Near Real-Time Speciation of Organic Aerosols for Source Apportionment

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EPA Atmospheric Science Progress Review Meeting, 6.21.07

Project Objective:
Highly Time Resolved Measurements of Ambient Organic Aerosol

Method	Analysis Procedure	Time Resolution	Reference	Molecular Specificity
Aerodyne AMS	Thermal desorption + 70 eV EI	2 min	Zurich 2005 Lanz (ACP, 2007)	Low (1)
PIAMS	Laser desorption + 10.5 eV PI	4 min	Wilmington 2006 Johnston	High (3)
TDPBMS	Temperature programmed desorption + 70 eV EI	30 min	Riverside 2006 Ziemann	Moderate (2)
TAG (GC/MS-FID)	GC separation + 70 eV EI	1 hour	ICARTT Williams (JGR, 2007)	Very high (4)

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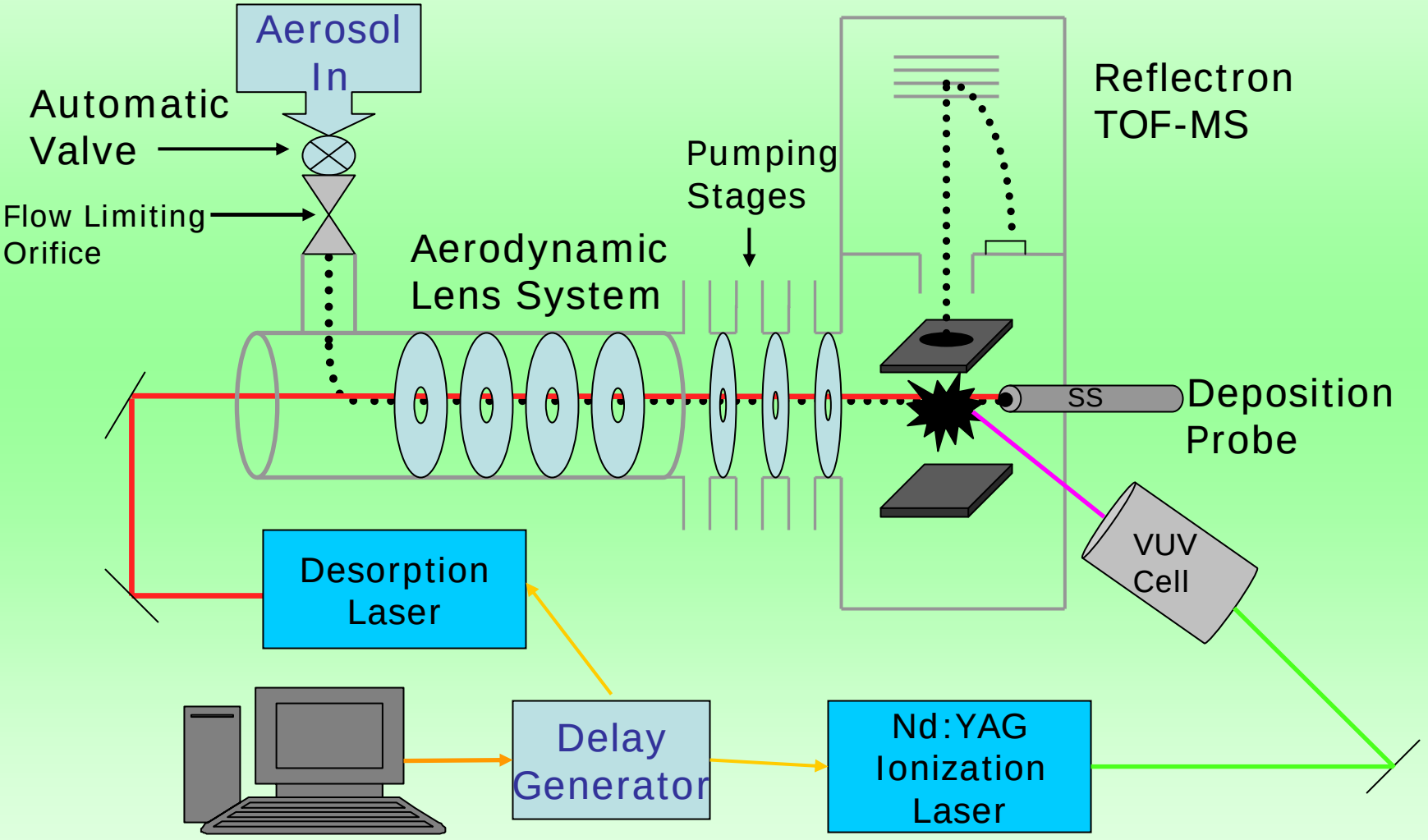
Photoionization Aerosol Mass Spectrometer (PIAMS)



Oktem et al, Anal. Chem. (2004) 76, 253-261

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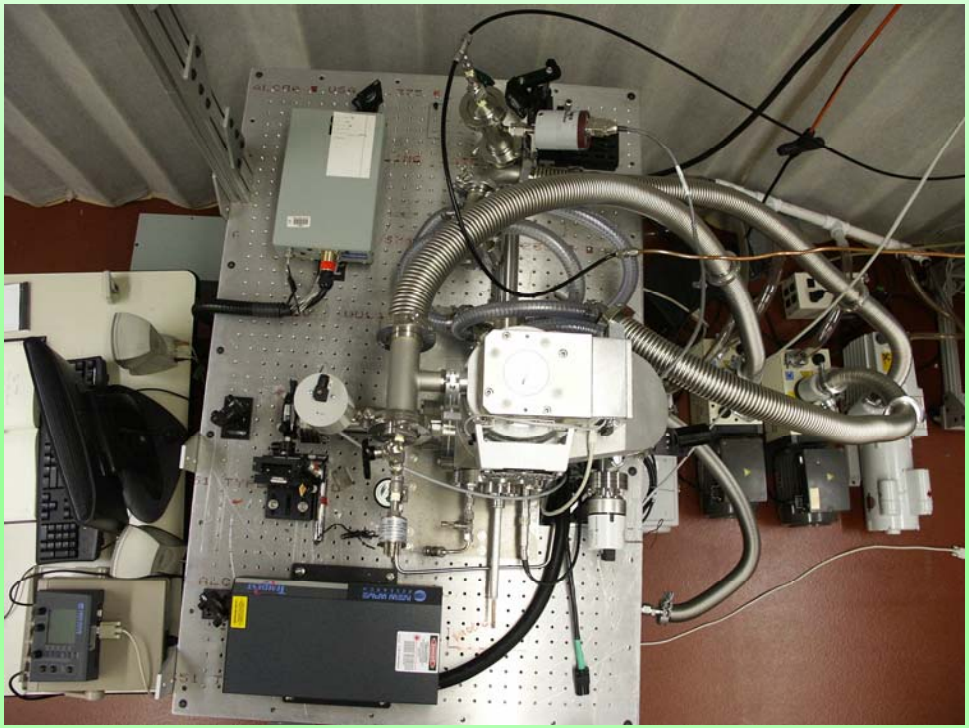
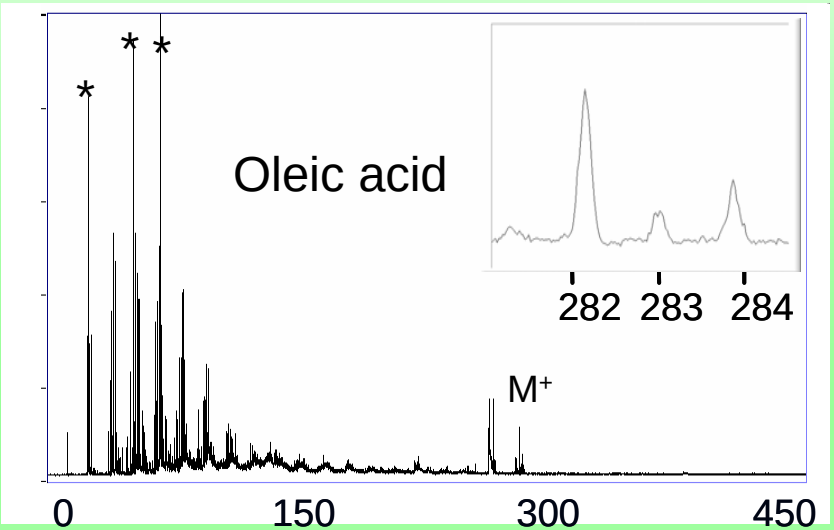
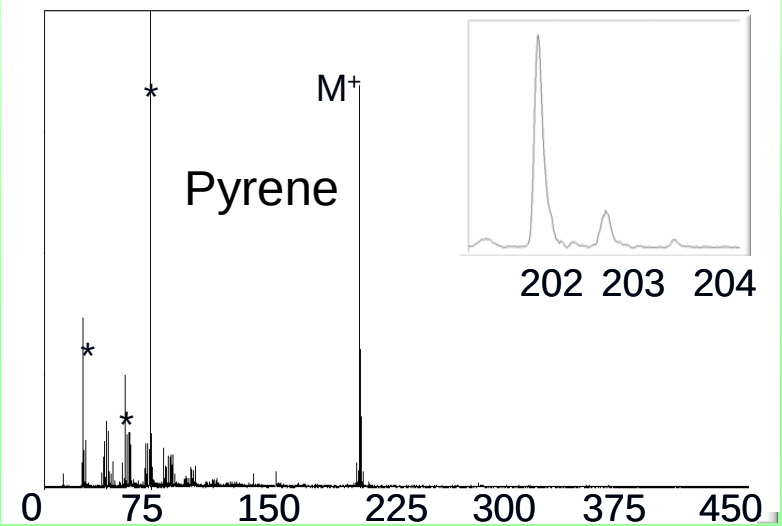
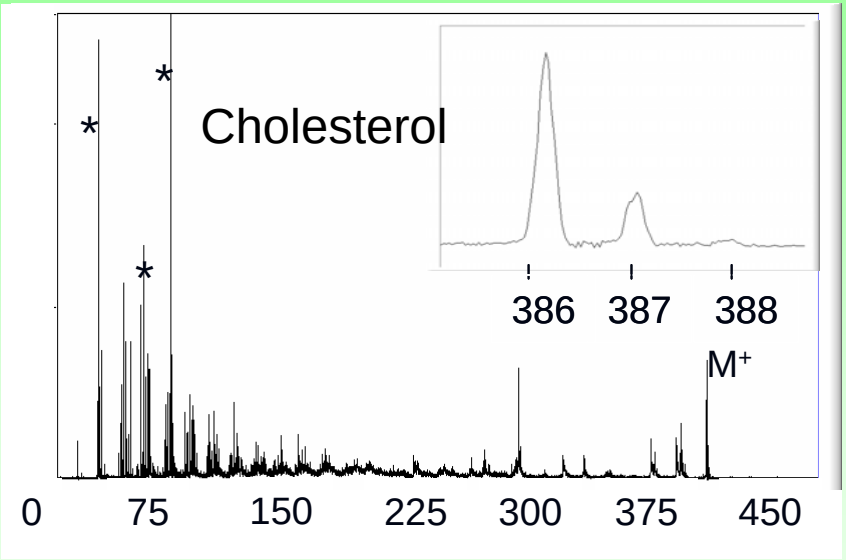


