Flash Pyrolysis Coupled to GC×GC-TOFMS and GC-High Resolution TOFMS for Characterization of Crude Oil and Petroleum Fractions

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Introduction

Petroleum is the most complex matrix in nature, constituted by many thousands of compounds, and presents an analytical challenge. For comprehensive analysis we need a chromatographic separation with high peak capacity, and for mass spectrometry analysis we need high resolving power and high mass accuracy.

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 of crude oils adds a new dimension for the complete characterization of crude oil. In this study we evaluated the use of a pyrolysis probe (Py) coupled to comprehensive two-dimensional gas chromatography (GC×GC) time-of-flight (TOF) and GC high resolution time-of-flight (HRTOF) mass spectrometry (MS) for the characterization of crude oils and asphaltene fractions.

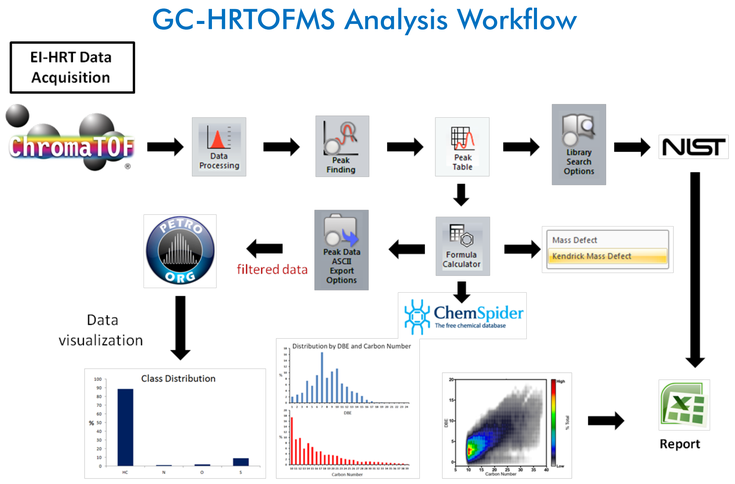
Experimental

Crude oil samples obtained from several countries were analyzed by Py–GC×GC–TOFMS and Py–GC–HRTOFMS. The samples were placed into a quartz tube of a Pyroprobe Model 5200 (CDS Analytical Inc., Oxford, PA, USA) interfaced to an Agilent 7890A GC (Palo Alto, CA, USA). Analyses were performed at 350°C and 500°C for thermal desorption, and 800°C for pyrolysis. Interface, valve oven, and transfer line were at 300°C. Helium was used as carrier gas from the pyroprobe to the GC at a flow rate of 1mL.min^{-1}.

For Py–GC–HRTOFMS analysis a Pegasus® GC-HRT (LECO Corporation, St. Joseph, MI, USA) was used in high resolution mode (≥25,000). Electron energy of 70 eV was applied. Separation by GC was achieved with a Restek (Bellefonte, PA, USA) Rxi-5MS 30 m column in the condition of 1mL.min $^{-1}$ of Helium at constant flow. The oven has an initial temperature of 50°C held for 1 minute, raised to 320°C at 5°C.min^{-1}, and held at the final temperature for 10 minutes. The temperature of the inlet, transfer line, and ion source were respectively 300, 320, and 250°C.

A Pegasus 4D (LECO Corporation, St. Joseph, MI, USA) was used for Py–GC×GC–TOFMS analysis with the experimental conditions of 70 eV in the ion source, and acquisition rate of 200 spectra/s in the mass range of 40 to 700 *m/z*. The separation in the first dimension used a 30 m Restek (Bellefonte, PA, USA) column Rxi-5MS. The second-dimension separation was done using a 1.25 m Restek Rxi-17MS column. The oven program has a initial temperature of 60°C for 1 minute, raised to 320°C at 4°C.min^{-1} and held at the final temperature for 10 minutes. The temperature of the inlet, transfer line, and ion source were respectively 300°, 320°, and 250°C. Secondary oven temperature offset was 5°C. The dual stage, quad-jet thermal modulator had a temperature offset of 15°C, modulation period of 4 s, with 0.6 seconds long hot pulse.

GC-HRTOFMS Analysis Workflow



Results and Discussion

Typically crude oil samples are analyzed in two steps of isothermal desorption (350°C and 500°C). After that the remaining residue is pyrolyzed at 800°C. Isomeric ratios of polycyclic aromatic hydrocarbons (PAHs) and polycyclic aromatic sulfur hydrocarbons (PASHs) were evaluated, and may reflect the diversity of organic source input, thermal maturity, biodegradation level, and depositional environments (Chiaberge et al, 2011; Sarmah et al., 2010).

