

Online atmospheric pressure chemical ionization high resolution mass spectrometry (APCI-Orbitrap-MS²) for characterization of the SOA molecular composition

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The emission of volatile organic compounds (VOCs) into the atmosphere, irrespective of biogenic or anthropogenic origin, acts as a well-established precursor for the formation of secondary organic aerosol (SOA). Particularly a detailed knowledge of the molecular composition of SOA is essential for elucidation of formation mechanisms (Zhang, 2015).

Providing high sensitivity and selectivity towards single chemical compounds, mass spectrometry (MS) is the most commonly applied technique for the chemical analysis of atmospheric aerosol particles (Farmer, 2010). Online mass spectrometry techniques avoid potential artefacts associated with offline analysis methods, such as evaporation and chemical reactions during long sample collection and analysis time periods (Pratt and Prather, 2012). One of the major advantages of online mass spectrometry is the ability to examine chemical changes in atmospheric environments in short timescales within seconds.

However, condensed phase reactions between inorganic (nitrate, sulfate and ammonium) and organic aerosol constituents, lead to the formation of low volatile irreversible products like monoterpene- and isoprene-derived organosulfates, nitroxy organosulfates (Surratt et al., 2008) or organonitrates (Szmigielski, 2010). Due to the fact that these compounds consist of more than just C-, H-, and O-atoms, a high mass resolution is needed to determine the exact sum formula.

Furthermore another current research interest is the identification and correct determination of highly oxidized molecules (HOMs) which are able to contribute significantly to organic mass in tropospheric particles (Mutzel, 2015). Especially in the analysis of atmospheric aerosols at mass to charge ratios (m/z) above 300 amu several compounds at the same nominal mass are basically possible whereby a high mass resolving power is needed to separate between two compounds.

Here we present the first coupled APCI-Orbitrap-MS²-technique for the online determination of SOA particle phase. This approach combines the high mass resolution ($R=70.000$ at m/z 200) and accuracy (<2 ppm) of an QExactive Orbitrap mass analyser (Thermo Scientific, Germany), which enables the determination of the elemental composition by exact mass measurements, and the advantages of online measurement techniques.

In this work, a modified, commercial APCI-ion source is used for the investigation of SOA derived organic molecules produced in environmental chamber experiments. As a soft ionization technique APCI

provides information about the molecular mass by producing either $[M-H]^-$ or $[M+H]^+$ ions, depending on the polarity of the ion source. Additionally the QExactive mass spectrometer allows MS² experiments for further structural elucidation of SOA products.

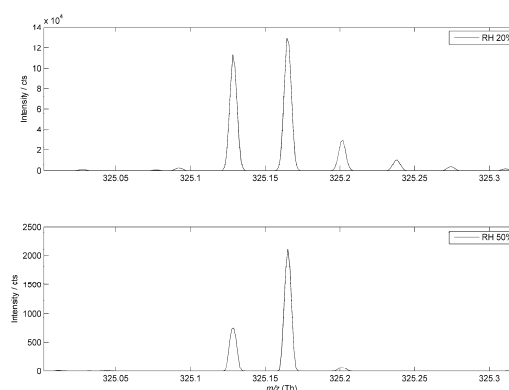


Figure 1. Comparison of the Dimer $C_{17}H_{26}O_6$ (m/z 325) measured with different relative humidity (RH) shows different molecular patterns.

First investigations were focussed on the influence of the water vapour concentration on the formation of α -pinene/ O_3 oxidation products in the mass range from m/z 300-450. Fig. 1 shows high resolution mass spectra of HOMs at m/z 325 whose structure is proposed by Zhang *et al.* (2015). The figure shows clearly a different molecular pattern which could only be observed with an appropriate mass resolution.

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