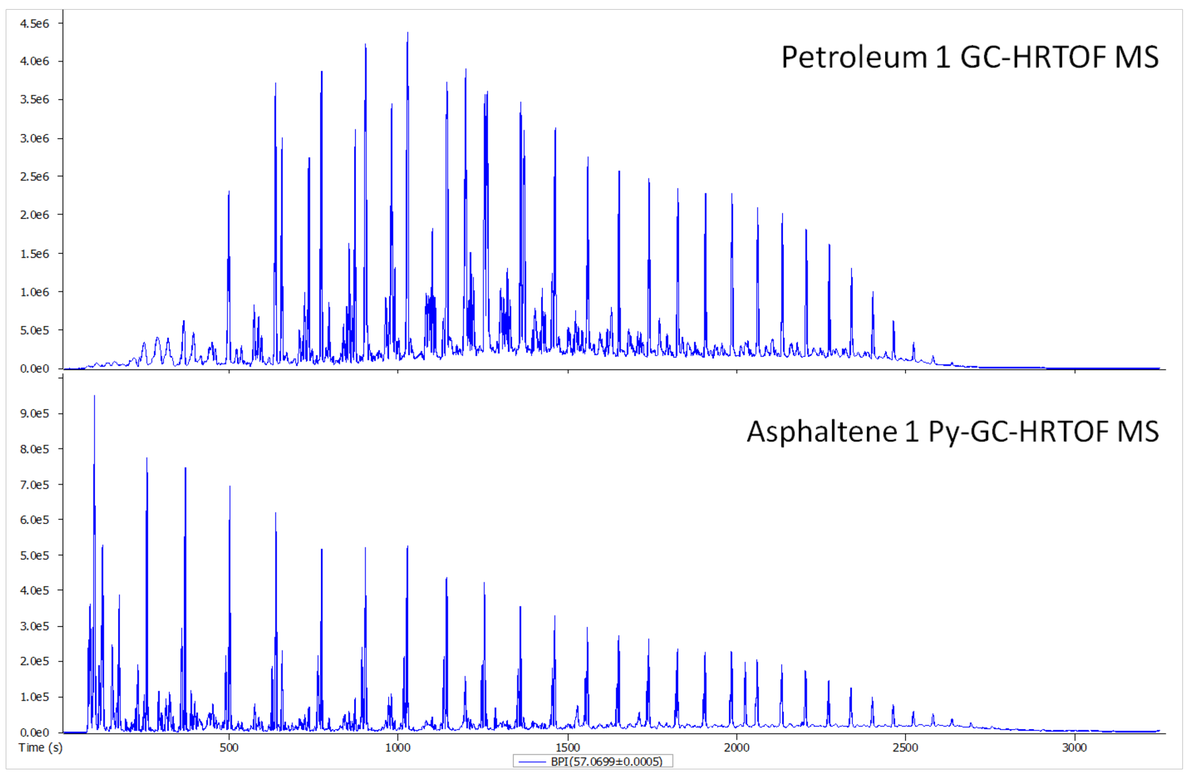
Methods

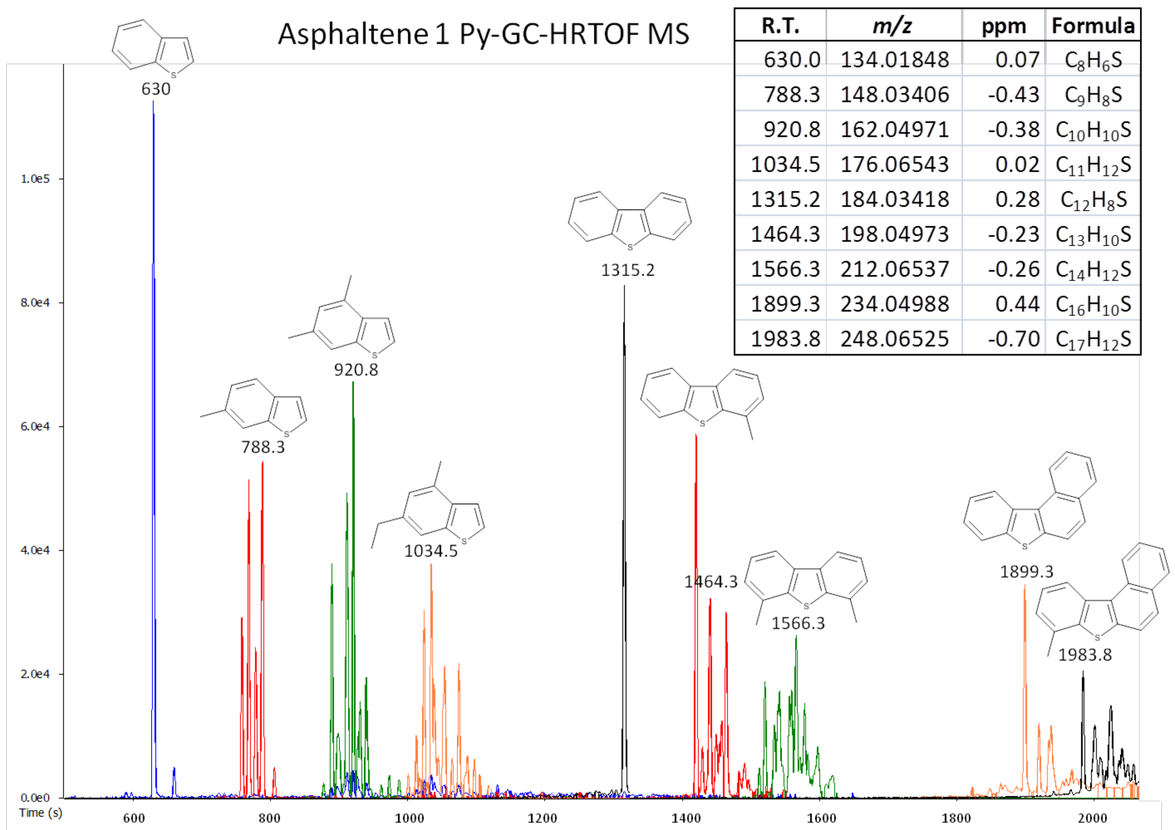
Thermal Desorption and Pyrolysis: Performed with a CDS Pyroprobe Model 5200 coupled to a LECO Pegasus® GC-HRT. Typically we run the crude oil samples in two steps of thermal desorption (350°C and 500°C). After that we pyrolyze the residue at 800°C. Asphaltene fractions were analyzed at 800°C. The pyroprobe injected the samples into the gas chromatograph's split/splitless inlet with Helium carrier gas (1 mL/min).
GC-HRT MS Analysis: GC with a Restek Rxi-5MS column (30 m, 250 μm, 0.25 μm). Data was acquired in high resolution mode yielding a nominal resolving power of 25,000 with mass accuracy of <1 ppm. Data were recorded in full MS mode from 45-650 *m/z* at 6 spectra/s acquisition rate, and 1.5 kHz extraction frequency.
Data Processing: Data were processed using ChromaTOF-HRT® 1.80 (LECO Corporation) and PetroOrg (Omics, LLC)

Results and Discussion

Preliminary results show compositional differences among crude oil samples. The comparison of pyrolysis products of asphaltene fractions shows compositional similarity with the pyrolysis of the residue after thermal desorption at 500°C, indicating that the residue is constituted mainly by asphaltene. The pyrolysis of asphaltenes from distinct crude oil samples shows distinct composition in terms of polycyclic aromatic sulfur heterocycles (PASHs), polycyclic aromatic nitrogen heterocycles (PANHs), and polycyclic aromatic hydrocarbons (PAHs).