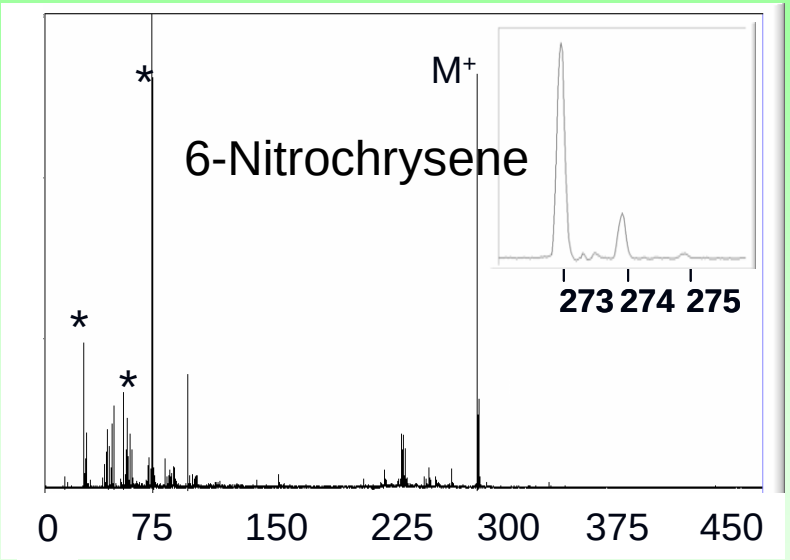
PIAMS Spectra of Organic Standards

Oktem et al, Anal. Chem. (2004) 76, 253-261





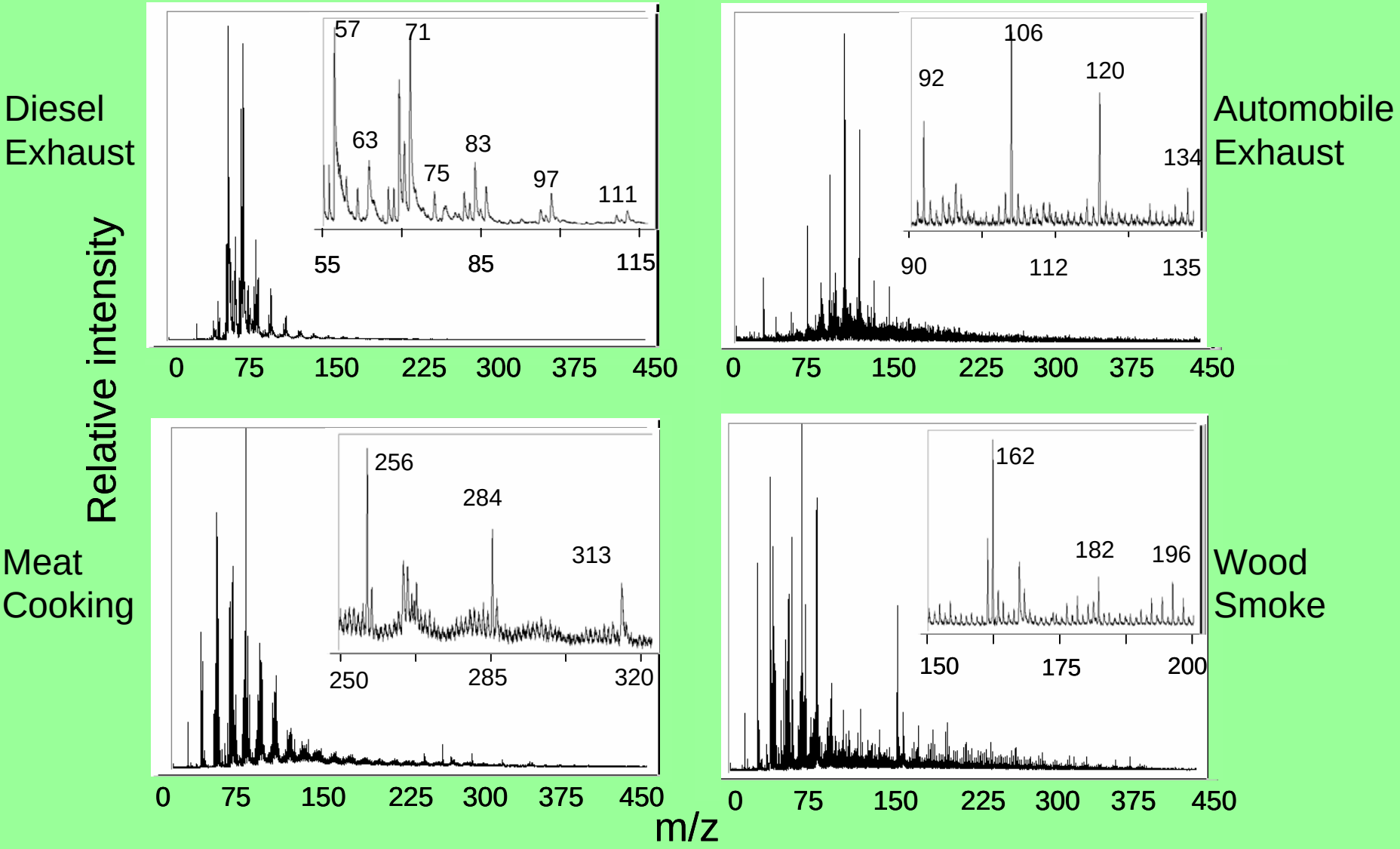




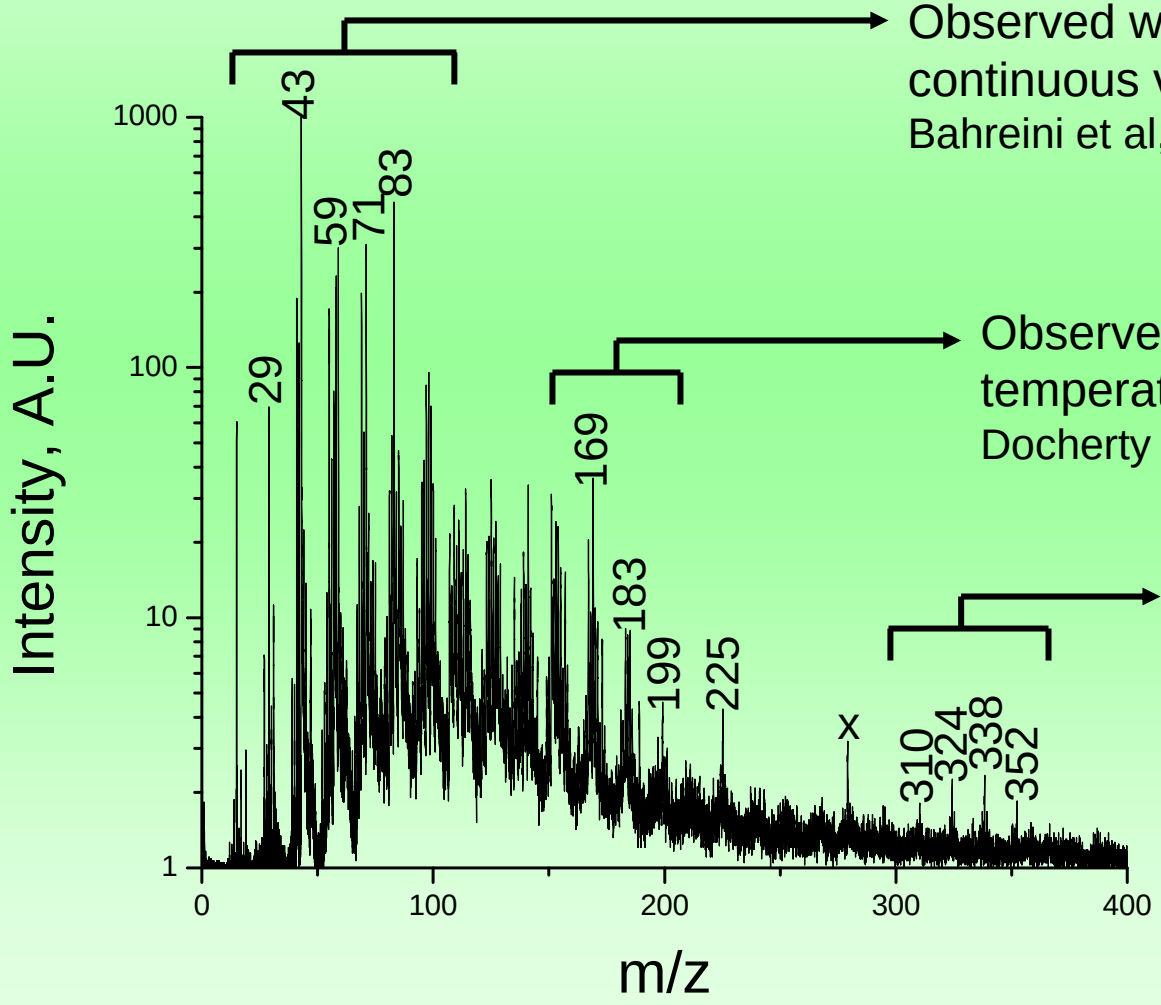
Ambient Sources of Organic Aerosol

On-line analysis by PIAMS

(Oktem et al, Anal. Chem. (2004) 76, 253-261)



