Scientific Innovation Through Integration

Molecular Characterization of Organic Aerosol

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ASR ALCWG 2010 Workshop

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EMSL is located at PNNL

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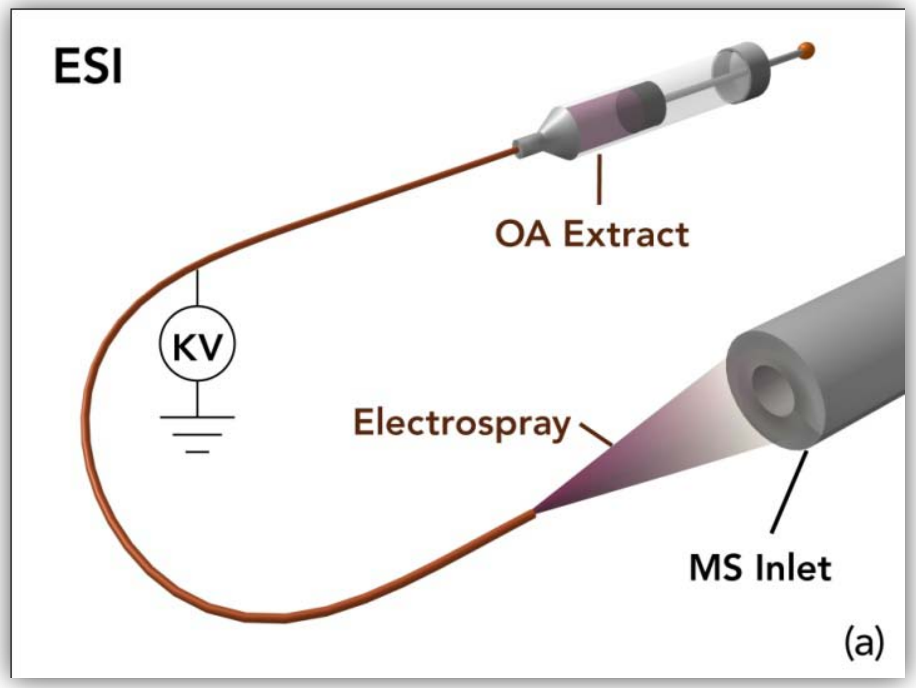
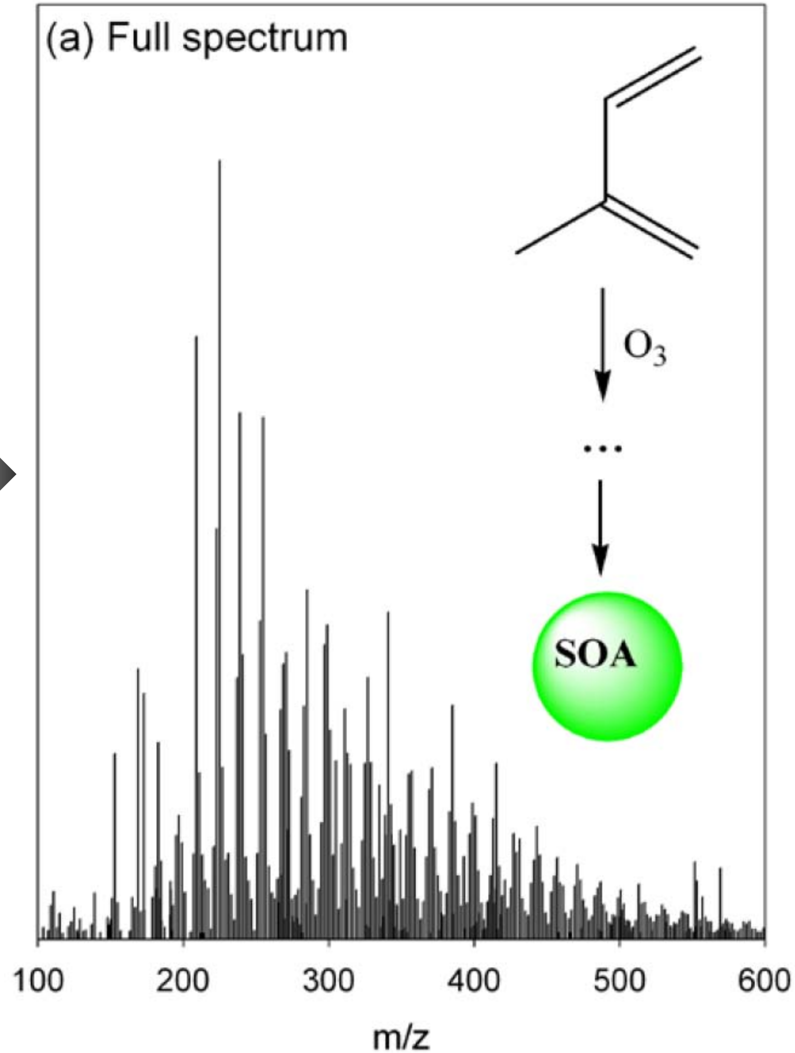
Understanding of fundamental relationship between the chemical composition and physicochemical properties of OA.

- Application of HR-MS for Molecular-level Characterization of OA, Unraveling Mechanisms of SOA Formation and Atmospheric Aging
- Development and Applications of Novel API-Surface Sampling Techniques for Analysis of OA
- Molecular Insights on Chemical Composition and Absorption Properties of "Brown Carbon"

ESI/HR-MS Analysis of OA





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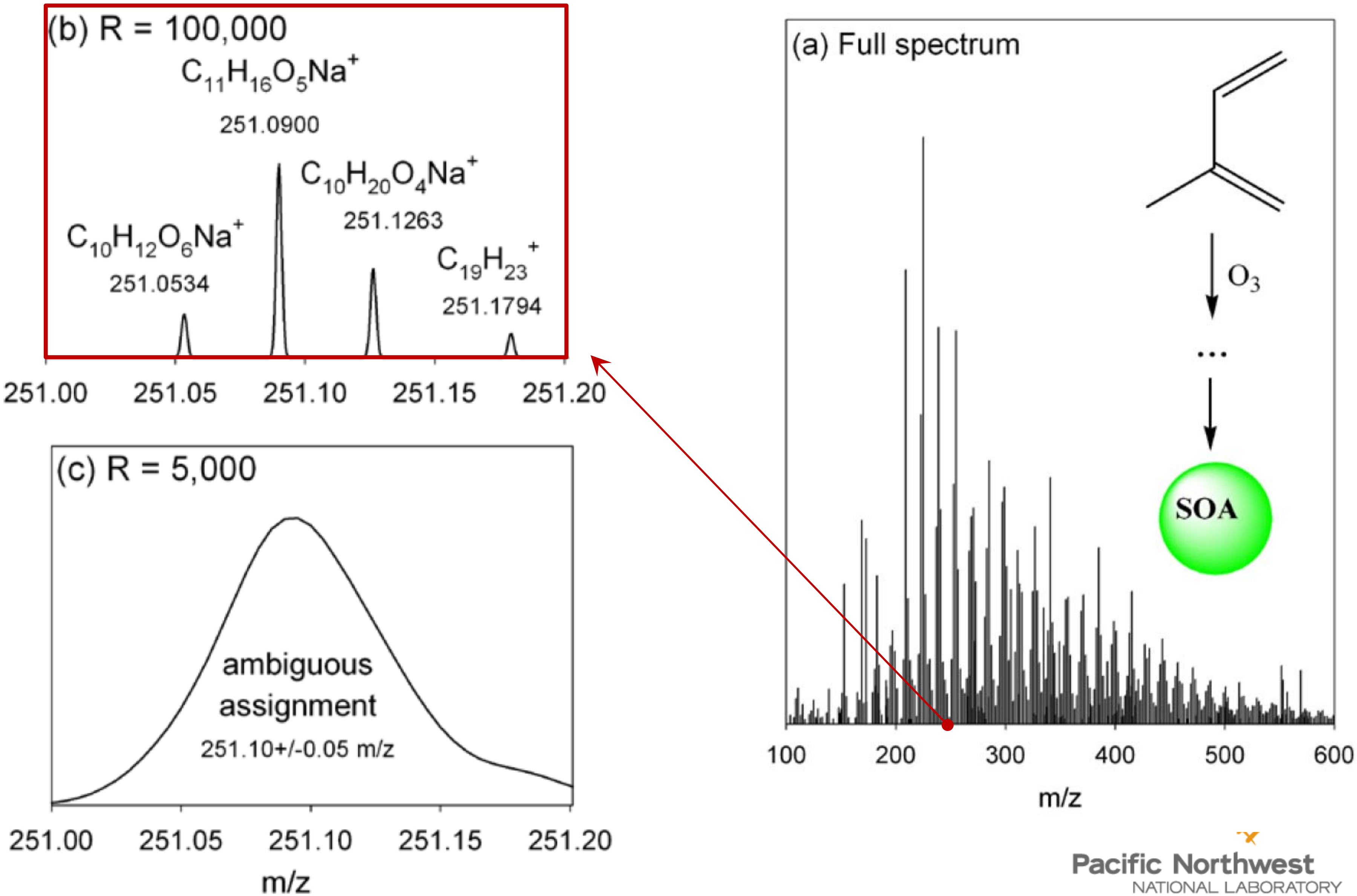
ESI/HR-MS Analysis of OA



