

## **Thermal Desorption Chemical Ionization Mass Spectrometry (TDCIMS) for organic nanoparticle chemical composition**

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Significant progress has been made in the past year in developing the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) into a quantitative tool for measuring the composition of secondary organic compounds on freshly nucleated nanoparticles. The TDCIMS technique is, currently, the only one that can measure the molecular composition of sub-20 nm diameter particles in near real-time. It does this by charging and, optionally, size selecting particles and then collecting these by electrostatic deposition on a metal filament. Once a sufficient mass of particles is collected the filament is transferred into the chemical ionization region of a mass spectrometer where it is resistively heated to evaporate the deposited particles. The desorbed molecules are then chemically ionized by reactions with  $\text{H}_2\text{O}^+(\text{H}_2\text{O})_n$  and  $\text{O}_2^-(\text{H}_2\text{O})_m$  where  $n$  and  $m$  are the range of 1 - 6. Once ionized, the species are first declustered in a drift cell and then mass analyzed using a triple quadrupole mass spectrometer (Extrel Corp.).

Activities in the past year have included studies of the chemical ionization process itself, which converts neutral species desorbed from particles into ions for mass analysis. The data show that the ion signal is proportional to analyte concentration as long as the chemical reagent is present in sufficient quantities, otherwise then the signal is degraded by competition with co-existing compounds. This fundamental study shows that, under conditions in which the reagent ions are of the same concentration as the neutral reactant compounds, the ion signal derived from a sample is dependent on the quantity and reactivity of the other compounds desorbed from the sample.

Another important accomplishment in the past year has been the successful demonstration of a technique for gradually desorbing compounds from the collection filament based on their volatility. This temperature programmed thermal desorption scheme is demonstrated in the figure below using a 100 pg sample of methylglyoxal. Methylglyoxal exists primarily as a monomer in dilute aqueous solution, but as it becomes more concentrated it will start to form oligomers. Presently there is speculation, based on laboratory experiments, that similar oligomers could comprise a significant amount of the non-volatile mass of organic atmospheric aerosol. In the figure below, a 100 pg sample of methylglyoxal is placed on the TDCIMS filament, and then slowly desorbed by resistively heating the filament. As the plot shows, the compound existed on the filament in two states: one which evaporated off at room temperature, and one that desorbed once the electrical current that is used to heat the filament is applied. The first state is probably the aqueous solution, whereas the second is a non-volatile oligomer that formed when the water evaporated from the sample. This result, while preliminary, confirm that a temperature programmed approach can be useful discriminating organics in particles. Future plans for the TDCIMS instrument include its deployment to the T1 site for MIRAGE-Mex.

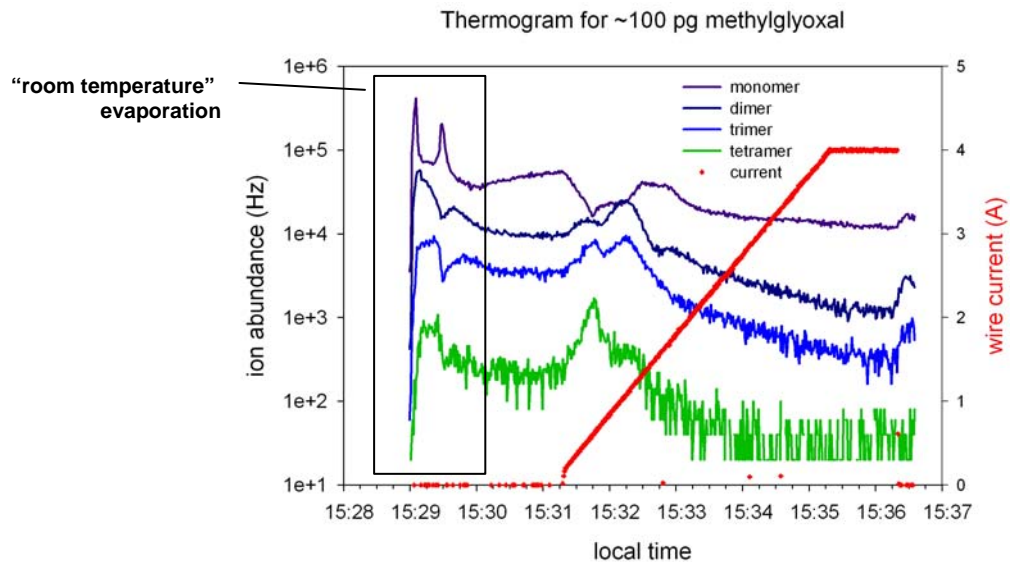


Figure: A plot of the abundance of methylglyoxal from a 100 pg sample applied to the collection filament of the TDCIMS. Wire current is directly proportional to filament temperature (ca. 100°C per amp of current).