Development of the GC-MS Organic Aerosol Monitor (OAM) For In-field Detection of Fine Particulate Organic Compounds

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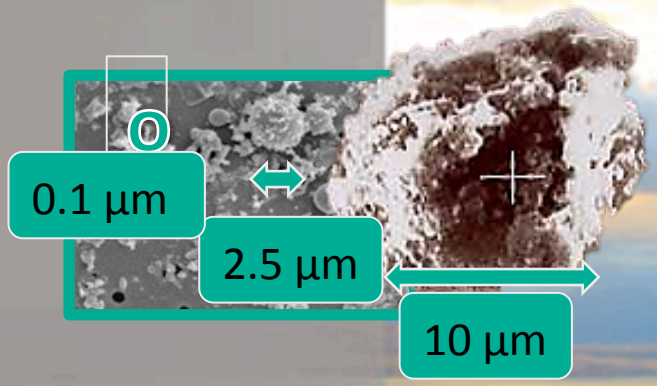
National Ambient Air Quality Standards (NAAQS)

Pollutant [final rule cite]		Primary/ Secondary	Averaging Time	Level	Form
Carbon Monoxide [76 FR 54294, Aug 31, 2011]		primary	8-hour	9 ppm	Not to be exceeded more than once per year
			1-hour	35 ppm	
Lead [73 FR 66964, Nov 12, 2008]		primary and secondary	Rolling 3 month average	0.15 µg/m^3 (1)	Not to be exceeded
Nitrogen Dioxide [75 FR 6474, Feb 9, 2010] [61 FR 52852, Oct 8, 1996]		primary	1-hour	100 ppb	98th percentile, averaged over 3 years
		primary and secondary	Annual	53 ppb (2)	Annual Mean
Ozone [73 FR 16436, Mar 27, 2008]		primary and secondary	8-hour	0.075 ppm (3)	Annual fourth-highest daily maximum 8-hr concentration, averaged over 3
Particle Pollution Dec 14, 2012	$PM_{2.5}$	primary	Annual	12 µg/m^3	annual mean, averaged over 3
		secondary	Annual	15 µg/m^3	annual mean, averaged over 3 years
		primary and secondary	24-hour	35 µg/m^3	98th percentile, averaged over 3 years
	PM_{10}	primary and secondary	24-hour	150 µg/m^3	Not to be exceeded more than once per year on average over 3
Sulfur Dioxide [75 FR 35520, Jun 22, 2010] [38 FR 25678, Sept 14, 1973]		primary	1-hour	75 ppb (4)	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		secondary	3-hour	0.5 ppm	Not to be exceeded more than once per year

http://www.epa.gov/air/criteria.html

Organic Aerosol



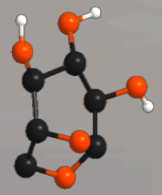
Particulate Matter (PM) Composition:

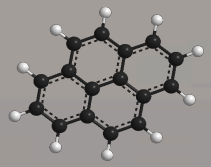
- Inorganic Material
- Soils & Dust
- Metals
- Black Carbon
- Organic Compounds

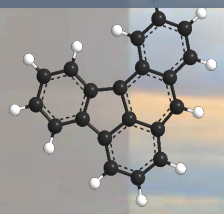
10-90%

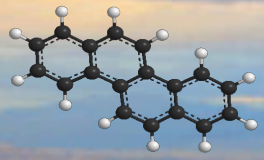
(1) Lee, S. H.; Allen, H. C. *Anal Chem* **2012**, *84*, 1196-1201.

