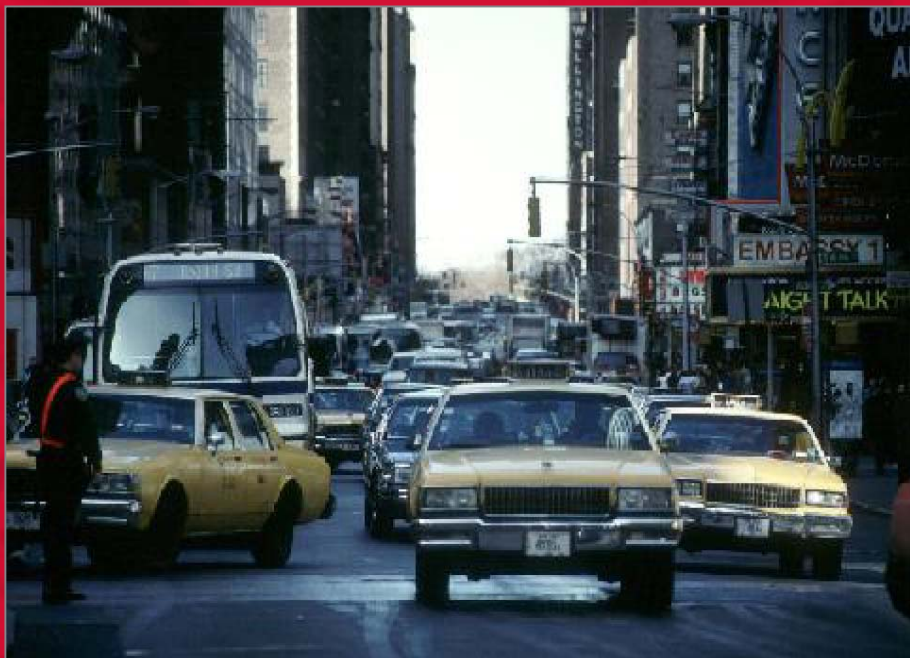


US EPA ARCHIVE DOCUMENT



**Polar Organic  
Fine Particles  
from the  
New York,  
New Jersey &  
Connecticut  
Regional Airshed**

**U.S EPA STAR PM Source Apportionment Review Meeting**  
Monica Mazurek, Civil & Environmental Engineering Department  
U.S. EPA Research Triangle Park  
June 21-22, 2007

# Project Goals -- Polar Organic Fine Particles

Identify and measure the ambient abundances of polar organic compounds found as PM<sub>2.5</sub> in the NY, NJ and CT regional airshed using Liquid Chromatography/Mass Spectrometry (LCMS) chemical analysis

Measure and identify both known and potential secondary organic aerosol markers found within the fine particle acidic organic fraction

Identify emissions of polar organic compounds from primary sources, including vehicular sources and wood combustion