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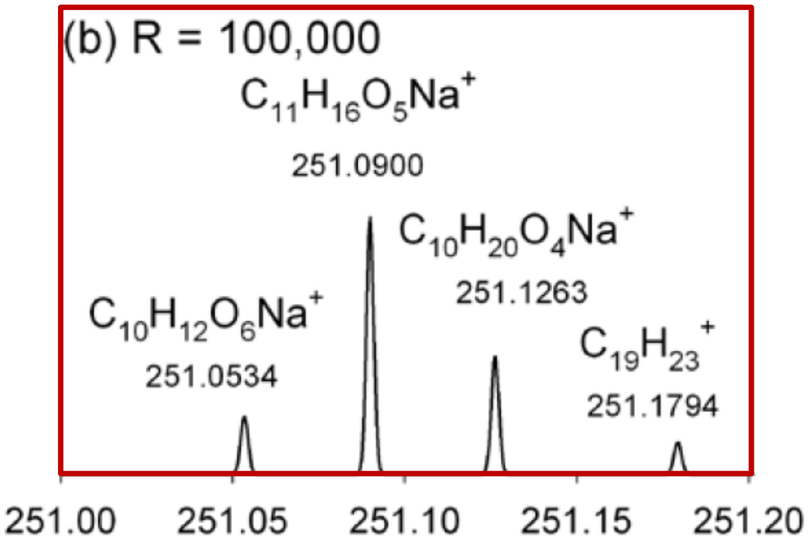
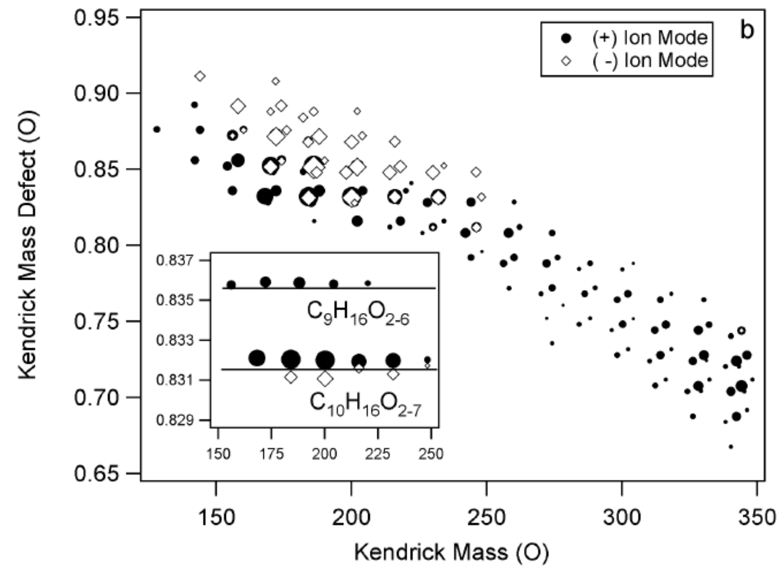
ESI/HR-MS Analysis of OA





First study in2004: M. Johnston and Co (*U. Delaware*)

- **Improved Understanding of OA Molecular Composition**
- **Mechanisms of SOA Formation and Atmospheric Aging:** **Effects of Seed Particles, Concentrations, RH, UV-light, etc.**
- **Closure Studies on OA Chemistry and their Physico-chemical Properties**
- **Applied in both Laboratory and Field studies** **(SOA, WSOC – rain/cloud water, BBA)**

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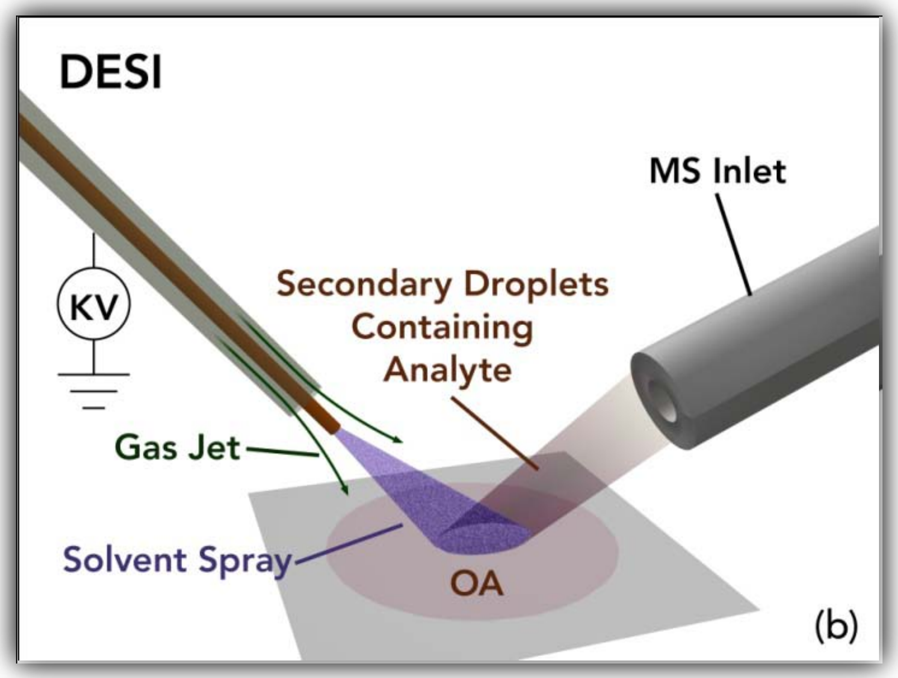
DESI MS - API/Surface Sampling Technique

Takats et al., *Science*, 2004 **Cooks et al.,** *Science*, 2006



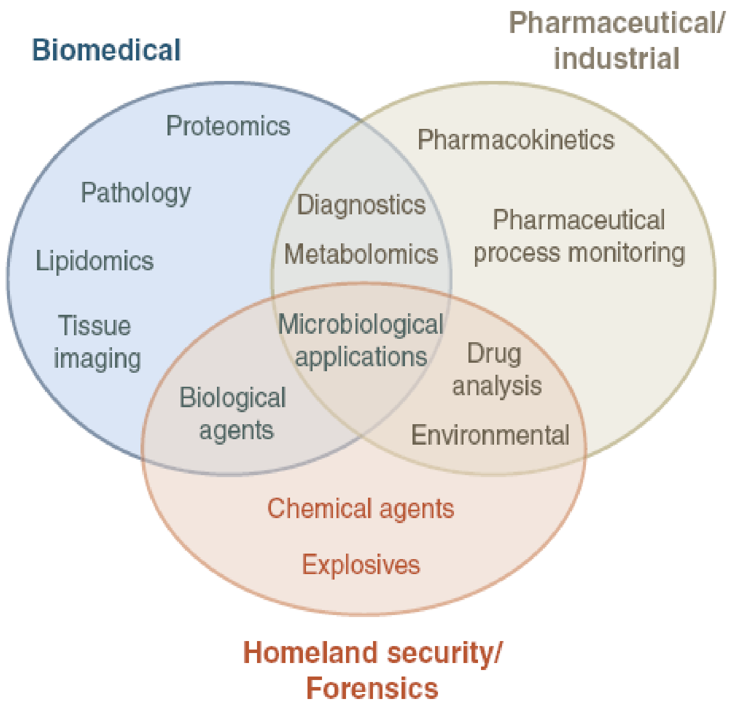


Fig. 4. Areas of application of the ambient MS method of DESI, grouped into three broad overlapping classes.

- ✓ **no sample prep is required**
- ✓ **ambient pressure ionization/sampling**

- **2004-2008: Has not been applied for analysis of aerosol samples…**
- **2009: Field samples - X. Yang et al, (*Fudan U.*)**
- **2010: SOA aging (*PNNL-UCI*)**
- **2010: Development and Application of Nano-DESI**

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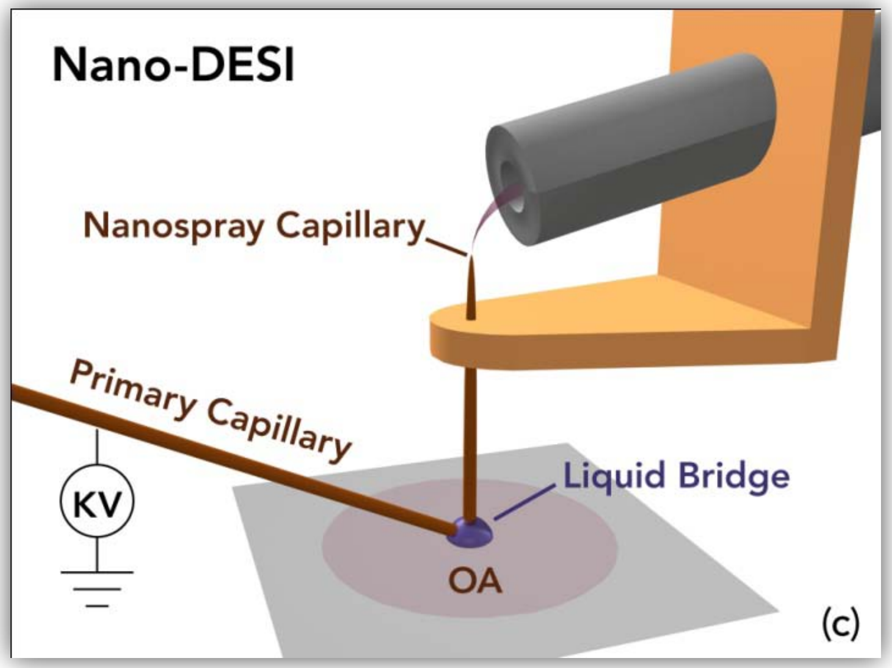
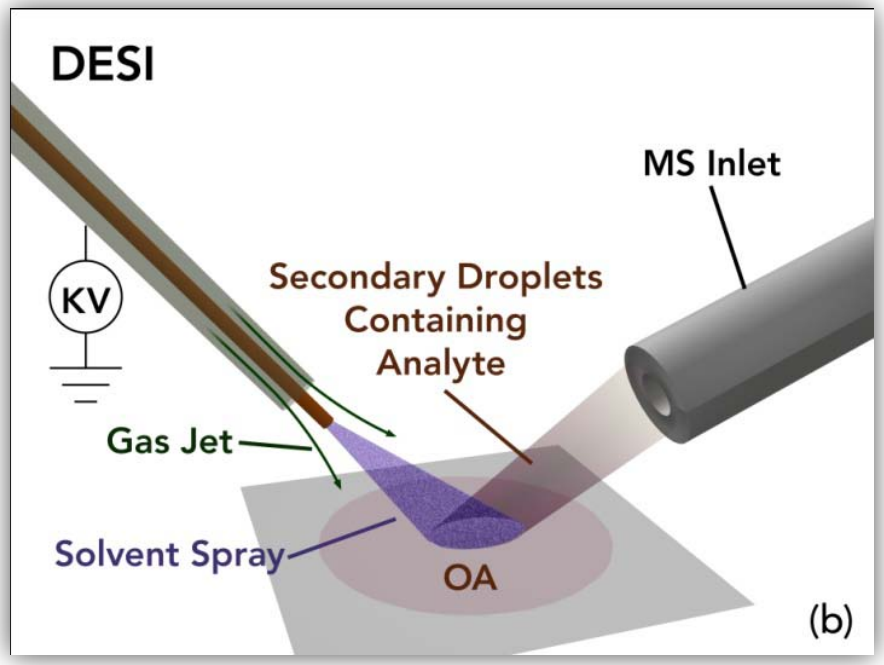
Nanospray-DESI Mass Spectrometry