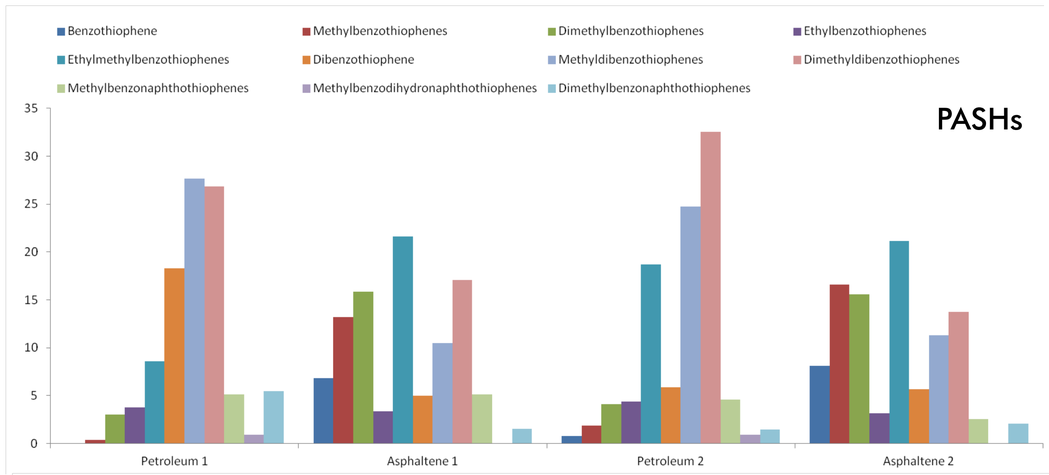
Example of Typical Chromatograms of Petroleum and Respective Asphaltene Fraction, and Py-GC-HRTOFMS Analysis of PASHs from Asphaltene