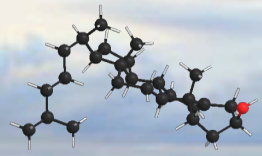
PM Organic Markers









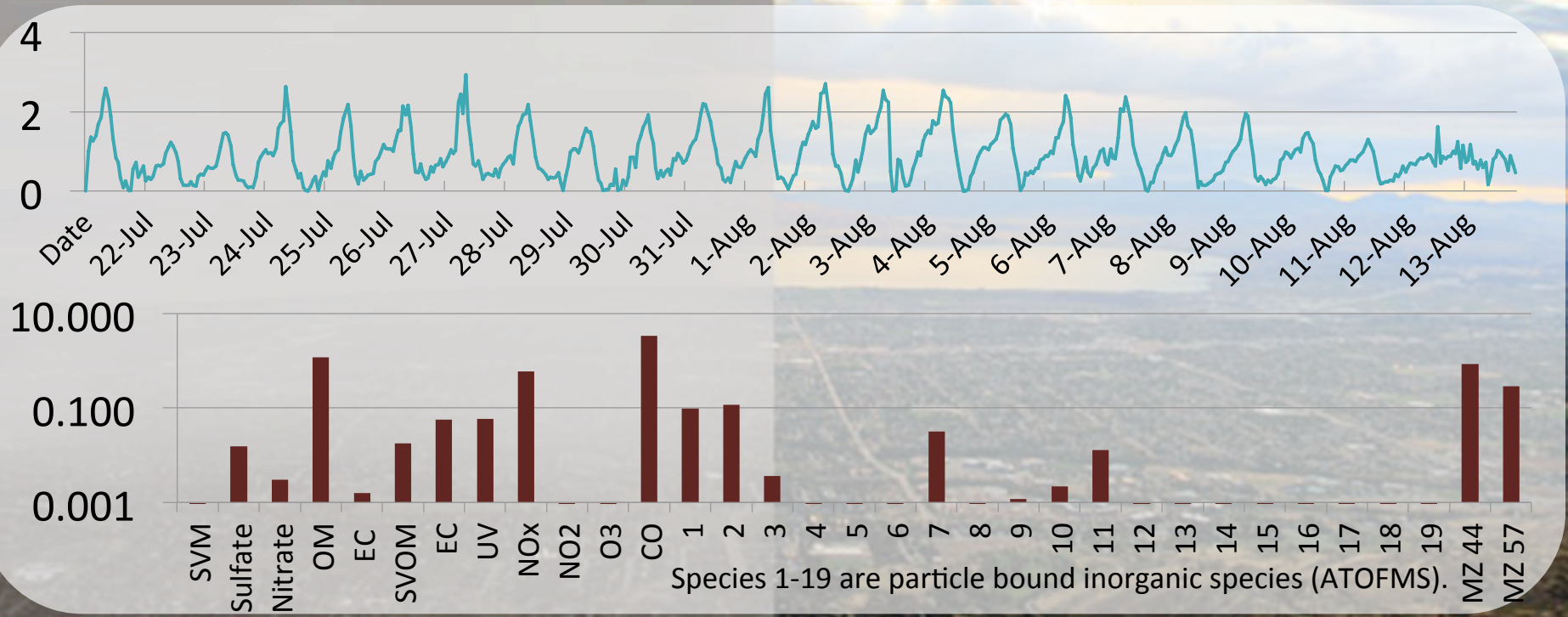


Levoglucosan

Polycyclic aromatic hydrocarbons (PAHs)

Cholesterol

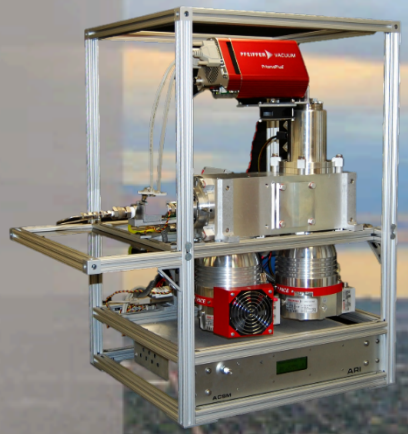
Organic Aerosol Composition For Source Apportionment



Example: One of 16 sources (mobile gas) identified using positive matrix factorization.

Eatough, D. J.; Grover, B. D.; Woolwine, W. R.; Eatough, N. L.; Long, R.; Farber, R. *Atmospheric Environment* **2008**, *42*

