Characterization of Laboratory-Generated Secondary Organic Aerosols Using a High Resolution Time-of-Flight Aerosol Mass Spectrometer

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Introduction

• Three intensive urban and rural field campaigns were conducted (EPA/NYSERDA PMTACS-NY Supersite program): Queens College (Summer 2001, Winter 2004) and Whiteface Mountain (Summer 2002);

• 45-50% of PM mass can be attributed to carbon-containing species (2001-2004).

• Q-AMS data collected during the field campaigns, showed that a significant PM carbon contributions comes from secondary organic production under summertime conditions at urban and rural sites.

• Objectives of this project:

- to find optimal parameters for generation, conditioning and characterization of secondary organic aerosols (SOA) generated from known atmospheric Volatile Organic Compounds (VOCs) of known composition in the controlled slow-flow chamber environment,

- to study physical and chemical properties of the generated SOA,

- to develop characteristic high resolution mass spectra for compound-specific secondary PM products.

• Information obtained in this study will be further used to

- provide basic knowledge of the production of organic PM from both anthropogenic and biogenic precursors,

- provide better estimates of the attribution of anthropogenic and biogenic sources to ambient aerosol measurements.

Generation of Polydisperse Secondary Organic Aerosols (SOA) at the ASRC Aerosol Research Facility

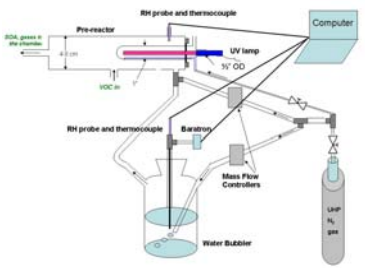
- *SOA generation method: reaction of OH radicals with VOCs;*
- *VOC source: heated permeation tubes*

Volatile Organic Compounds for SOA Generation

VOC	Formula	MW	Structure
Toluene	C_7H_8	92	
m-Xylene	C_8H_{10}	106	
Lemonene	$C_{10}H_{16}$	136	
α-Pinene	$C_{10}H_{16}$	136	

ASRC OH Radical Generation System

• *OH radicals produced via UV photolysis of water vapor:* $H_2O \xrightarrow{h\nu} OH + H$

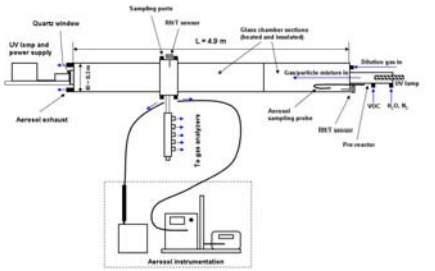


• Nitrogen flow: 3.2 l/min;

• Pre-reactor conditions: RH 35-45%, Temperature 21-22°C;

• Generated [OH] is estimated to be appr. 10^8 molecules/cm^3

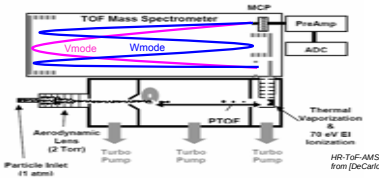
Measurements of Secondary Organic Aerosols and Gaseous Precursors



Aerosol and Gas Instrumentation

- Aerodyne HR-ToF-AMS ,
- TSI Scanning Mobility Particle Sizers with Nano DMA (NanoSMPS) and Long DMA (LDMA SMPS),
- TSI Condensation Particle Counter (CPC),
- R&P Differential TEOM Mass Monitor
- Thermo Environmental Instruments gas analyzers: ozone, NO-NO_2-NOx and Methane/Non-Methane Hydrocarbon (NMHC)

Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)



HR-ToF-AMS schematics is taken from [DeCarlo et al., 2006]

For current experiment:

• HR-ToF-AMS was sampling at the slow-flow chamber inlet.

• HR-ToF-AMS was switching between the two ion optical modes: V and W.

• W-mode data were used for High Resolution mass spectrometric analysis of laboratory-generated SOA.

• AMS heater temperature was maintained at ~600oC.

• Data were saved every minute.

• Mass spectra of experiment blanks ([VOC]>0, all flows are on, UV lamp is off) were recorded and subtracted from the corresponding mass spectra of SOA prior to the High Resolution analysis.

• A multiple-peak Gaussian curve fit algorithm similar to that reported in DeCarlo et al., (2006) was used to deconvolve a unit mass peak into separate contributions for specific elemental compositions based on small differences in mass defect.

• Criteria for "major" m/z selection: signal intensity ≥ 2% of total 'Organics' signal.

Reference: DeCarlo, P.F., et al., A Field-Deployable High-Resolution Time-of-Flight Aerosol Mass Spectrometer, *Analytical chemistry*, 10.1021/ac061249n, 2006.

