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

C. Zuth¹, S. Ockenfeld¹, A. L. Vogel², T. Hoffmann¹

¹Institute of Inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg-University of Mainz
²Laboratory for Environmental Chemistry & Laboratory for Atmospheric Chemistry, Paul Scherrer Institute, Villigen

Motivation

The organic fraction of atmospheric aerosols contains hundreds to thousands of species in a m/z range of 100-500 amu, frequently more than 16 compounds within 0.2 Daltons, clearly illustrating the necessity of high mass resolution techniques to investigate its chemical composition. The emission of volatile organic compounds (VOCs) into the atmosphere, a cross-section of biogenic or anthropogenic origin, acts as a well-established precursor for the formation of secondary organic aerosol (SOA). However, condensed phase reactions between inorganic (nitrate, sulfate and ammonium) and organic aerosol constituents lead to the formation of low volatile irreversibly products like monoterpene- and isoprene-derived organosulfates, nitroxy organosulfates, or organonitrates. The identification of these products as well as the correct determination of highly oxidized molecules (HRMVs) would benefit from this new technique.

Innovation

Here we show the first coupled APCI-Orbitrap-MS² technique for the online determination of SOA particle phase. As a soft ionization technique a modified, commercial APCI-source provides information about the molecular mass of aerosol compounds. Very little or no fragmentation is observed with this ionization, which simplifies the interpretation of mass spectra. This approach combines the high mass resolution (7000 @ m/z 200) and accuracy (< 2 ppm) of an Orbitrap mass spectrometer and the advantages of online measurement techniques.

Instrumental setup:

Experimental:

I Chamber experiments

- SOA was generated in the laboratory from α-pinene oxidation under dark conditions and two distinct relative humidities (RH).
- High Resolution Mass Spectra of two possible SOA dimers show different molecular patterns depending on the relative humidity.
- minor distribution at higher RH.
- molecular patterns of two possible SOA dimers changes by turning on the UV-Clamp.
- High Resolution Mass spectra changes to higher molecular masses and less oxidized molecules.

II APCI-Orbitrap-MS² Characterization

- Several atmospheric relevant VOC oxidation products were tested to assess the ionization.

Conclusion & Outlook

- First successful application of APCI-Orbitrap-MS² in chamber experiments for real-time analysis of submicron organic aerosol particles.
- Soft ionization technique shows the deprotonated molecular ions.
- Further experiments for calibration of the APCI-ion source.
- Intercomparison studies with other aerosol instruments like Aerosol Mass Spectrometry (AMS) to evaluate the obtained data.
- High-resolution spectra of NO₃⁻ / SO₄²⁻ mixed experiments with different monoterpene concentrations.

References: