Analysis of Suwannee river fulvic acid (SRFA) with ESI-ICR/FTMS after fractionation with free-flow electrophoresis (FFE) and size exclusion chromatography (SEC)

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The level of intricacy in the analysis of large molecules and of mixtures can be classified according to their polydispersity and heterogeneity. The structures of complicated, but monodisperse, natural products and biopolymers are readily accessible by a combination of analytical methods, which primarily rely on NMR spectroscopy and mass spectrometry. Supramolecular structures, composed of (modified) biopolymers aligned in aggregates, which are supported and defined by weak interactions, require a more elaborate characterization, further fractionation studies for more sophisticated descripion. Consequently, the characterization and structural analysis of geopolymers, which feature a substantial extent of both polydispersity and molecular heterogeneity, is most demanding with respect to methodology and concepts. In an ongoing evolution, future high quality structural analyses of NOM/HS will have to provide a characterization of individual molecules and a description of the extent and mechanisms of their interactions. Although complementary organic structural spectroscopy of NOM creates data sets of high information density, adding extra dimensions of the analysis possibly simplify this condensed group of information. Free zone electrophoretic techniques allow a separation of NOM on the basis of their own chemical surface properties (charge) and configuration (size) under different solution conditions without interaction with an active phase such as in liquid chromatography. Also, size exclusion chromatography (SEC) is one of the most widely used techniques for the investigation of MWD of HS, enabling a fractionation based on size only.

The wealth of inherent multivariate profiling capabilities is of adequate potential and richness to fundamentally advance knowledge and understanding of NOM/HS. These extended applications provide alternative interpretations and their combination advocate molecular composition and structure information. We demonstrate the significance of the outlined complementary approaches (FFE and SEC combined with FT/MS and NMR) for the characterization of complex natural materials on the example of Suwannee river FA.