Field Techniques

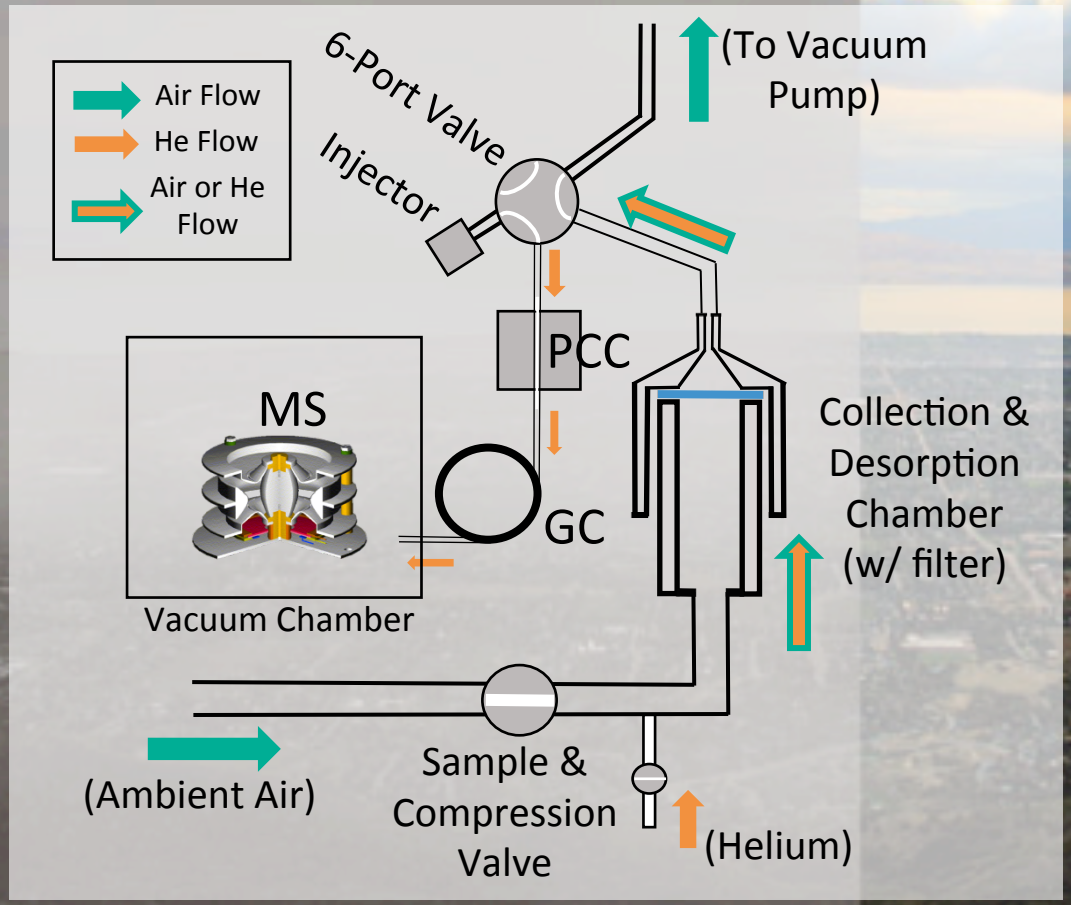


Current Instrumentation:

- Aerodyne Aerosol Chemical Speciation Monitor
- Aerodyne Aerosol Mass Spectrometer
- TSI Aerosol ToF Mass Spectrometer (discontinued)

(1) Williams, B. J.; Goldstein, A. H.; Kreisberg, N. M.; Hering, S. V. *P Natl Acad Sci USA* **2010**, *107*, 6676-6681.

GC-MS Organic Aerosol Monitor (OAM)



Thermal Desorption Chamber

↓

Pre-column Concentrator (PCC)

↓

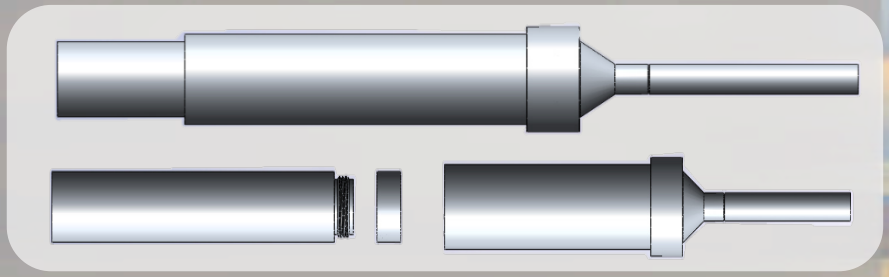
Gas Chromatograph (GC)

↓

Mass Spectrometer (MS)

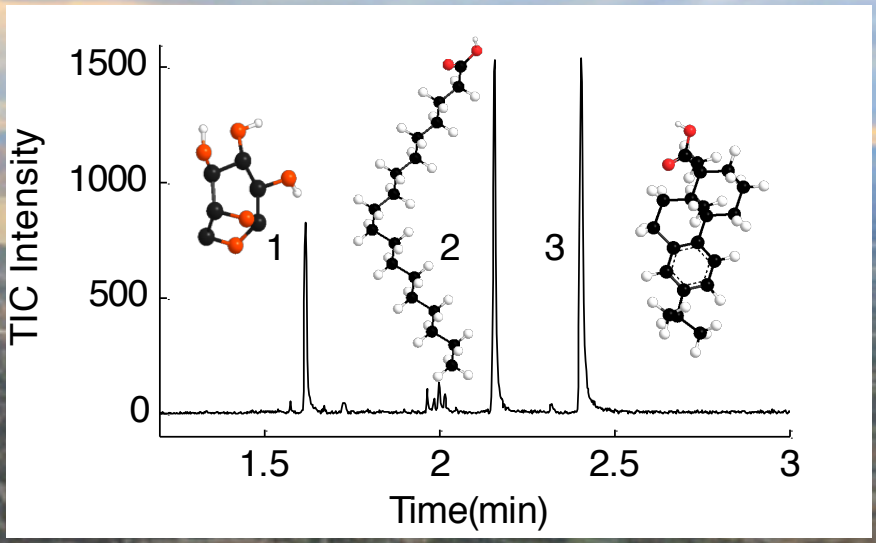
Collection/Thermal Desorption Chamber

Chamber
↓
PCC
↓
GC
↓
MS



Chamber Specifications:

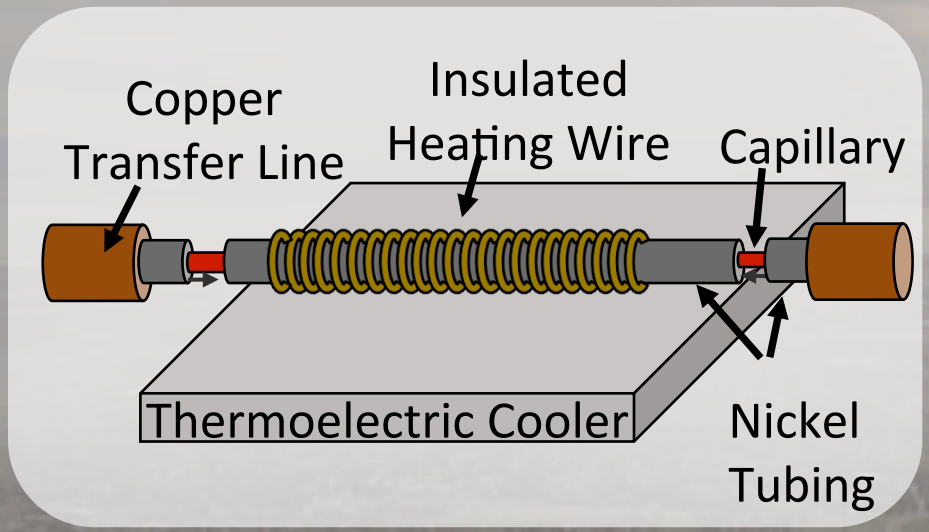
- Deactivated Quartz Filter
- Inertium Treated Stainless Steel Chamber
- Resistively Heated
- Desorb at 150- 280 °C
- Condition/Clean at 280-350 °C

