Development of an Online Extractive Electrospray Ionization Time of Flight Mass Spectrometer (EESI-TOF): Application to Atmospheric Aerosol

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Thermal desorption of aerosol components for analysis is typical in most online aerosol sampling instruments (e.g. AMS, ATOFMS, SPLAT, PALMS). Most single particle instruments utilize simultaneous laser desorption/ionization, which is not quantitative due to matrix effects, while quantitative approaches like the AMS cause extensive thermal decomposition and fragmentation due to the high temperatures and hard ionization techniques used. While recent developments in semi-continuous measurements coupled to GC or soft ionization techniques like CIMS (e.g. TAG, SV-TAG, FIGAERO) have provided very useful tracer analysis on the ground and chambers, thermal decomposition during desorption even at low temperatures significantly changes measured aerosol composition. Key molecular information is lost, hindering mechanism development and source apportionment. Therefore there is a fundamental need in the atmospheric chemistry community for online, rapid response chemical characterization of atmospheric aerosol without artifacts from thermal decomposition.

To fill this gap in the measurement capabilities of the community, we describe the development of an online extractive electrospray time-of-flight mass spectrometer (EESI-TOF) for fast molecular analysis of aerosol organics without fragmentation or thermal desorption. This instrument couples an EESI inlet, recently developed at PSI, to a robust, commercially available high-resolution time of flight mass spectrometer. Briefly, the extractive electrospray instrument operating principle involves the collision of atmospheric aerosol with charged electrospray droplets. The soluble components are extracted into the electrospray droplet, and as the solvent from the electrospray evaporates, ion ejection by the coulomb explosion mechanism results in gas phase ions formed from the extracted aerosol. Therefore aerosol are ionized rapidly, and transferred into the gas phase without any need for heating.

The EESI-TOF provides rapid response (1Hz) measurements of highly oxidized organic species and oligomers with individual compound detection limits as low as 1 ng m⁻³ in 5 seconds, allowing for the simultaneous retrieval of molecular compositions for hundreds of compounds that comprise organic aerosol at high time resolution. Figure 1 shows an example of the level of detail this single instrument provides. An example mass spectrum collected at 1 Hz of 5 µg m⁻³ of SOA from the reaction of α-pinene and ozone yields a suite of over 500 individual molecules (150 to 500+ Th) which are detected by the EESI-TOF with excellent signal to noise even for oligomeric species which are clearly identifiable in the mass spectrum.

We present the detailed characterization of the EESI-TOF instrument and its application to atmospheric aerosol, both from chambers and ambient measurements. We discuss the instrument performance in the context of current aerosol measurement shortfalls, and potential applications of the instrument to the chemical speciation of organic aerosol at atmospherically relevant conditions.

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