C38 Biotic and Abiotic Compositional Changes in Heavy Crude Oil Determined by ESI-FT-ICR Mass Spectrometry

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After attending this presentation, attendees will learn basic principles of ESI FT-ICR MS and applications to environmental and forensic complex mixture analysis.

This presentation will impact the forensic community and/or humanity by demonstrating ultra-high mass resolving power (greater than one million), high mass accuracy (less than 1 ppm) and rapid analysis of environmental and forensic complex mixtures.

Crude oil is a complex and geographically unique combination of saturates, aromatics, resins, and asphaltenes. The great diversity of chemical classes present and the concentration range over which they exist make compositional analysis by traditional analytical methods difficult. Routinely used bench top analytical techniques such (such as GC-MS and LC-MS) are ineffective in characterizing crude oils due to limited peak capacity and resolving power and thus commonly result in the detection of a large unresolved complex mixture (UCM) "hump." The recent application of (ESI) Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) to petrochemical analyses has assisted in unraveling the complexity of crude oil and petroleum products, detecting >20,000 compositionally distinct polar acyclic, polycyclic, and polyaromatic polar –NSO compounds in a single sample. Such analysis serves to generate a detailed compositional fingerprint without the need for pre-chromatographic separation. However, environmental stressors such as bacterial remediation, solar UV photochemical transformations, and volatilization "smear" this fingerprint by generating new and removing previously identified components. For example, photochemical and bacterial mineralization of petroleum products result in decreased alkyl carbon chain length, dearomatization, denitrogenation, desulfurization, and increase in carboxylic acid content, whereas removal of short chain paraffinic compounds is attributed to volatilization. These changes further complicate source-to-sink forensic identification of crude oil spills as well as combusted particulate organic matter in the environment. Environmental modifications that increase the polar nature of a crude oil are of concern since they may result in increased water-solubility and toxicological impact. ESI FT-ICR MS provides ultrahigh-resolution mass analysis of polar species in complex mixtures, such as crude oil, achieving high resolving power $m/\Delta m_{50\%} > 300{,}000$ and high mass accuracy (< 1 ppm). Therefore FT-ICR MS provides an effective method of monitoring (on a component by component basis) environmentally induced changes in complex organic materials.

Here ESI negative-ion FT-ICR MS is applied to heavy South American and medium Arabian crude oils and their water-soluble acidic –NSO containing species, before and after photochemical modifications. The analysis of a seven oil biodegradation sample ranging in quality from undegraded to severely biodegraded is included to emphasize changes in polar –NSO containing species as a function of increased biodegradation. Molecular formulas (elemental compositions) from each sample are assigned from accurate mass measurement combined with a Kendrick mass sorting procedure. Both class based, aromaticity, and carbon number variations in the samples are highlighted by a combination of three-dimensional van Krevelen, Kendrick and aromaticity plots. The NSF National High Field FT-ICR Facility (CHE-99-09502), Florida State University, and the National High Magnetic Field Laboratory in Tallahassee, FL supported this work.

FT-ICR MS, Petroleum, Environmental Chemistry

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