Molecular-level Analysis of Size Resolved Secondary Organic Aerosol (SOA) Samples from CALNEX Bakersfield Using High Resolution Mass Spectrometry

Rachel Sellon, Alex Laskin, Julia Laskin, Allen Goldstein
University of California Berkeley and Pacific Northwest National Laboratory

Introduction

- Samples were collected during CalNex 2010 in Bakersfield California.
- It has been estimated that a large fraction (>30%) of unidentified organic matter in SOA can be attributed to humic like substances (HULIS) and oligomers.[1]
- A soft ionization method such as electrospray ionization combined with a high resolution mass spectrometer can be used to measure the exact mass of the HULIS compounds.

Method:

Six hour samples were collected with a MOUDI on aluminum foil substrates. Substrates were analyzed at the EMSL facility at Pacific Northwest National Labs in Washington.

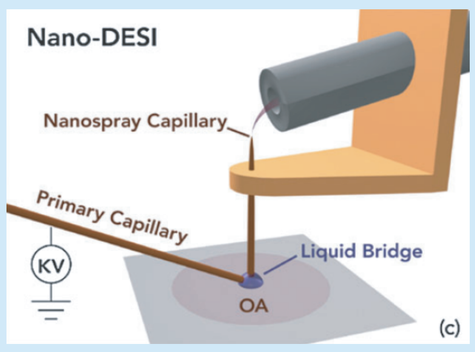

Figure 1. Schematic of Nano-DESI set-up showing two capillaries, liquid junction, mass spectrometer inlet, and where electrospray voltage is applied [2, 3, 4]

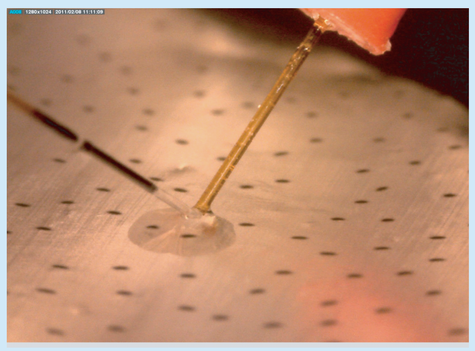

Figure 2. Close up view of Nano-DESI sampling on a substrate. Small black dots are impacted samples from the non-rotating MOUDI.

Mass spectra were collected using a novel sampling technique developed by the Laskin group at PNNL.

Nano-DESI uses a liquid bridge to desorb the sample and transport it to an electrospray ionization source coupled to an Orbitrap mass spectrometer.

A mass resolution of 60,000 enables the determintation of exact masses for elemental formula calculation.

Results

Peaks with S/N ratio of 3 and higher were extracted using Decon2LS.
An average of 600 peaks were found in the mass range of 120-800 *m/z*.

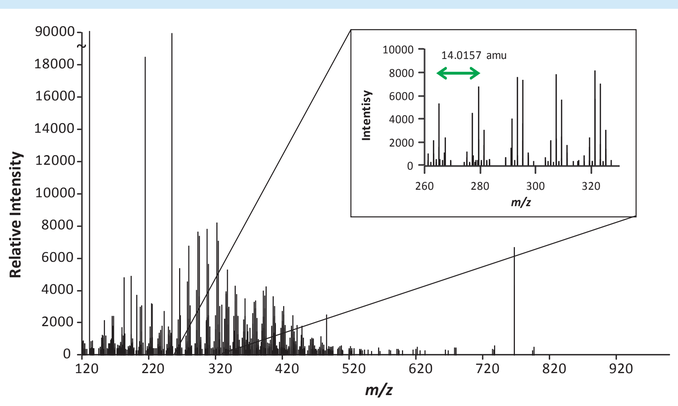

Figure 3. Reconstructed mass spectrum for sample collected June 5, midnight to 6 am. Expanded section shows perodicity of 14 amu (CH_2 groups).

All compounds are singly charged.

There is a regular spacing between peaks of 14.0157 amu (CH_2 groups)

Even mass ions contain odd numbers of nitrogen.

Peaks were assigned emperical formulas using a formula calculator and Kendrick diagrams.
On average 80% of the peaks in a mass spectra can be assigned using C, H, O, N and S.

References

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(3) Roach, P. J.; Laskin, J.; Laskin, A. *Analyst*, **2010**, 135, 2233-2236
(4) Laskin, J.; Laskin, A.; Roach, P. J.; et. al. *Anal. Chem.*, **2010**, 82 (5) 2048-2058
(5) Mazzoleni, L. R.; Ehrmann, B. M.; Shen, X.; Marshall, A. G.; Collett, J. F. Jr.; *Environ. Sci. Technol*. **2010**, 44, 3690-36097

Acknowledgments

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Results

Kendrick Analysis

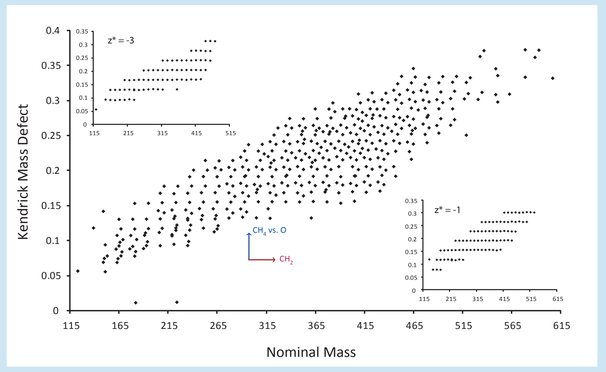

Figure 4. Kendrick mass defect vs. nominal mass for select compounds from June 8, 6 pm to midnight. The insets are subsets that are separated based on the remainder of the nominal mass divided by 14. Left to right = increase in CH_2, up and down = exchange CH_4 and O.

