

Extractive electrospray ionisation: A novel mass spectrometry technique for the online characterisation of organic aerosol composition and reactivity

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Organic compounds are often the dominant fraction of tropospheric aerosol. Despite this, our understanding of the composition of organic aerosol is limited. A lack of detailed knowledge of the chemical composition of aerosols limits our understanding of their effect on climate and air quality.

We present a new technique for online measurement of the compounds present in organic aerosol: Extractive Electrospray Ionization (EESI) coupled to Mass Spectrometry (MS). In this method, a plume of charged solvent droplets is generated using an Electrospray Ionisation source. Aerosol particles are directed into this spray and particle-into-droplet extraction occurs, dissolving the soluble aerosol components. The volatile solvent evaporates and gas-phase aerosol analyte ions are formed and sampled at the MS inlet (Figure 1). We present here a custom-designed EESI source which has been designed and optimized to interface with a commercial Ultra-High Resolution Mass Spectrometer.

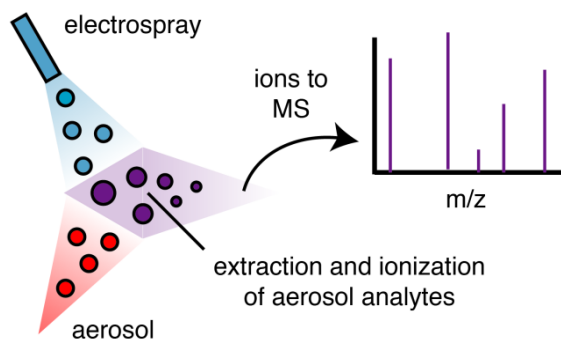


Figure 1: Illustration of the EESI-MS principle applied to organic aerosols.

EESI-MS offers a number of advantages: The online ionization mechanism provides composition information on aerosols in flow-tube and chamber studies with a time resolution of seconds, without the potentially large sampling artefacts introduced by collecting aerosols onto substrates for offline analysis. The ionization process produces molecular ions with minimal fragmentation, which greatly aids the interpretation of spectra for complex mixtures.

We have demonstrated that the MS ion signal scales linearly with particle mass concentration in the range tested and is independent of particle diameter and liquid water content, suggesting that the entire particle bulk is extracted for analysis. High sensitivity for aerosols composed of oxygenated organic compounds is achieved. For example, tartaric acid aerosol can be

detected in the sub- $\mu\text{g}/\text{m}^3$ range, with a dynamic range of about 3.5 orders of magnitude, using tandem MS experiments¹.

EESI was also used to understand the chemical mechanisms of reactions occurring in the particle phase. These are increasingly being recognized as making an important contribution to observed organic aerosol composition. Measurements of oleic acid aerosol ($20\mu\text{g}/\text{m}^3$) after ozonolysis reveal the formation of a variety of oxidation products in good agreement with previous offline studies. Time-resolved measurements of the same system reveal the growth of oligomers as the reaction time between aerosol and ozone is increased. The average molecular weight and oxygen:carbon ratio of these oligomers increase over time (Figure 2), which has implications for particle viscosity, hygroscopicity and phase.

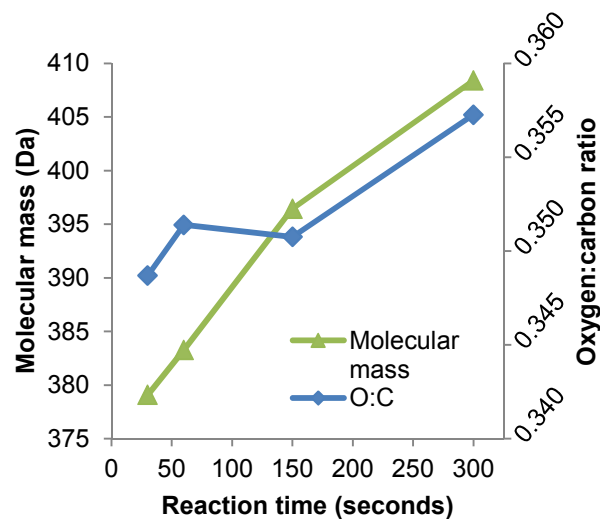


Figure 2: Time-resolved EESI-MS measurements of oligomers formed during oleic acid ozonolysis reveal that on average they become heavier and more oxygenated at longer reaction times.

Future work will study the product-resolved kinetics of aerosol-phase chemistry at a molecular level and implement a simple model to obtain rate constants for oligomer formation and other reactions in particles. This will allow us to assess their importance in influencing the chemical composition of aerosols.

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[1] Gallimore, P.J. and Kalberer, M. (submitted).