

Urban organic aerosols ultrafine particles compositions: a high-resolution mass spectrometry characterization

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Organics compounds represent the major fraction of atmospheric aerosol particles; a large part is still not well characterized. A detailed understanding of the sources, transformations processes and fates of organics aerosols is needed.

Investigating the chemical composition of fine and ultrafine particle matter can be expected by using electrospray ionization coupled with high-resolution linear ion trap Orbitrap™ (Thermo Corp.) mass spectrometer (ESI-HRMS). ESI-HRMS is an innovative, recent and powerful tool for describing the organic matter. Chemical and physical properties of organic aerosols are determined with ESI-HRMS by molecular composition. We present here the chemical composition of ultrafine aerosols particles collected on filters at an urban site in Grenoble, France, during winter and summer 2012.

Prior to the MS analysis, aerosols are sampled and segregated upon three sizes (<0.1 μm; 0.1 to 1 μm; 1 to 2.5 μm) using a DA-80 DIGITEL™ collector and a BGI High Volume Cascade Impactor. Firstly, chemical speciation is run on each sample to measure EC, OC, ions and metals. The water-soluble fraction is isolated using Accelerated Solvent Extractor (ASE 200 – Dionex) and diluted in acetonitrile before the ESI injection.

Orbitrap-HRMS provides a resolution of 100,000 at m/z 400, with a mass range 50 – 2000 amu. The ESI-HRMS is known as a “soft” ionization method, leading to very little fragmentation. Thus this technique is more used for the chemical characterization of individual molecules in complex mixtures of SOA. Acquisition is made for both positive and negative ionization mode.

For our moderately complex mixture (~ 2000 peaks), containing O, C, H, N, S and Na, unambiguous elemental formula assignments were established below 350 Da within 1 mDa using a custom computer software (Attributor v1.05) developed by F.R. Orthous-Daunay (2011) and described in Danger et al. (submitted). It is based on a suite of scripts that allow to evaluate the most probable attribution of a high resolution peak, based on its mass, the presence and relative intensity of isotopic peaks, as well as chemical rules (nitrogen rule, even electron ions, etc.) Using a Kendrick analysis (Hughey et al., 2001) based on the CH₂ and C₂H₄O pattern on the unambiguous attribution of most peaks below 350 Da as shown in figure 1, series of regularly spaced peaks were identified in the spectrum, and used to extend the

formula attribution toward higher masses. This extension into Kendrick series was also checked against isotopic patterns. Typical standard deviation of the Kendrick mass defect in any such identified series was lower than 0.5 mDa which ensures the proper attribution of all the members of a series, to within less than 1 mDa in the full mass range explored (i.e. 50-800 Da).

The identified elemental formulas are classified into elemental sub-groups referring to the CHONS composition. The obtained results show seasonal variation of chemical moieties and allow a comparison upon particle size. Finally, a comparison will be realized on ambient OA collected at an urban kerbside site (Grenoble, France) in the course of the MOCOPO .

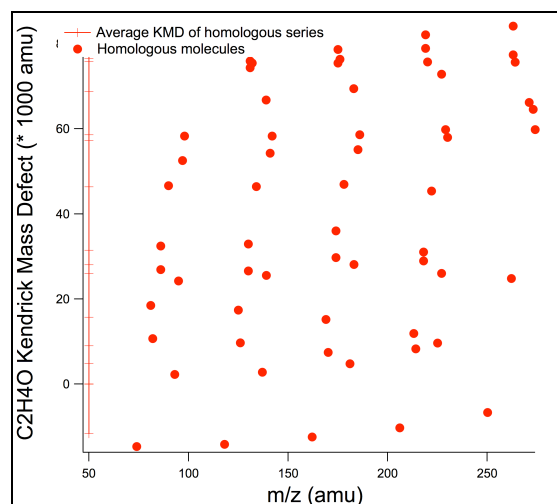


Figure 1. C₂H₄O Homologous series by ESI(+)-HRMS

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