

Towards a Molecular-Level Understanding of Organic Aerosol Evolution Using a Field-Deployable High Resolution Time-of-Flight Chemical Ionization Mass Spectrometer

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Summary

Atmospheric aerosols affect climate and human health, but their source and chemical evolution is poorly understood. Organic aerosols (OA) constitute a major fraction of submicron atmospheric aerosols and are either emitted directly from the source (primary organic aerosol, POA) or formed from oxidation of precursor organic gases in the atmosphere (called secondary organic aerosols, SOA),¹ which is often a major fraction of OA.² Despite this progress, SOA formation mechanisms and dominance in atmospheric aerosols are poorly simulated by models. In collaboration with Aerodyne Research Inc., the UW group has been developing a new instrument to measure a suite of multifunctional organic compounds in both the gas and particle phases simultaneously. Here I present recent laboratory and field results obtained using this new instrument. We investigated the SOA yields, formation, reaction mechanisms and products, and gas-particle partitioning of the products from photo-oxidation of several alkanes in the Caltech environmental chamber. Previous smog-chamber studies^{3,4} have shown that the oxidation of alkanes has a high SOA yield and can produce highly oxygenated SOA. We also took part in a recent field study to examine wintertime urban outflow in the UK, known as "Aeroflo/Clearflo" which occurred January – February, 2012. Preliminary data from that campaign are shown here and discussed in a breakout session.

New Instrumentation

MOVI-HRToF-CIMS Technique

- Pre-concentration and gas-particle separation using inertial impaction
- Temperature programmed desorption for volatility information
- Chemical ionization high-resolution time of flight mass spectrometry

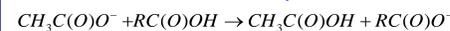
Micro-Orifice Volatilization Impactor⁵

100 nozzles, 150 μm diameter; Cutpoint (d_{50}): 0.13 μm ; Flow: 10 L/min, $\Delta P = 15\%$

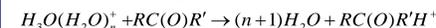
Thermally isolated impaction surface; surface and body temperature controlled to within +/- 1K

Chemical Ionization

Proton abstraction – selectively reacts with acids⁶



Proton transfer – general ionization scheme



High Resolution Time-of-Flight Mass Spectrometer

Similar to the high resolution Aerodyne-AMS⁷, but with an atmospheric pressure interface

Mass accuracy from manufacturer ~ 20 ppm

Mass resolving power ($m/\Delta m_{\text{FWHM}}$) > 3500

High sensitivity

– detection limits at sub ng/m^3 for particle phase compounds at 10 min sampling

– detection limits at sub pptv ($<10^9 \text{ cm}^{-3}$) for gas phase compounds in 10 min average

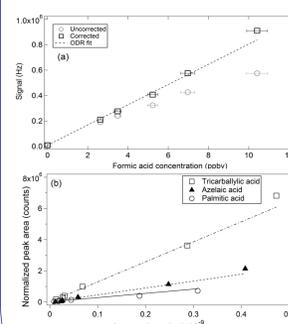
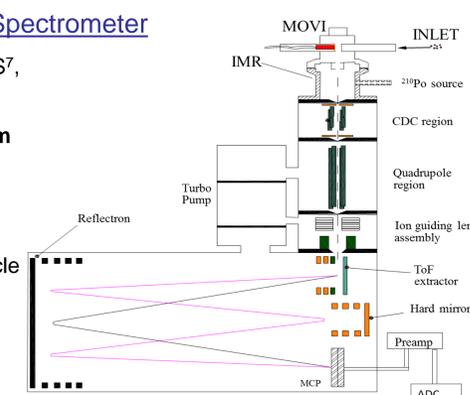
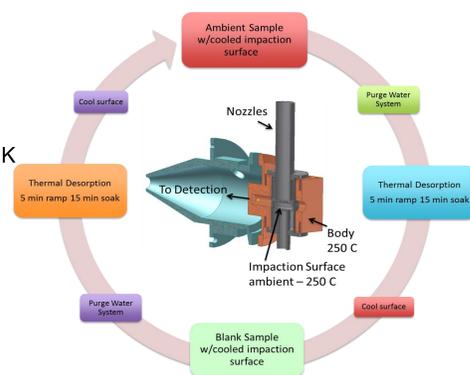


Fig. 1: Instrument response (ion count rate) for different amounts of gas and particle-phase carboxylic acids.

