Ion Molecule Reaction H/D exchange as a Probe for Isomeric Fractionation in Chromatographically Separated Natural Organic Matter

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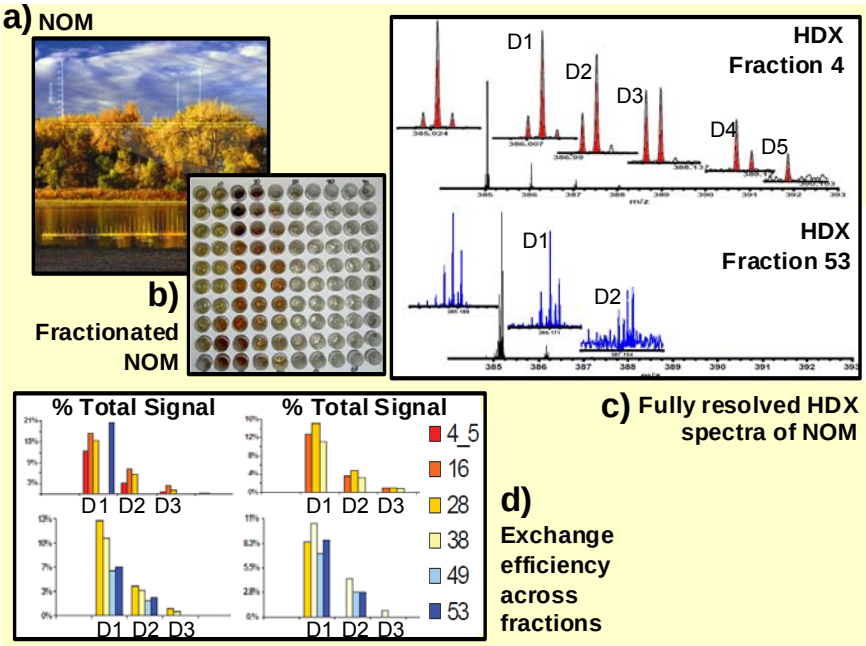
Introduction

High-resolution mass spectrometry disperses and resolves analyte ions with far greater peak capacity than any chromatographic technique. Unfortunately, even the highest-resolution mass spectrometer cannot separate isomers. For the characterization of complex mixtures, tandem chromatography and MS techniques must be developed that combine isomeric separation with detailed compositional characterization. To develop such techniques, a means of identifying isomeric separation is required. Hydrogen/Deuterium exchange (HDX) is an attractive means to distinguish isomers because the ability to exchange hydrogen(s) depends critically on structure.



Experimental

Suwannee River Fulvic Acid was fractionated through a phenyl column [(X-BridgeTM, (3.5µm, 4.6 x 150mm)] as previously described[1]. For solution HDX experiments, both spray-solvent components were deuterated (D_2O and ISP-d8). For in-cell, gas-phase HDX, isobars of interest were isolated through stored waveform inverse Fourier transform then exposed to ND_3 collision gas for 120s at ≤ 3 x 10^{-7} Torr. The NHMFL's custom-built 9.4 Tesla FT-ICR mass spectrometer was used for all experiments.

Results and Discussion

As shown in Figure 1, isobaric resolution is maintained. Such resolution had not been possible in previous HDX studies without recent advances in FT-ICR MS.[2-3] The data furthermore show that compounds with the same elemental compositions eluting in different fractions do not necessarily exchange the same total number of Hand do not have identical exchange efficiencies for any given exchange. Rather, late-eluting fractions and early-eluting fractions appear to have comparable exchange efficiencies; middle-eluting fractions, meanwhile, exchange with the highest efficiency.

Conclusions

The results encompass the first gas-phase H/D exchange results for fully resolved natural organic matter (NOM) isobars and the first direct evidence of isomeric separation of NOM through reversed-phase chromatography.

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