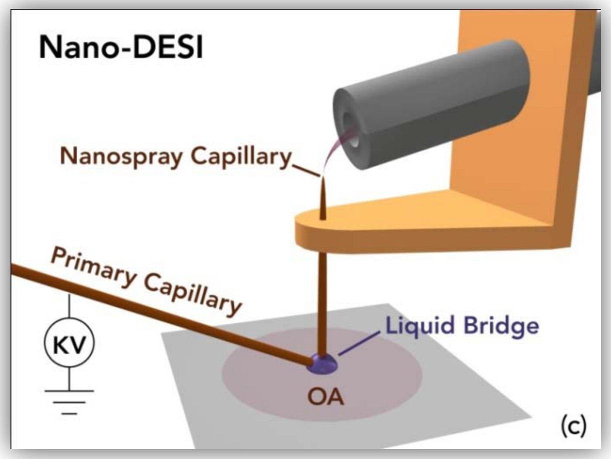
Roach et al., *Analyst*, 2010; *Anal. Chem.*, 2010



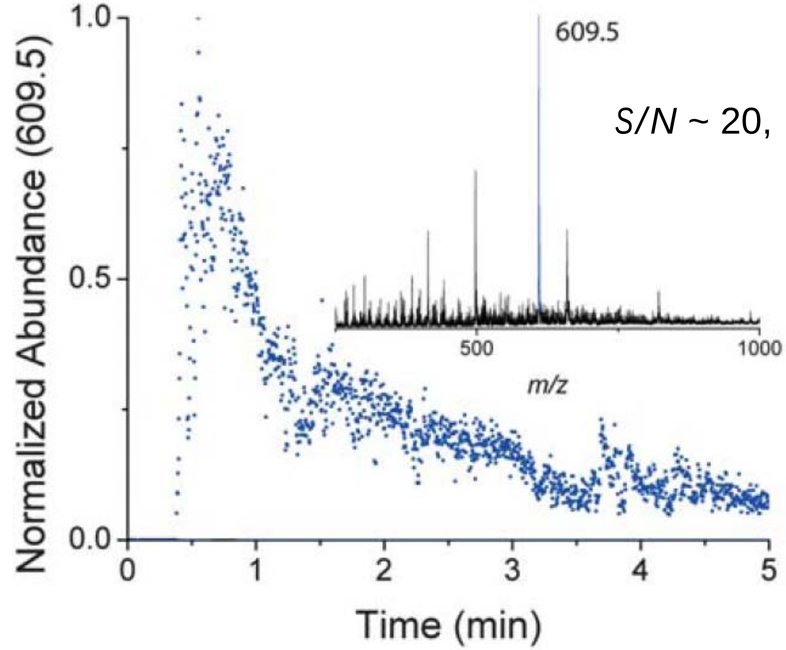


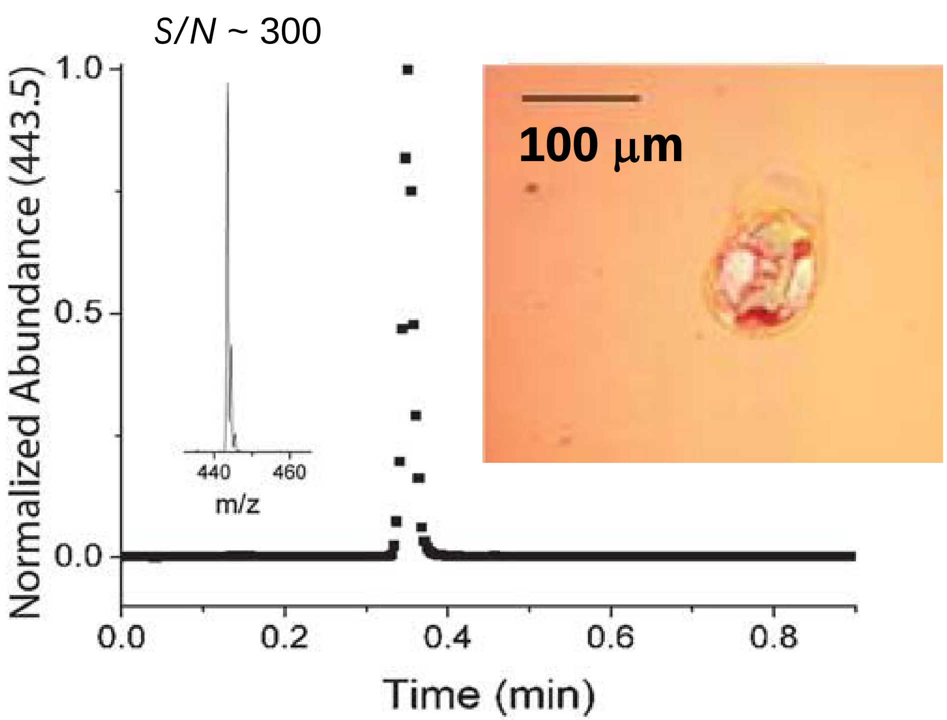
- Precise control of desorption/ionization
- No analyte transport on the substrate; Minimal analyte consumption
- Improved sensitivity
- Reduced spot size
- Readily scaled to smaller volumes

Nano-DESI: Analytical Capabilities



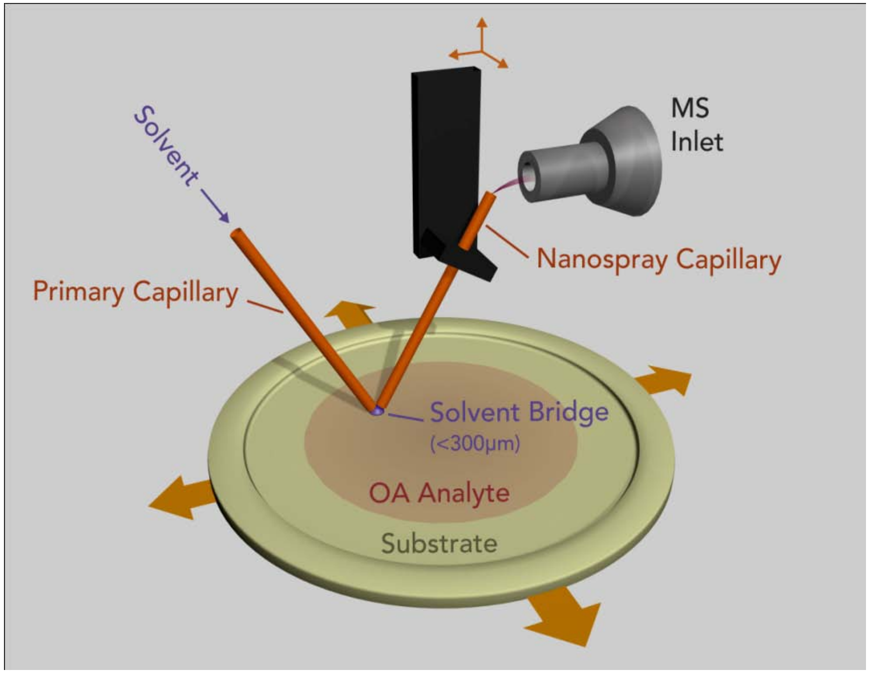
Improved Sensitivity
(10 pmol (0.7 ng) of reserpine)

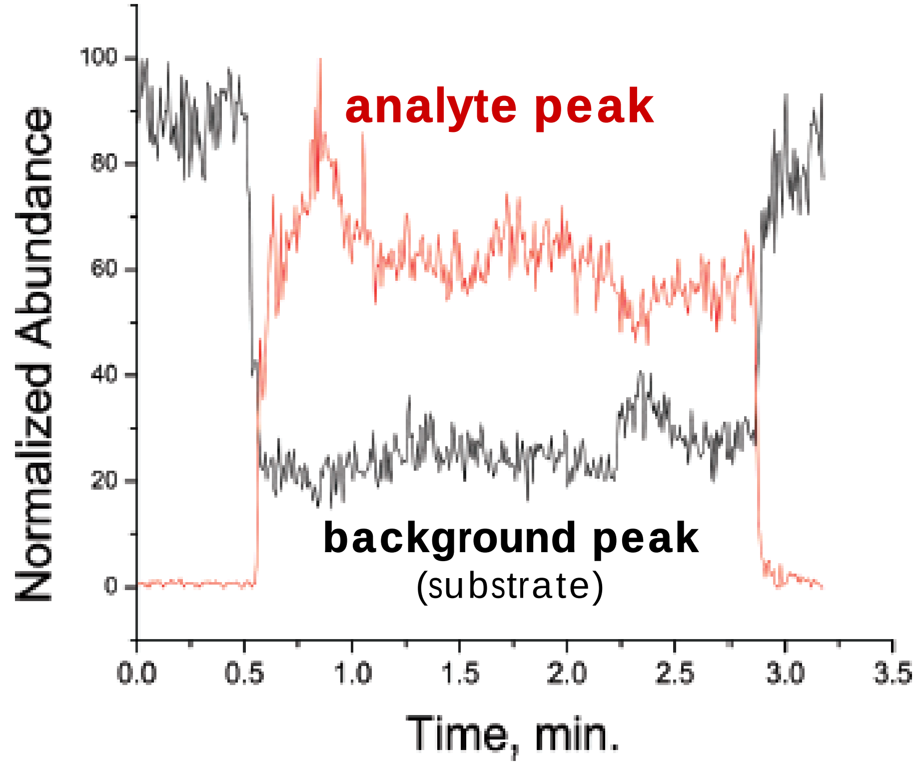




Reduced Spot Size
(rhodamine film on glass)

