Selective Ionization of Dissolved Organic Nitrogen by Positive Ion Atmospheric Pressure Photoionization Coupled with Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

D. C. Podgorski (FSU, NHMFL, Chemistry), A.. M. McKenna (NHMFL, Chemistry), R. P. Rodgers (FSU, NHMFL, Chemistry), A. G. Marshall (FSU, NHMFL, Chemistry), and W. T. Cooper (FSU, Chemistry)

Results and Discussion

Dissolved organic nitrogen (DON) comprises a heterogeneous family of organic compounds that includes both well known biomolecules such as urea or amino acids as well as more complex, less characterized compounds such as humic and fulvic acids. Typically, DON represents only a small fraction of the total dissolved organic carbon pool and therefore presents inherent problems for chemical analysis and characterization. Here, we demonstrate that DON may be selectively ionized by atmospheric pressure photionization (APPI) and characterized at the molecular level by Fourier transform ion cyclotron resonance mass spectrometry. Unlike electrospray ionization (ESI), APPI ionizes polar and nonpolar compounds, and ionization efficiency is not determined by polarity. Both positive (APPI) and negative (ESI) ion mass spectral are needed to access the full range of elemental compositions (see **Figure 1**). APPI is tolerant to salts, due to the thermal treatment inherent to nebulization, and thus avoids salt-adduct formation that can complicate ESI mass spectra. Here, for dissolved organic matter from various aquatic environments, we selectively ionize DON species that are not efficiently ionized by other ionization techniques, and demonstrate significant signal to noise increase for nitrogen species by use of APPI relative to ESI.[1]

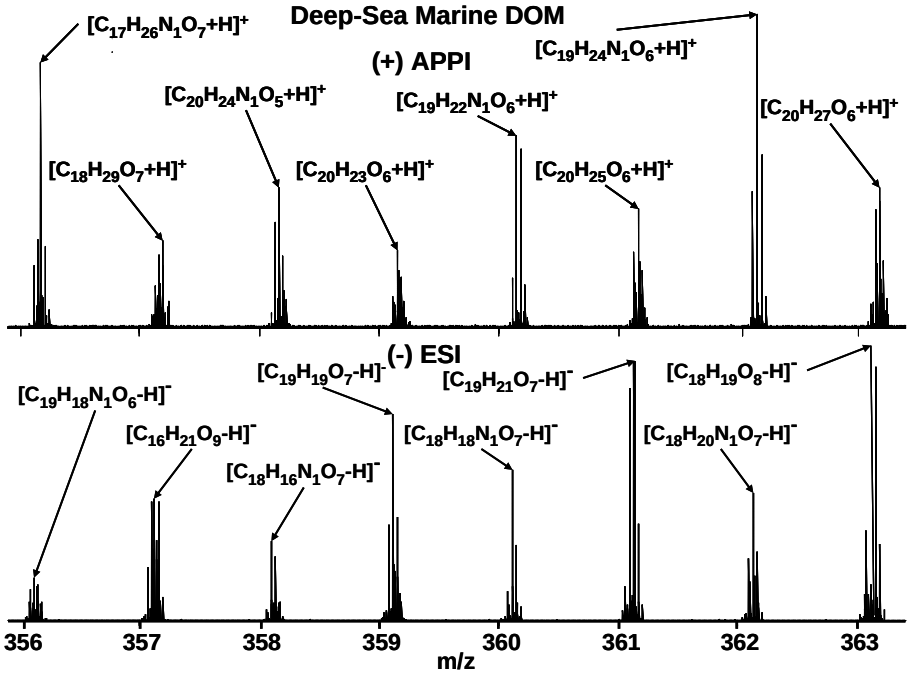

Figure 1. FT-ICR MS expanded mass spectral segments for deep-sea marine DOM produced by positive ion APPI (top) and negative ion ESI (bottom). For APPI, the most abundant ions have even nominal mass, e.g., $[C_cH_hN_1O_o + H]^+$. For ESI, the most abundant ions have odd nominal mass, e.g., $[C_cH_hO_o - H]^-$.

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References

[1] Podgorski, D. C., *et al.*, Anal. Chem., **84**, 5085-5090 (2012).