C6 Recent Advances in High Resolution FT-ICR Mass Spectrometry and Their Applications to Environmental Forensics

Ryan P. Rodgers, PhD, Geoffrey C. Klein, BS, and Lateefah A. Stanford, BS, Department of Chemistry and Biochemistry, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, FL 32310; Christopher L. Hendrickson, PhD, National High Magnetic Field Lab, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, FL 32310; Alan G. Marshall, PhD, Department of Chemistry and Biochemistry, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, FL 32310*

After attending this presentation, attendees will understand the fundamentals of high resolution FT-ICR mass spectrometry. Fundamental limitations of traditional analytical techniques, and how FT-ICR MS overcomes many of those limitations will be discussed.

This presentation will impact the forensic community and/or humanity by describing how the amount of information that can be obtained from complex environmental samples has drastically increased as a result of FT-ICR MS applications to environmental forensics. Thousands of different compounds may now be identified and used for fingerprint-based identification of heavy crude oil or other complex contaminants.

Traditional analytical techniques such as Liquid Chromatography (LC) and Gas Chromatography (GC) have inadequate chromatographic resolution for the baseline separation of all species present in complex mixtures composed of hundreds or even thousands of individual components. 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 mass spectral interpretation and component identification through traditional library based searches. This is especially true for complex materials that have undergone abiotic or biotic modification in the environment. 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. Even if the traditional analytical techniques succeed in both separating and resolving an individual species in a complex mixture, the low mass accuracy provided by the commonly employed mass spectrometers prevents elemental composition assignment. 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; these attributes make it an attractive alternative for the analysis of complex mixtures such as crude oil. For example, we recently resolved almost 20,000 different elemental compositions in a single positive-ion electrospray FT-ICR mass spectrum of a heavy crude oil.

Here we report environmental forensic applications of FT-ICR MS in the compositional analysis of heavy crudes, their water-soluble fraction, and abiotic changes in the crude oil polar species as a function of increased weathering in both soil and water (simulated sea water). High resolution (>300,000) and high mass accuracy (sub-ppm) mass spectra of electrospray (ESI) ionized samples are obtained on a homebuilt 9.4T ESI FT-ICR MS equipped with a MIDAS data station. Crude oil standards consisted of thousands of peaks over hundreds of compound classes. Five geochemically different crudes were analyzed in an effort to differentiate them from one another based on their compositions provided from the FT-ICR MS analysis. The crudes showed significant differences that directly relate to their geochemical source histories. We also report the compositional determination of water-soluble organics leached from a heavy crude oil. Contrary to previous reports in the literature, the composition of the water-soluble species is very complex and is composed of both the expected CO_2 series (carboxylic acids) as well as higher oxygen containing hydrocarbons and many SO_X species. Similar weathering experiments in sterilized soil will also be presented. Relevant instrumental advances will be discussed that both expand the compound classes that can be identified and make the analysis more informative and routine. Advances discussed include selective ion accumulation, a new octapole ion accumulator that increases the efficiency of ion ejection, and a new field desorption/ionization/atmospheric pressure ion source. Work supported by ExxonMobil Research and Engineering, NJ, NSF (CHE-99-09502), FSU, and the National High Magnetic Field Laboratory in Tallahassee, FL.

High Resolution Mass Spectrometry, Environmental Forensics, FT-ICR MS

 ** Presenting Author*