Example of an Organic Aerosol Mass Spectrum
Aerosol from α-pinene ozonolysis

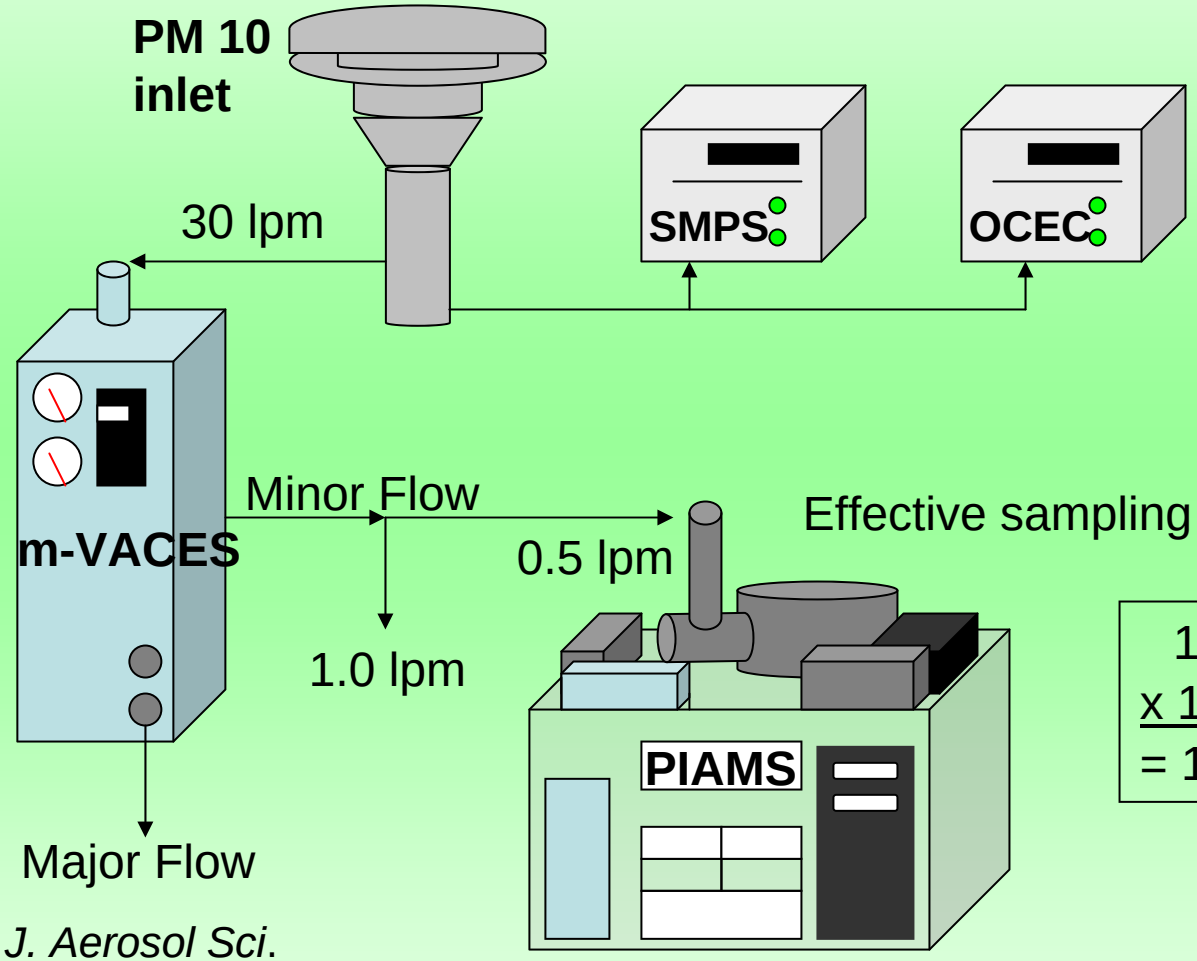


Observed with 70 eV EI +
continuous vaporization (AMS)
Bahreini et al, ES&T (2005) 39, 5674-5688

Observed with 70 eV EI +
temperature programmed desorption
Docherty et al, ES&T (2005) 39, 4049-4059

Observed with 10.5 eV PI +
laser desorption (PIAMS)
Tolocka et al, ES&T (2006) 40,
1843-1848

Ambient Sampling

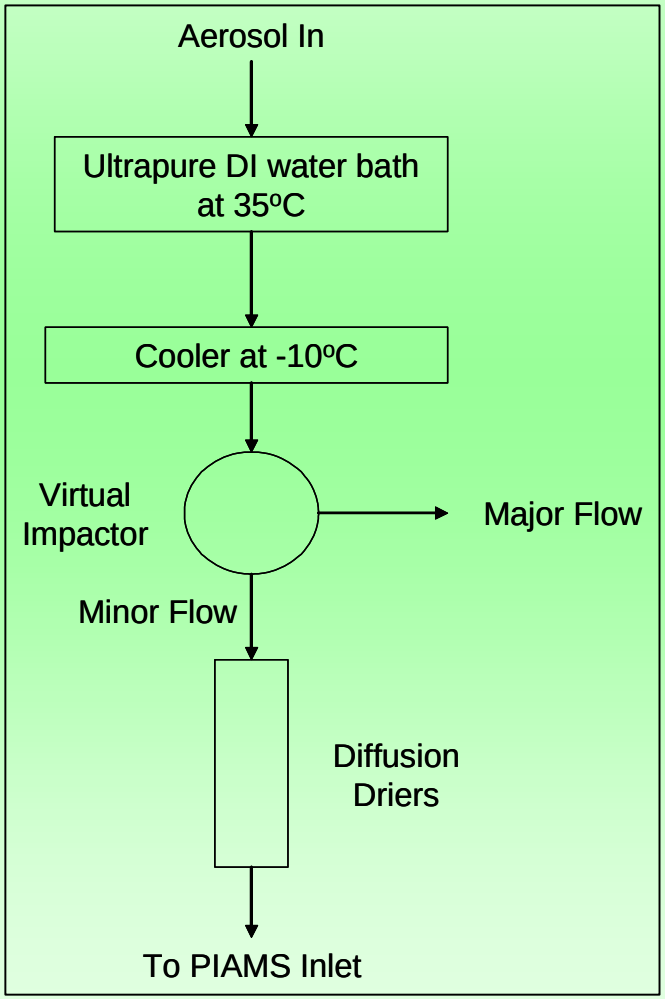


Effective sampling rate: 10 lpm

1 ng/m^3
x 10^{-2} m^3/min
= 10 pg/min

Geller et al., *J. Aerosol Sci.* (2005) 36, 1006-1022

Versatile Aerosol Concentration Enrichment System (VACES)



Geller et al, A new compact aerosol concentrator for use in conjunction with low flow-rate continuous aerosol instrumentation, J. Aerosol Sci. (2005) 36, 1006-1022

Khlystov et al, In situ concentration of semi-volatile aerosol using water condensation technology, J. Aerosol Sci. (2005) 36, 866-880

Zhao et al, Field evaluation of the versatile aerosol concentration enrichment system (VACES) coupled to the rapid single particle mass spectrometer (RSMS-3), J. Geophys. Res. – Atmospheres (2005) 110, D07S02

Ambient Air Analysis with PIAMS

1. **Collect sample** **2.0 minutes**

   Ambient aerosol sampled through aerodynamic lens and deposited on probe

2. **Analyze sample** **0.3 minutes**

   Multiple desorption/ionization laser shot sequences to vaporize and analyze organic compounds

3. **Clean Probe** **1.2 minutes**

   Multiple desorption laser shots to remove any remaining material; acquire background spectrum