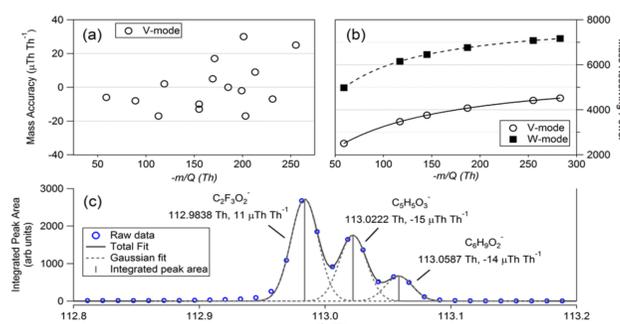


Fig. 2: Mass accuracy based on known m/Q exact masses compared to predicted (a), mass resolving power as a function of m/Q (b), and an example ion resolution and composition assignment (c).

Dodecane Low- NO_x 18hr Oxidation

- Experiments used 28 m^3 Caltech chambers
- Oxidation time scales of 18 and 36 hr
- Low and high- NO_x conditions, using $\text{H}_2\text{O}_2 + \text{h}\nu$ and $\text{HONO} + \text{h}\nu$ as OH source, respectively
- Neutralized ammonium sulfate seed aerosol
- Dry conditions, $\text{RH} < 7\%$ and $T = \text{ambient}$
- SOA and OH maintained at ambient levels

Mass Spectra – Positive Mode

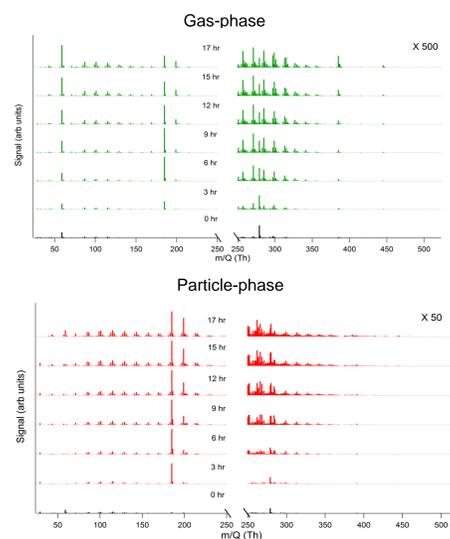


Fig. 3 (above): SOA mass concentration and fractional yield during the 18hr oxidation of Dodecane under Low- NO_x conditions. SOA mass concentration reached $25 \mu\text{g m}^{-3}$ by the end of the 18 hr oxidation. The maximum fractional yield is approximately 0.12. OH concentrations were $2 \times 10^6 \text{ molec cm}^{-3}$.

Fig. 4: Evolution of mass spectra in gas and particle-phases as a function of experiment time are presented here. Note the split in the mass axis and the signal on the right axis are multiplied by a factor of 500 and 50 relative to the left axis

Oxygenated products up to 450 Th are detected. There are differences between gas and particle-phase products, but the major products, 185 Th, 199 Th, and 203 Th are observed in both phases. The distribution and molecular composition of products evolves over 18hr, suggesting multiple generations arise from functionalization and fragmentation

Product Formation and Evolution

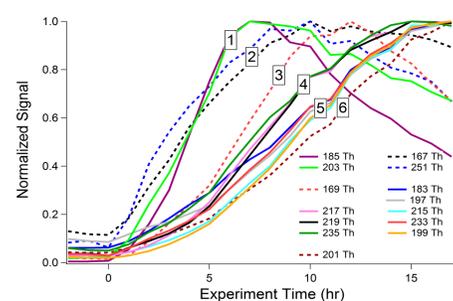


Fig. 5: Unit mass resolution time traces of a few products showing their evolution during the experiment. Six different types of profiles were identified probably corresponding to a mix of different generations of products.

High-Resolution Analysis "Fragmentation vs Functionalization"

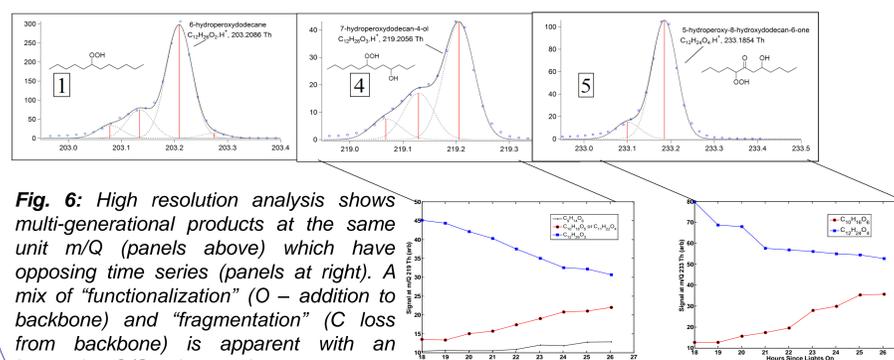


Fig. 6: High resolution analysis shows multi-generational products at the same unit m/Q (panels above) which have opposing time series (panels at right). A mix of "functionalization" (O – addition to backbone) and "fragmentation" (C loss from backbone) is apparent with an increasing O/C ratio as aging progresses.

