



High-field FT-ICR-MS and aromaticity equivalent approach for structural identification of water soluble organic compounds (WSOC)

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Organic aerosol (OA) makes up a large and often dominant fraction, (20 to 90%) of the submicron atmospheric particulate mass, and its effects are becoming increasingly important in determining climatic and health effects of atmospheric aerosols. Despite the abundance of OA, our understanding of the sources, formation processes and atmospheric properties of OA is limited. Atmospheric OA has both primary (directly emitted) and secondary (formed in the atmosphere from precursor gases) sources, which can be natural (e.g. vegetation) and/or anthropogenic (e.g. fossil-based vehicle exhaust or biomass burning). A significant fraction of OA contains as much as 20-70% of water soluble organic compounds (WSOC). The WSOC fraction is a very complex mixture of low volatility, polyfunctional aliphatic and aromatic compounds containing carboxyl, alcohol, carbonyl, sulfo, nitro, and other functionalities. This high degree of chemical complexity of atmospheric organics has inspired a number of sophisticated approaches that are capable of identifying and detecting a variety of different analytes in OA. Accordingly, one of the most challenging areas of atmospheric particulate matter (PM) analysis is to comprehend the molecular complexity of the OA, especially WSOC fraction, a significant component of atmospheric fine PM (PM_{2.5}). The sources of WSOC are not well understood, especially the relative contributions of primary vs. secondary organic aerosol. Therefore, the molecular characterization of WSOC is important because it allows gaining insight into aerosol sources and underlying mechanisms of secondary organic aerosols (SOA) formation and transformation. In this abstract, molecular characterization of WSOC was achieved using high-field mass spectrometry FT-ICR-MS and aromaticity equivalent approach. Aromaticity equivalent (X_c), defined recently as a new parameter calculated from the assigned molecular formulas (complementary to the aromaticity index [1]), is introduced to improve identification and characterization of aromatic and condensed aromatic compounds in WSOC [2]. We proposed threshold values of $X_c \geq 2.5000$ and $X_c \geq 2.7143$ as ambiguous minimum criteria for the presence of aromatic structure and condensed aromatic compounds, respectively. The advantage of employing this parameter is that X_c would have a constant value for each proposed core structure regardless the degree of alkylation, and thus visual representation and structural interpretations of the spectra become advantageous for characterizing and comparing complex samples. Diesel particulate matter (DPM) and two atmospheric aerosols collected in the industrial area affected by biomass burning events were used to study the applicability of the proposed criteria for the improved identification of aromatic and condensed aromatic structures in complex mixtures in the FT-ICR mass spectra.

References

- [1] Koch.BP, Dittmar.T. From mass to structure: an aromaticity index for high-resolution mass data of natural organic matter. *Rapid Commun. Mass Spectrom.* 2006, 20, 926-932
- [2] Yassine.MM, Harir.M, Dabek-Zlotorzynska.E, Schmitt-Kopplin.Ph. Structural characterization of organic aerosol using Fourier transform ion cyclotron resonance mass spectrometry: Aromaticity equivalent approach. *Rapid Commun. Mass Spectrom.* 2014. 28. 2445-2454