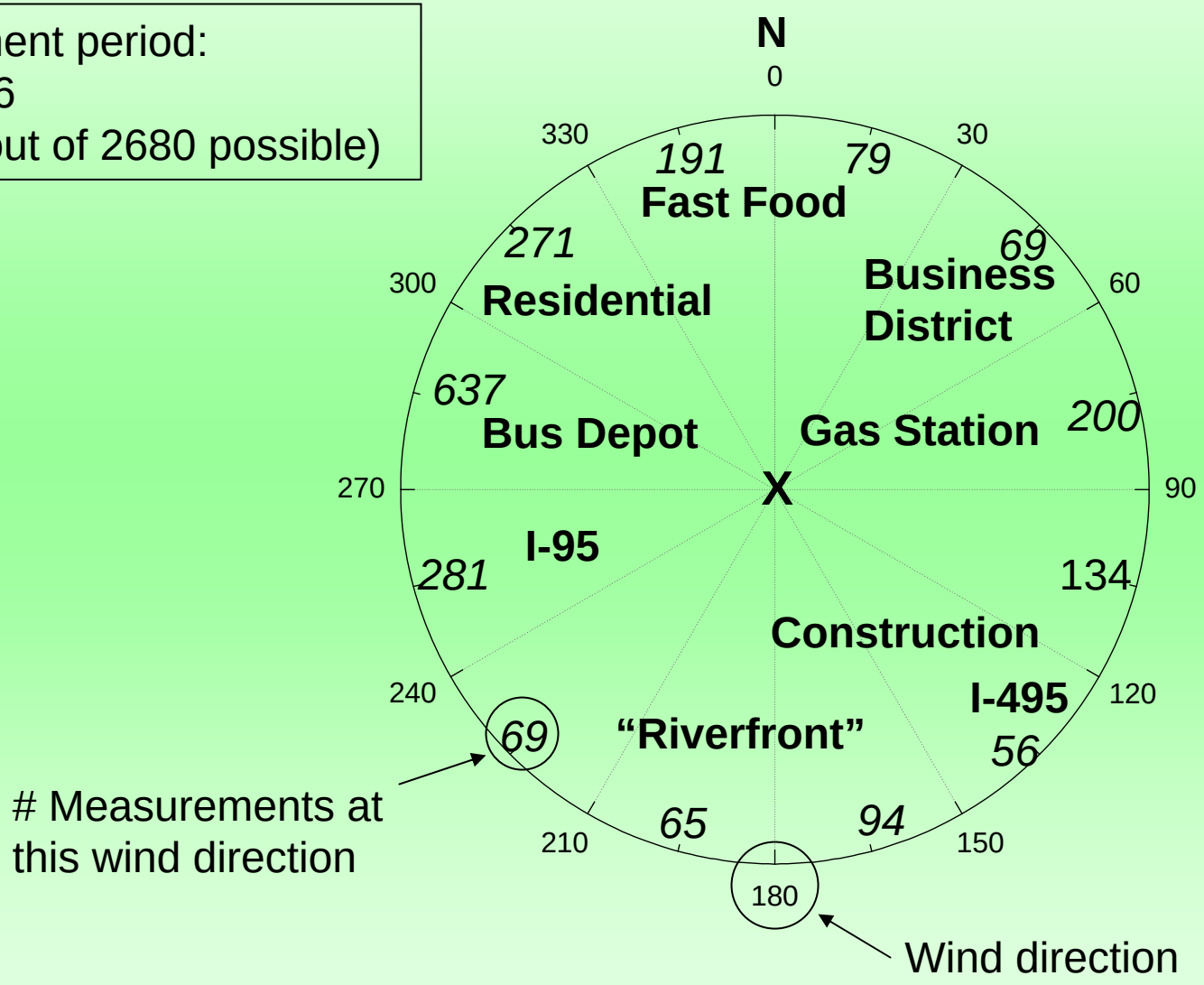
Total Cycle Time **3.5 minutes**

Measurement Site

State of Delaware
Air Quality Monitoring Site
Wilmington, Delaware

Possible stationary sources within 1 mile of sampling site

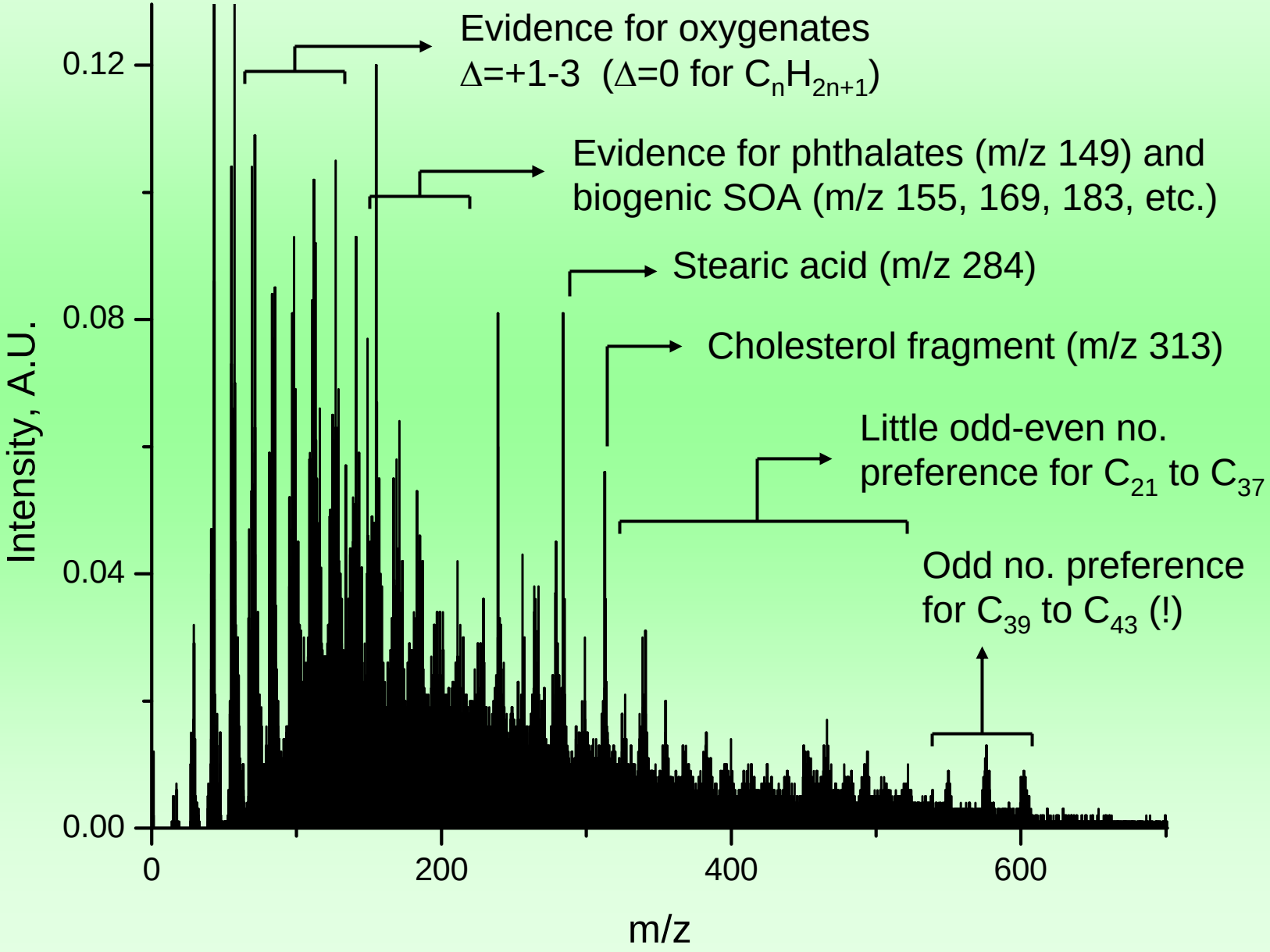
First measurement period:
June 4-11, 2006
2259 spectra (out of 2680 possible)



Single Particle Contributions to PM1 in Wilmington, DE

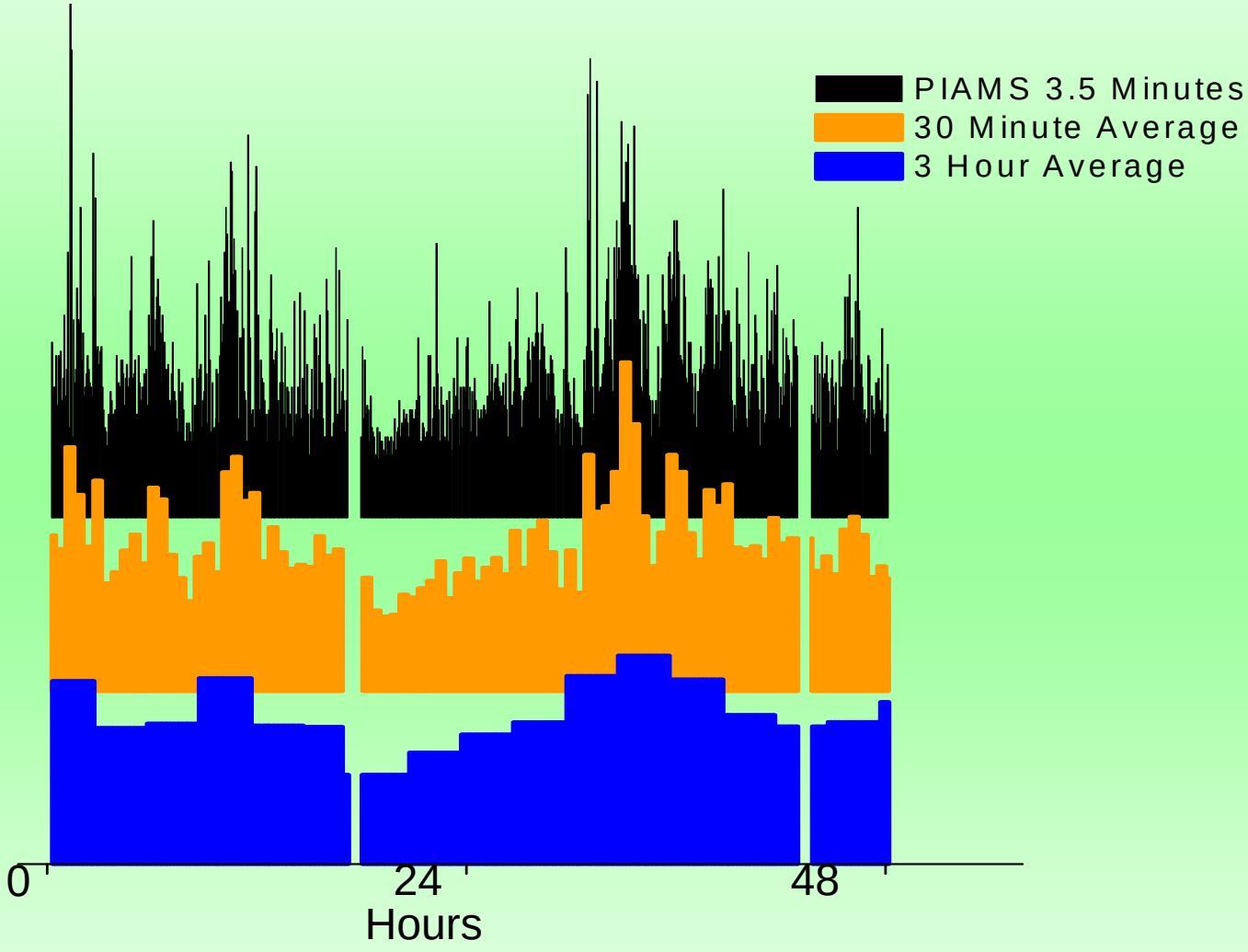
Particle Type	Single-Particle Classes	Approximate Fraction of PM_1
Internally Mixed, Secondary Aerosol		67%
Fine particles (mostly regional)	OCANS+Nitrate (220, 440, 770 nm)	38%
Ultrafine particles (mostly local)	OCANS+Nitrate (50, 110 nm)	29%
Externally Mixed, Primary Particles		33%
Biomass burning	K	13%
Fossil Fuel Combustion and other sources of POA	EOC	7%
Industrial Sources		13%
Alkyl Amines	Amine	(5%)
Alkali Metals	Na+K, K+Na, Li	(5%)
Transition/Heavy Metals	Various (V, Fe, Zn, Pb, etc.)	(3%)