Analysis of OA Using Nano-DESI MS



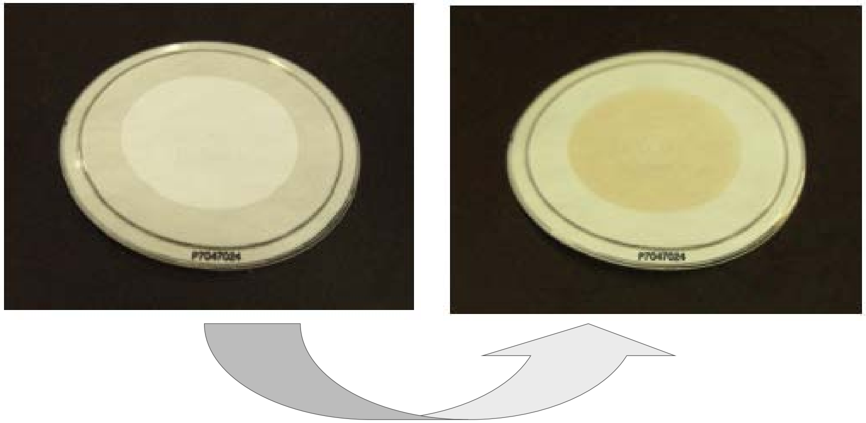


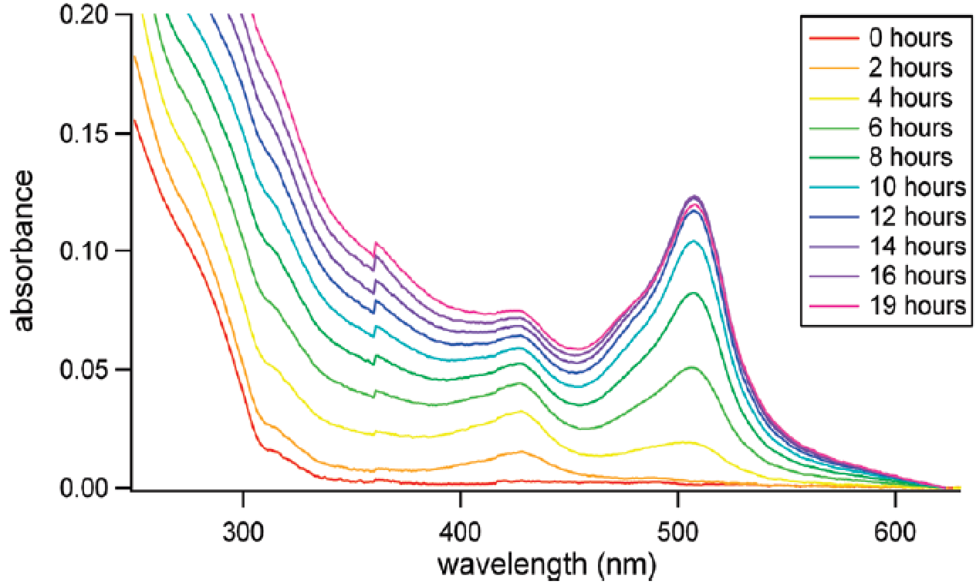
- ✓ **Routine analysis of <10 ng OA**
- ✓ **Probe size < 500 μm**

Brown SOA in Laboratory

Limonene/O_3 (LSOA)

White LSOA (fresh) → Brown LSOA (aged)



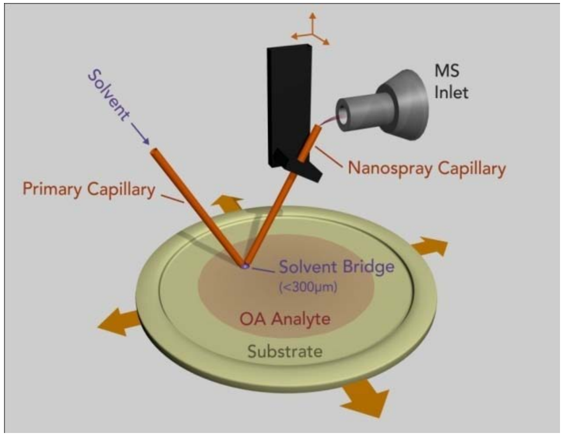


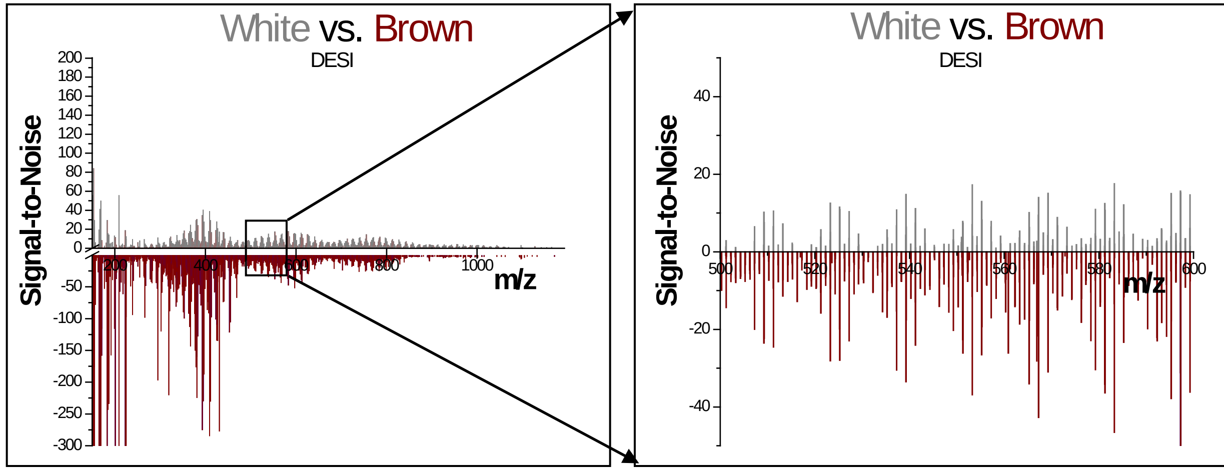
$[NH_3]_g = 5\times10^{-7}$ atm, $[HNO_3]_g = 2\times10^{-11}$ atm, RH ~ 85%, t = 1-24 hours

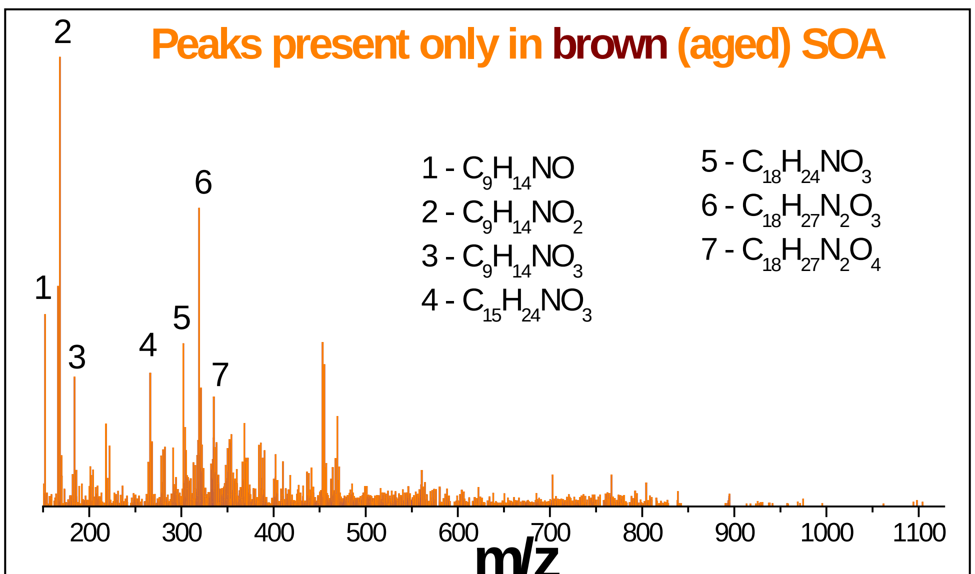
UV-Vis detection of the "browning" extent

✓**Aging at atmospherically relevant experimental conditions**

Nano-DESI/HR-MS of white vs. brown SOA

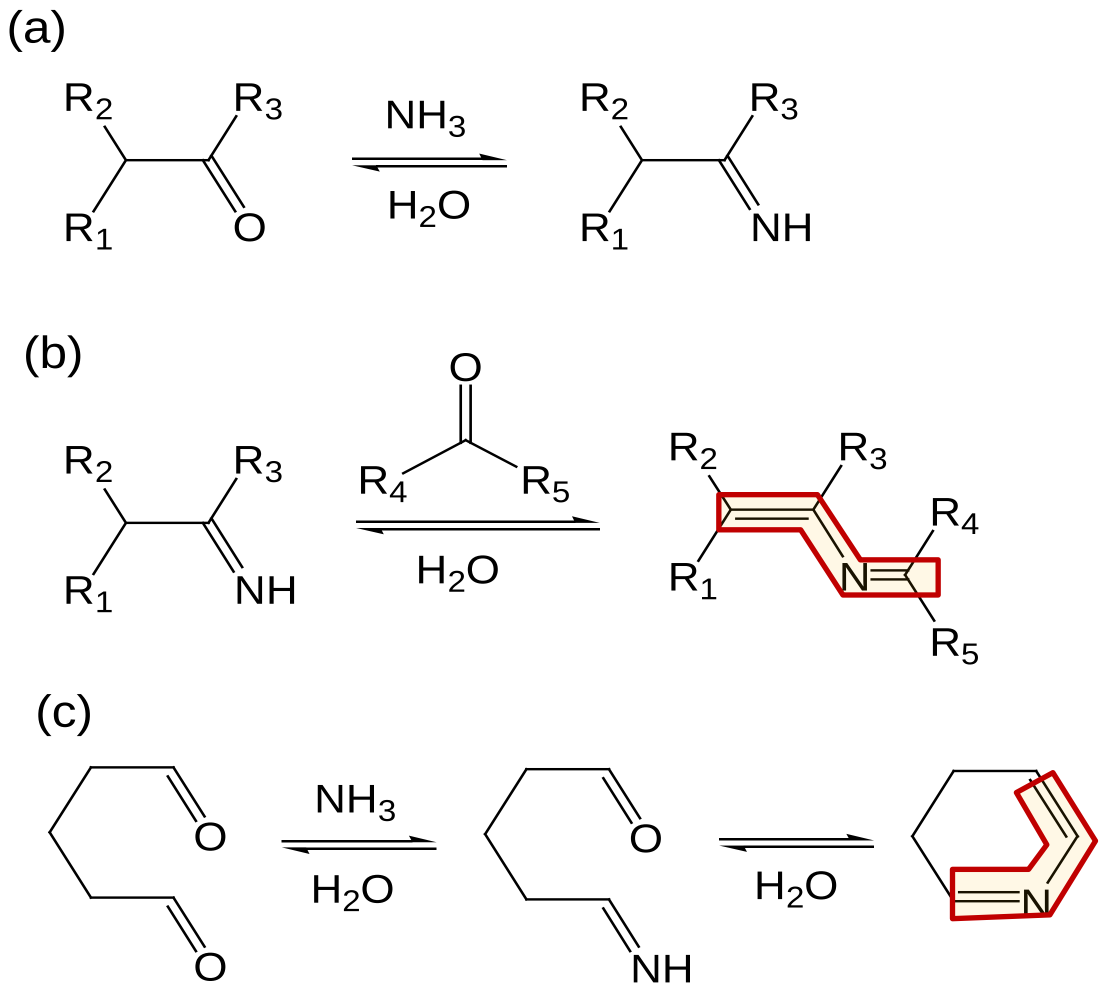






- **~1200 new peaks, 70% assigned**
- **Dominant compounds with one or two N-atoms**
- **Abundant homologous series of N- containing peaks**

