C6 Petroleomics: Environmental Forensic Applications of High Resolution FT-ICR Mass Spectrometry

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The goal of this presentation is to introduce FT-ICR mass spectrometry and its applications in the environmental forensic arena.

The number of distinct chemical components of petroleum is already approaching tens of thousands, and is thus becoming roughly comparable to the number of genes (genome) or proteins (proteome) in a given biological species. Therefore, the inherent complexity of crude oil and its derived products has until now made environmental analysis difficult or in some cases, impossible. Once introduced to the environment, subsequent biotic and abiotic modifications of the petroleum product further complicate an already complex mixture. Traditional analytical techniques such as Liquid Chromatography (LC), Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS) have inadequate chromatographic resolution for the baseline separation of all species present in most petroleum distillates above diesel fuel. As a result, combined techniques (such as GC-MS and LC-MS) are ineffective due to co-eluting species that complicate the mass spectrum and hinder component identification. Furthermore, mass spectrometers commonly employed for GC-MS and LC-MS are low resolution / low mass accuracy quadrupole mass filters or quadrupole ion trap type mass analyzers that are unable to adequately resolve complex mixtures for individual component identification. As a result, the utilization of traditional analytical techniques provides a limited amount of compositional information and is often dominated by a large unresolved "hump," commonly referred to as an unresolved complex mixture (UCM). Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) benefits from ultra-high mass resolving power (greater than one million), high mass accuracy (less than 1 ppm) and rapid analysis which make it an attractive alternative for the analysis of petroleum products that range from crude oil to gasoline. For example, the authors recently resolved almost 20,000 different elemental compositions in a single positive-ion electrospray FT-ICR mass spectrum of a heavy crude oil.

The presenter will report three environmental forensic applications of FT-ICR mass spectrometric analyses in the initial site characterization of a U.S Air Force jet fuel (JP-8) spill site, the initial results from forensic typing of crude oils, and recent instrument advances that aide in the analysis. High-resolution mass spectra of electron-ionized jet fuel samples are obtained from as little as a 1 microliter septum injection into an all-glass heated inlet system. Molecular formulas (elemental compositions) are assigned from accurate mass measurement alone. From a compositional analysis of an unweathered standard, components are identified and monitored as a function of weathering. Identifying the leachable and volatile components present in such a complex mixture is useful in fate and risk assessment and environmental impact studies. JP-8 contaminated soil samples were obtained from Eglin Air Force Base, Soxhlet extracted, and analyzed for compositional similarities to weathered standards. Crude oil standards were provided by ExxonMobil and Petrobras and analyzed by electrospray ionization (ESI) FT-ICR mass spectrometry. Each crude consisted of thousands of peaks and hundreds of compound classes. Ten crudes were analyzed in an effort to differentiate the crudes from one another based on their compositions provided from the FT-ICR MS analysis. Instrumental advances discussed include selective ion accumulation, a new octapole ion accumulator, and the addition of a field desorption / ionization ion source.

Mass Spectrometry, High Resolution, FT-ICR MS

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