Pyrolysis of crude oil and asphaltene samples show distinct composition in terms of light and heavy PAHs, PASHs, and isomers related to sample characteristics. Preliminary results show that the pyrolysis products of asphaltene samples have compositional similarity with the pyrolysis of the crude oil residue, indicating that the residue obtained after thermal desorption at 500°C is constituted mainly by asphaltene.

Country	Crude Oil	°API	Sulfur Content (wt %)
Colombia	Vasconia	26.3	0.56
Ecuador	Oriente	25.9	1.01
Venezuela	Leona	24.0	1.52
Country	Merey	14.7	2.74

Conclusions

- The pyrolysis of asphaltenes from discrete crude oil samples shows distinct composition in terms of light and heavy aromatic hydrocarbons and alkyldibenzo-thiophenes.
- The use of Py–GC×GC–TOFMS is crucial for the determination of isomeric composition, and Py–GC–HRTOFMS with high resolution and high mass accuracy complements the identification by unequivocal chemical formula assignments.
- The study of the relationships of the crude oil and asphaltene composition are in progress.

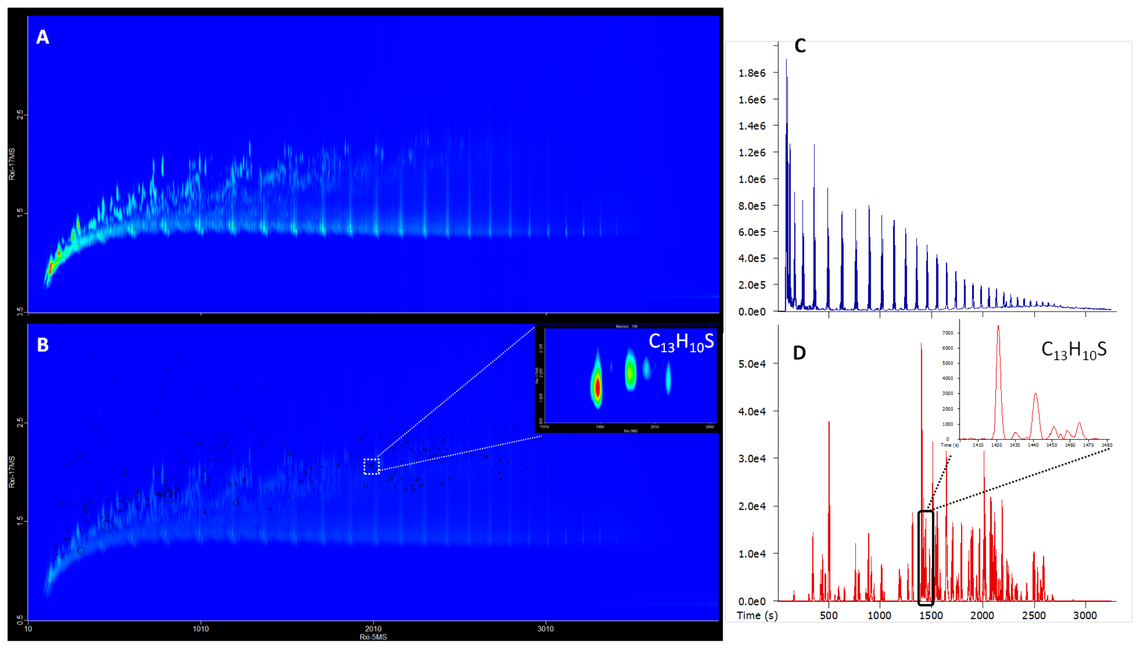
References

Chiaberge, S.; Fiorani, T.; Cesti, P., 2011. Methyldibenzothiophene isomer ratio in crude oils: gas chromatography tandem mass spectrometry analysis. Fuel Processing Technology. **92**, 2196-2201.