Reaction Mechanism

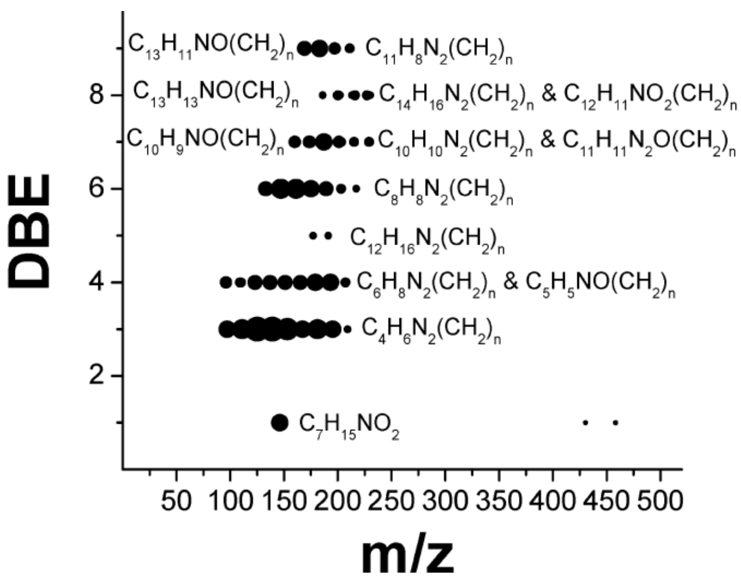


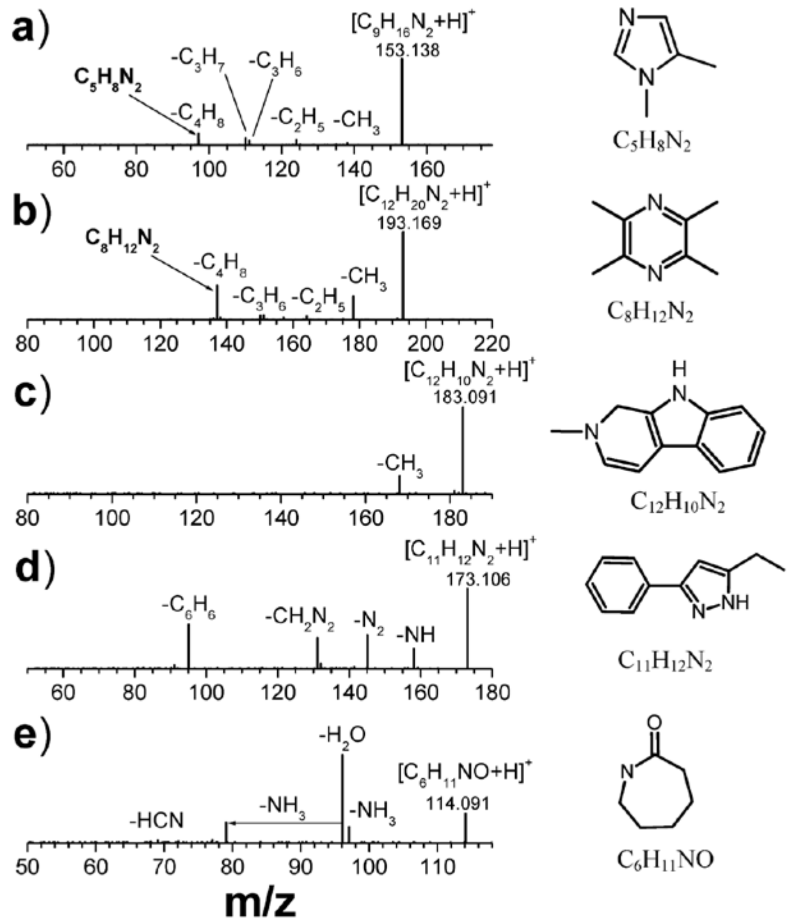
- ✓ **N-heteroatom compounds are products of NH_3/SOA aging**
- ✓ **Some of them are Brown Carbon chromophores**

Detection of N-heteroatom Compounds in Ambient OA

Biomass Burning

Laskin et al., *EST*, 2009





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Detection of N-heteroatom Compounds in Ambient OA

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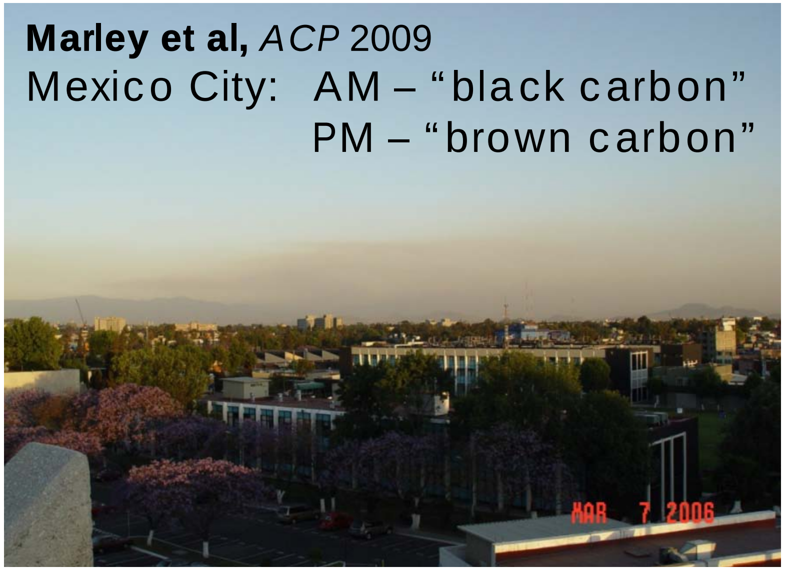
SOA from Mexico City

Roach et al., *Anal.Chem*, 2010



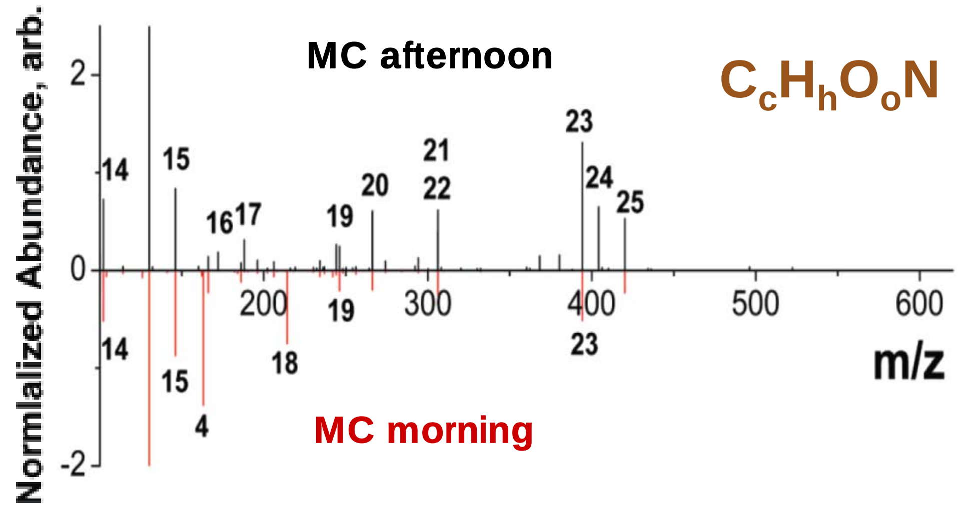


Table 2. Abundant Peaks Observed in Nano-DESI Mass Spectra of Mexico City OA Samples[a]

no.	*m/z*	formula	no.	*m/z*	formula	no.	*m/z*	formula
1	130.1589	$C_8H_{15}NH^+$	10	351.2009	$C_{16}H_{30}O_8H^+$	19	246.1699	$C_{12}H_{23}NO_4H^+$
2	203.0525	$C_6H_{12}O_6Na^+$	11	363.2373	$C_{18}H_{34}O_7H^+$	20	266.1961	$C_{12}H_{27}NO_5H^+$
3	147.1014	$C_7H_{14}O_3H^+$	12	373.2579	$C_{20}H_{36}O_6H^+$	21	306.1912	$C_{14}H_{27}NO_6H^+$
4	**163.1228**	$\mathbf{C_{10}H_{14}N_2H^+}$	13	387.0866	$C_{23}H_{14}O_6H^+$	22	306.2274	$C_{15}H_{31}NO_5H^+$
5	217.1798	$C_{12}H_{24}O_3H^+$	**14**	**102.1277**	$\mathbf{C_6H_{15}NH^+}$	23	394.2215	$C_{21}H_{31}NO_6H^+$
6	135.1014	$C_6H_{14}O_3H^+$	15	146.1174	$C_7H_{15}NO_2H^+$	24	404.2059	$C_{22}H_{29}NO_6H^+$
7	171.1016	$C_9H_{14}O_3H^+$	16	172.1333	$C_9H_{17}NO_2H^+$	25	420.2009	$C_{22}H_{29}NO_7H^+$
8	249.1696	$C_{12}H_{24}O_5H^+$	17	188.1283	$C_9H_{17}NO_3H^+$			
9	261.1697	$C_{13}H_{24}O_5H^+$	18	214.2529	$C_{14}H_{31}NH^+$			

[a] Numbered peaks correspond to labels in Figure 6. Species in OA from an urban environment of Shanghai reported by Wang et al.[16] are marked in bold.

