Investigation of SOA from Anthropogenic Precursors using online Extractive Electrospray Ionization Mass Spectrometry

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Keywords: Anthropogenic SOA, PAM, EESI-TOF
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Secondary organic aerosol (SOA) is formed by the oxidation of gaseous precursors and constitutes a large fraction of the global submicron aerosol. Quantifying the contribution of individual sources to the total SOA requires the determination of SOA yields from individual precursors and/or identification of source-related signatures in the generated SOA. SOA formation has traditionally been investigated by the oxidation of atmospherically-relevant precursors under controlled conditions in smog chambers. However, these experiments must typically be operated in batch mode, making the exploration of a complex reaction space extremely time-consuming. Further, existing online instrumentation relies on thermal desorption and/or hard ionization techniques, resulting in extensive decomposition and/or fragmentation, thus destroying the detailed chemical signatures needed to link SOA to its source.

Here we investigate SOA formation from a set of nine compounds related to major anthropogenic emissions sources, including wood burning (phenol, naphthalene, syringol, guiacol), vehicle emissions (benzene, toluene), and cooking (decadienal, nonanal, sesquiterpenes), as well as the biogenic molecule alpha-pinene. These molecules have been identified as likely SOA precursors in recent emissions studies (e.g. Bruns et al., submitted). SOA is generated using a potential aerosol mass (PAM) flow reactor, which uses higher-than-ambient concentrations of OH radicals to simulate several days of atmospheric aging on an experimental timescale of approximately 90 s. The rapid response of the PAM enables exploration of a complex reaction space, including the effects of precursor concentration, VOC/NO_x ratios, and relative humidity on SOA formation.

Gas and particle composition was monitored using a proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS), a high resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS), and an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF) that was recently developed at PSI. The EESI-TOF provides highly time-resolved mass spectra of the particle phase using a soft ionization source with no thermal desorption step. This allows online measurement of the chemical composition without thermal decomposition or fragmentation.

Figure 1 shows a sample time series of EESI-TOF measurements of 8 selected ions measured during the photooxidation of toluene in the presence of increasing amounts of NO_x. The top panel shows four C7 organonitrates ($C_7H_9NO_x$), while the bottom panel shows four C7 oxygenates ($C_7H_{10}O_x$), all measured as sodium adducts. Time periods where the concentration drops to near-zero correspond to instrument blanks. As expected, the concentration of organonitrates increases with increasing NO_x, while a slight decrease of the oxygenates is observed.

We will present concentration-dependent SOA yield curves determined as a function of VOC/NO_x ratio, relative humidity, and OH exposure. EESI-TOF spectra will be used to assess proposed reaction mechanisms and identify potential tracers for source apportionment. The PAM oxidation results will be compared to selected smog chamber experiments to assess the similarity of PAM and chamber oxidation mechanisms.
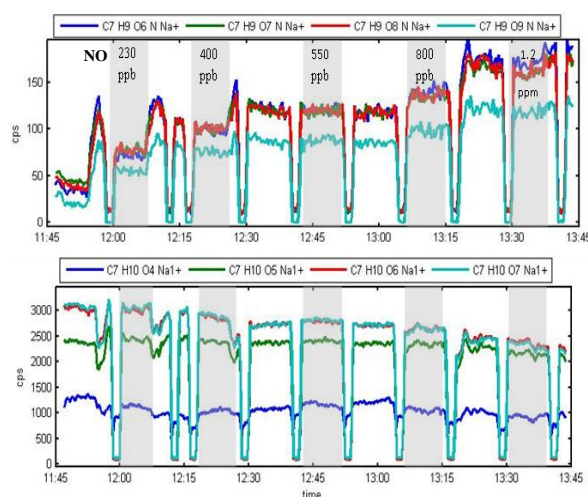

Figure 1. EESI-TOF time series of selected organonitrate (top) and oxygenate (bottom) ions generated by PAM oxidation of toluene in the presence of increasing NO_x.

Bruns, E. A., et al (submitted), Nature Sci. Rep.