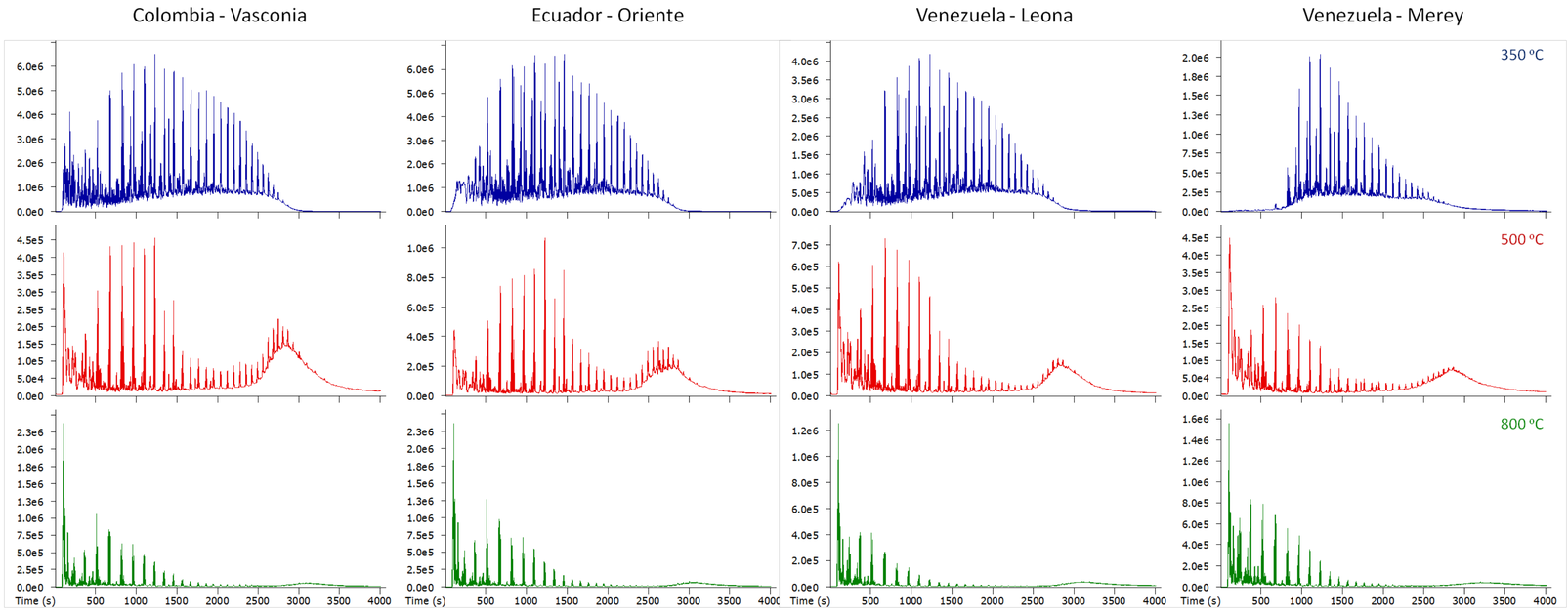
Sarmah, M.K.; Borthakur, A.; Dutta, A., 2010. Pyrolysis of petroleum asphaltenes from different geological origins and use of methylnaphthalenes and methyl-phenanthrenes as maturity indicators for asphaltenes. Bulletin of Materials Science **33**, 509-515.

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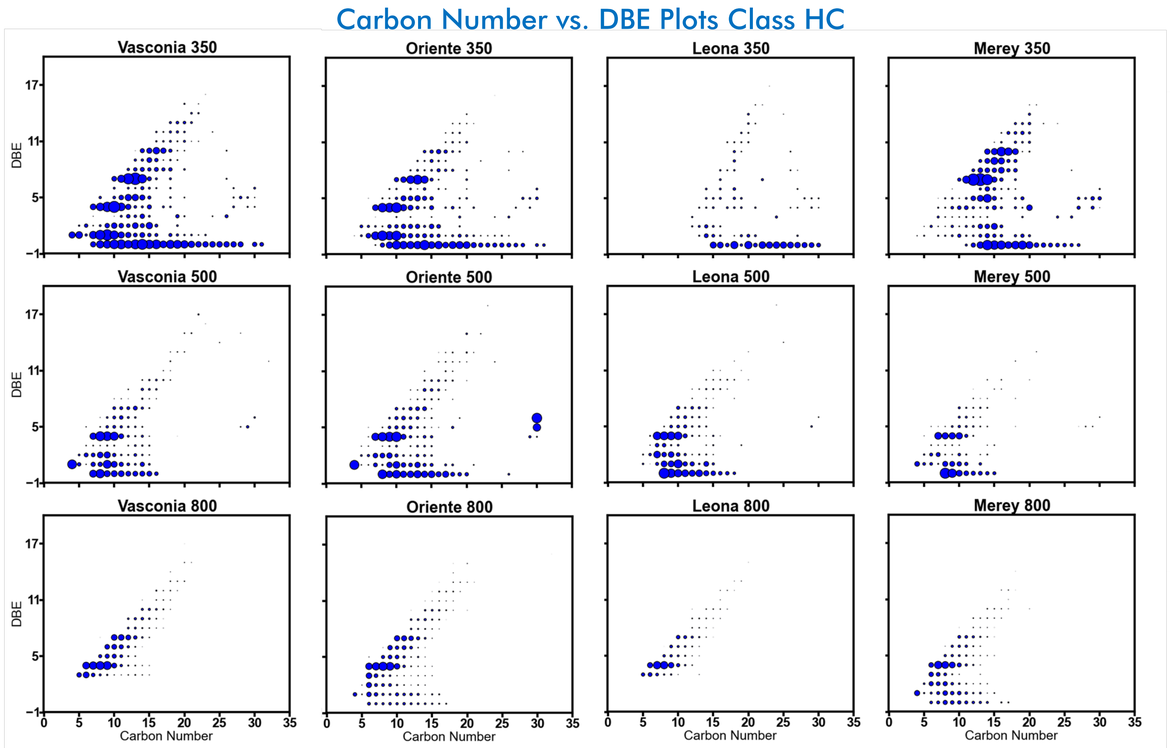
Comparison of GC×GC-TOFMS Contour Plot and GC-HRTOFMS Chromatogram