The mass of CH_2 is converted from 14.01565 to 14.000

Species with different numbers of CH_2 groups will have the same Kendrick mass defect.

An additional level of separation is generated using the modulus.

Van Krevelen diagrams

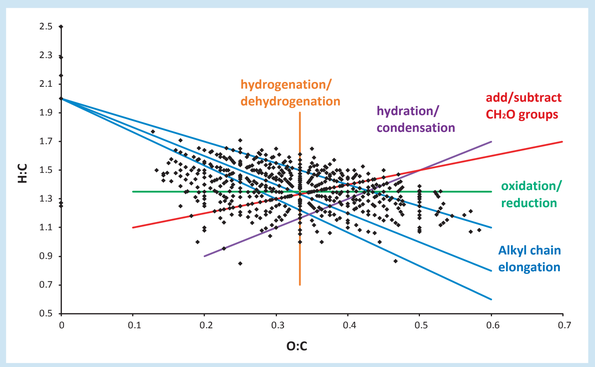

Figure 5. Van Krevelen, (O:C vs H:C) diagram for June 8, 6pm to midnight. Clear patterns are visible, the colored lines indicate homologous series [5]

Plot of the H:C vs O:C for each compound

Colored lines indicate homologous series.

Series used in Kendrick analysis include:
CH_2O, Oxygen, and CH_2

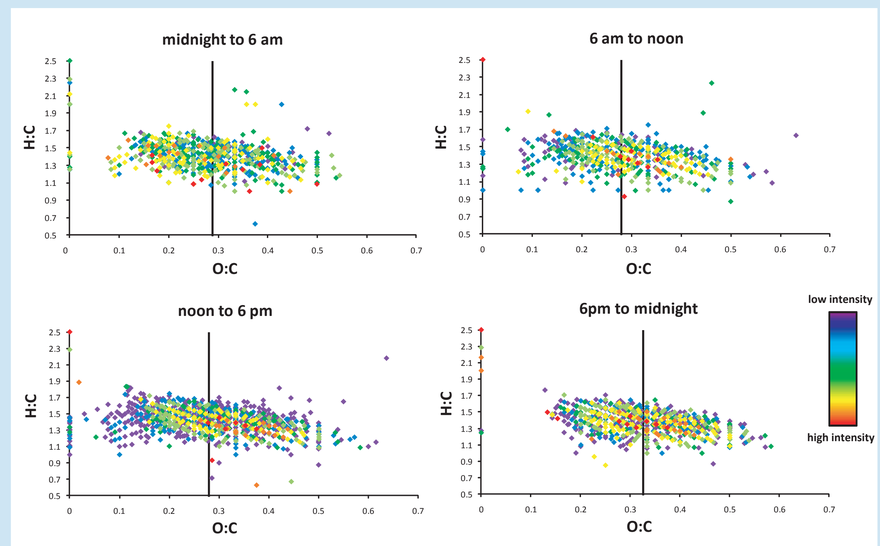

Figure 6. Van Krevelen, (O:C vs H:C) diagrams for June 8, 6 hour samples. Compounds are weighted by relative peak intensities. Vertical black lines indicate the average O:C ratio for that sample.

There is higher average intensity from 6 am to midnight.

Lack of low O:C peaks in the 6 pm to midnight sample provides evidence of more aged particles.

Double Bond Equivalency

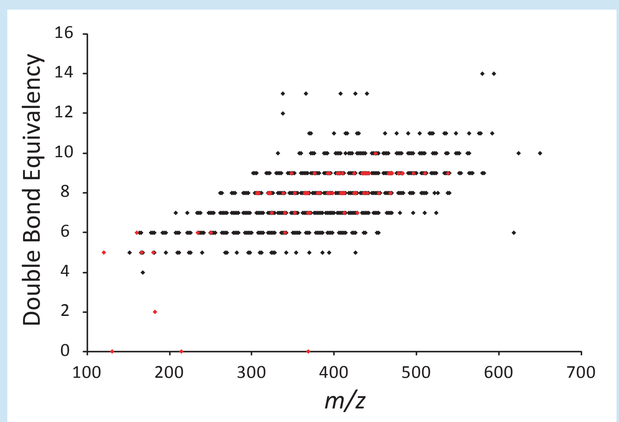

Figure 7. Double bond equivalency vs. m/z for June 8, 6 pm to midnight. Black dots correspond to compounds with C, H, and O. Red dots correspond to compounds with C, H, O, and N.

DBE gives information on the number of rings and unsaturated bonds in a molecule.
DBE = 1 - (h/2) + (n/2) + c

DBE increases linearly with molecular weight. Most nitrogen containing species (red) fall on top of C, H, O species except for a few amines.

Conclusions

The sampling technique developed at PNNL enables the measurement of high-resolution mass spectra from samples with no prior processing.
Samples from the beginning of the campaign show similar mass spectra with regular 14 amu spacings, a pattern seen in oligomeric species.
The O:C ratio spans roughly 0 to 0.6 and the H:C spans 0.5 to 2.5.
There is evidence of atmospheric aging in the 6pm to midnight sample.
The linear increase in DBE with increasing mass indicates that the larger molecules have more rings and double bonds, potentially as a result of the reactions that form them.