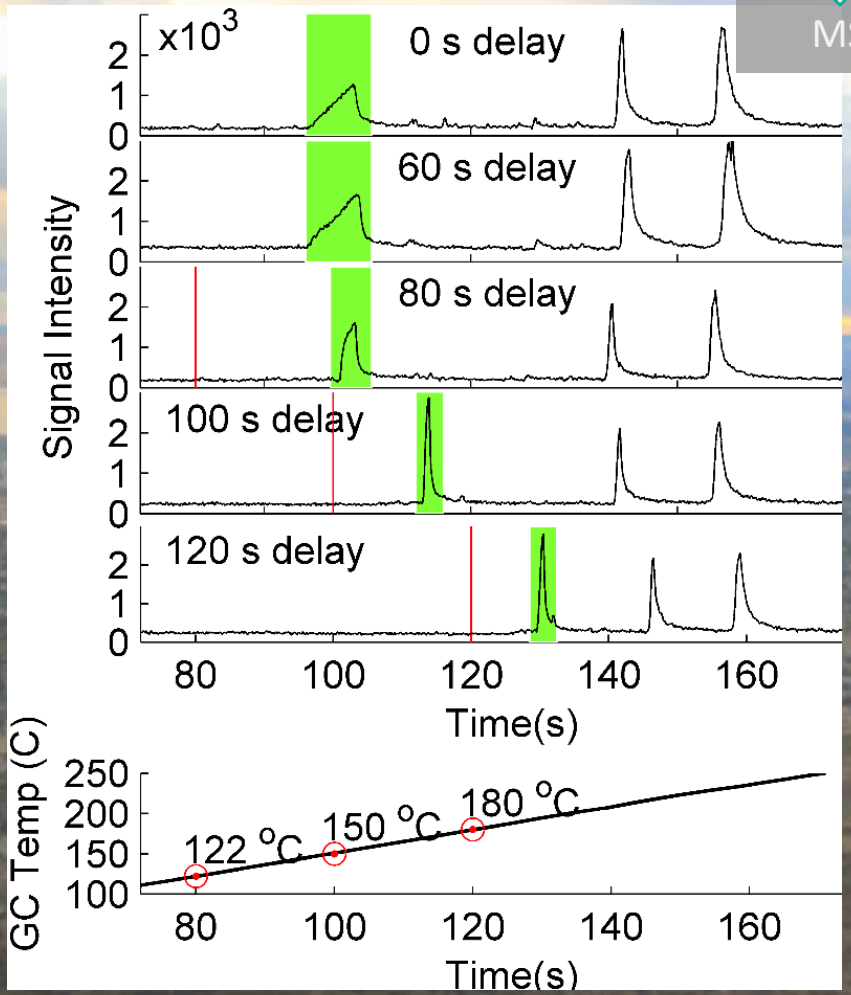


1- Levoglucosan
2- Stearic Acid
3- Dehydroabietic acid

Pre-Column Concentrator

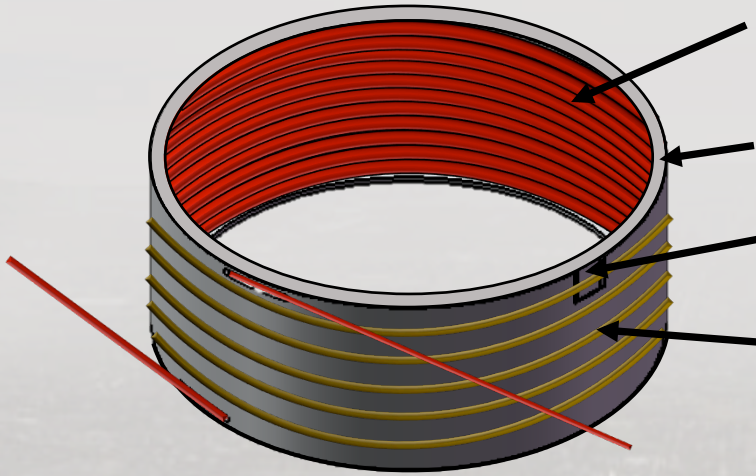
Chamber
PCC
GC
MS



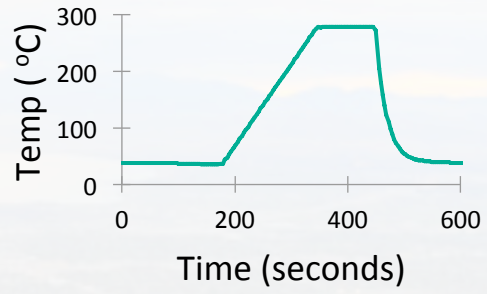


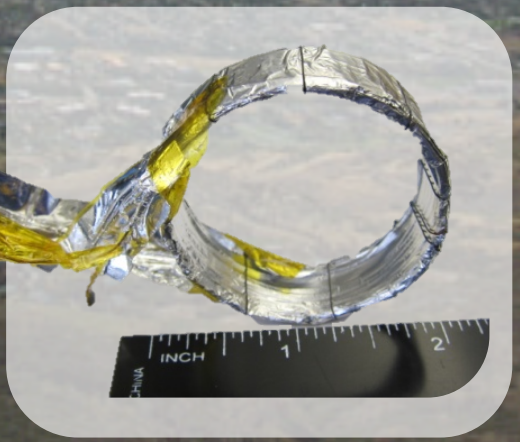
Compact Gas Chromatograph

Chamber