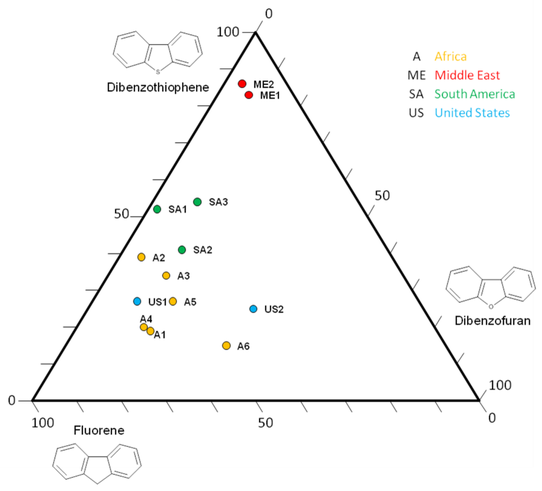
Example of Py–GC-HRTOFMS Chromatograms Using Thermal Desorption and Pyrolysis Temperature



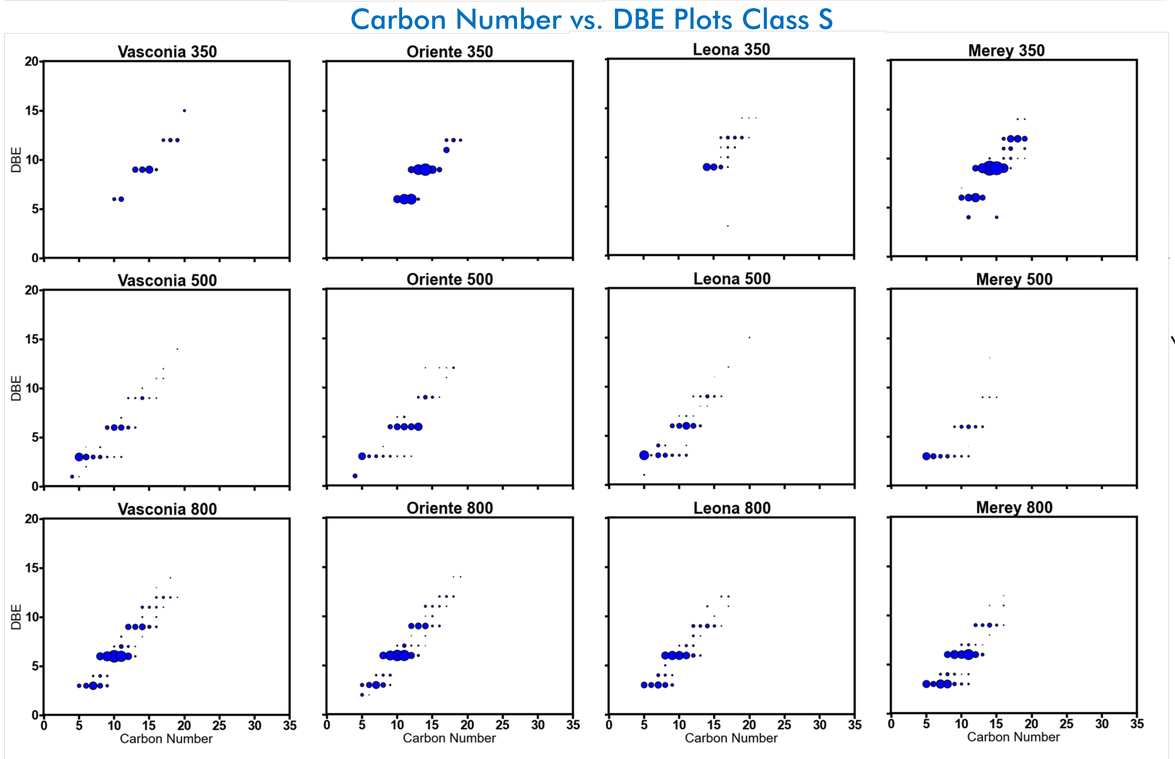
Carbon Number vs. DBE Plots Class HC



Depositional Environment Based on Relative Content of Fluorene, Dibenzothiophene, and Dibenzofuran



Carbon Number vs. DBE Plots Class S



Level of Maturity and Biodegradation using MDBT Isomer Ratio

