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Volatility Measurements of Individual Components in Organic Aerosol Mixtures

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Primary and secondary organic aerosols (POA and SOA) comprise anywhere from 20% to 90% of atmospheric particulate matter. As they age in the atmosphere, POA and SOA undergo transformations through atmospheric multi-phase reaction chemistry such as oxidation, fragmentation, oligomerization, gas-to-particle partitioning, and cloud processing, which modify their composition and eventually blur original identity of aged organic aerosol (OA). Quantitative assessment of gas-particle equilibrium of OA components is critical to understand formation, growth, distribution, and evolution of the OA composition in the atmosphere. In this work, we present a novel ambient pressure measurement platform developed and tested for untargeted screening of components of complex OA mixtures, followed by targeted chemical speciation of components with identified chemical composition, and assessment of their physicochemical properties such as vapor pressure and heats of sublimation. Presented method employes temperature programmed desorption (TPD) experiments coupled to 'direct analysis in real time' (DART) ionization technique and high-resolution mass spectrometry (HRMS).

We demonstrate successful applications of the TPD-DART-HRMS platform for analysis of selected standards, i.e. organic compounds with known ambient vapor pressure and apparent heat of sublimation, which showed excellent agreement of our experimental results with the literature tabulated values. We extend these experiments to interrogate individual organic components in complex samples of SOA generated in the laboratory-controlled ozonolysis of monoterpenes. Obtained results indicate very promising applicability of the reported TPD-DART-HRMS method for untargeted analysis of organic molecules in OA and other environmental mixtures, enabling rapid detection and quantification of organic pollutants in the real-world condensed-phase samples with no sample preparation.