Chemical Composition of Limonene Secondary Organic Aerosol using High-Resolution Electrospray Ionization Mass Spectrometry

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What is Aerosol?

Stable suspension of solid or liquid particles in a gas

Gas

Particle

Aerosol

Particulate matter (PM)
Complex set of interactions between aerosol, solar light, relative humidity and atmospheric conditions => Hard to study
Laboratory Aerosol Chamber

Aerosol generated under controlled conditions and collected via a number of filter and impaction techniques.
# SOA Collection Techniques

<table>
<thead>
<tr>
<th>PILS</th>
<th>Drum Impactor (PNNL)</th>
<th>MOUDI (MSP Corp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Stage</td>
<td>3 Stages</td>
<td>10 Stages</td>
</tr>
<tr>
<td>No Cut-point diameters</td>
<td>Cut-point diameters 2.5, 1.15, 0.34, 0.07 µm</td>
<td>Cut-point diameters of 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1 and 0.056 µm</td>
</tr>
<tr>
<td>1 – 45 mins collection</td>
<td>4 - 60 mins collection</td>
<td>10 min – 2 hrs collection</td>
</tr>
</tbody>
</table>
Images of SOA from CC-SEM

Stage 10 (100 - 56 nm)

Collected using MOUDI
Factor of 4 difference in size distribution
SOA particles described as amorphous solid
Flattens on impact

Stage 7 (560 - 320 nm)
Orbitrap ESI-MS

Resolution = 0.001 amu!

Two Modes: Positive Ion Mode
Negative Ion Mode
High Resolution Data Analysis

Raw data → Deconvolution → Background Subtraction → Assignment

- Kendrick Analysis
- Van Krevelen Analysis
- Bulk Analysis

Molecular Formula Sorting

Assignment
- m/z = 87.008357
- C₇H₅O₃⁻ = [M-H]⁻

Assignment Verification
1. Lewis / Senior rules
2. H:C / O:C / DBE constraints
3. Isotopic pattern
4. Chemical families
   - Oxygenated hydrocarbons
   - N-containing hydrocarbons

Structural Assignments
1. Known mechanisms
   - C₃H₄O₃ pyruvic acid

- MS/MS, MS³
Mass Spectra

Positive ion mode ESI MS of SOA collected by Drum Impaction and extracted in acetonitrile

Each Peak ~ 1 Molecule

\[ \text{M} \rightarrow \text{M} - \text{Na}^+ \]
\[ \text{M} \rightarrow \text{M} - \text{H}^+ \]

High accuracy mass measurements allows the determination of elemental composition for hundreds of peaks

(b) \( R = 100,000 \)

- \( \text{C}_{11}\text{H}_{16}\text{O}_5\text{Na}^+ \) 
  - 251.0900
- \( \text{C}_{10}\text{H}_{12}\text{O}_6\text{Na}^+ \) 
  - 251.0534
- \( \text{C}_{10}\text{H}_{20}\text{O}_4\text{Na}^+ \) 
  - 251.1263
- \( \text{C}_{19}\text{H}_{23}^+ \) 
  - 251.1794

(c) \( R = 5,000 \)

Ambiguous assignment
- 251.10 +/- 0.05 m/z
SOA is a complex mixture of oxygen-rich organic compounds i.e. acids, carbonyls, peroxides, alcohol...
Solvent-Analyte Reactions

## Reactions between carbonyl/carboxyl and methanol

### Ester Formation

\[
\text{R-C(=O)OH} + \text{CH}_3\text{OH} \rightleftharpoons \text{R-C(=O)OCH}_3 + \text{H}_2\text{O}
\]

\(\Delta (m/z) = 14.0156\)

Acid Catalyzed

Extent of reaction depends on solvent concentration

Use this to the advantage of detecting carbonyls!

### Hemiacetal Formation

\[
\text{R-C(=O)R'} + \text{CH}_3\text{OH} \rightleftharpoons \text{R-C(=O)R'OH} + \text{OCH}_3
\]

\(\Delta (m/z) = 32.0262\)

### Acetal Formation

\[
\text{R-C(=O)R'} + \text{CH}_3\text{OH} \rightleftharpoons \text{R-C(=O)R'OCH}_3 + \text{H}_2\text{O}
\]

\(\Delta (m/z) = 46.0419\)

Extraction of SOA into methanol provides a suitable medium for reaction but not necessarily atmospherically relevant.
Water Soluble Organic Compounds

95% of compounds detected using acetonitrile as extraction solvent were found in water extracted SOA as well.

<table>
<thead>
<tr>
<th></th>
<th>&lt;O:C&gt;</th>
<th>&lt;H:C&gt;</th>
<th>&lt;DBE&gt;</th>
<th>OM:OC</th>
</tr>
</thead>
<tbody>
<tr>
<td>PILS</td>
<td>0.39</td>
<td>1.59</td>
<td>3.69</td>
<td>1.64</td>
</tr>
<tr>
<td>Filter/ACN</td>
<td>0.38</td>
<td>1.57</td>
<td>4.10</td>
<td>1.65</td>
</tr>
</tbody>
</table>
Chemical Composition as a Function of Particle Size

No distinct trends in Van Krevelen diagrams for particles in the size range studied (560 - 56 nm)

Two Step Process:
1. Gas Phase reaction of limonene and ozone
2. Oxidized material partitions into particle phase

Result:
Particles grow from same subset of oxidized material
Chemical Composition as a Function of Particle Size and Time

