Characterization of Oxygenated Organic Compounds 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).

• PM organic carbon characterization was done using an Aerodyne Aerosol Mass Spectrometer (Q-AMS).

• It has been shown that natural hydrocarbons are an important contributor to PM organic fraction in rural and urban environments.

• Objectives of this project:

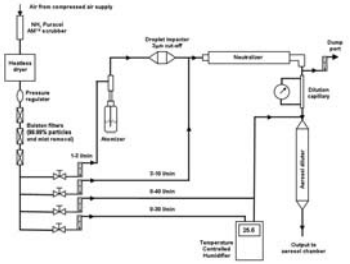
- to study physical and chemical properties of laboratory-generated oxygenated organic aerosols of known composition and of ambient importance;

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

• Information obtained in this study will be further used to quantify the AMS-measured organic mass fraction of PM2.5 made in urban and rural environment during the PMTACS-NY field campaigns.

Generation of Polydisperse Oxygenated Organic Compound (OOC) Aerosols at the ASRC Aerosol Research Facility

ASRC Aerosol Generation System



• OOC aerosol generation method: spray-atomization

• Solvent: distilled/de-ionized water, except for oleic acid (acetone) and palmitic acid (ethanol)

• Sampling from a slow-flow glass chamber (4.9 m length, 0.30 m diameter)

• Generation and chamber dilution conditions varied depending on a compound

Organic Compounds Used for Generation of Organic Aerosols

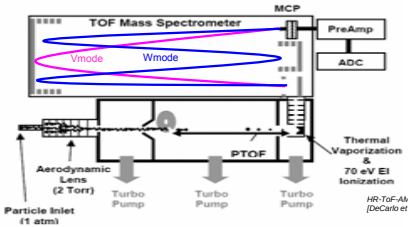
Compound	Formula	Mw	Structure
Oxalic Acid	$C_2H_2O_4$	90	
Malonic Acid	$C_3H_4O_4$	104	
Succinic Acid	$C_4H_6O_4$	118	
Glutaric Acid	$C_5H_8O_4$	132	
Adipic Acid	$C_6H_{10}O_4$	146	
Glyoxylic Acid	$C_2O_3H_2$	74	
DL-Malic Acid	$C_4H_6O_5$	134	
Cis-Pinonic Acid	$C_{10}H_{16}O_3$	184	
Phthalic Acid	$C_8H_6CO_4$	166	
Levoglucosan	$C_6H_{10}O_5$	162	
Palmitic Acid	$C_{16}H_{33}O_2$	256	
Oleic Acid	$C_{18}H_{34}O_2$	282	

Measurements of OOC Aerosols

Aerosol Instrumentation

- Aerodyne HR-ToF-AMS ,
- TSI Scanning Mobility Particle Sizer (SMPS),
- TSI Condensation Particle Counter (CPC),
- Sunset Labs OC/EC monitor,
- R&P Differential TEOM Mass Monitor

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 is switching between the two ion optical modes: V and W.

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

• AMS heater temperature ~600ºC.

• Data are saved every 5 min.

• Mass spectrum of a solvent blank were recorded and subtracted from a mass spectrum of an OOC of interest prior to the High Resolution analysis.

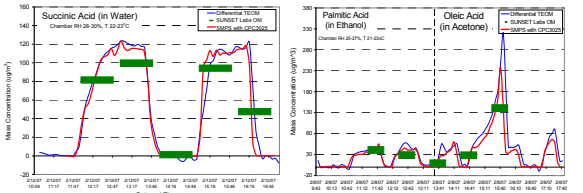
• A multiple-peak Gaussian curve fit algorithm similar to that of DeCarlo et al. [2006] was used to deconvolve a unit mass peak into separate contributions for specific elemental compositions based on small differences in mass defect.

• Data are collected at a resolution > 1000. Results in figures and table at right are from analysis of high resolution data subsequently combined into single m/z bins.

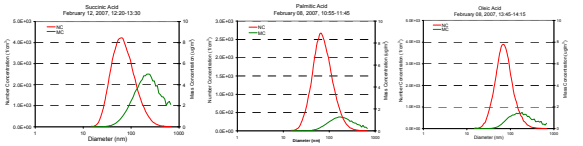
• Criteria for "major" m/z selection: signal intensity ≥ 3% of total 'Organic' signal.

