High Performance Time-of-Flight Mass Spectrometry for Comprehensive Petroleum Analysis

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Background

Petroleum is the most complex matrix in nature, constituted by many thousands of compounds. Full knowledge of composition of crude oil is the key in the rational use of reserves, optimization of production, the refining process, reduction of byproducts, quality control of derivatives, and many other crucial aspects of the petrochemical field. Advances in the performance of time-of-flight mass spectrometry (TOFMS) such as high resolution, high mass accuracy, and high acquisition rate provide an alternative for most routine studies of volatile and semi-volatile compounds of crude oil and derivatives. In this work we investigate the composition of crude oils and derivatives by pairing High Resolution GC-TOFMS with a petroleomic software tool. Complementary GC×GC-TOFMS data provided isomeric composition.

Experimental

Crude oil samples were diluted in $CHCl_2$ and injected into the gas chromatograph's split/splitless inlet with helium carrier gas. The analyses were performed in both EI and CI (CH_4) modes with a LECO Pegasus® GC-HRT MS (resolving power of up to 50,000 and mass accuracy of <1 ppm), and in EI with a LECO Pegasus 4D GC×GC-TOFMS. Asphaltene fractions were pyrolyzed at 800°C with a CDS Pyroprobe Model 5200 coupled to a LECO Pegasus GC-HRT. The pyroprobe injected the samples into the gas chromatograph's split/splitless inlet with helium carrier gas (1 mL/min). Data were processed using ChromaTOF-HRT® 1.80 (LECO Corporation) and PetroOrg (Omics, LLC).

Results

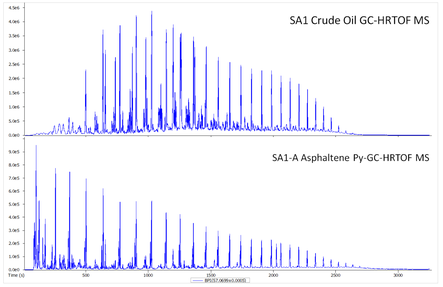
Preliminary results show that High Resolution GC-TOFMS was extremely useful for petroleomic studies allowing evaluation of class distribution and composition of the homologous series (carbon number versus DBE plots). The hydrocarbons and aromatics are the most abundant class, and heteroatomic class in abundance greater than 1% can be analyzed. Chemical ionization provides additional information of class composition showing the relative distribution of hydrocarbons and (N, O, S)-heterocyclic compounds. Members of homologous series are better distinguished and compared using CI in conjunction with EI. These results show that petroleomic software complements the traditional workflow analysis. GC×GC-TOFMS complements the results of High Resolution GC-TOFMS.

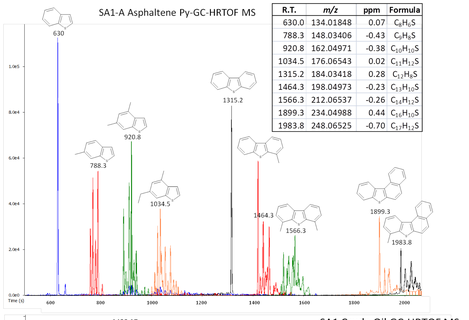
Conclusions

High Resolution GC-TOFMS and GC×GC-TOFMS are useful for a non-target comprehensive characterization of petroleum through a petroleomic approach, and can also provide targeted analysis of chemical markers.

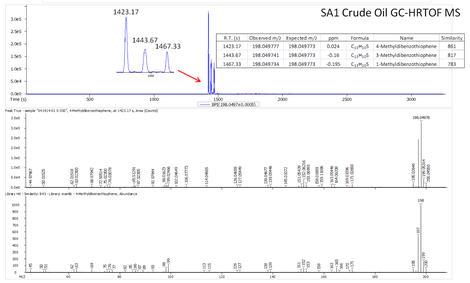
High Resolution GC-TOFMS analysis with high resolution and high mass accuracy is crucial for identification of crude oil and asphaltene pyrolysis products by unequivocal chemical formula assignment, with enhancement of sensitivity and selectivity.