PIAMS Spectrum of Ambient Aerosol
6/8/06, 8:59 pm

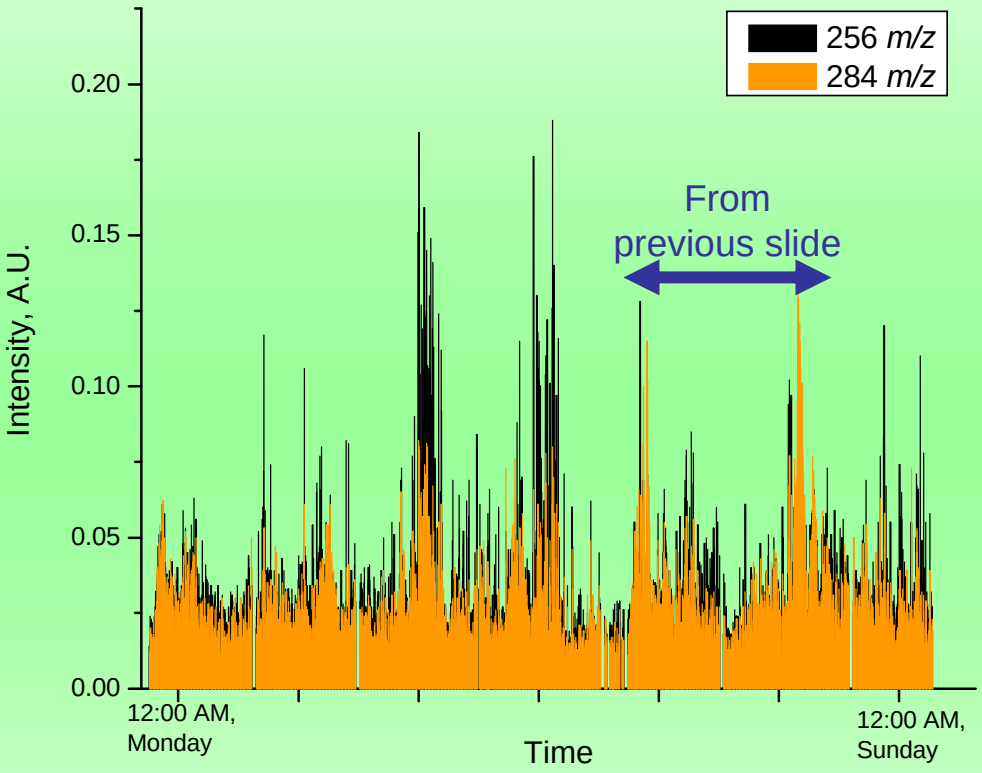


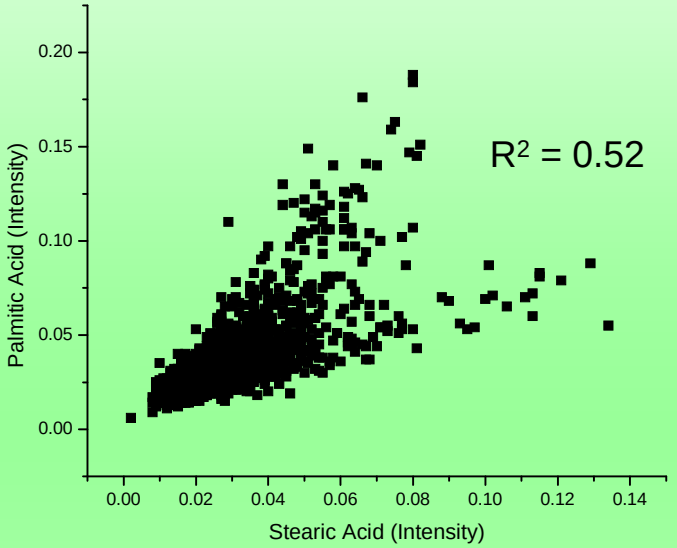
Time resolution above 30 minutes begins to loose information

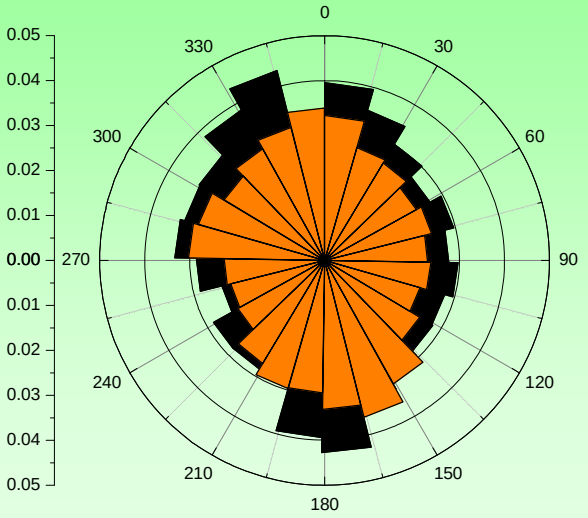
Palmitic Acid (m/z 256)



Time resolved analysis of palmitic (m/z 256) and stearic (m/z 284) acids June 4-11, 2006

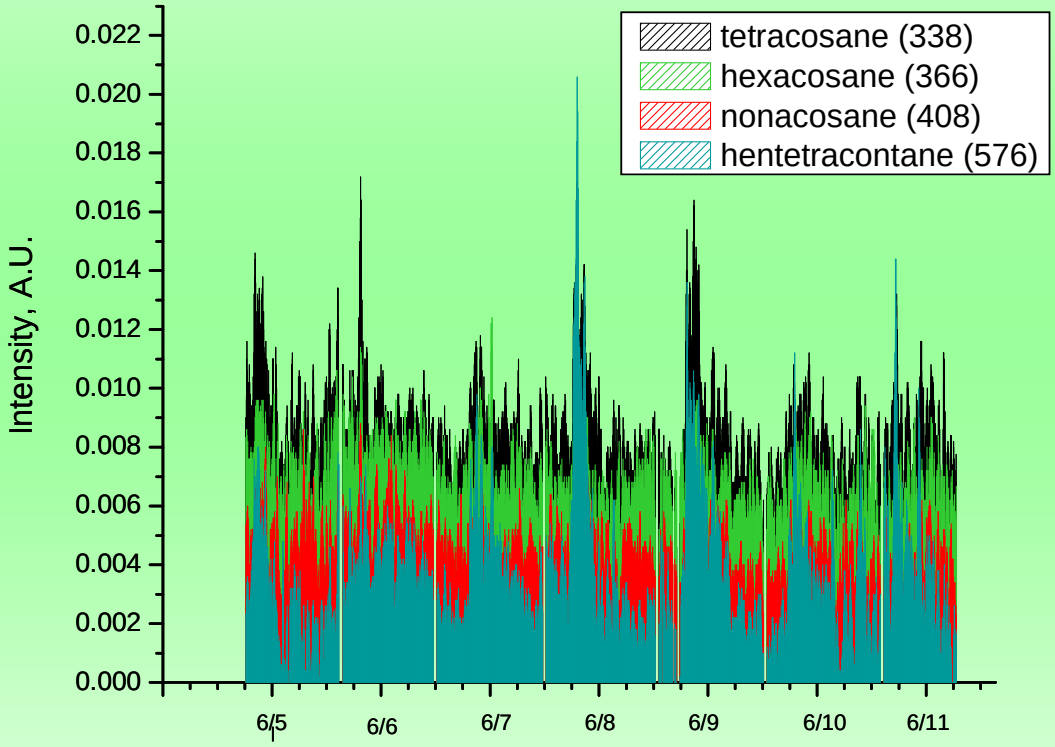


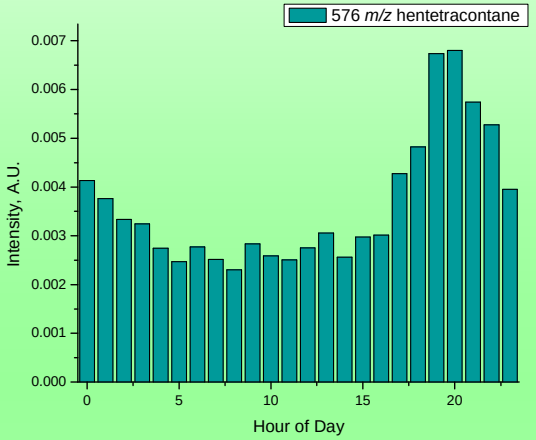


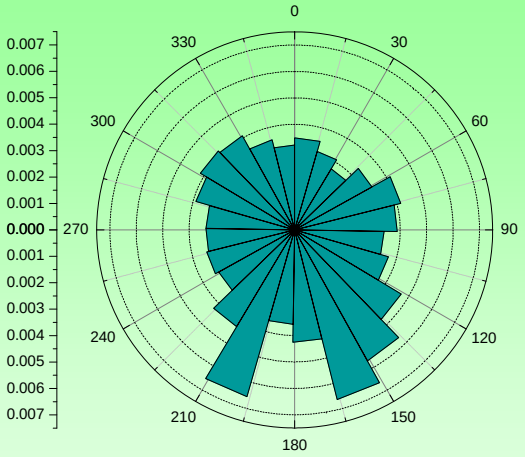


Multiple sources suggested
Stationary and nonstationary sources (?)

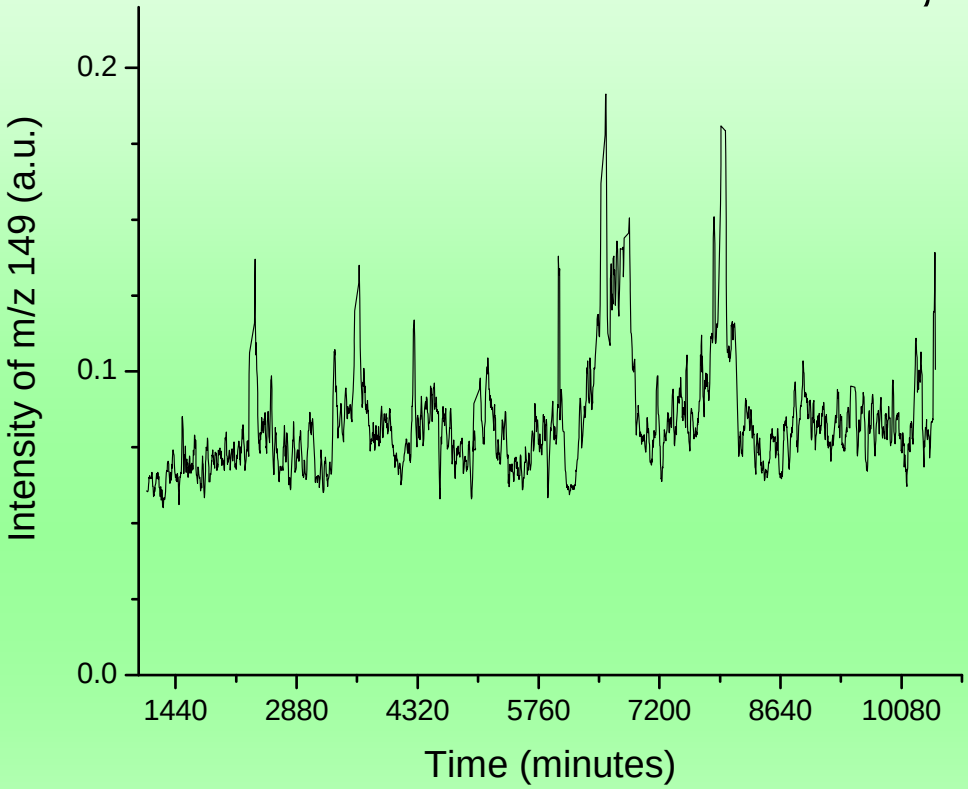
Time resolved analysis of
High molecular weight alkanes / alkanoic acids
June 4-11, 2006