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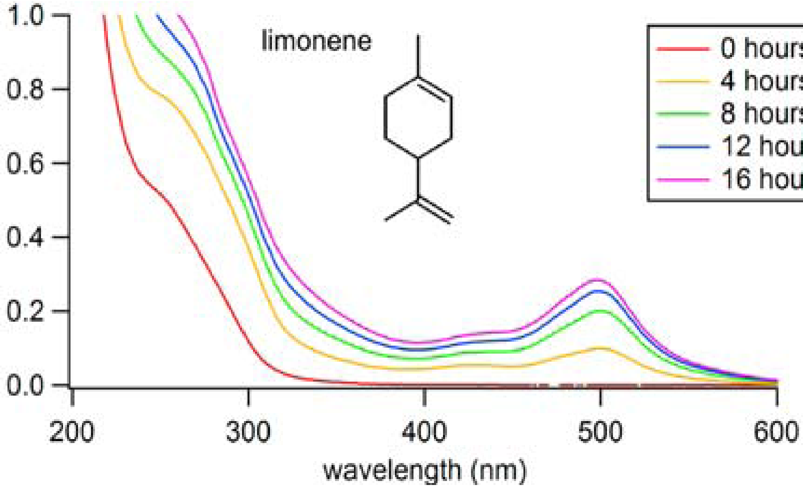
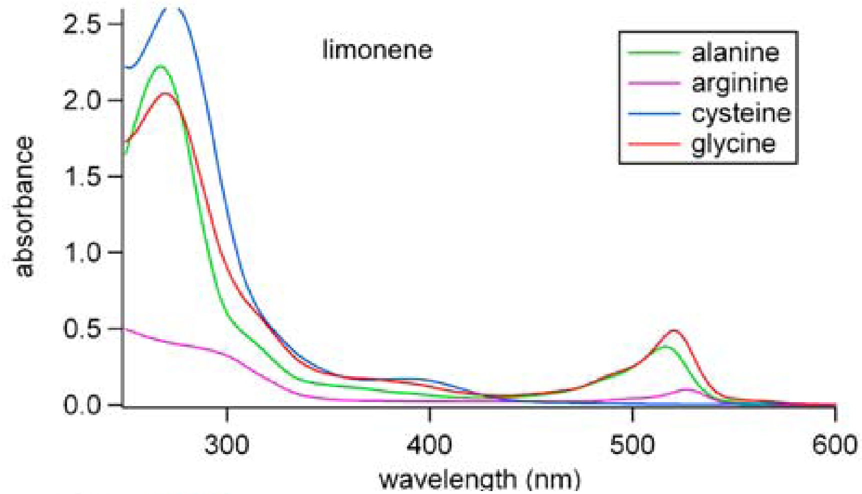
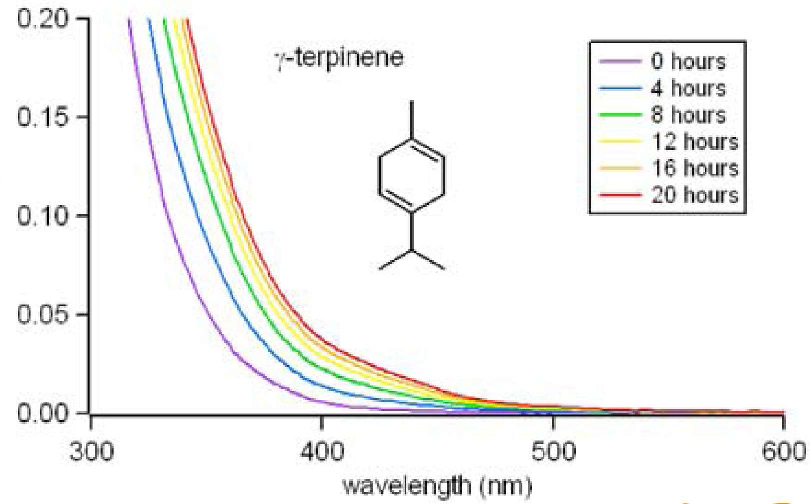
N-heteroatom Compounds in other SOA material

Bones et al., *JGR*, 2010







- ✓ **Molecular structures of individual N-heteroatom compounds determine light-absorption properties of SOA**

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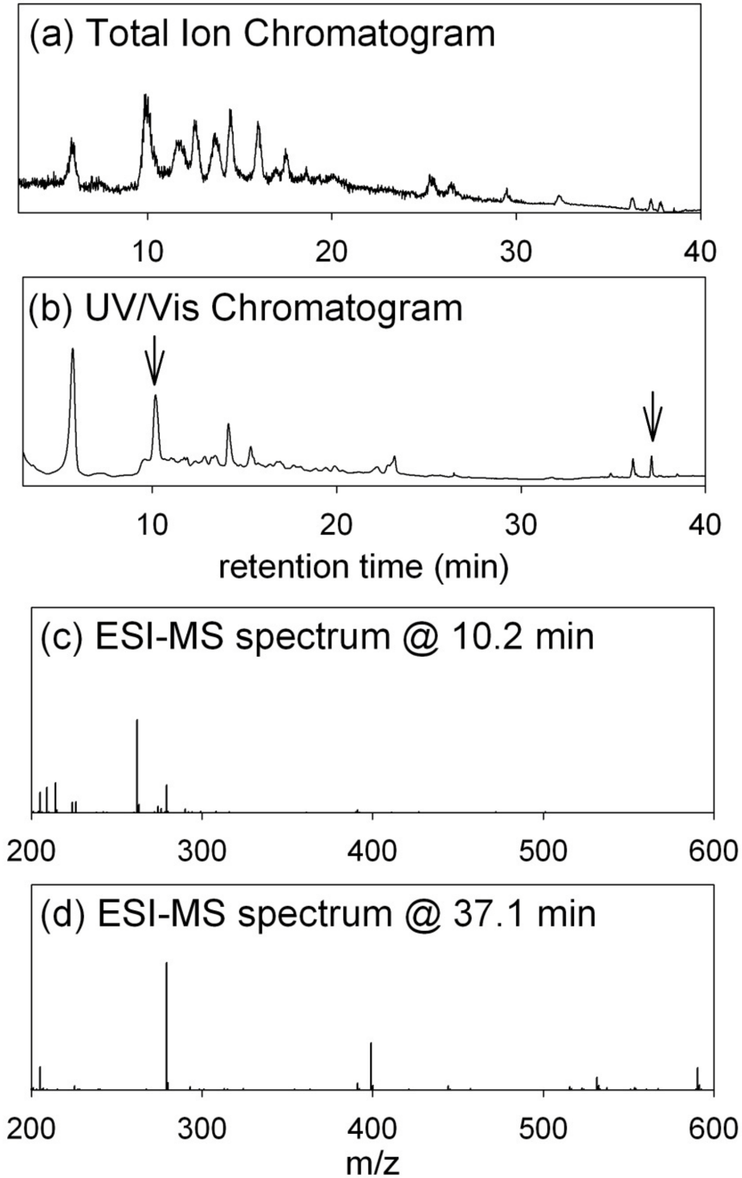
Ongoing Efforts



HPLC - UV-Vis – ESI/HR-MS

Identification and quantification of molecular species with light absorbing properties (chromophores) in OA

Conclusions

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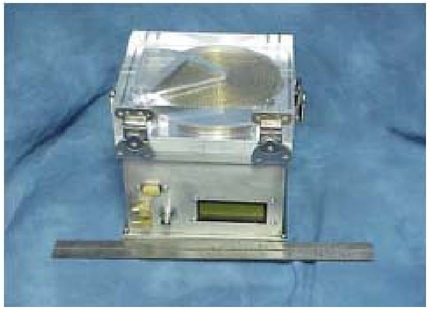
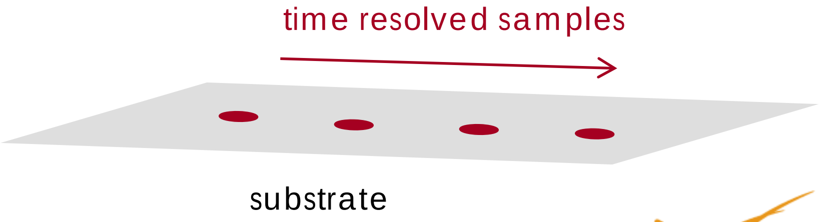
- Selected <u>individual molecules</u> (chromophores) are responsible for light-absorption of OA (brown carbon)
- Improved analytical methods are needed for quantitative analysis of chromophores

<u>Nano-DESI</u>

- Rapid analysis of ng level of OA without sample preparation; Simultaneous detection of hundreds of molecules
- Stable signal over 3-5 min – sufficient for MS^n analysis
- Suitable for high throughput analysis of time-resolved OA samples





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BES DOE, the Chemical Sciences Division

UCI:

National Science Foundation (ATM-20 0831518)

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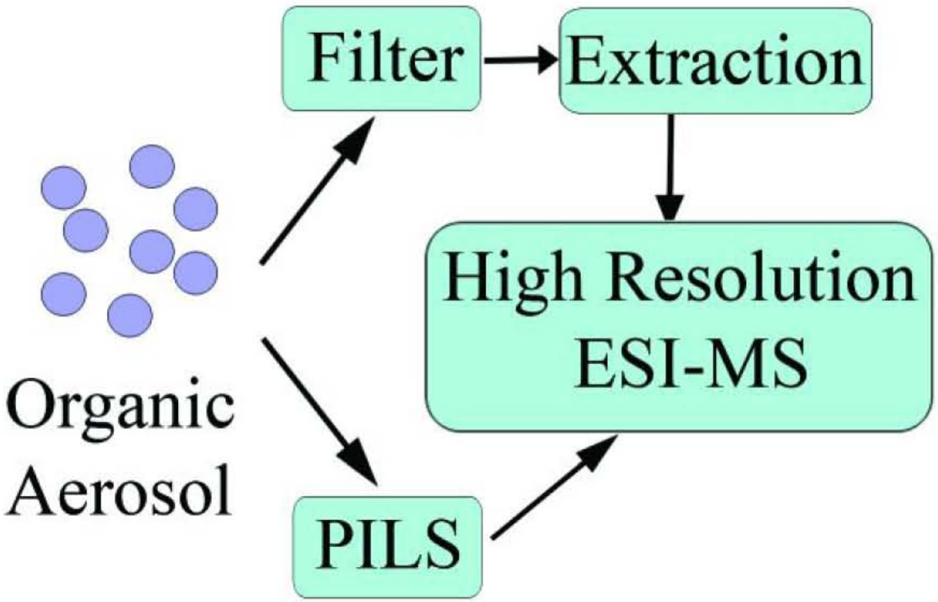
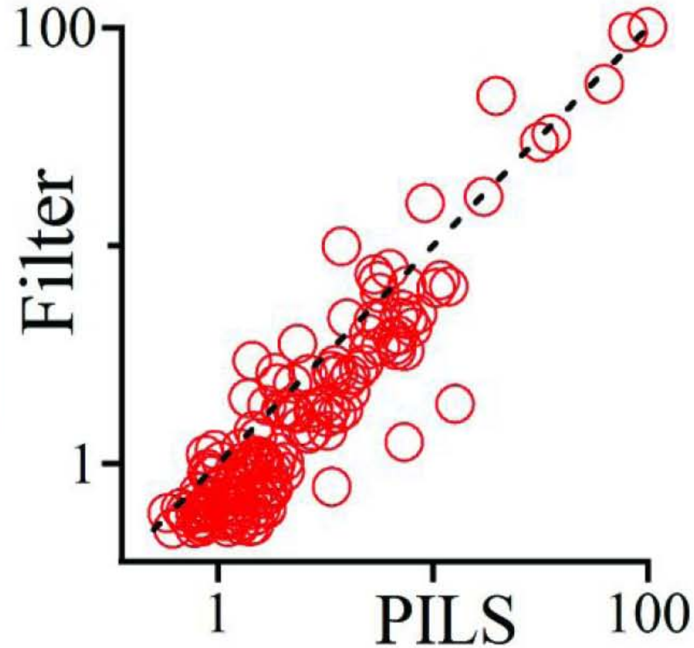
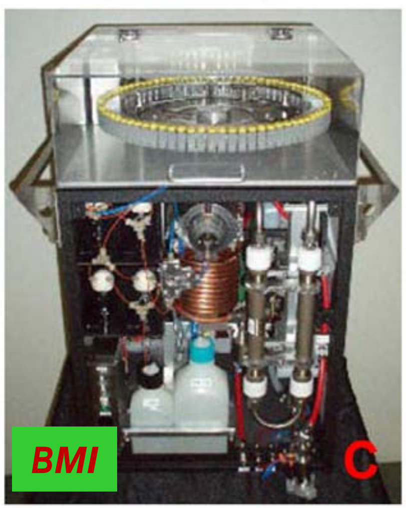