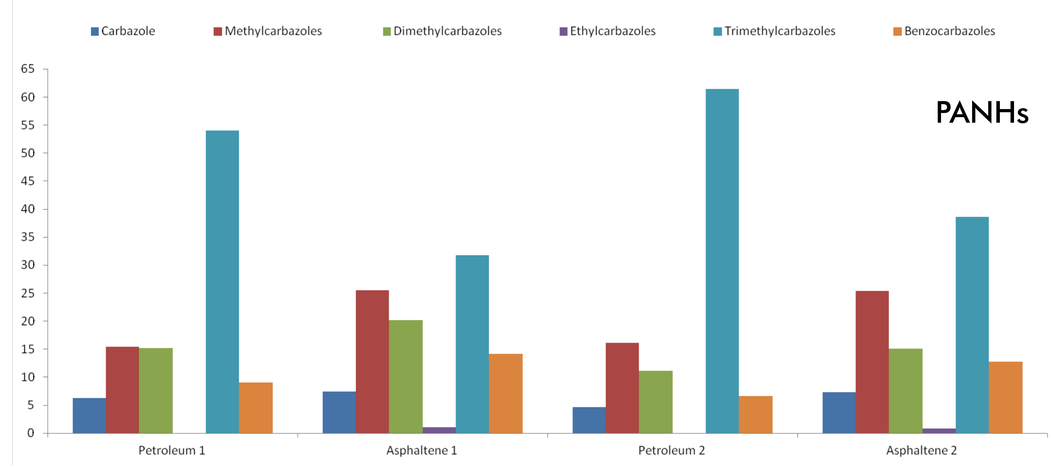


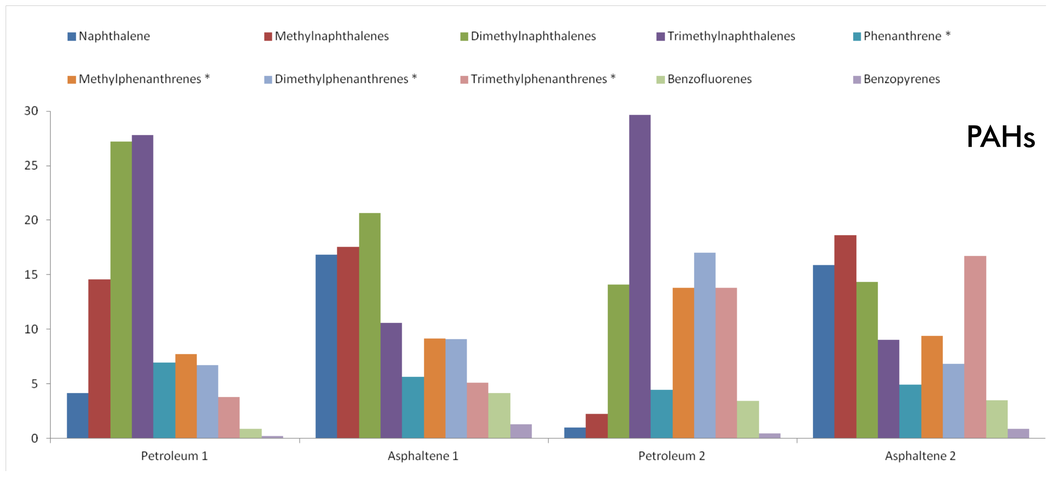


R.T.	*m/z*	ppm	Formula
630.0	134.01848	0.07	C_8H_6S
788.3	148.03406	-0.43	C_9H_8S
920.8	162.04971	-0.38	$C_{10}H_{10}S$
1034.5	176.06543	0.02	$C_{11}H_{12}S$
1315.2	184.03418	0.28	$C_{12}H_8S$