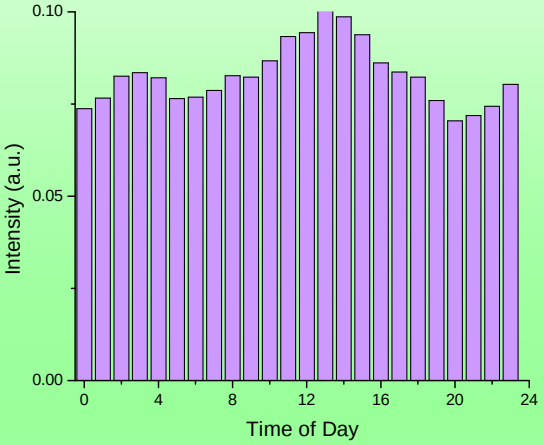


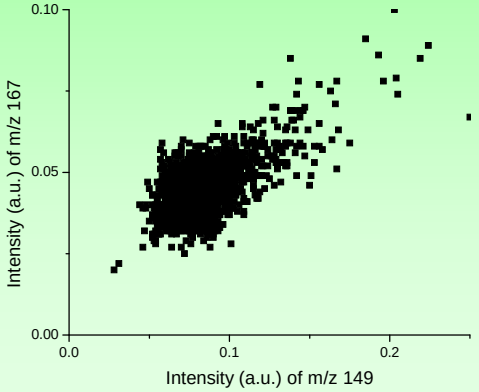


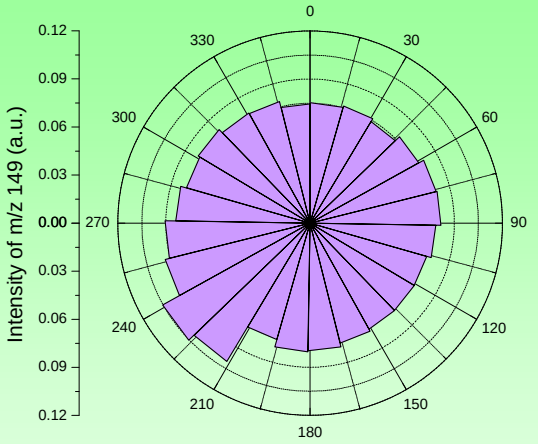


Time resolved analysis of Phthalates (m/z 149, 167) June 4-11, 2006



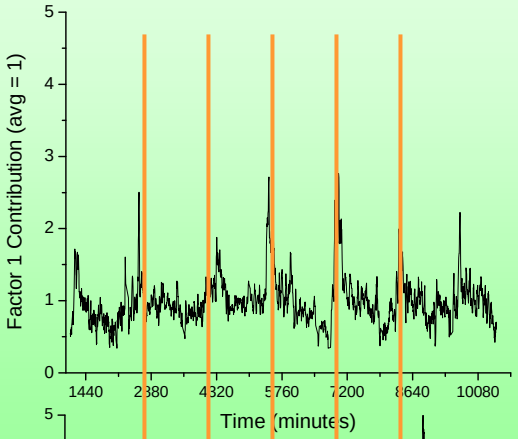


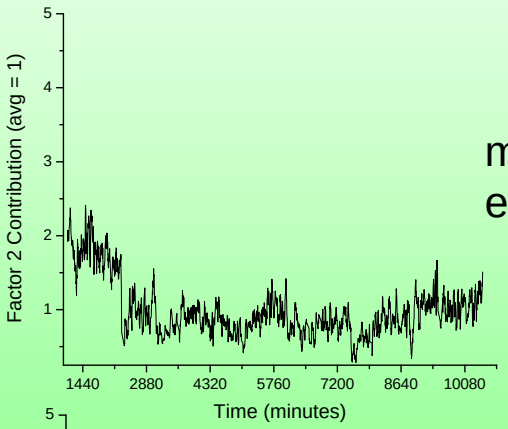




Factor Analysis (Preliminary)

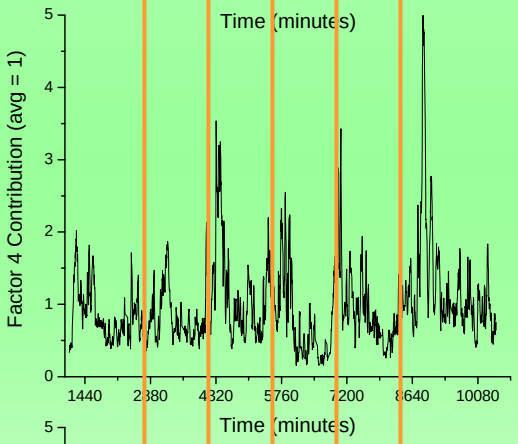
239, 265, 313, **576**

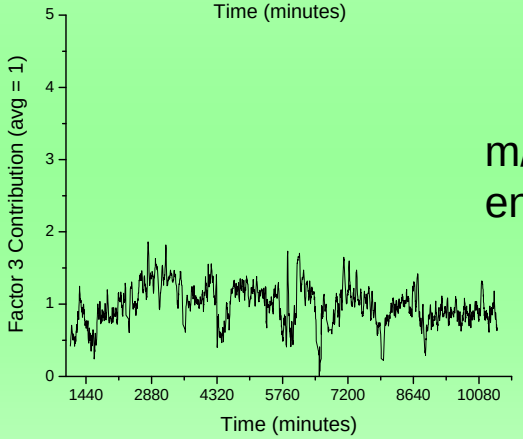




m/z < 400 enhanced

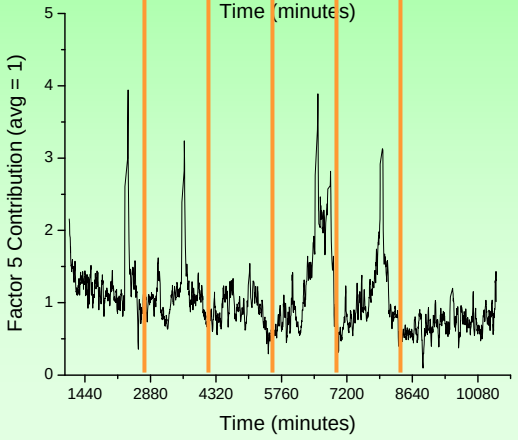
256, 284 alkanoic acids





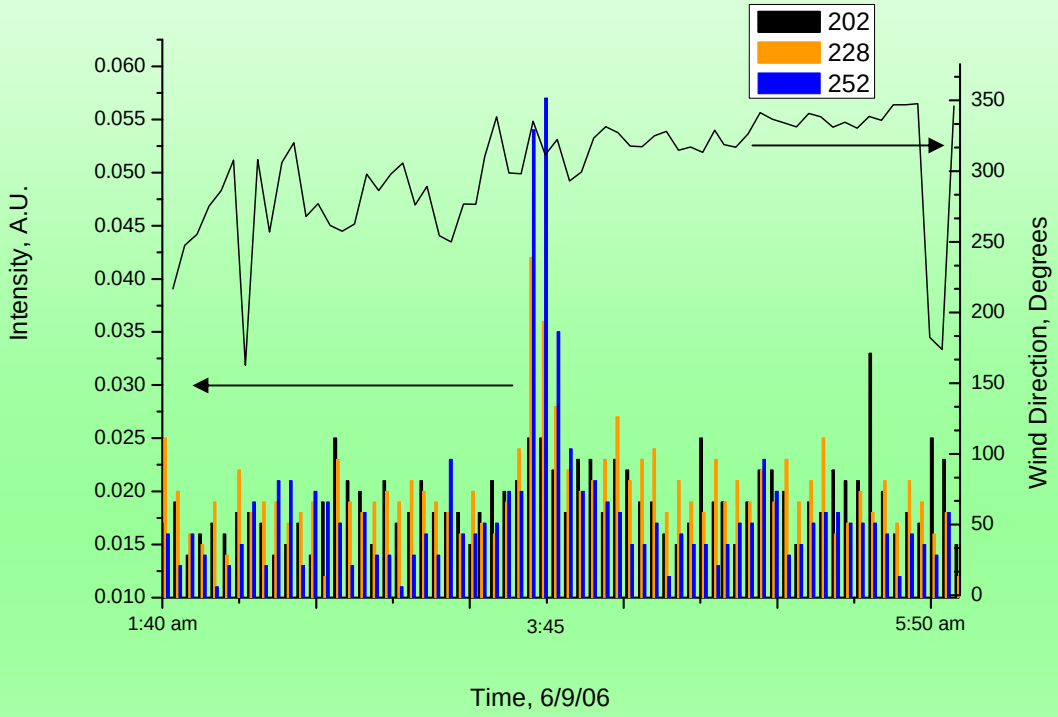
m/z > 400 enhanced

149, 167, 279 phthalates

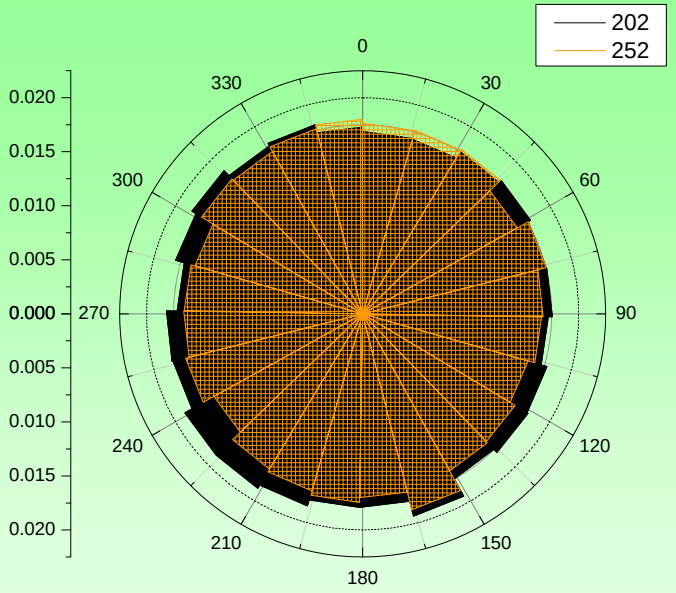


EPA PMF 1.1
2259 spectra
80 m/z values:
alkyl fragments, alkanes (alkenoic acids), alkanoic acids, PAHs, phthalates, biogenic SOA “markers”, molecular markers from GC-MS studies

A Possible PAH “Event”