Field Measurements: Aeroflo/Clearflo U.K.



Fig. 7 The Aeroflo field site was located ~45 km ESE of London in Kent (Detling). The area is rural and the meteorology during the campaign provided a range of source regions, air mass ages, temperature, and precipitation. The MOVI-HRToF-CIMS operated nearly continuously from January 22 – February 15.

DOE-ASR funded Aeroflo – an aerosol focused augmentation of the U.K. Clearflo field study of urban air quality and outflow in the U.K. A multi-institution team deployed a state-of-the-art suite of in-situ and remote sensing instrumentation to study the sources and evolution of aerosol downwind of London and the European Continent from January 10 – February 15, 2012.

Preliminary Results: MOVI-HR-ToF-CIMS Time Series

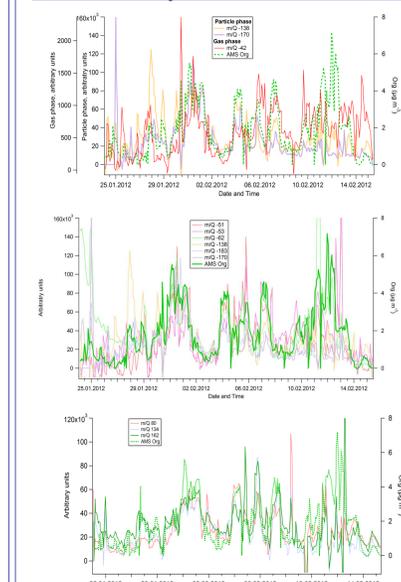


Figure 8. The three panels at left show a very small subset of ion signal time series recorded by the MOVI-HR-ToF-CIMS including gas and particle components detected using the acetate reagent ion (top and middle), and proton-transfer by $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ clusters.

In the top panel, two ions (m/Q 138 and 170) detected analyzing the particle phase showed significant variations over the campaign that were fairly well correlated with AMS total organic aerosol mass. These ions also correlated well with that at m/Q 42 detected almost entirely in the gas-phase corresponding to isocyanic acid (HNCO), a biofuel combustion tracer. The ability to simultaneously monitor gas and particle phase composition with one instrument enhances the ability for robust source identification.

The middle and bottom panels illustrate that there are a number of ions detected in the particle phase that correlate well with AMS total organic aerosol mass loading (many not shown). Statistical techniques are currently being used to decompose these multidimensional data into classes for a detailed source apportionment of organic aerosol in this study.

High-Resolution Analysis of m/Q 138 During Sampling and Desorption

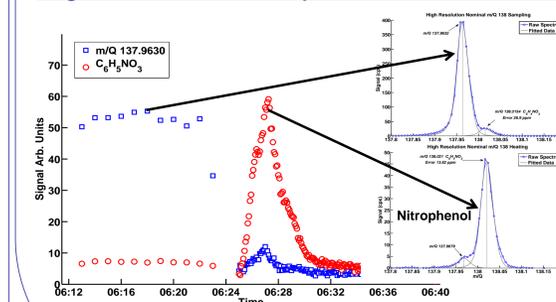


Fig. 9 As a final demonstration of the capabilities of the instrument, at left is plotted a high-resolution time series of ion signal with unit m/Q of 138 (see Fig. 8 above). Two different ions compose the signal at this m/Q . During sampling, the ion at 137.96 Th dominates the signal. During a temperature-programmed desorption (6:25AM), the ion signal becomes dominated by that corresponding to a nitrophenol. This finding is consistent with the particle signal of m/Q 138 being correlated with a biofuel combustion tracer.

Conclusions

Dodecane oxidation under low- NO_x conditions shows formation of numerous highly oxygenated products in gas and particle-phases. The MOVI-HRToF-CIMS is able to resolve differences in the time evolution of multigenerational products that contribute to SOA. Future analyses will address functionalization vs. fragmentation and volatility information obtained with MOVI (not shown). In addition, the MOVI-HRToF-CIMS successfully measured a large suite of compounds in the gas and particle phases during the Aeroflo deployment that will likely give unprecedented information on organic aerosol sources and evolution.

Acknowledgements / References

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