Example of Typical Chromatograms of Petroleum and Asphaltene and Analysis of PASHs



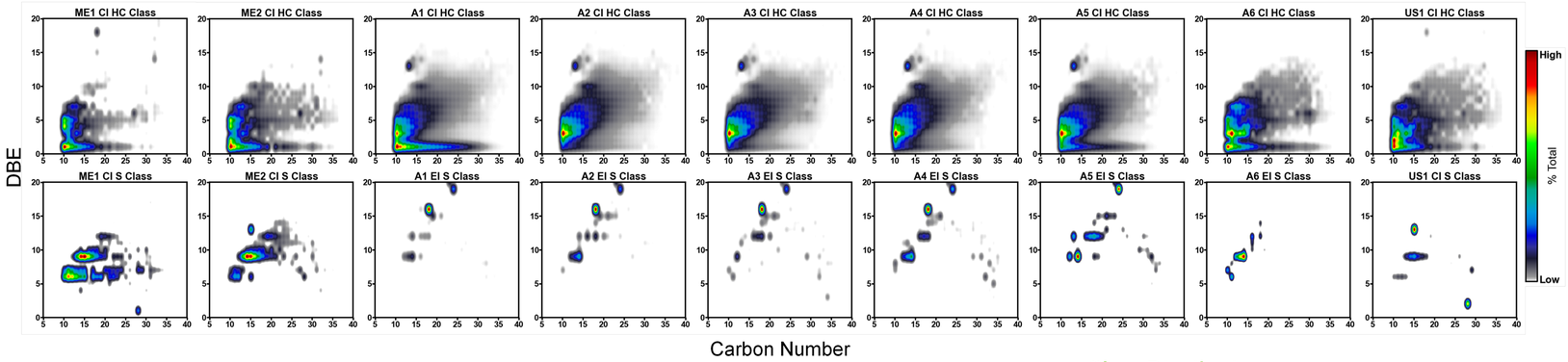


R.T.	m/z	ppm	Formula
630.0	134.01848	0.07	C_9H_9S
788.3	148.03406	-0.43	$C_{10}H_9S$
920.8	162.04971	-0.38	$C_{10}H_{11}S$
1034.5	176.06543	0.02	$C_{11}H_{11}S$
1315.2	184.03418	0.28	$C_{12}H_9S$
1464.3	198.04973	-0.23	$C_{13}H_{11}S$
1566.3	212.06537	-0.26	$C_{14}H_{13}S$
1899.3	234.04988	0.44	$C_{16}H_{11}S$
1983.8	248.06525	-0.70	$C_{17}H_{13}S$

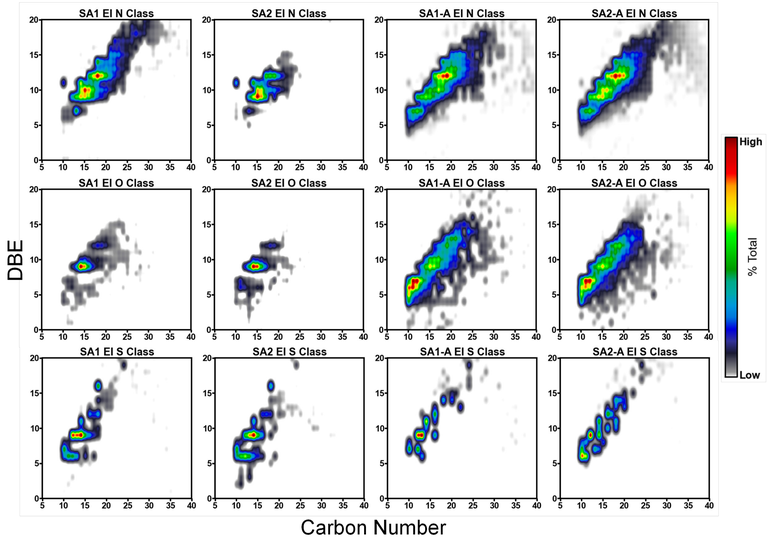


R.T. (s)	Observed m/z	Expected m/z	ppm	Formula	Name	Similarity
1423.17	198.049777	198.049773	0.024	$C_{14}H_{10}S$	4-Methyldibenzothiophene	861
1443.67	198.049741	198.049773	-0.16	$C_{14}H_{10}S$	3-Methyldibenzothiophene	817
1467.33	198.049734	198.049773	-0.195	$C_{14}H_{10}S$	1-Methyldibenzothiophene	783

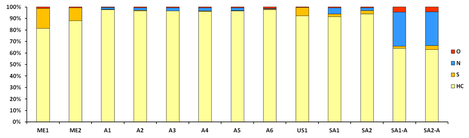
Carbon Number vs. DBE Plots Showing Hydrocarbon and Sulfur Classes



Carbon Number vs. DBE Plots Showing Nitrogen, Oxygen, and Sulfur Classes



Class Distribution



Plots Showing the Level of Maturity and Biodegradation Using MDBT Isomer Ratio, and Depositional Environment Using the Relative Content of Fluorene, Dibenzothiophene, and Dibenzofuran