Organic
Aerosol
Filter
Extraction
High Resolution
ESI-MS
PILS


100
1
Filter
1
PILS
100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Ongoing Efforts and Projects:
2. Aerosol Photochemistry Studies

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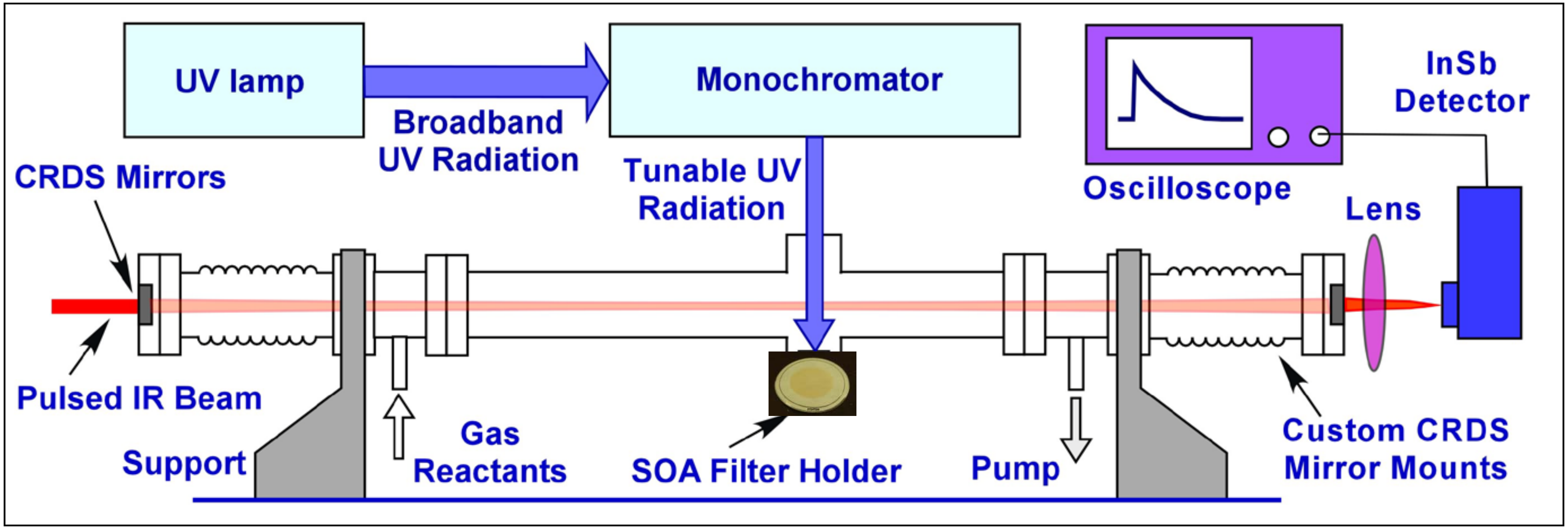
T. Nguen – *UCI* grad student

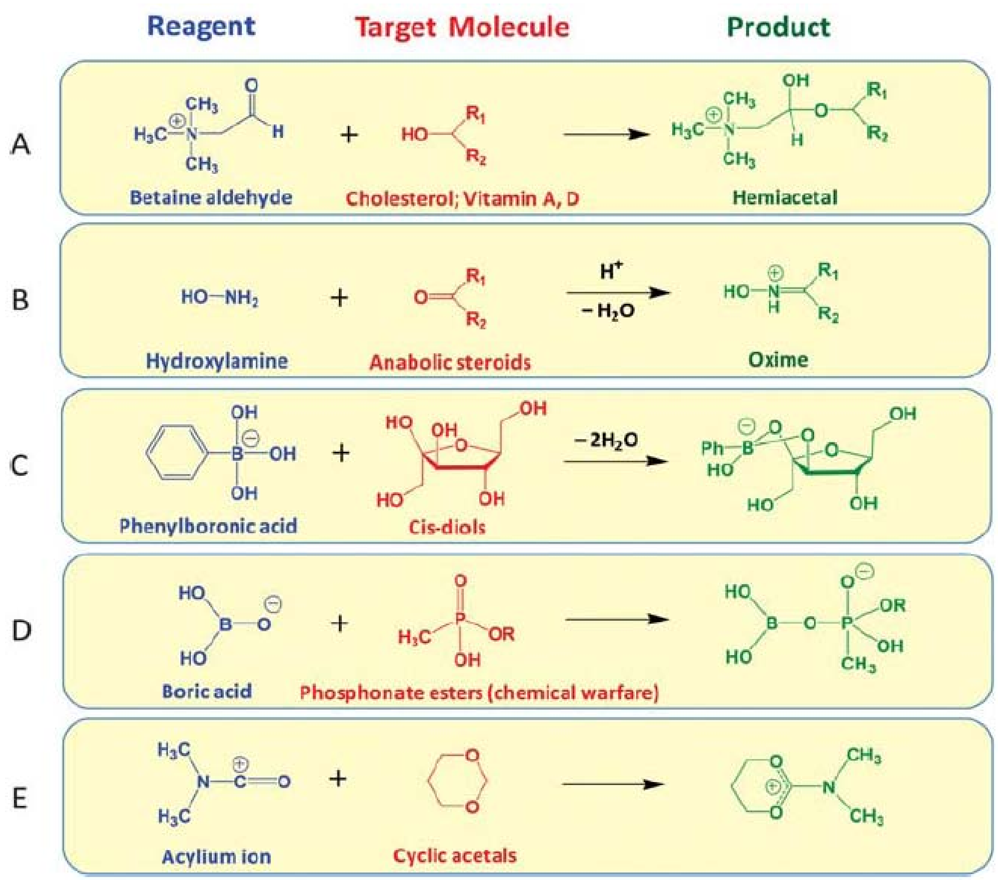


CRDS reactor in UCI

- **aging of OA by photochemistry**
- **effects of RH**
- **molecular analysis of both gas and condensed phases**

Reactive Nano-DESI

with SULI students: B. Heath (Sept-Dec)