↓
PCC
↓
GC
↓
MS



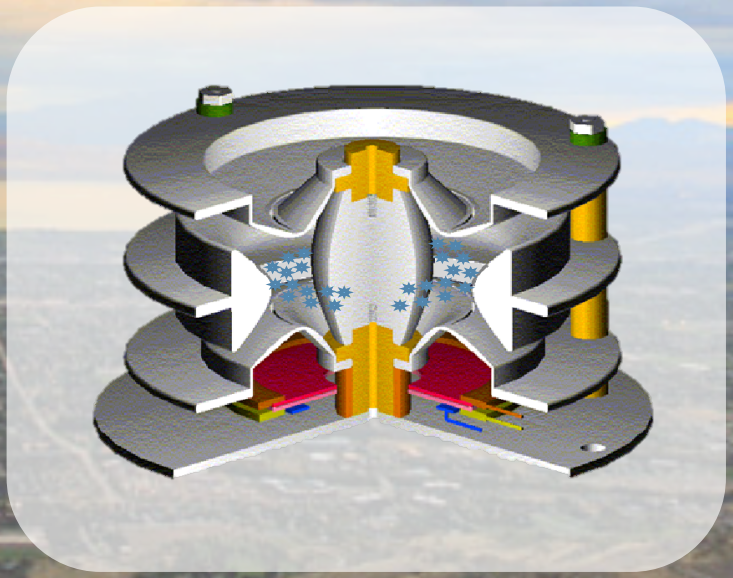
Column Heating





Toroidal Ion Trap Mass Spectrometer

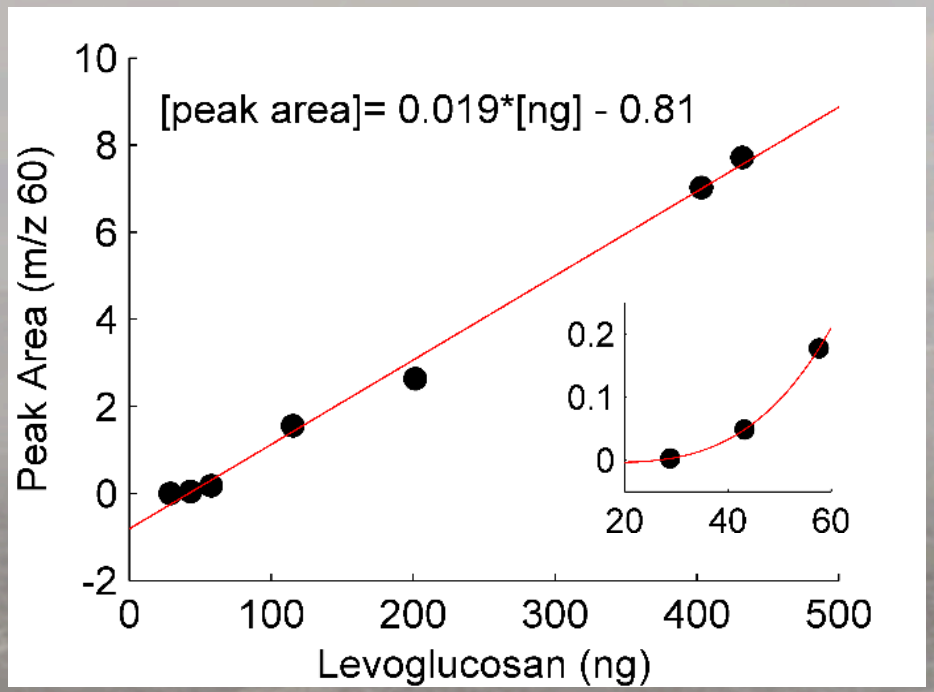
Chamber
⇩
PCC
⇩
GC
⇩
MS



Modified Guardian 7, Torion Technologies (Perkin Elmer)

OAM System Testing

Levoglucosan Desorption Calibration:

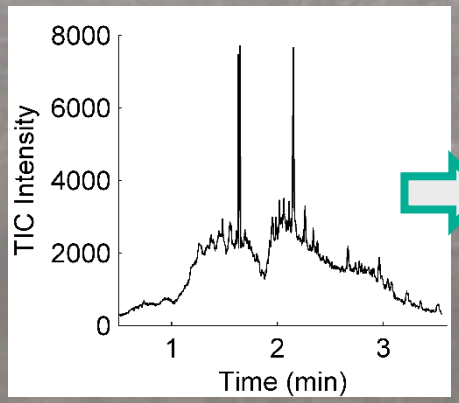


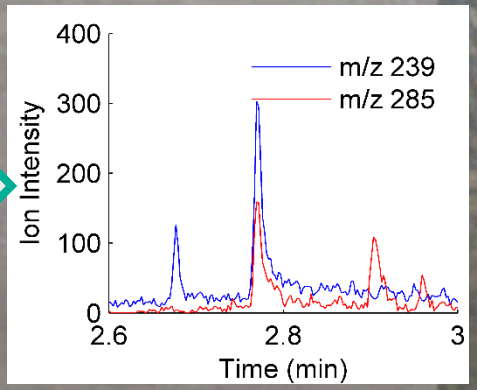
Calibration Curve:

1. Linear from 60-400+ ng
2. Nonlinearity at low concentrations
   a. Ion Trap Response
   b. Discriminator level
   c. Degradation

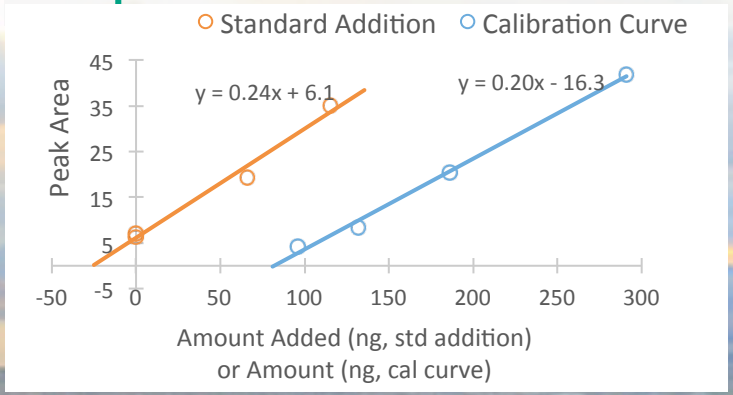
OAM System Testing

Atmospheric Chamber

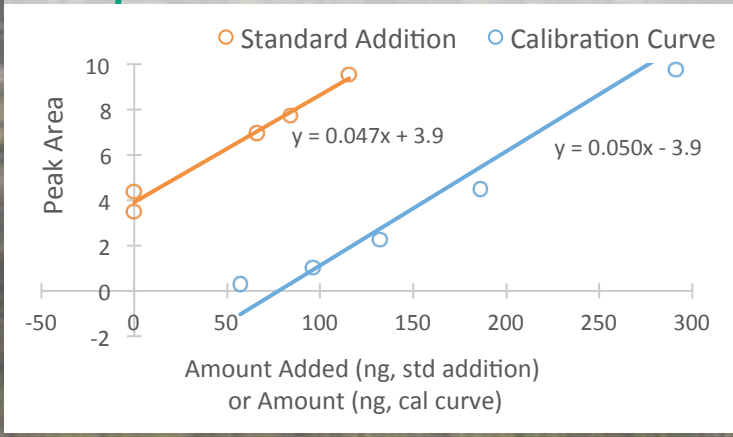




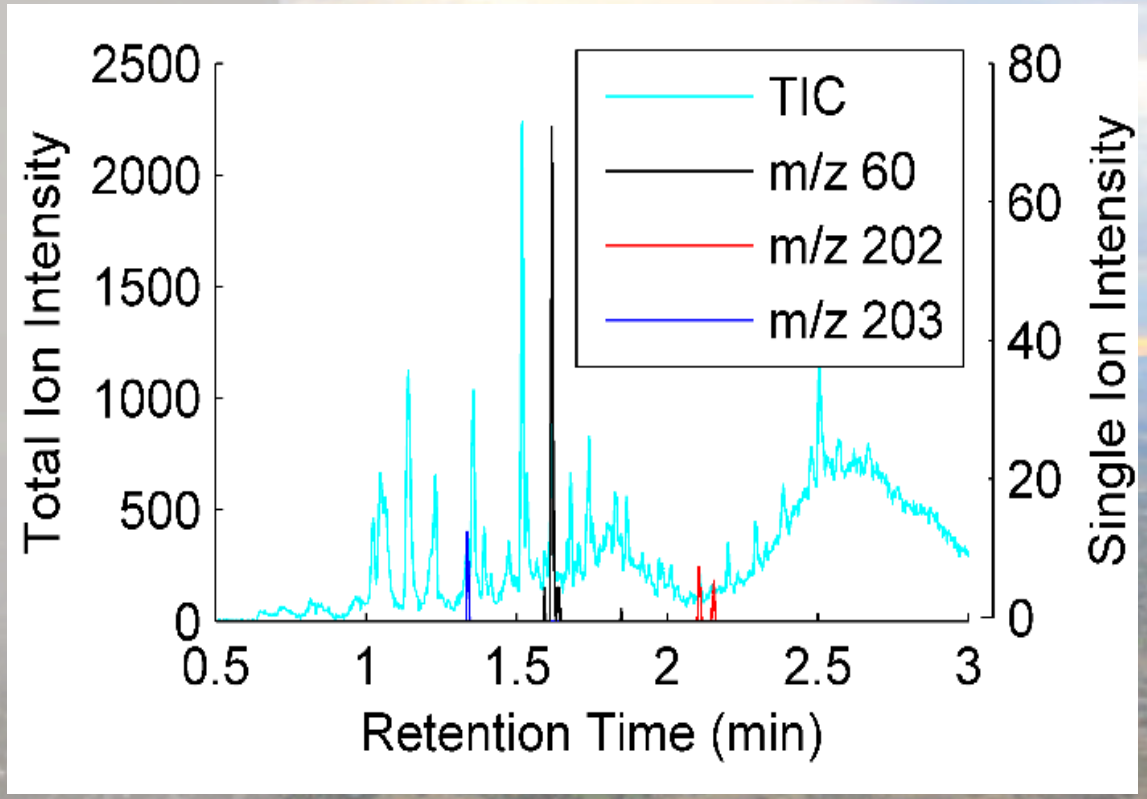
Dehydroabietic acid: slopes same at 95% CI