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

Time Series of Mass Concentrations of Selected OOC Aerosols

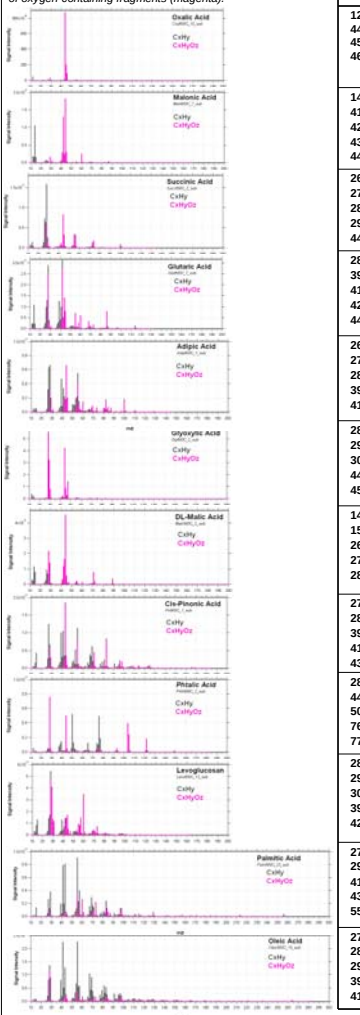


Size Distributions of Selected Generated OOC Aerosols



High Resolution Mass Spectrometric Analysis of OOC Aerosols

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).



Major m/z	Organic Fragments	Major m/z	Organic Fragments
12	C^+		
44	CO_2^+		
45	CO_2H^+		
46	$CH_2O_2^+$		
14	CH_2^+	45	CO_2H^+
41	C_2HO^+	60	$C_2H_4O_2^+$
42	$C_2H_2O^+$		
43	$C_2H_3O^+$		
44	CO_2^+		
26	$C_2H_2^+$	45	CO_2H^+
27	$C_2H_3^+$	55	$C_3H_3O^+$
28	CO^+, $C_2H_4^+$, $C^{13}CH_3^+$	56	$C_3H_4O^+$
29	$C_2H_5^+$, CHO^+		
44	CO_2^+		
28	CO^+, $C_2H_4^+$	45	CO_2H^+, $C_2H_5O^+$
39	$C_3H_3^+$	55	$C_3H_3O^+$
41	$C_3H_5^+$, C_2HO^+	86	$C_4H_6O_2^+$
42	$C_2H_2O^+$, $C_3H_6^+$		
44	CO_2^+		
26	$C_2H_2^+$	42	$C_2H_2O^+$, $C_3H_6^+$
27	$C_2H_3^+$	44	CO_2^+
28	CO^+, $C_2H_4^+$, $C^{13}CH_3^+$	54	$C_4H_6^+$, $C_3H_2O^+$
39	$C_3H_3^+$	55	$C_3H_3O^+$, $C_4H_7^+$
41	$C_3H_5^+$		
28	CO^+	47	$CH_3O_2^+$
29	CHO^+		
30	CH_3O^+		
44	CO_2^+		
45	CO_2H^+		
14	CH_2^+	29	CHO^+
15	CH_3^+	42	$C_2H_2O^+$
26	$C_2H_2^+$	43	$C_2H_3O^+$
27	$C_2H_3^+$	44	CO_2^+, $C_2H_4O^+$
28	CO^+	71	$C_3H_3O_2^+$
27	$C_2H_3^+$	53	$C_4H_5^+$
28	CO^+	55	$C_4H_6^+$
39	$C_3H_3^+$	69	$C_5H_9^+$
41	$C_3H_5^+$	83	$C_5H_7O^+$
43	$C_2H_3O^+$		
28	CO^+	104	$C_7H_4O^+$, $C_8H_8O_2^+$
44	CO_2^+	105	$C_7H_5O^+$
50	$C_4H_2^+$	122	$C_7H_6O_2^+$, $C_4H_{10}O_4^+$
76	$C_6H_4^+$		
77	$C_6H_5^+$		
28	CO^+	43	$C_2H_3O^+$
29	CHO^+	44	CO_2^+, $C_2H_4O^+$
30	CH_3O^+	57	$C_3H_5O^+$
39	$C_3H_3^+$	60	$C_2H_4O_2^+$
42	$C_2H_2O^+$		
27	$C_2H_3^+$	57	$C_4H_9^+$
29	$C_2H_5^+$	60	$C_2H_4O_2^+$
41	$C_3H_5^+$	69	$C_5H_9^+$
43	$C_3H_7^+$	83	$C_6H_{11}^+$, $C_5H_7O^+$
55	$C_4H_7^+$, $C_3H_3O^+$		
27	$C_2H_3^+$	43	$C_3H_7^+$
28	CO^+	55	$C_4H_7^+$, $C_3H_3O^+$
29	$C_2H_5^+$	67	$C_5H_7^+$
39	$C_3H_3^+$	69	$C_5H_9^+$
41	$C_3H_5^+$		

Summary

• Twelve pure oxygenated organic compounds of known composition and commonly found in ambient air were used to generate polydisperse aerosols in controlled laboratory conditions;
• Optimal parameters for polydisperse aerosol generation and conditioning were found;
• Physical and chemical characterizations of generated aerosols were performed;
• Characteristic mass spectra for each compound were developed using the HR-ToF-AMS;
• Major m/z peaks and their elemental compositions for each OOC were identified;
• Results of the High Resolution mass spectrometric analysis are consistent with expectations based on chemical structure of OOCs (for example, very few oxygenated fragments in palmitic and oleic acids mass spectra, mostly oxygenated fragments in oxalic and glyoxylic acids mass spectra, etc.).

Acknowledgements

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