# Speciation of Organics for Apportionment of PM<sub>2.5</sub> in the NY City Area (SOAP) **SOAP 2002-2003**

Sources of fine carbonaceous particles

Ambient concentrations  
TC, EC, OC

Ambient concentrations  
molecular markers

**NY, NJ CT Fine Particulate Matter Study**



Toll Plaza 13, NJ Turnpike

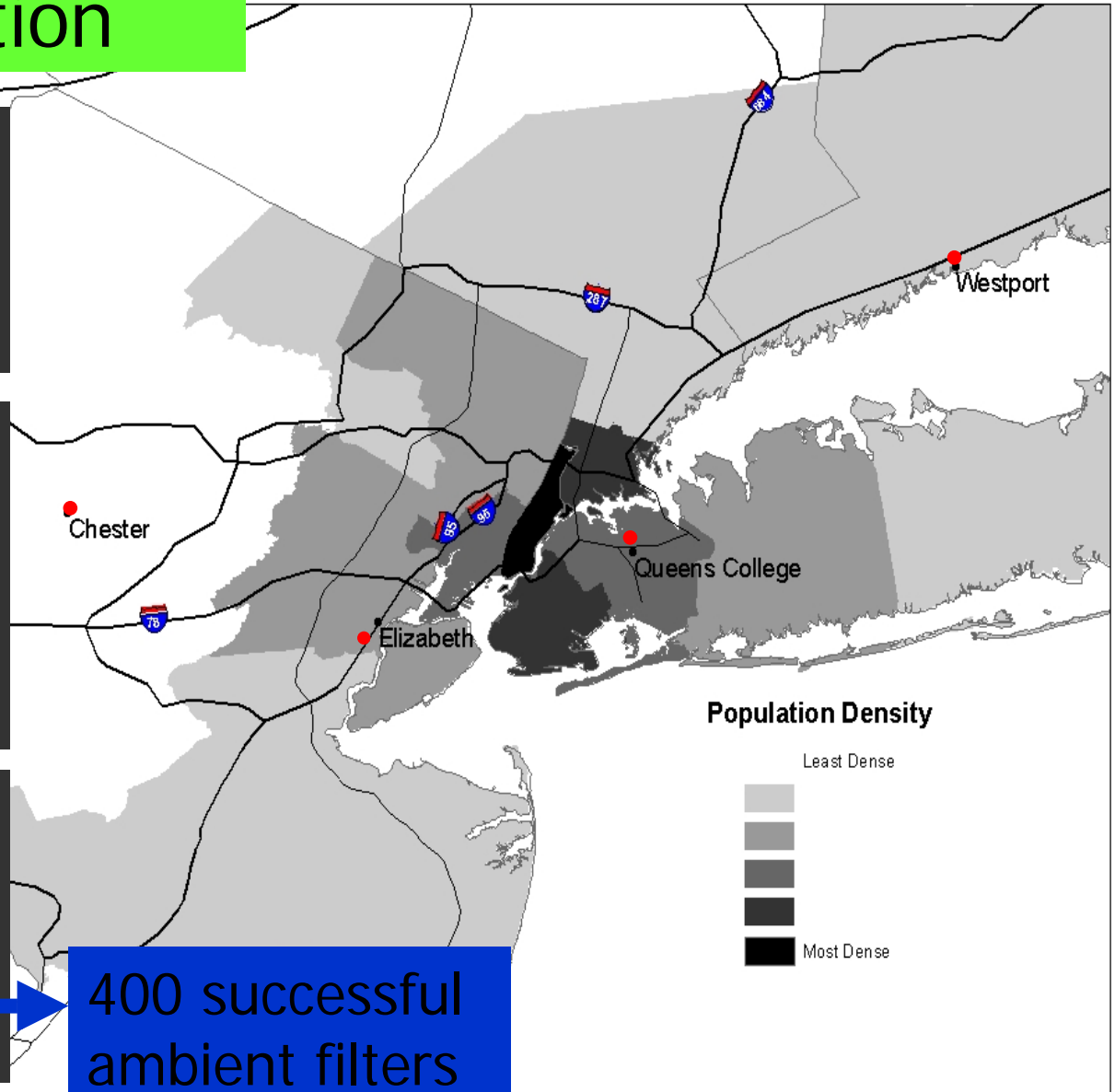
# PM-2.5 Collection

SOAP 2002-  
2003 network  
field program

Queen's College  
NY Supersite  
Elizabeth, NJ  
Chester, NJ  
Westport, CT

Completed full  
annual cycle May  
2002-2003 using  
Speciation Trends  
Network Schedule