Levoglucosan: slopes same at 85% CI

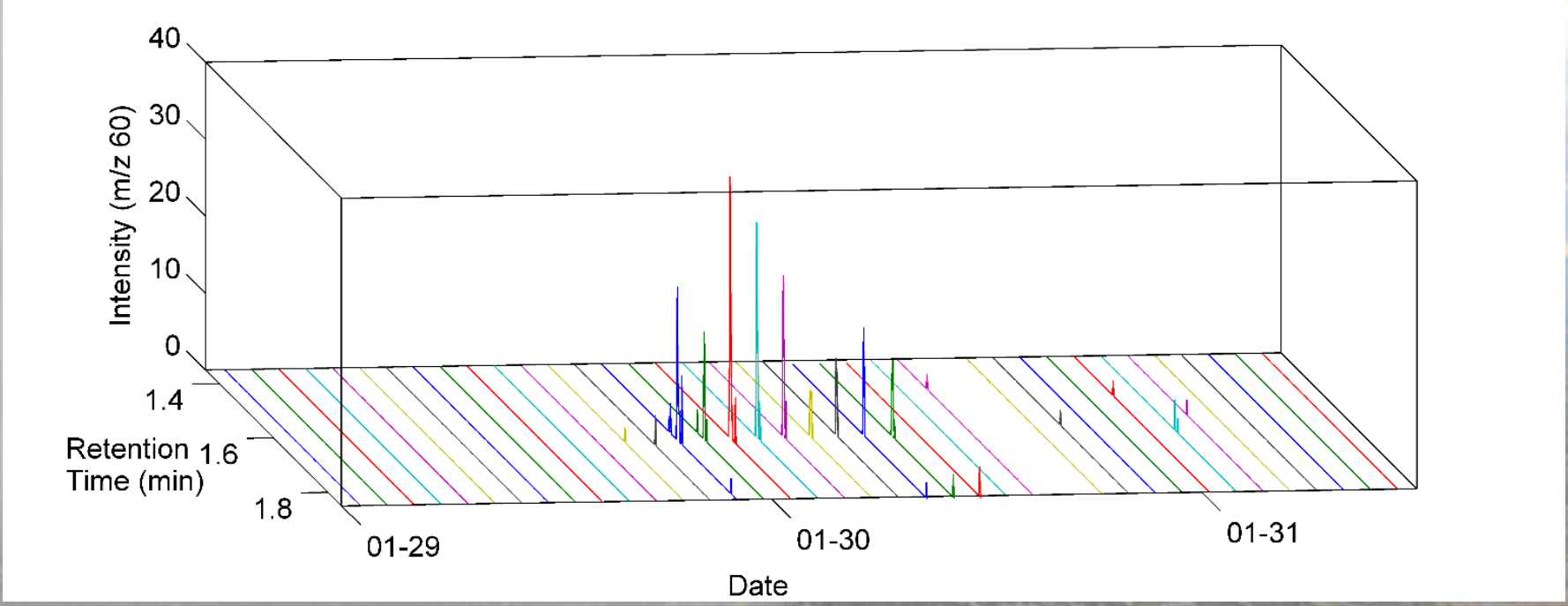


OAM Field Results



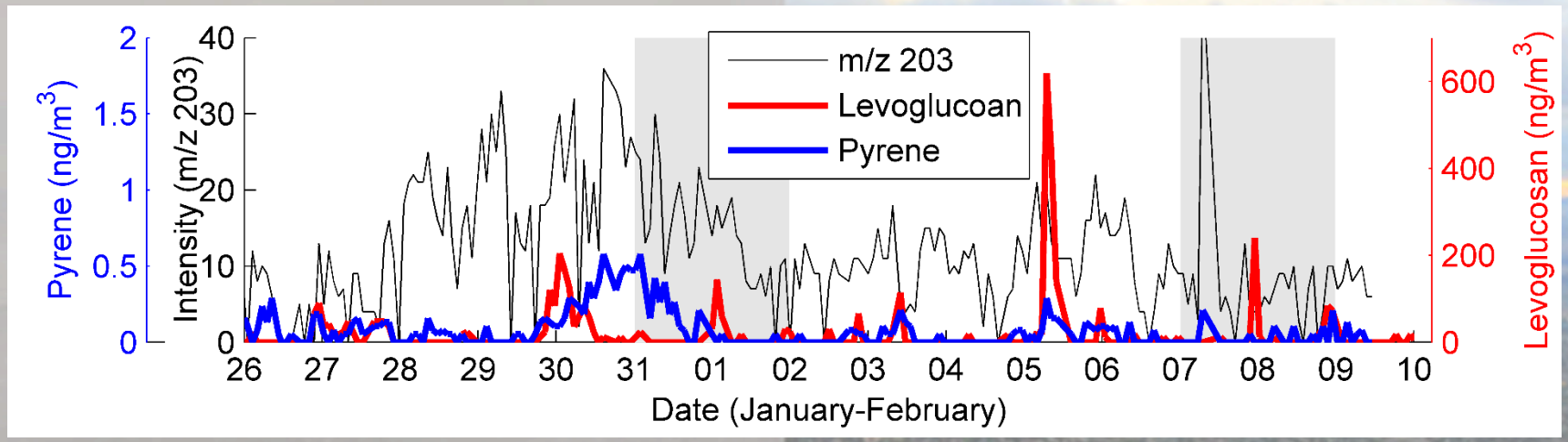
Total Ion Chromatogram (TIC) for an ambient sample collected 2/5/2015 from 10:00- 11:00 a.m.

OAM Field Results



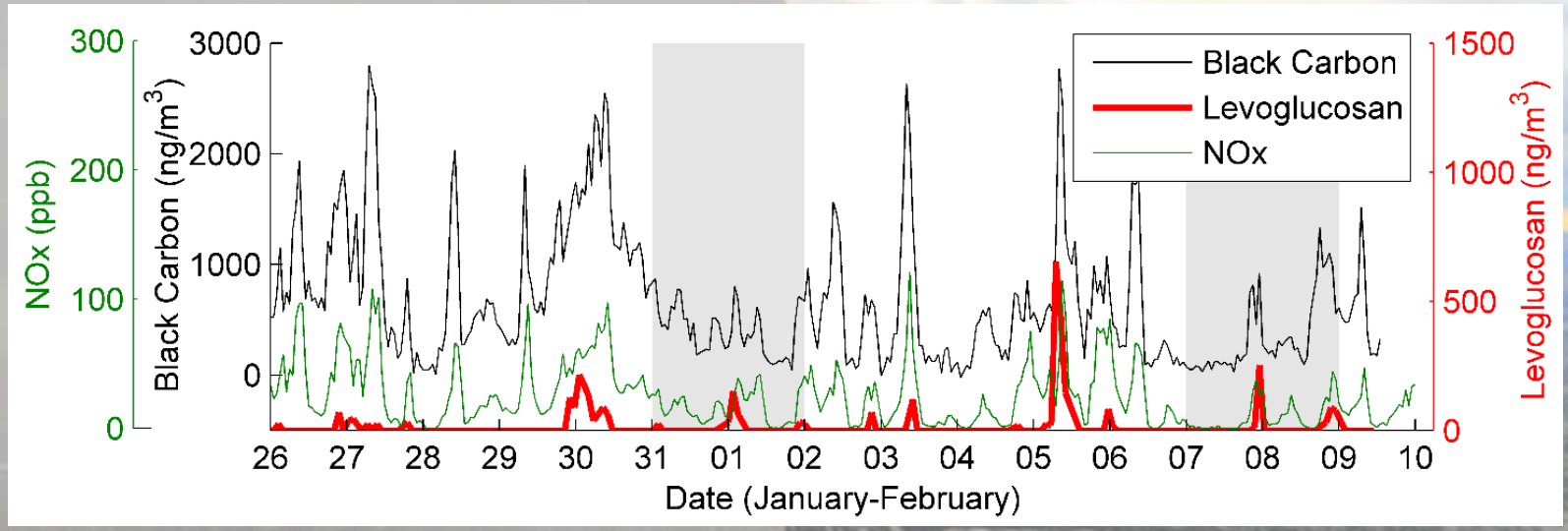
Series of chromatograms (m/z 60) demonstrating levoglucosan detection.

OAM Field Results



Semi-continuous concentrations of pyrene, levoglucosan, and an unidentified compound.

OAM Field Results



Semi-continuous concentrations of levoglucosan, black carbon, and NOx.

Conclusions

- Autonomous operation
- In-field reliability
- Semi-continuous concentrations of organic markers
- High sensitivity & selectivity

OAM Future Development

- Integration of sorbent tube for autonomous VOC sampling
- Further filter testing for higher temperatures
- Use for source apportionment (PMF analysis)

Acknowledgements

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NSF

SOUTHERN CALIFORNIA EDISON

TORION