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

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Motivation

The organic fraction of atmospheric aerosols contains hundreds to thousands of species in a *m/z* range of 100-500 and, frequently more than 10 compounds within 0.1 Dalton (Da), clearly illustrating the necessity of high mass resolution techniques to investigate its chemical composition[1]. 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)[2].

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, nitrooxy organosulfates[3] or organonitrates[4]. The identification of these products as well as the correct determination of highly oxidized molecules (HOMs)[5] 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-Ion 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 (70000 @ *m/z* 200) and accuracy (< 2 ppm) of an QExactive Orbitrap mass spectrometer and the advantages of online measurement techniques.

Experimental

Instrumental setup:

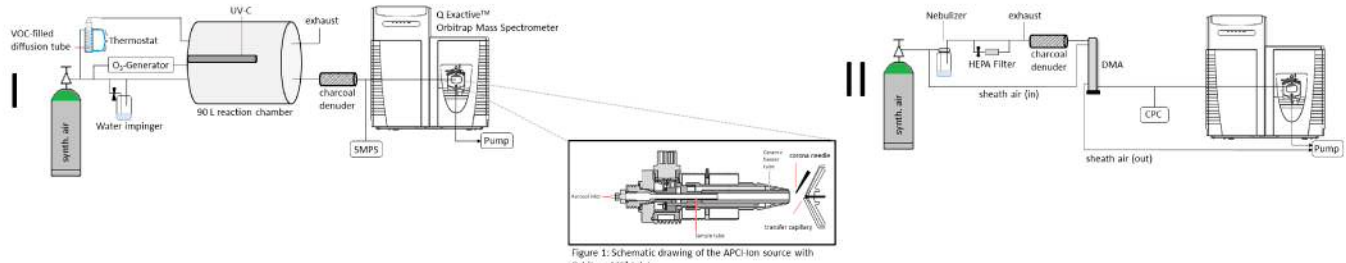


Figure 1: Schematic drawing of the APCI-Ion source with Orbitrap-MS² inlet.

I Chamber experiments

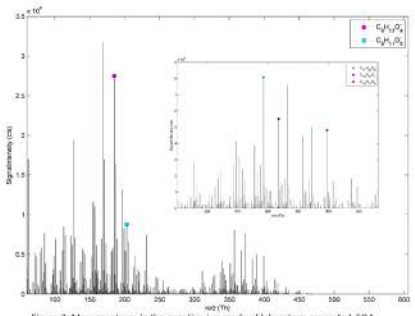


Figure 2: Mass spectrum in the negative ion mode of laboratory-generated SOA (background subtracted). The inset shows a detailed view of the "dimeric region". Colored dots show typical α-pinene oxidation products (magenta = pinic acid, cyan = MBTCA, green = $C_{17}H_{25}O_9^-$, blue = $C_{19}H_{29}O_9^-$, red = $C_{19}H_{27}O_9^-$).

- SOA was generated in the laboratory from α-pinene ozonolysis under dark conditions
- soft ionization process shows mainly the deprotonated molecular ions
- monomeric region in the range between *m/z* 140 and *m/z* 230 and dimeric oxidation products of α-pinene in the range between *m/z* 300 and *m/z* 450
- typical α-pinene oxidation products are observed in both regions

- SOA was generated in the laboratory from α-pinene ozonolysis 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

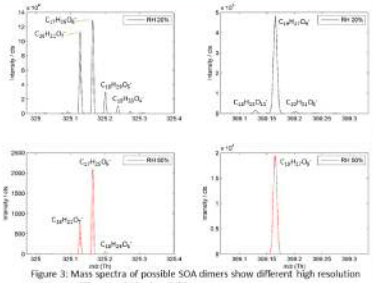


Figure 3: Mass spectra of possible SOA dimers show different high resolution pattern at different relative humidities.

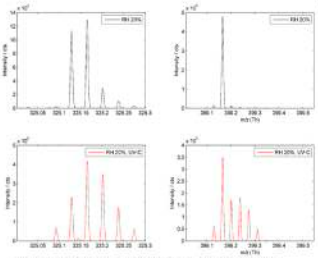


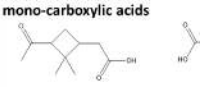
Figure 4: Mass spectra of possible SOA dimers show different high resolution pattern with UV-C lamp switched on/off.

- molecular pattern of two possible SOA dimers changes by turning on the UV-C lamp
- High Resolution Mass spectra changes to higher molecular masses and less oxidized molecules

II APCI-Orbitrap-MS² Characterization

several atmospherically relevant VOC-oxidation products were tested to assess the ionization

mono-carboxylic acids

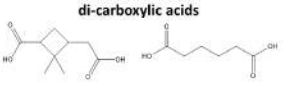


pinonic acid

***m/z* ([M-H]⁻) 183.1026 Th**

- Precursors are α-pinene, ß-pinene, 3-carene and cyclohexene
- Intermediate Volatile Organic Compounds (IVOC)

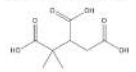
di-carboxylic acids



pinic acid — adipic acid

***m/z* ([M-H]⁻) 185.0819 Th** — ***m/z* ([M-H]⁻) 145.0506 Th**

tri-carboxylic acids



3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)[6]

***m/z* ([M-H]⁻) 203.0561 Th**

- Precursors are α-pinene and β-pinene
- MBTCA is considered as a SOA-aging marker
- O/C ratio > 0.7
- Low Volatile Organic Compounds (LVOC)

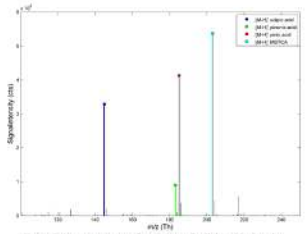


Figure 5: Mass spectrum of a mixture of adipic acid, pinonic acid, pinic acid and MBTCA aerosol at 10 nm particle diameter in the negative ionization mode.

- laboratory aerosol is generated by nebulization of a methanol solution of 4 analytical standards
- Mass Spectrum shows no significant fragmentation
- deprotonated quasi-molecular ions show the major signal for each compound ([M-H]⁻)

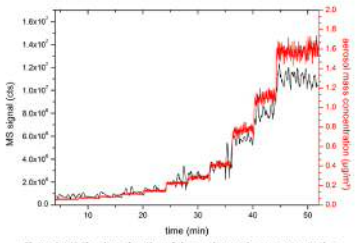


Figure 6: MS Signal as a function of time and aerosol mass concentration for the analysis of MBTCA aerosol at 100 nm particle diameter.

- the APCI-Orbitrap-MS² setup enables the analysis of submicron aerosol particles in real-time
- the aesosol mass delivered to the ion source was varied by adjusting the flow rate through a HEPA filter
- changing aerosol mass concentrations induce immediate response in MS signal
- limits of detection for carboxylic acids in aerosol particles in ng/m³ range

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 NOx / SO_2 mixed experiments with different monoterpene concentrations

References:

[1] Nozière *et al.*, **2015**, *Chem. Rev.*, 115(10), 3919-3983.
[2] Zhang *et al.*, **2015**, *PNAS*, 112, 14168-14173
[3] Surratt *et al.*, **2008**, *J.Phys.Chem. A*, 112, 8345-8378
[4] Szmigielski *et al.*, **2010**, *Atmospheric Research*, 98, 183-189
[5] Mutzel *et al.*, **2015**, *Environ. Sci. Technol.*, 49, 7754-7761
[6] Szmigielski et al., **2007**, *Geophys. Res. Lett.*, 34, L24811