400 successful  
ambient filters





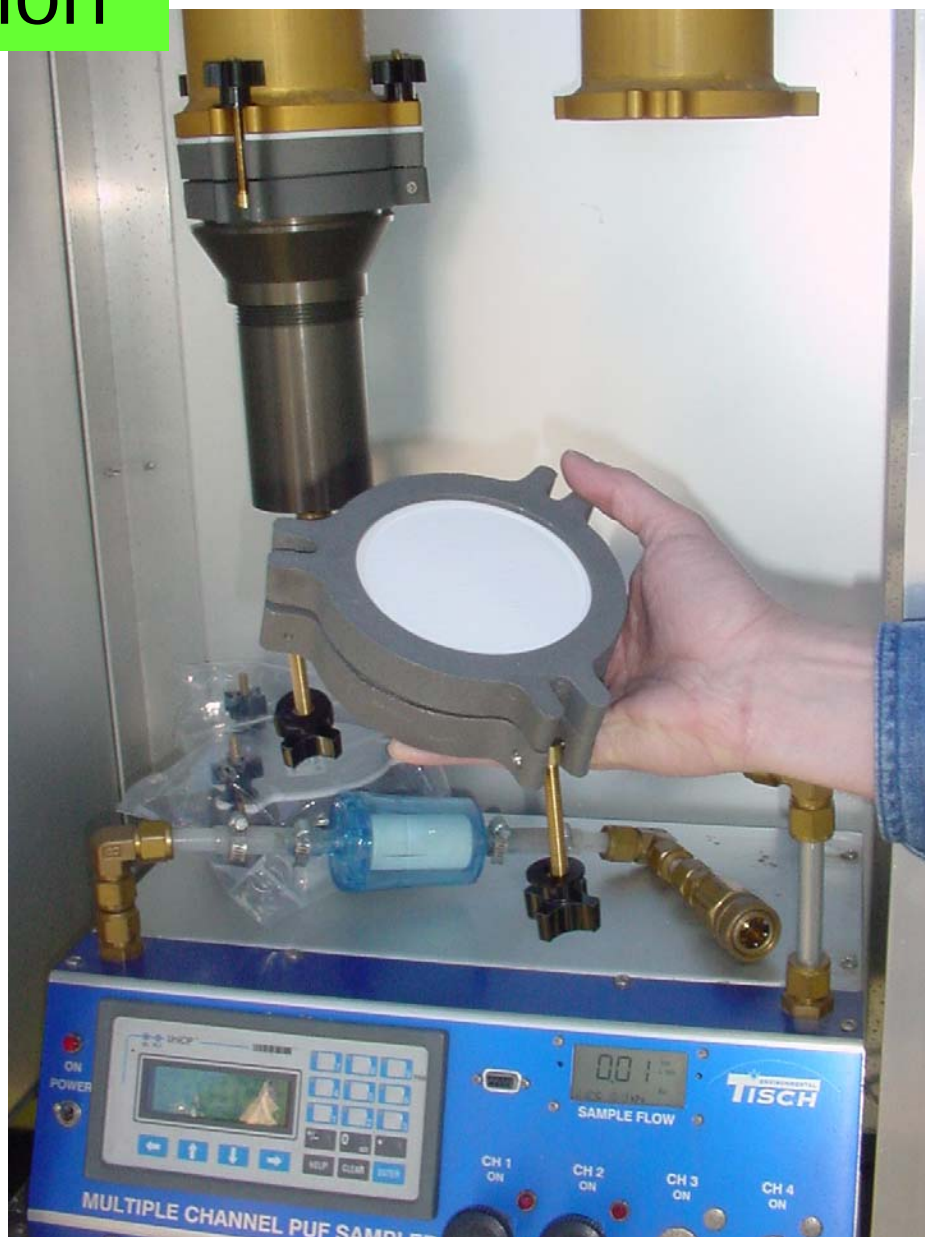
# Fine Particle Collection

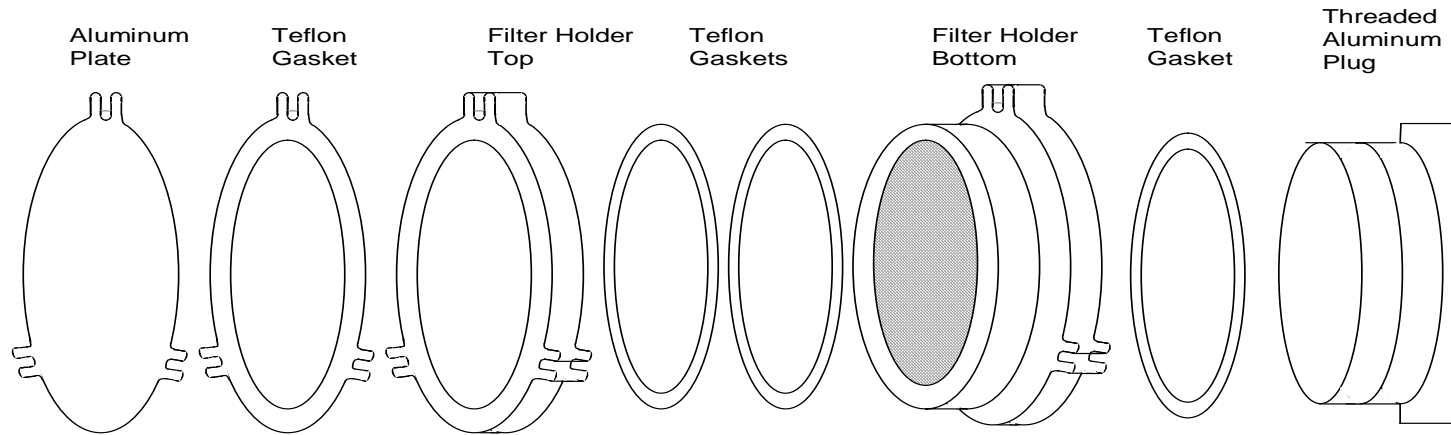
## Tisch 2 or 4 Channel Sampler

Quartz fiber filter collection substrate, 102mm

24 hr, 113 lpm

Sampling, transport, sample handling, and analytical procedures for ppt ( $10^{-12}$ ) level organics