1464.3	198.04973	-0.23	$C_{13}H_{10}S$
1566.3	212.06537	-0.26	$C_{14}H_{12}S$
1899.3	234.04988	0.44	$C_{16}H_{10}S$
1983.8	248.06525	-0.70	$C_{17}H_{12}S$

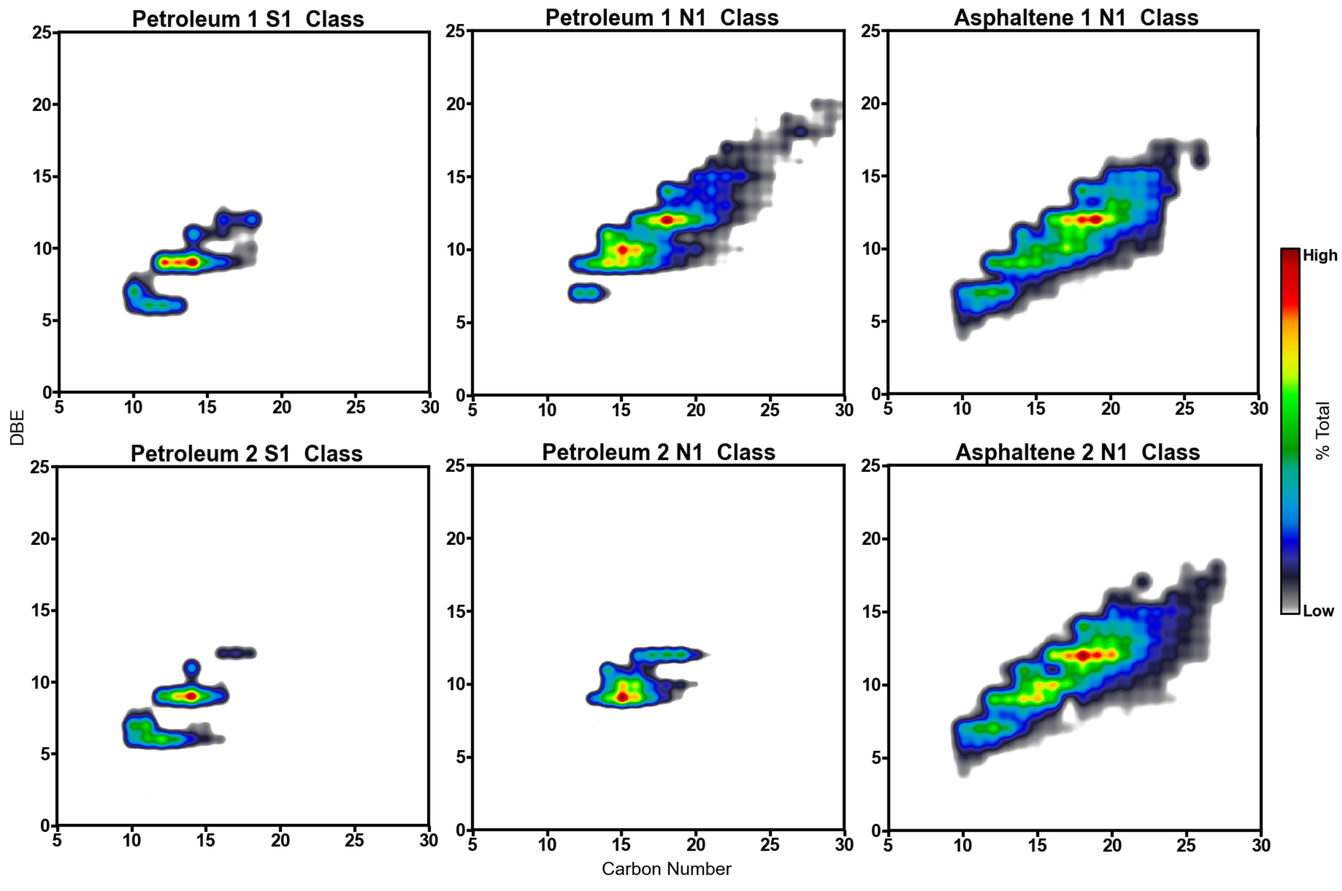
Distribution of PASHs, PANHs and PAHs in Two Petroleum Samples and Respective Asphaltene Fractions



