Tetramethylammonium Hydroxide as a Reagent for Complex Mixture Analysis by Negative Ion Electrospray Ionization Mass Spectrometry

V.V. Lobodin (NHMFL, Chemistry); P. Juyal (Nalco Energy Services); A.M. McKenna (NHMFL, Chemistry); R.P. Rodgers (FSU, NHMFL, Chemistry); A.G. Marshall (FSU, NHMFL, Chemistry)

Results and Discussion

Ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) enables the direct characterization of complex mixtures without prior fractionation. High mass resolution can distinguish peaks separated by as little as 1.1 mDa) and high mass accuracy enables assignment of elemental compositions in mixtures that contain tens of thousands of individual components (crude oil). Negative electrospray ionization (ESI) is particularly useful for the speciation of the most acidic petroleum components that are implicated in oil production and processing problems. Here, we replace conventional ammonium hydroxide by tetramethylammonium hydroxide (TMAH, a much stronger base, with higher solubility in toluene) to more uniformly deprotonate acidic components of complex mixtures by negative ESI FT-ICR MS. The detailed compositional analysis of four crude oils (light to heavy, from different geographical locations) reveals that TMAH reagent accesses 1.5-6 times as many elemental compositions, spanning a much wider range of chemical classes than does NH_4OH (see Figuer 1). For example, TMAH reagent produces abundant negative electrosprayed ions from less acidic and neutral species that are in low abundance or absent with NH_4OH reagent. More important, the increased compositional coverage of TMAH modified solvent systems maintains, or even surpasses the compositional information for the most acidic species. The method is not limited to petroleum-derived materials and could be applied to the analysis of dissolved organic matter, coal, lipids, and other naturally occurring compositionally complex organic mixtures.

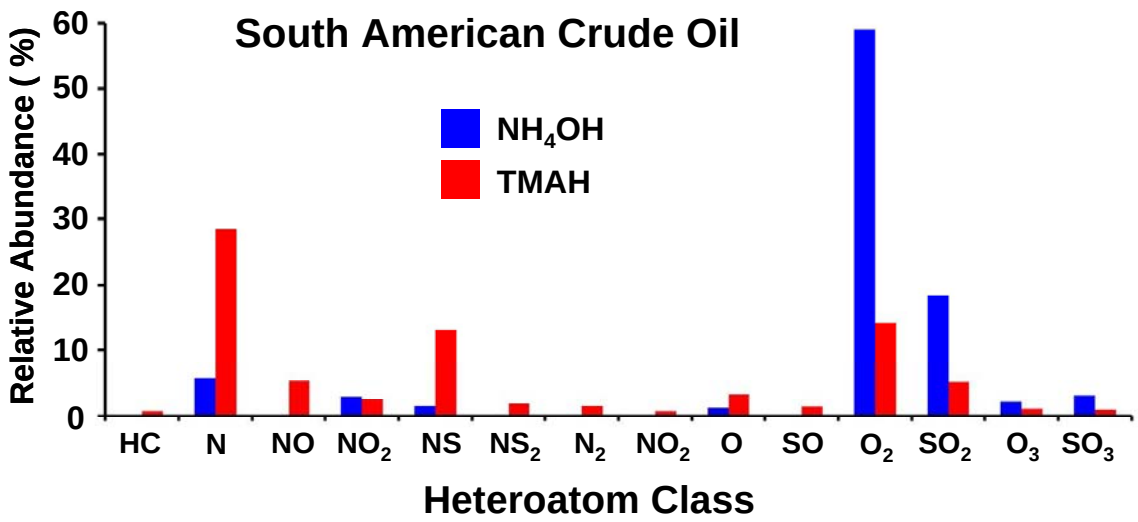

Figure 1. Heteroatom class distributions for the 14 most abundant classes from a South American crude oil analyzed by (-) ESI FT-ICR MS with NH_4OH (blue) and TMAH (red). The most acidic classes, O_2 and SO_2, are the most abundant with ammonium hydroxide, but are more than 3x lower in relative abundance with the TMAH modified solvent system, for which N_1 (pyrrolic nitrogen) species are the most abundant.

Acknowledgments

This work was supported by NSF Division of Materials Research through DMR 11-57490, BP/The Gulf of Mexico Research Initiative, the Florida State University Future Fuels Institute, Nalco (An Ecolab Company), and the State of Florida..

References

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