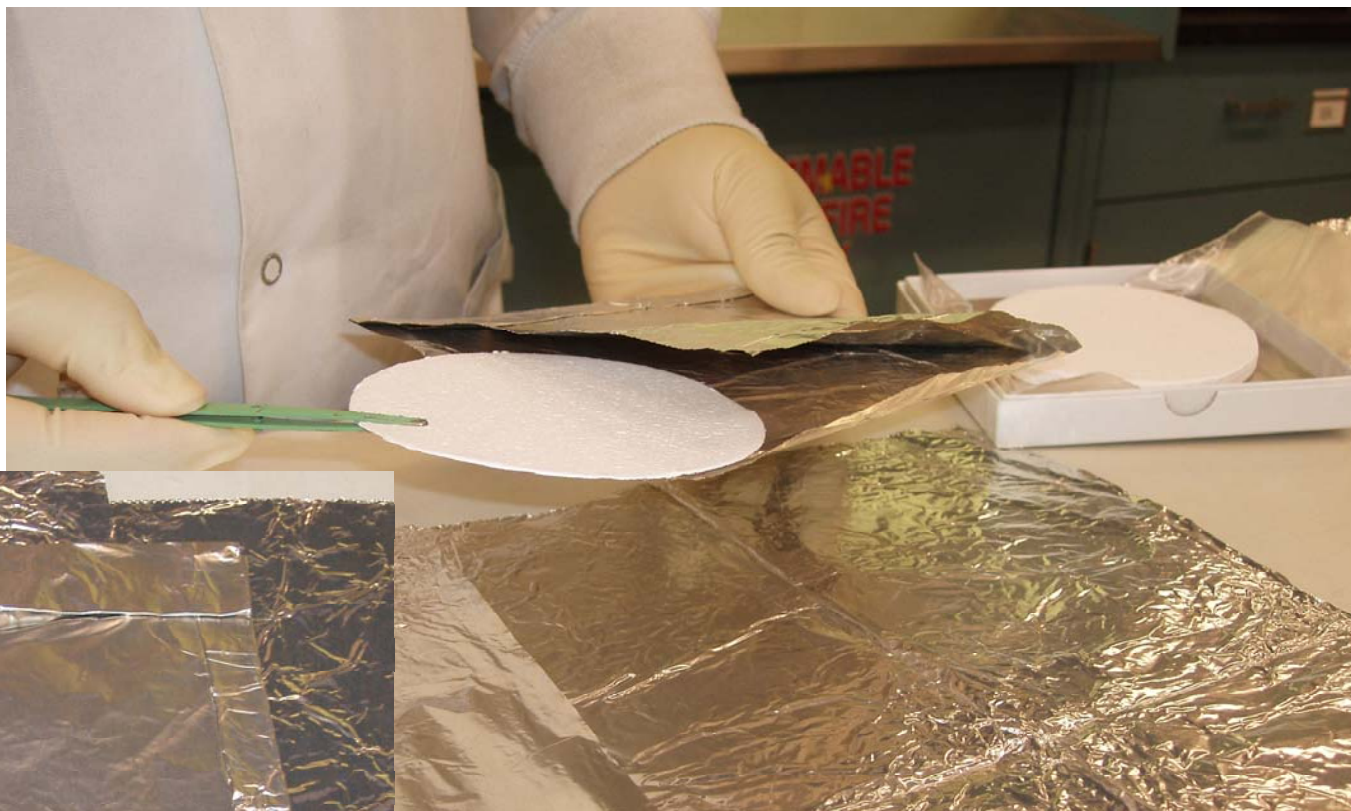




## Shipping Module for Filter Holder



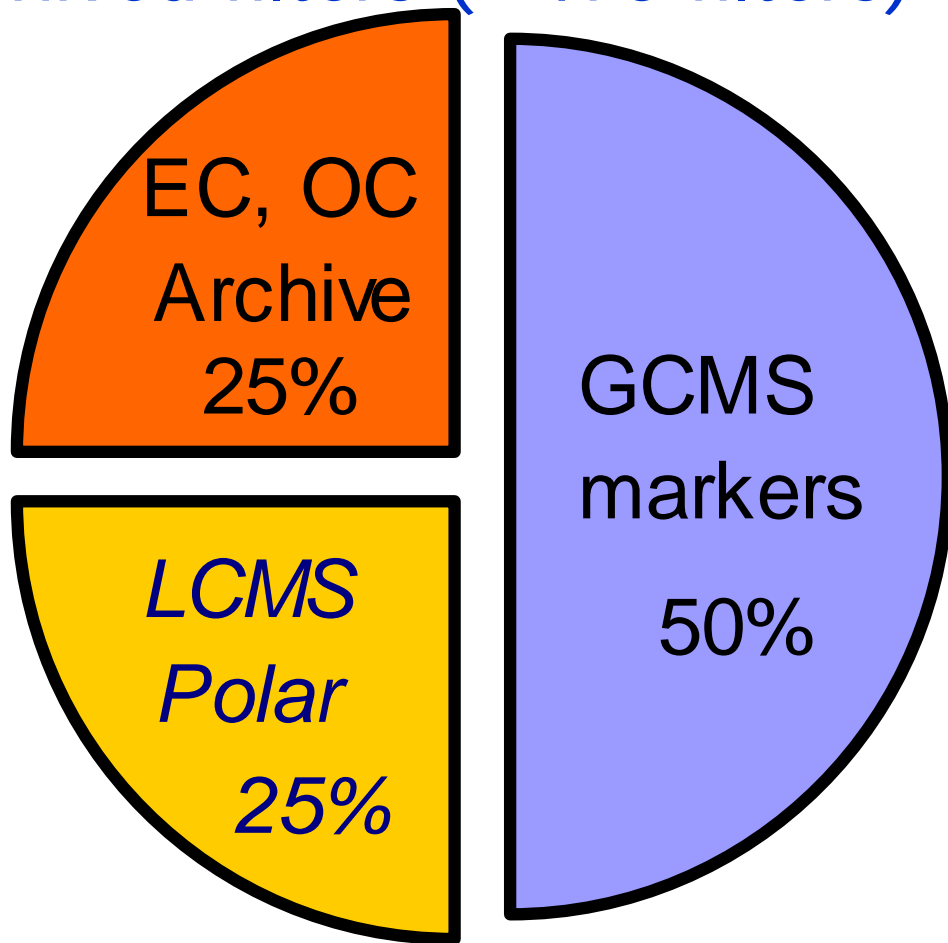
# Reducing carbon background...



... filter handling,  
preparation & storage  
steps critical



# EC, OC and TC filter mass loadings ( $\mu\text{g}/\text{cm}^2$ ) SOAP network archived filters (~470 filters)



NYC Fine Particle Filters

Color range chart



# Filter Handling, EC/OC Punch and Storage



# SOAP fine particle composites

| Identical days, 6-10 filters per composite |                        |
|--|------------------------|
| Early summer '02                           | Eliz, Qns, Chs         |
| Summer '02                                 | Eliz, Qns, Wpt, Chs    |
| Early fall, '02                            | Eliz, Qns, Wpt, Chs    |
| Fall, '02                                  | Eliz, Qns, Wpt, Chs    |
| Fall, '02 precision                        | Eliz, Qns, Wpt, Chs(2) |
| Early winter, '02-'03                      | Eliz, Qns, Wpt, Chs    |
| Winter, '03                                | Eliz, Qns, Wpt, Chs    |
| Early spring, '03                          | Eliz, Qns, Wpt, Chs    |
| Spring, '03                                | Eliz, Qns, Wpt, Chs    |
| Late spring, '03                           | Eliz, Qns, Wpt, Chs    |