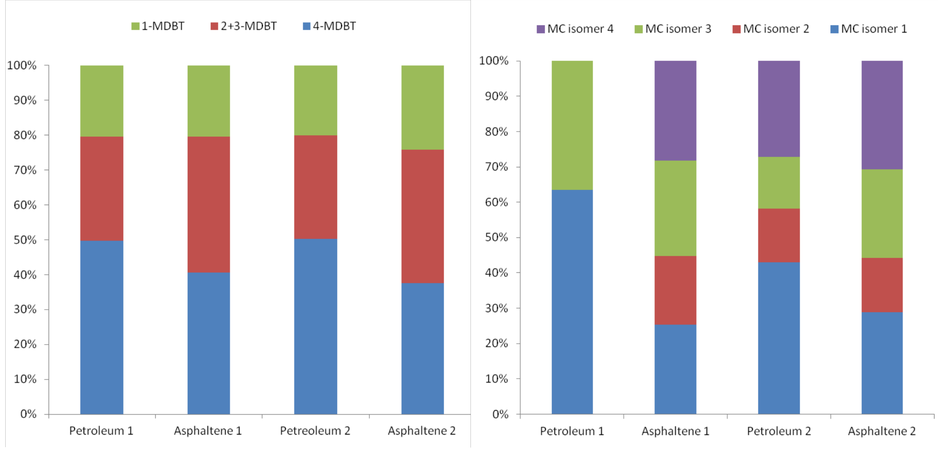




Carbon Number vs. DBE Plots



Distribution of Methyldibenzothiophene (MDBT) and Methylcarbazole (MC) Isomers



Conclusions

Py-GC-HRTOFMS analysis with high resolution and high mass accuracy is crucial for identification of crude oil and asphaltene pyrolysis products by unequivocal chemical formula assignment, with enhancement of sensitivity and selectivity. Analysis of petroleum and respective asphaltene fractions from diverse geographical origins are under evaluation as part of future work.