C18 Molecular Level Compositional and Structural Characterization for the Deepwater Horizon Oil Spill By GC-GC and FT-ICR Mass Spectrometry

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The goal of the presentation is to provide information on the first compositionally comprehensive inventory of the Deepwater Horizon crude oil, and monitor molecular level changes in the crude as a function of biotic and abiotic modifications from the wellhead to terminal point in the environment.

This presentation will impact the forensic science community by understanding how Ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) enables detailed compositional characterization of complex petroleum samples (all acidic, basic, aromatic and aliphatic species) at the level of molecular formula assignment. Comprehensive 2D gas chromatography (GCxGC) provides exhaustive structural characterization of nonpolar oil components below a carbon number of ~35. Such information is critical for source appointment and quantification of water washing and evaporative losses. Combined, the two techniques provide a wealth of compositional information that provides forensic fingerprinting of petroleum releases and monitors compositional changes at the molecular level. For the first time, comprehensive 2D GC and ultrahigh-resolution FT-ICR MS are combined to provide molecular level information on a real world oil spill.

An oil spill changes its chemical composition continuously, due to evaporation and dissolution. Furthermore, “weathering” (biotic and abiotic modifications) changes the composition of a crude oil and increases the relative abundance of polar species that are readily addressed by FT-ICR MS, but that are problematic for GC separations (requiring chemical derivatization prior to analysis). In work completed under an NSF RAPID Grant (#CHE-1049753), we have resolved and identified 72,000 acidic, basic, and nonpolar species in the Deepwater Horizon parent crude oil. Subsequent fractionations by micro-distillation and HPLC-2 have revealed thousands more species as well as structural information not provided by high resolution mass spectrometry alone and provide relevant fractions for more detailed analysis by FT-ICR MS and GC x GC. Collectively, the compositional results provided a detailed fingerprint and inventory of species released into the Gulf of Mexico. Water washing experiments have revealed water-soluble species that cannot be directly analyzed by gas chromatographic methods. Collaborative efforts reveal acidic/basic species compositional changes from the wellhead to being washed ashore in Pensacola, FL, where the compositional complexity of the basic species increased by 50%. Compositional analysis of tidal beach sediments at various depths exposes compositional changes due to weathering and sea water solubility, critical for enhanced model development. Most notably, the carbon number and aromaticity (double bond equivalents = rings plus double bonds to carbon) for the species identified below the initial oil contamination zone are lower than for the primary oiled sediment layer. Such compositional changes have been previously documented by our research in simulated oil spills performed in the laboratory (Stanford *et al.*, 2005). FT-ICR MS enables access to high boiling, polar species that have eluded environmental studies in the past due to their complexity and acidic/basic nature. That very character can now be exploited and combined with the highest performance FT-ICR mass spectrometry, to provide detailed compositional information for tens of thousands of acidic, basic and nonpolar species that lie within and far beyond the range of state-of-the-art gas chromatographic techniques. However, the resolution and structural analysis of lower boiling, nonpolar species (less than 35 carbons) is critical to determine the identity of suspect crude oils and measure weathering phenomena of volatile/semi-volatile species not easily analyzed by FT-ICR MS. Work supported by NSF (CHE-10-49753 and DMR-06-54118).

GC-GC, High Resolution Mass Spectrometry, Deepwater Horizon Oil Spill

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