# Part 1:

## LCMS versus GCMS for quantitative analysis of atmospheric polar organic compounds in complex mixtures

### Target Compound Classes

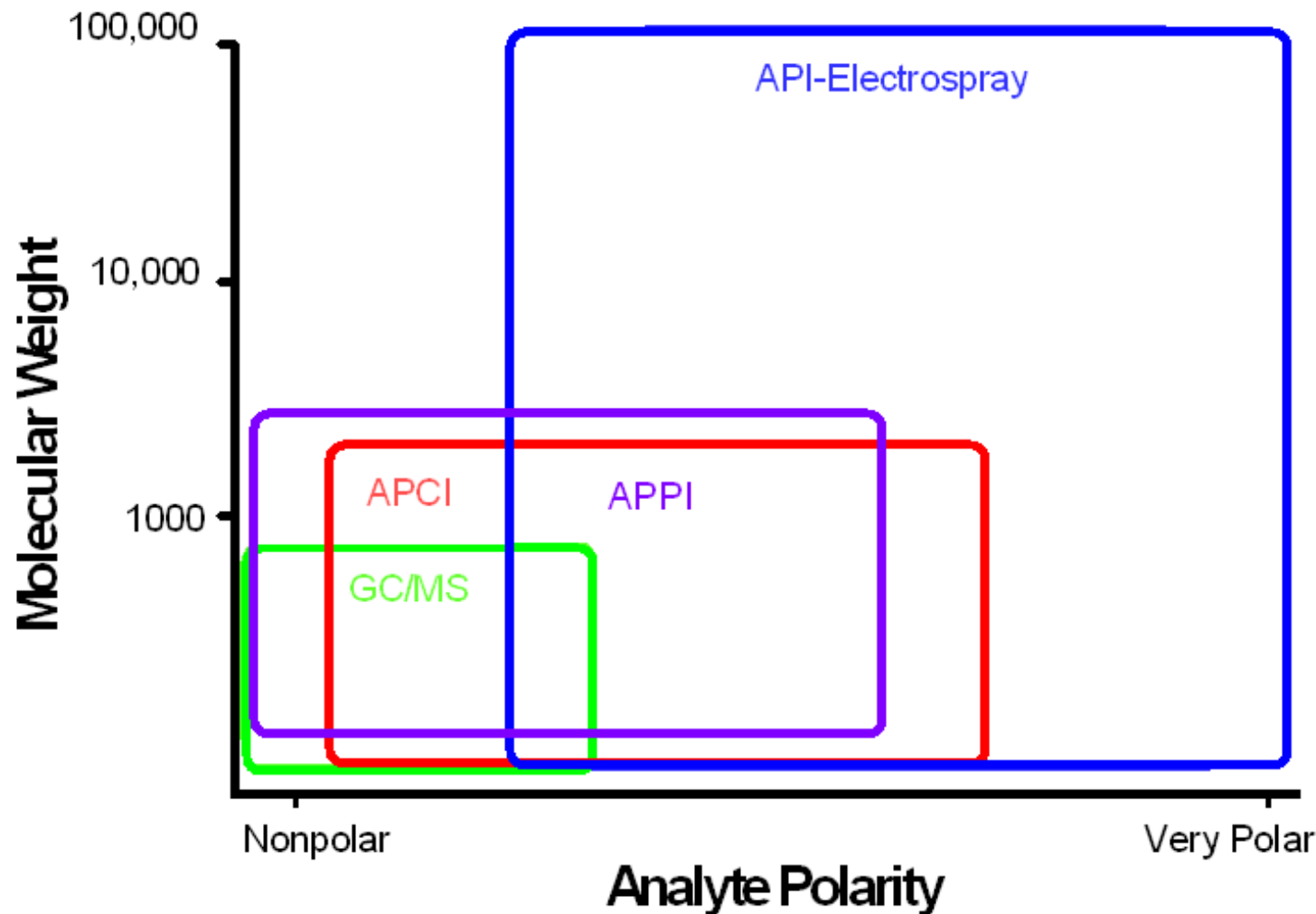
- C3-C10 aliphatic dicarboxylic acids
- Aromatic (aryl) acids
- Hydroxy and oxoacids
- Alcohols, polyols
- Carbohydrates (sugars, levoglucosan)
- Humic acids, fulvic acids (HULIS compounds)
- Basic organic compounds (amines, amino acids)

### Measurement Goal

Achieve high sensitivity & precision for quantitation of individual marker compounds



