Fact or Artifact: The Representativeness of ESI-MS for Complex Natural Organic Mixtures

Stenson, A.C.; Novotny, N.R.; Capley, E.N. (University of South Alabama, Chemistry)

Introduction

Because mass spectrometers provide their own dispersion and resolution of analytes, electrospray ionization mass spectrometry (ESI-MS) has become a workhorse for the characterization of complex mixtures from aerosols to crude oil. Unfortunately, ESI mass spectra commonly contain multimers, adducts, and fragments. For the characterization of complex mixtures of unknown initial composition, this presents a significant concern. Mixed-multimer formation could potentially lead to results that bare no resemblance to the original mixture. Conversely, ESI-MS has continually reflected subtle differences between natural organic matter (NOM) mixtures that are in agreement with prediction or theory. Knowing the real limitations of the technique is therefore critical to avoiding both over-interpretation and unwarranted skepticism. Here, data were collected on four mass spectrometers under a battery of conditions.

Experimental

Quasi bottom-up approach: Two sets of experiments were conducted on mixtures of slightly more than 40 synthetic standards. The first set of experiments involved a battery of solution conditions on three different instruments to ascertain whether any condition produced spectra approaching NOM complexity and/or exhibiting NOM-typical mass spacing patterns. For the second set, the number of variables was reduced to allow for analysis of the extent to which spray solvent, solution age, and acid or base modifiers affected spectrum cleanliness and coverage.

Quasi top-down approach: 40 different nominal masses (from m/z 163 to 911) in a NOM spectrum were chosen for collision-induced dissociation (CID) to determine whether they dissociate as non-covalent adducts would.

Results and Discussion

Results indicate (1) under no conditions did simple mixtures rival the complexity of NOM, (2) unrepresentative peaks, when present, were generally of low relative abundance, (3) unrepresentative peaks were essentially insignificant under NOM-typical instrument settings which allowed for source induced dissociation of non-covalent adducts and (4) NOM do not fragment as non-covalent multimers would. However, the data also show that the formation of unrepresentative peaks cannot entirely be ruled out and must be taken into consideration during data interpretation.

Conclusions

Together the top-down and bottom-up data suggest that, although formation of unrepresentative ions is likely for simple mixtures, most of those ions appear to be susceptible to source induced dissociation and do not appear to form a significant fraction of observed NOM ions. However, because unrepresentative peaks cannot be ruled out completely, it is best to base compositional inferences on ions that appear under a number of complimentary instrument and/or solvent conditions and pair ESI-MS with data from different ionization sources, various prefractionation/isolation steps, and/or non-mass spectral data (e.g., NMR & fluorescence).

Acknowledgements

A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490, and the State of Florida. In addition, financial support was provided by NSF EAR-0848635, NSF CHE-1039944, NSF-EPSCoR 0091853-353, and the University of South Alabama. The authors thank Vanessa Jarvis, Eva V. Osilla, Dr. Jeremiah D. Tipton and Dr. Amy M. McKenna for assisting in data collection and providing detail for segments of this manuscript; Dr. Alan G. Marshall and the ICR staff at the National High Magnetic Field Laboratory for granting access to the high-resolution instruments; Dr. June Ayling for providing access to a low-resolution instrument; and Dr. David Stranz and Sierra Analytics for access to the Composer software used to calibrate SRFA data and obtain molecular formulae.