Molecular Analysis of Aerosol Compositions in CLOUD-Chamber Experiments using UHPLC-Orbitrap-MS

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Various Oxidation products of monoterpenes and isoprene have an important influence on nucleation, the formation of Secondary Organic Aerosol (SOA) particles and cloud condensation nuclei (CCN), which affect global climate and human health. A detailed knowledge of the SOA molecular composition is crucial for its characterization and elucidation of formation mechanisms. Here we present the first ultrahigh performance liquid chromatography coupled to electrospray ionization ultrahigh resolution (Orbitrap) mass spectrometry (UHPLC/ESI-UHRMS) data based on filter sampling for precisely controlled particle formation experiments performed at the CLOUD (Cosmics Leaving Outdoor Droplets) chamber at CERN (European Organisation for Nuclear Research).

The experiments were focussed on pure biogenic nucleation events with oxidation products of alpha-pinene, delta-3-carene, isoprene as well as mixed runs with sulfuric acid vapour, NO_x and ammonia. The data were obtained during the CLOUD 10 campaign between September and December 2015.

UHRMS offers new possibilities to characterize the complexity of atmospheric organic samples due to its ability to assign molecular formulas to the majority of the peaks measured in the sample. The measurements were performed in the mass range *m/z* 80-800 with a mass resolution of R=70.000 at *m/z* 200 and a mass tolerance of 2 ppm. However, even at higher molecular masses the high accuracy coupled with high resolution allows to determine unambiguous elemental formulas for each ion peak due to further data processing.

The soft ionization technique results in the formation of ions with very little or no fragmentation and offers the advantage to perform MS^2-experiments for structural elucidation. The coupling to UHPLC enables chromatographic separation of isobaric organic compounds, which generates additional information to other mass spectrometric techniques used at the chamber. In this case the retention time of the compounds act as a third dimension in addition to the intensity and the exact molecular mass.

Several data filtering approaches, e.g. restrictions for the number of possible elements assumed to be present in the molecule (C, H, O, N and S), analysis of isotopic patterns, double bond equivalent checks, reasonable oxygen to hydrogen and oxygen to carbon ratios, etc. reduce the number of matching formulas, which increase exponentially with the mass.

Additional insights into the sources and compositions of SOA are provided by various visualization methods for the large UHRMS data sets. Mass defect plots, van Krevelen Diagrams and plots describing the carbon oxidation state are given here as an example.

A special focus lies on the detection and molecular composition of highly oxidized compounds, often referred to as extremely low-volatile organic compounds (ELVOCs) (Ehn *et al*., 2014), highly oxidized Organosulfates (HOOS) (Mutzel *et al*., 2015) and nitrated organic species in the particle phase. For this reason the data sets were compared to the complementary Filter Inlet for Gases and Aerosols (FIGAERO) (Lopez-Hilfiker *et al.*, 2014) coupled to a chemical ionization time of flight mass spectrometer to resolve the organic species related to particle growth.

Ehn, M. *et al*. (2014) *Nature.* **506**, 476-479.

Mutzel, A., Poulain, L., Berndt, T., Iinuma, Y., Rodigast, M., Böge, O., Richters, S., Spindler, G., Sipilä, M., Jokinen, T., Kulmala, M., and Herrmann, H. (2015) *Environ. Sci. Technol.* **49**, 7754-7761.

Lopez-Hilfiker, F.D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T.F., Lutz, A., Hallquist, M., Worsnop, D.R. and Thornton, J.A. (2014) *Atmos. Meas. Tech.* **7**, 983-1001.