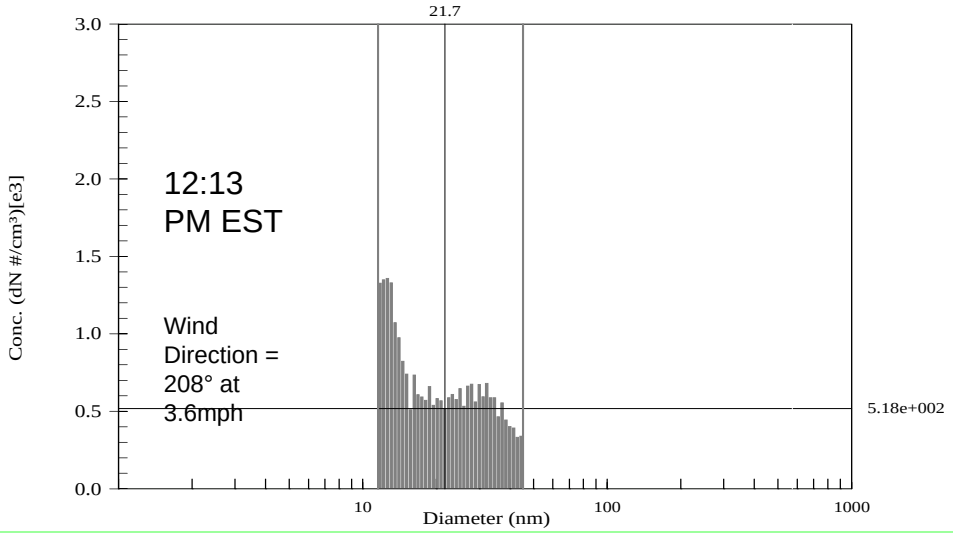
Not likely a plume from a unique stationary source

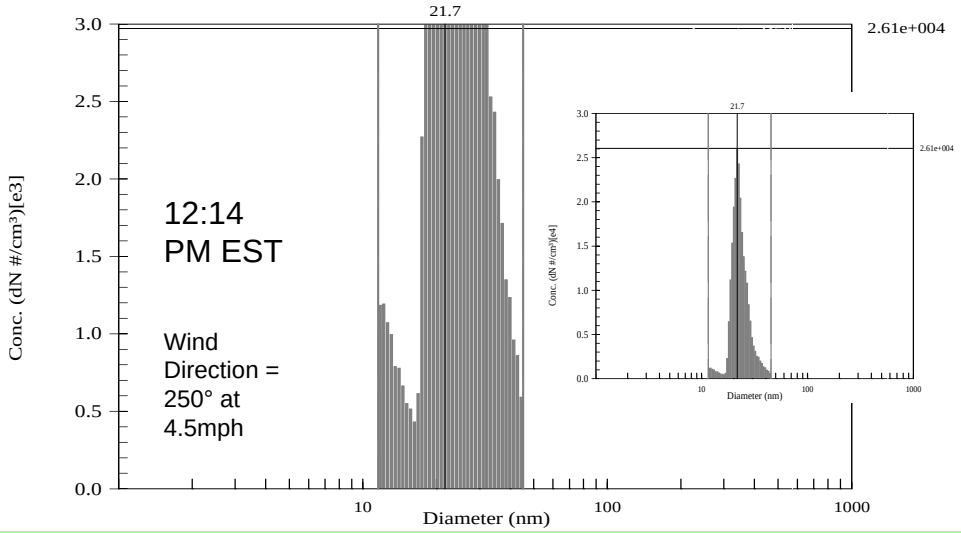


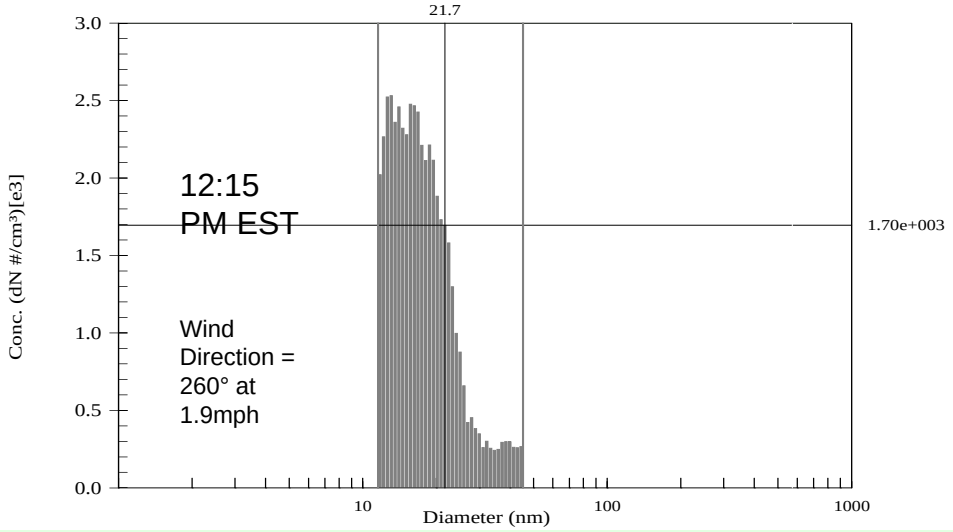
No discernible time or wind direction dependence over the measurement period

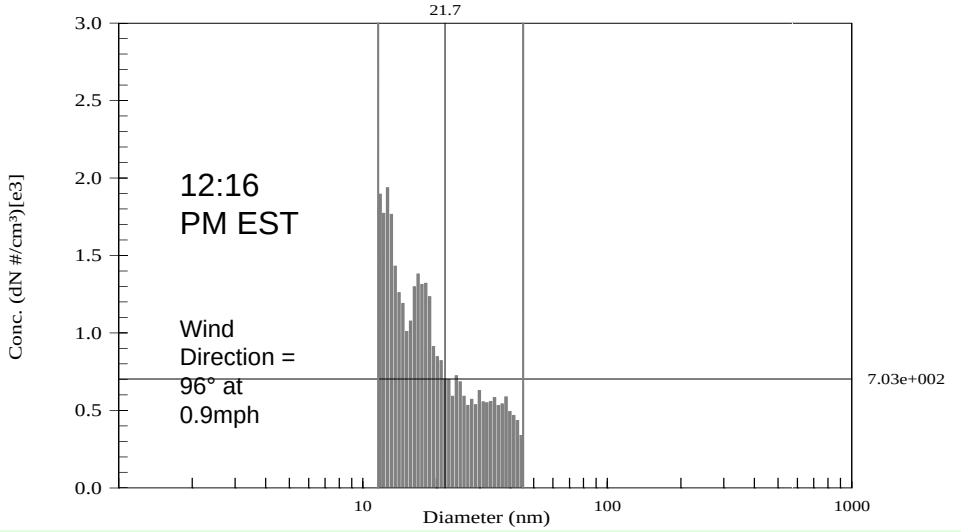
Particle Emission from a Diesel Locomotive

Diesel engine passes monitoring site at 12:14 PM EST (6/08/05)



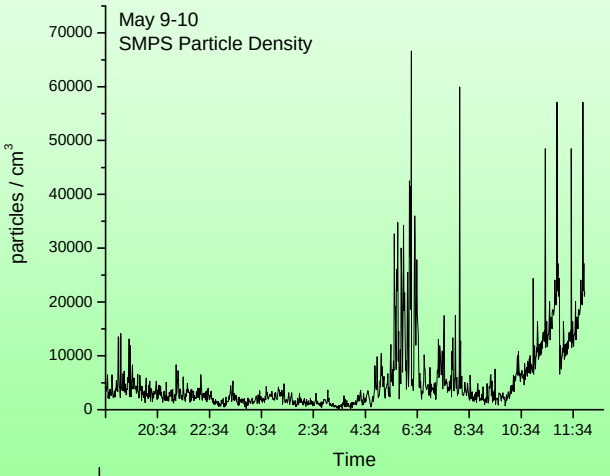


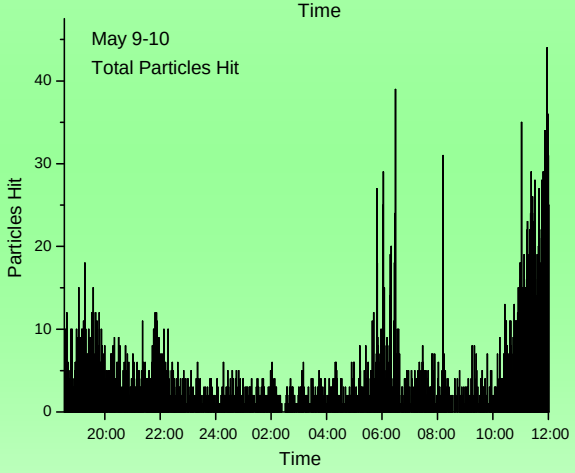




Resolving Individual Mobile Emitters

- Requirements
  - Size range: < 50 nm diameter
  - Time resolution: 1 minute
  - See also: Ogulei et al., JAWMA 2007, AS&T 2007
- PIAMS is not particularly well suited
  - Size range: 50-500 nm diameter
  - Time resolution: 3.5 minutes
- NAMS (nanoaerosol mass spectrometer) is better suited
  - Size range: 10-35 nm diameter
  - Time resolution: ≤ 1 minute





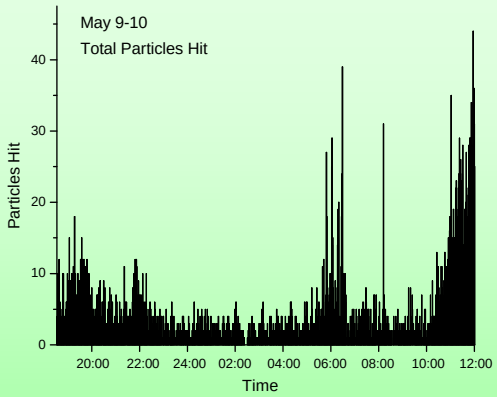
May 9-10, 2006: 5002 particles in 17 hr

$dN/d(\log d_p)$ vs. Time

d_m = 21 nm (d_{mn} = 25 nm for ρ = 1.7 g/cm^3)

NAMS Particle Hits per min vs. Time

d_{mn} = 25 nm (*f* = 10 kHz)



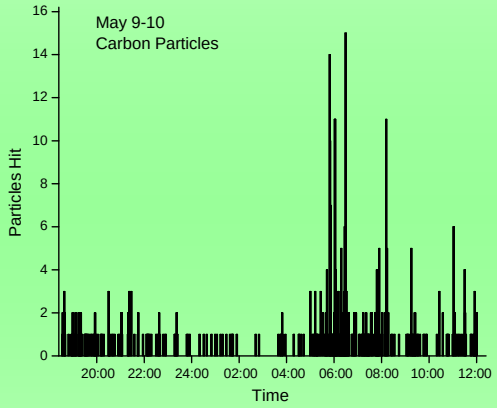
Particle “spikes” = hydrocarbon (vehicles?)