"Chamber Blank" Tests

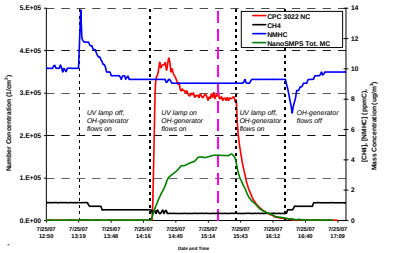
• Extensive "Chamber blank" tests were conducted:
- Flows (OH generation system and slow-flow chamber) on,
- Chamber dilution air: passed through a set of filters and charcoal scrubbers,
- [VOC] = 0,
- UV lamp switched on;

• Small particles were detected in the chamber after the UV lamp was switched on;

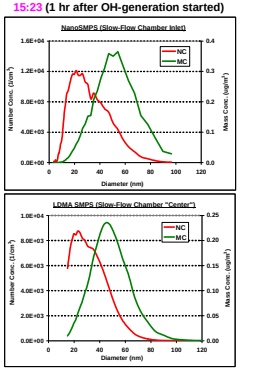
• Mass median diameter 25-35 nm, Mass concentration 0.02-0.05 μg/m^3 (total chamber flow of 18 l/min);

•This "chamber blank" did not affect results of the current experiments.

Selected Time Series of SOA and Precursor Gas Concentrations and Selected SOA Size Distributions



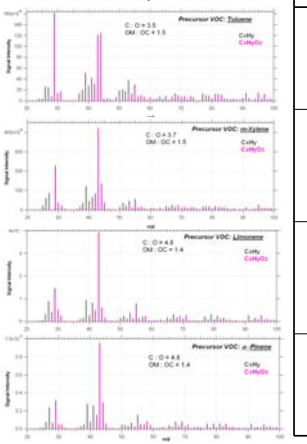
Particle size distribution measured at 15:23 (1 hr after OH-generation started)



VOC: Toluene,
OH generator flow: 3.2 l/min,
Pre-reactor RH: 35-45%,
Total chamber flow: 18.2 l/min,
Chamber RH: ~9%,
Assumed particle density: 1 g/cm^3

High Resolution Mass Spectrometric Analysis of OOC Aerosols

Mass spectra of SOA in the slow-flow chamber 60 min after the UV lamp was switched on



Major m/z	Organic Fragments	Major m/z	Organic Fragments
26	$C_2H_2^+$	42	$C_2H_2O^+$
27	$C_2H_3^+$	43	$C_2H_3O^+$
29	CHO^+	44	CO_2^+
39	$C_3H_3^+$	53	$C_4H_5^+$, C_3HO^+
40	$^{13}CC_2H_3^+$, $C_3H_4^+$, C_2O^+	55	$C_3H_3O^+$, $C_4H_7^+$
41	$C_3H_5^+$		
26	$C_2H_2^+$	42	$C_2H_2O^+$, $C_3H_6^+$
27	$C_2H_3^+$	43	$C_2H_3O^+$
29	CHO^+	44	CO_2^+, $^{13}CCH_3O^+$, $C_2H_4O^+$
39	$C_3H_3^+$	53	$C_4H_5^+$, C_3HO^+
40	$^{13}CC_2H_3^+$, $C_3H_4^+$, C_2O^+	55	$C_3H_3O^+$, $C_4H_7^+$
41	$C_3H_5^+$		
27	$C_2H_3^+$	42	$C_2H_2O^+$, $C_3H_6^+$
28	$C_2H_4^+$, CO^+	43	$C_2H_3O^+$
29	CHO^+, $C_2H_5^+$	44	CO_2^+, $^{13}CCH_3O$, $C_2H_4O^+$
30	CH_2O^+	55	$C_3H_3O^+$, $C_4H_7^+$
39	$C_3H_3^+$		
41	$C_3H_5^+$		
27	$C_2H_3^+$	42	$C_2H_2O^+$, $C_3H_6^+$
29	CHO^+, $C_2H_5^+$	43	$C_2H_3O^+$
39	$C_3H_3^+$	44	CO_2^+, $^{13}CCH_3O$, $C_2H_4O^+$
41	$C_3H_5^+$	55	$C_3H_3O^+$, $C_4H_7^+$

Signal intensities at each m/z value consist of fragments containing carbon and hydrogen only (gray) added to the signal of oxygen-containing fragments (magenta).

Summary

- **Four volatile organic compounds (VOCs) commonly found in ambient air were used to generate secondary organic aerosols via reaction with OH radicals in controlled laboratory conditions;**
- **Sampling of generated SOA was done from a slow-flow chamber;**
- **Physical and chemical characterizations of generated aerosols were performed;**
- **High m/z resolution mass spectra for generated SOA were recorded using the HR-ToF-AMS;**
- **Major m/z peaks for the SOA were identified;**
- **Results of the High Resolution mass spectrometric analysis of four SOA showed that**
  - **general appearance of mass spectra of SOA formed from m-Xylene, Limonene and α-Pinene is similar,**
  - **major m/z peaks are essentially the same (with few exceptions) for all four SOA,**
  - **there are no major peaks at m/z>55 in the chamber SOA mass spectra (the signal at 12<m/z<55, accounts for 75-80% of the total signal)**
  - **the fraction of oxygenated organic fragments increases for higher m/z,**
  - **OM:OC ratio is very similar for all four SOA (1.4-1.5). C:O ratio is varies for precursor compound groups (3.5 for Toluene/m-Xylene; and 4.8 for Limonene/α-Pinene).**

Acknowledgements

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