Intensity Weighted Average Values

\[ \langle O:C \rangle = \frac{\sum (O:C) \cdot \text{(Relative Intensity)}}{\sum \text{(Relative Intensity)}} \]

Allows comparison of the chemical composition of many mass spectra

Not Quantitative – Yet

ESI-MS Intensity = [Concentration] * Sensitivity

No clear size dependence of the chemical composition of SOA, but there is definite time dependence: further oxidation with time
Chemical Composition as a Function of Initial Reaction Conditions

- Initial Conditions: Dark vs. UV-light
  Dry vs. Wet air (RH)

- Collection Methods
  Drum Impactor
  MOUDI

- Similar reaction kinetics regardless of initial reaction conditions

- Same concentrations of limonene and ozone
### Chemical Composition as a Function of SOA Mass Loading

<table>
<thead>
<tr>
<th>Initial Concentrations (Ozone = Limonene)</th>
<th>Particle Collection Time (min)</th>
<th>PILS Water Flow Rate (µL/min)</th>
<th>SOA Mass Concentration at Collection (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ppm</td>
<td></td>
<td></td>
<td>6032</td>
</tr>
<tr>
<td>0.5 ppm</td>
<td></td>
<td></td>
<td>2289</td>
</tr>
<tr>
<td>0.1 ppm</td>
<td></td>
<td></td>
<td>275</td>
</tr>
<tr>
<td>0.1 ppm</td>
<td></td>
<td></td>
<td>267</td>
</tr>
<tr>
<td>0.05 ppm</td>
<td></td>
<td></td>
<td>90</td>
</tr>
<tr>
<td>0.05 ppm</td>
<td></td>
<td></td>
<td>75</td>
</tr>
</tbody>
</table>

Increase in partitioning from condensed phase to gas phase of less oxygenated species at lower mass loadings
Simulated Cloud Processing

[Diagram showing the process of simulated cloud processing involving ozone (O₃) and hydroxyl (OH) radicals reacting with organic compounds to form secondary organic aerosol (SOA) and cloud droplets. The diagram also illustrates the separation of processed SOA into dissolved organic matter (DOM).]

Key steps:
- Ozonolysis (O₃) and hydroxyl (OH) reactions form SOA and cloud droplets.
- High RH environment enhances SOA formation.
- Low RH promotes deposition of processed SOA into DOM.]
Chemical Composition – UV photolysis

SOA generated at four concentrations and collected using PILS

Photolyzed directly in water

UV-vis measurements taken before and after photolysis

Visual changes to mass spectra are obvious as photolysis progresses

What happens to UV-vis spectra and atomic ratios?
Chemical Composition – UV photolysis

Rate of photolysis can be determined from slope of ln(ABS) vs. time. From this a Quantum Yield for photolysis of limonene SOA in water can be estimated (~.01) and a characteristic lifetime for SOA in the atmosphere can be calculated.

Photolysis suggests loss of carbonyls/conjugation.
Chemical Composition – UV photolysis

Increase in average O:C ratio with increasing photolysis time

Less change in O:C ratio for lower SOA mass loading

Decrease in average DBE ratio with increasing photolysis time

Again less change in DBE ratio for lower SOA mass loading

Average atomic ratios suggest increase in acids and loss of high molecular weight oligomers
**Limonene SOA Chemical Composition**

<table>
<thead>
<tr>
<th>Topic</th>
<th>Details</th>
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<tbody>
<tr>
<td><strong>Extraction Solvent</strong></td>
<td>- Methanol – Limonene SOA is soluble but reacts</td>
</tr>
<tr>
<td></td>
<td>- Water – Limonene SOA is water-soluble</td>
</tr>
<tr>
<td><strong>Particle Size</strong></td>
<td>- No clear dependence of chemical composition (50-500 nm)</td>
</tr>
<tr>
<td><strong>Initial Reaction Conditions (UV light, Relative Humidity)</strong></td>
<td>- No clear dependence under our reaction conditions</td>
</tr>
<tr>
<td><strong>SOA Mass Loading</strong></td>
<td>- More volatile components (small O:C) do not condense in low mass loading experiments</td>
</tr>
<tr>
<td><strong>Reaction Time</strong></td>
<td>- Initial oxidation happens very quickly (&lt; 5 min) slower oxidation due to reaction of second double bond or conversion of aldehyde - acid</td>
</tr>
<tr>
<td><strong>Photolysis (λ &gt;295nm) Time</strong></td>
<td>- Destruction of carbonyls and high molecular weight oligomers; formation of acids and possibly peroxides</td>
</tr>
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Further Research

- Evaluate the role of photodissociation processes in evolution of SOA; including fully dissolved SOA in cloud droplets
- Determine whether photochemical aging of limonene SOA is dominated by peroxides or carbonyls
- Verify whether O:C ratios can be measured with ESI-MS quantitatively

Preliminary Results
- Increase in peroxide concentration with increased mass loading
- Increase in peroxide with UV photolysis
- Increase in Acids with UV photolysis
- Compounds sensitivity is a complex function of chemical structure (seems to correlate with octanol/water partition coefficient)
Acknowledgements

AirUCI, National Science Foundation, University of California, Irvine

Global Change Education Program, U.S. Department of Energy-Office of Biological and Environmental Research

PNNL group acknowledges support from the Chemical Sciences Division of the office of Basic Energy Science of US DOE.

The experimental part of this work was performed in the William R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by OBER DOE and located at Pacific Northwest National Laboratory (PNNL).
Thanks