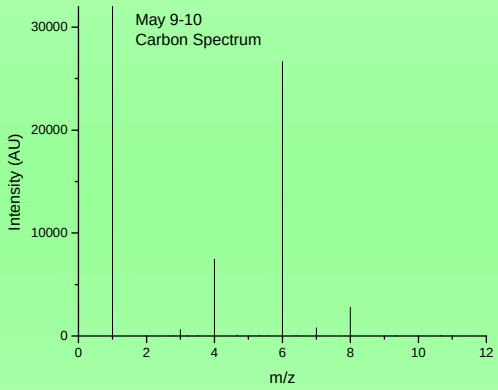
Low but detectable S, Si (core?)

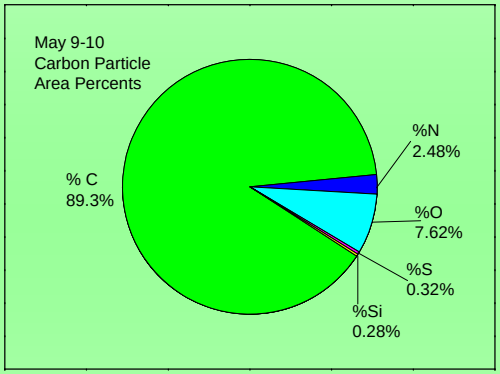
N, O concentrations appear to scale

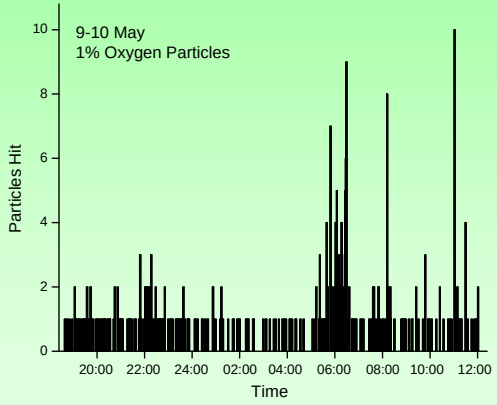
- significant organic nitrates or NH_4NO_3 (?)

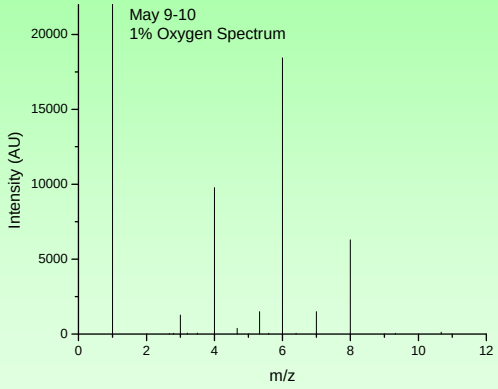
O:C ratio (residual) 0.04-0.17

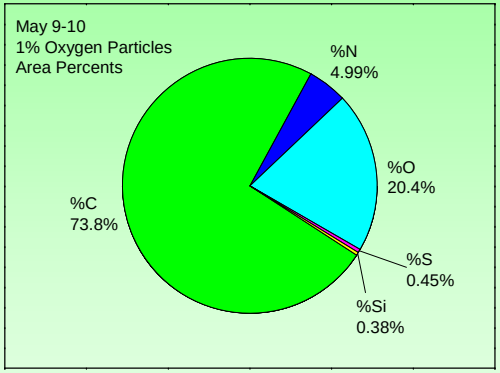


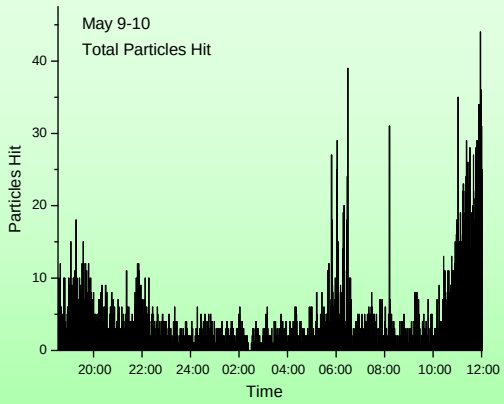


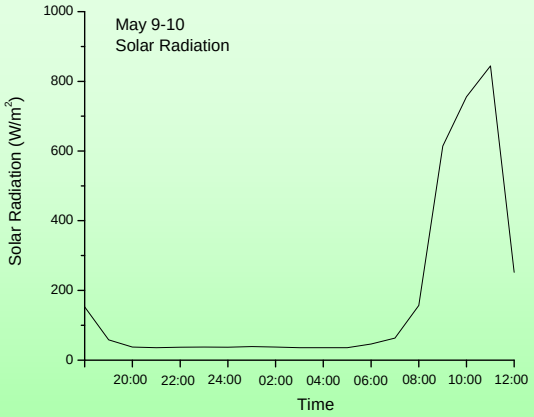








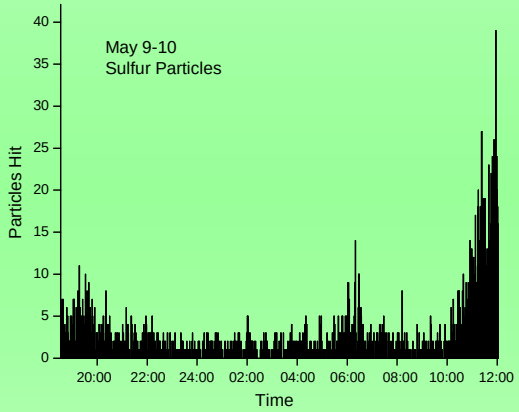


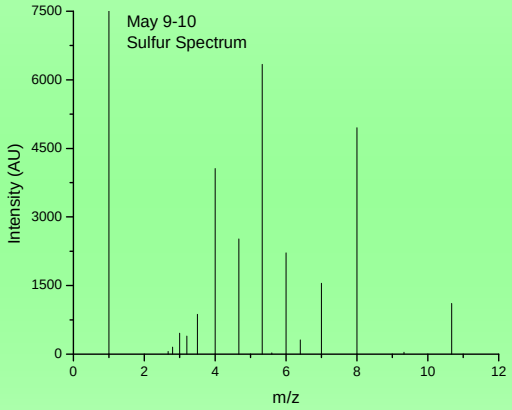


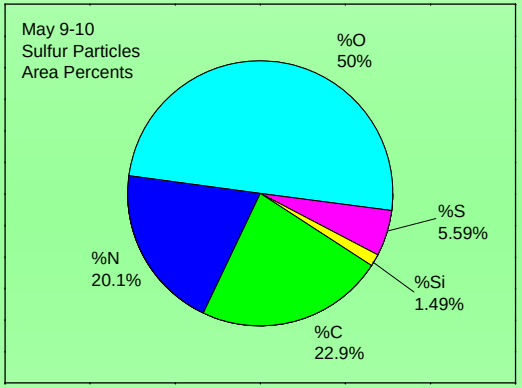
Photochemically generated secondary aerosol (?)

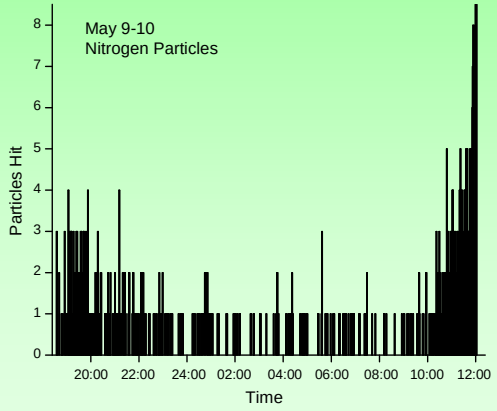
Sulfate and nitrate are indicated

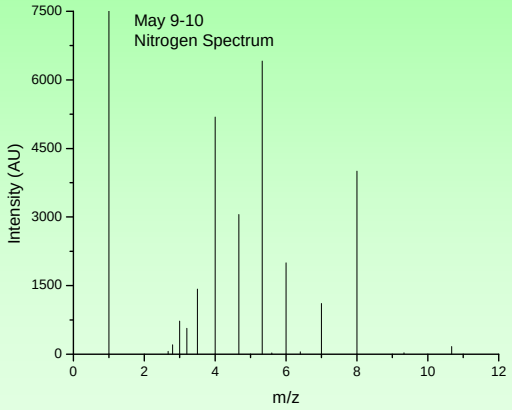
O:C (residual) ~0.6

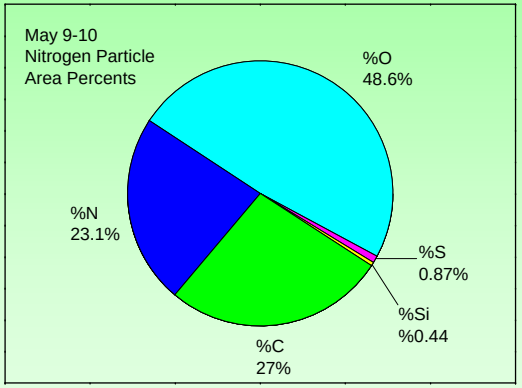












Conclusions

1. PIAMS has permitted ambient organic aerosol analysis at the molecular level with <5 min time resolution.
2. Rapid changes in molecular composition are observed for several species, most notably phthalates, alkanoic acids, high and MW alkanes.
3. In most cases, 30 min time resolution appears sufficient to capture the variations observed.
4. Characterizing carbonaceous emissions from individual mobile emitters requires fast time resolution (1 min) and nanoparticle detection (<50 nm). NAMS shows good potential for these measurements.

Remaining Work

1. Finish current round of ambient measurements.
2. Correlate PIAMS results with other parameters:
   - NOx, SO_2, O_3, CO, VOC
   - PM2.5, SMPS
   - OCEC, GC-MS (filter samples)
   - Meteorology

Acknowledgements

- **Matthew Dreyfus (UD)**
- Kouame Adou (UD)
- Michael Tolocka (LSU)
- EPA Grant No. RD-83216601