

## Molecular characterization of chromatographic fractions of deasphalted crude oils by FT-ICR Mass Spectrometry

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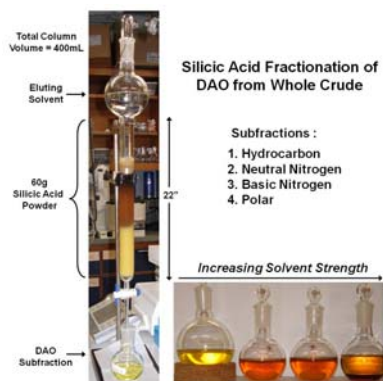
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The immense compositional complexity of crude oil prohibits direct detailed characterization by routine analytical techniques. Ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) allows detailed characterization of complex petroleum samples at the level of elemental composition assignment. Species in crude oil range from saturated hydrocarbons and naphthenic rings to highly aromatic, condensed structures with varying degrees of alkylation and heteroatom content (nitrogen, oxygen, sulfur and metals such as nickel and vanadium).

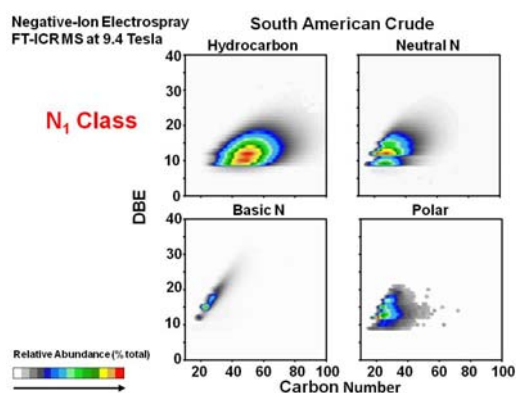


**Fig. 1.** Schematic diagram of column chromatography separation scheme used to fractionate deasphalted crude into four subfractions of increasing polarity.

Column chromatography when combined with FT-ICR MS provides enhanced speciation of the various chemical functionalities in crude oil. Here, we present a column chromatography method that separates deasphalted crude oils into nonpolar and polar subfractions based on aromaticity, polarity, and molecular weight [1]. The polar components of each fraction (i.e., pyridinic nitrogen, carboxylic acids) were characterized by positive and negative Electrospray Ionization (ESI), whereas Atmospheric Pressure Photoionization (APPI) was used to characterize the nonpolar species (i.e., polyaromatic hydrocarbons, thiophenes).

Fractionation and subsequent characterization by (+/-) ESI and APPI FT-ICR mass spectrometry was performed for three whole crudes from different geographic regions and for two high-boiling distillate fractions. Three FT-ICR mass spectra were collected for each subfraction to reveal compositional differences between the fractions as well as the

various crude oils. Enhanced characterization of the acidic species by negative ESI was facilitated by modification of the solvent system with the addition of tetramethylammonium hydroxide (TMAH) to increase the ionization efficiency of slightly acidic nitrogen-containing classes (Figure 2).



**Fig 2.** Double bond equivalents (DBE, number of rings plus double bonds) vs. carbon number plots for the N<sub>1</sub> class, based on negative ion ESI FT-ICR MS with TMAH.

APPI FT-ICR MS analysis of each LC fraction reveals that the hydrocarbon fraction is composed of alkyl-substituted aromatic hydrocarbons with a low relative abundance of polar components. Non-basic (pyrrolic) nitrogen dominates the neutral nitrogen fraction whereas the basic nitrogen is dominated by aromatic pyridines, hydrocarbons, thiophenes and furans. Trends in molecular weight and aromaticity as a function of LC elution across and between each crude oil fraction will be discussed. Positive-ion ESI shows highly abundant structures with DBE values that correspond to quinoline/acridine and a slight shift to lower carbon number with increasing solvent strength. Negative-ion ESI for the nonpolar fractions shows bimodal DBE distributions consistent with carbazole and benzocarbazole structures with highly aromatic structures dominant in the basic nitrogen fraction. APPI results differ from ESI and show highly aromatic structures in early eluting fractions. An overview of the column chromatography separation method and its associated benefits will be discussed, highlighting its role in the separation and characterization of the nonpolar and polar species in crude. (Work supported by NSF DMR 06-54118 and the State of Florida.)