Ifa et al, *Analyst*, 2010, 135, 669–681

- Quantitative Characterization of Different Functional Groups Present in OA of

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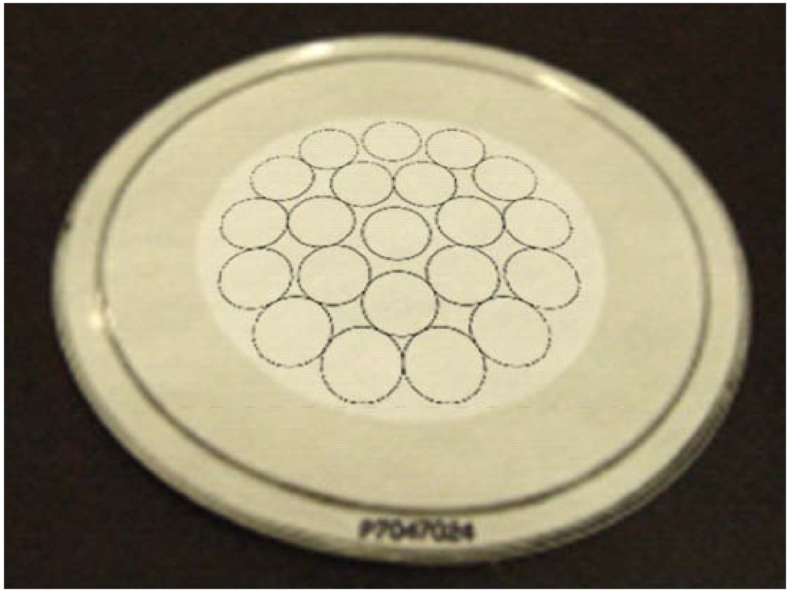
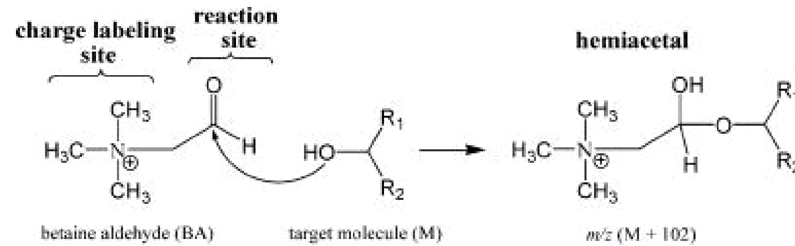
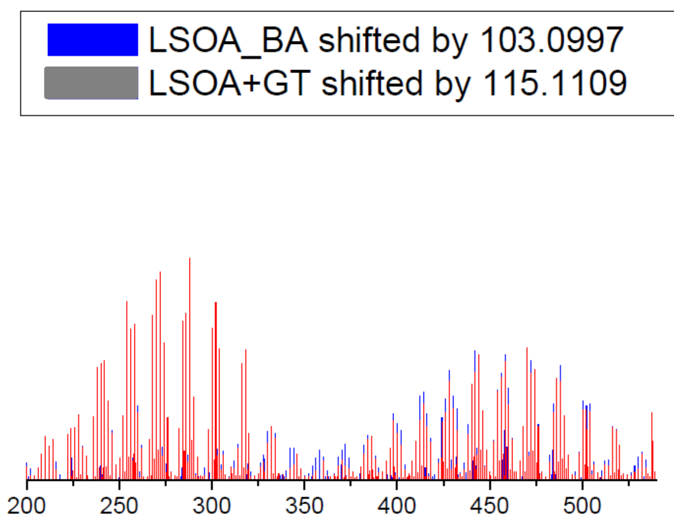
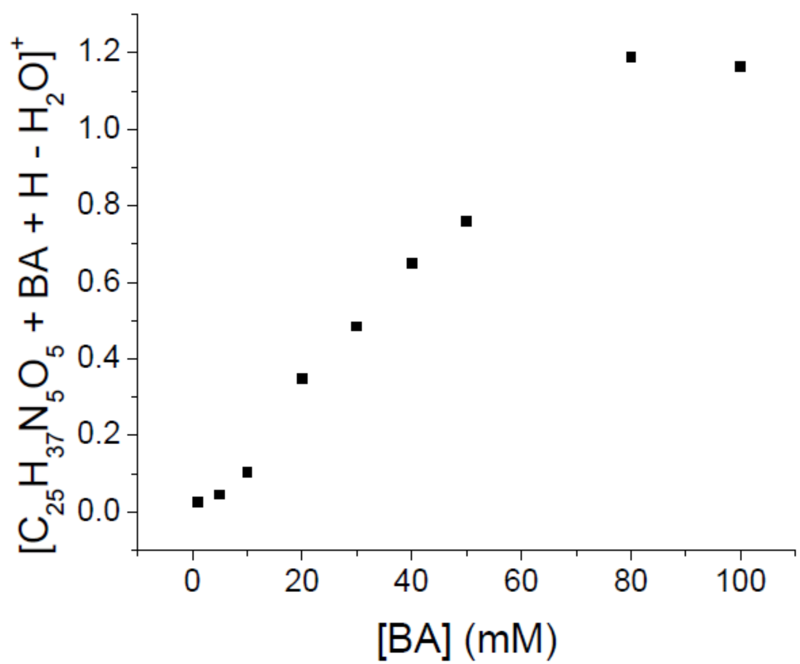
Reactive nanoDESI

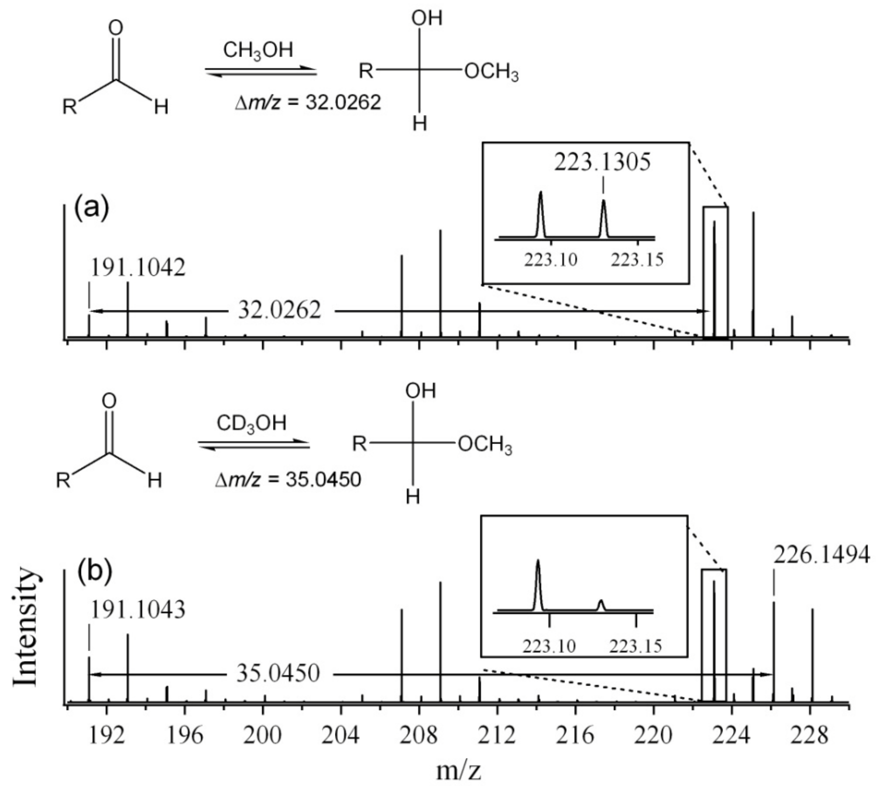


Betaine Aldehyde + Alcohol





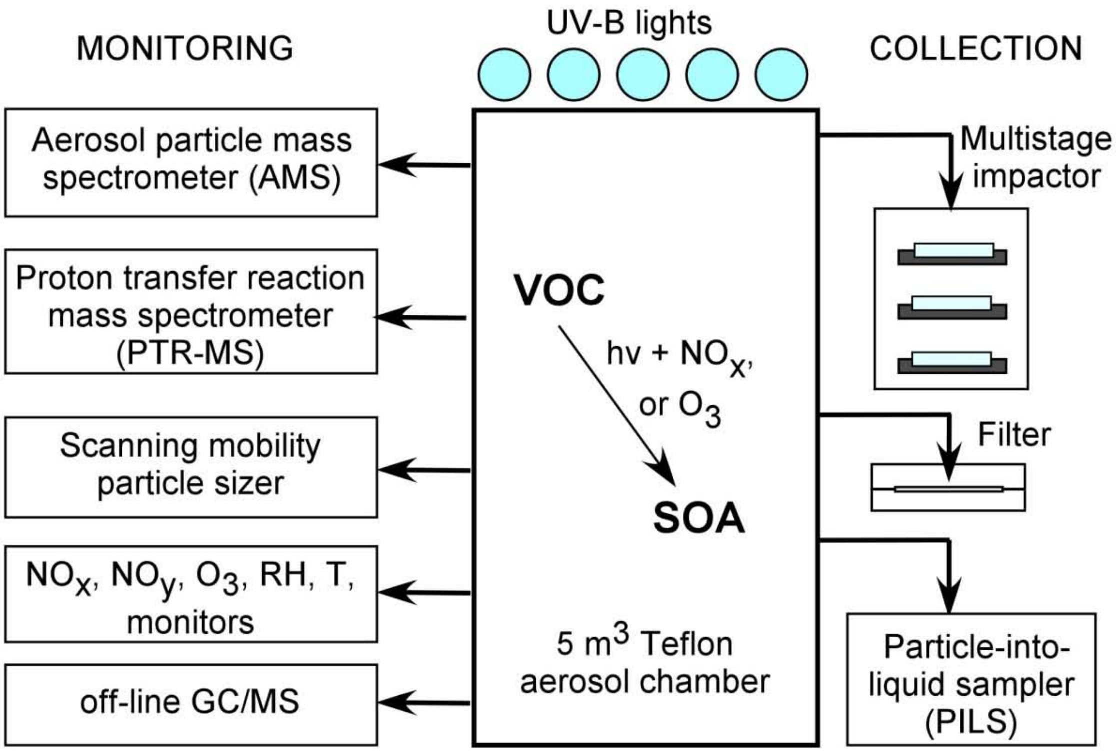


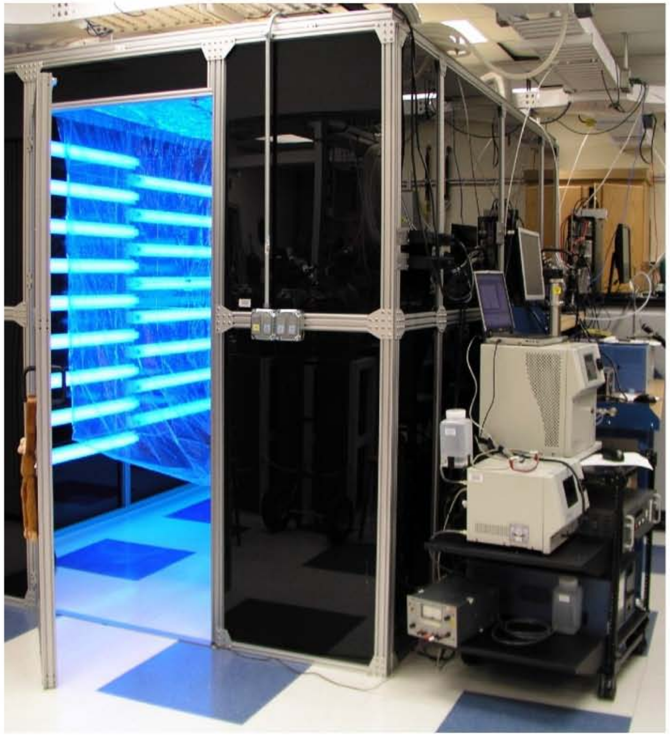

O
R
H
CH3OH
Δm/z = 32.0262
OH
R
OCH3
H
(a)
223.1305
223.10
223.15
191.1042
32.0262
O
R
H
CD3OH
Δm/z = 35.0450
OH
R
OCH3
H
(b)
226.1494
191.1043
35.0450
223.10
223.15
Intensity
192
196
200
204
208
212
216
220
224
228
m/z

Mass "Splits"

O and CH_4	36.4×10^{-3} amu	14,000
N and ^{13}CH	8.2×10^{-3} amu	60,000
C_3 and SH_4	3.4×10^{-3} amu	147,000

Laboratory Studies of SOA Chemistry





***UCI** smog chamber*

- **Formation and Aging of Terpenes/O_3 SOA**
  - **Cloud Chemistry of Organics**

Analysis of Field OA Samples

Figure 1 (A) –10 stage cascade Multi Orifice Uniform Deposition Impactor (MOUDI); (B) modified Davis Rotating drum Universal size-cut Monitoring impactor (DRUM); (C). Particle-to-Liquid Sampler (PILS).

ESI/HR-MS studies of OA: 2004-2010