# Mass spectrometric instrumentation for molecular marker analysis



Credit: Agilent Technologies 2001

# Why LCMS for polar compounds?

- Mass spectrometer more sensitive than other LC detectors (2 to 3 orders of magnitude better than UV/Vis detection)
- Can analyze compounds without a chromophore (carbohydrates, wood smoke sugars, diacids, diols)
- Can “resolve” coeluting peaks using mass selective filtering techniques and multi-stage MS
- Highly polar compounds well-suited to LCMS-ESI allowing for aqueous atmospheric solutions with broad pH range (pH 2 to pH 10)
- Suitable for high molecular weight compounds (“HULIS”), thermally unstable compounds (N-containing)

# LC methods development

## Changes in Sample Preparation and Solution Chemistry

- Analyte concentration sufficient for quantitative analysis (multi-level standard response curves)
- Maximize ionization through careful evaluation of solvents, buffers and modifiers ( $pK_a$  of compound must be known; mobile phase pH must be 1.5 units above or below compound  $pH_a$ )
- Minimize presence of compounds that compete for ionization or suppress signal through gas-phase reactions
- Analyte MW > 90 amu for ion trap collection; desolvation process loss mechanism for low MW compounds

# Agilent 1100 LC Ion Trap Mass Spectrometer with post-column addition, ESI & APPI sources, UV/VIS diode array detector

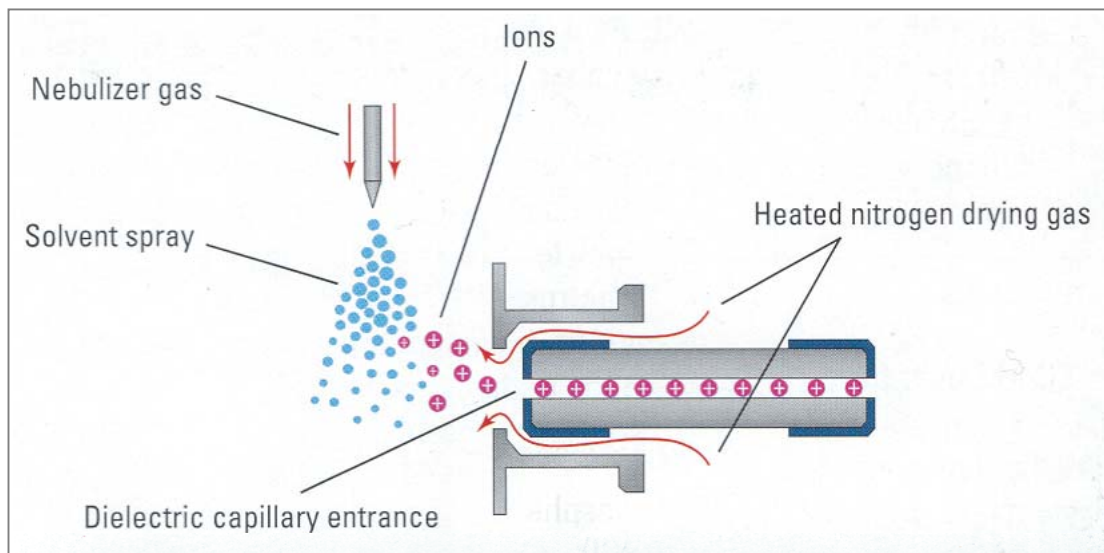




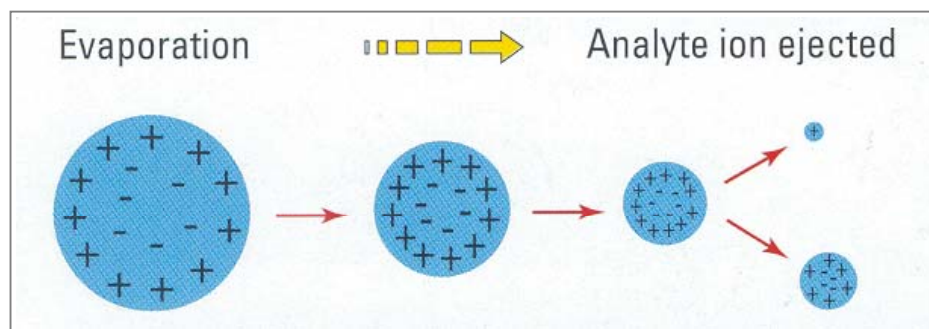
# Electrospray Ionization (ESI)

## Electrospray Ion Source

- Positive & negative modes
- Must generate ions in solution or induce ion formation in source; generate charged species (adducts, dimers, ion-pairing)

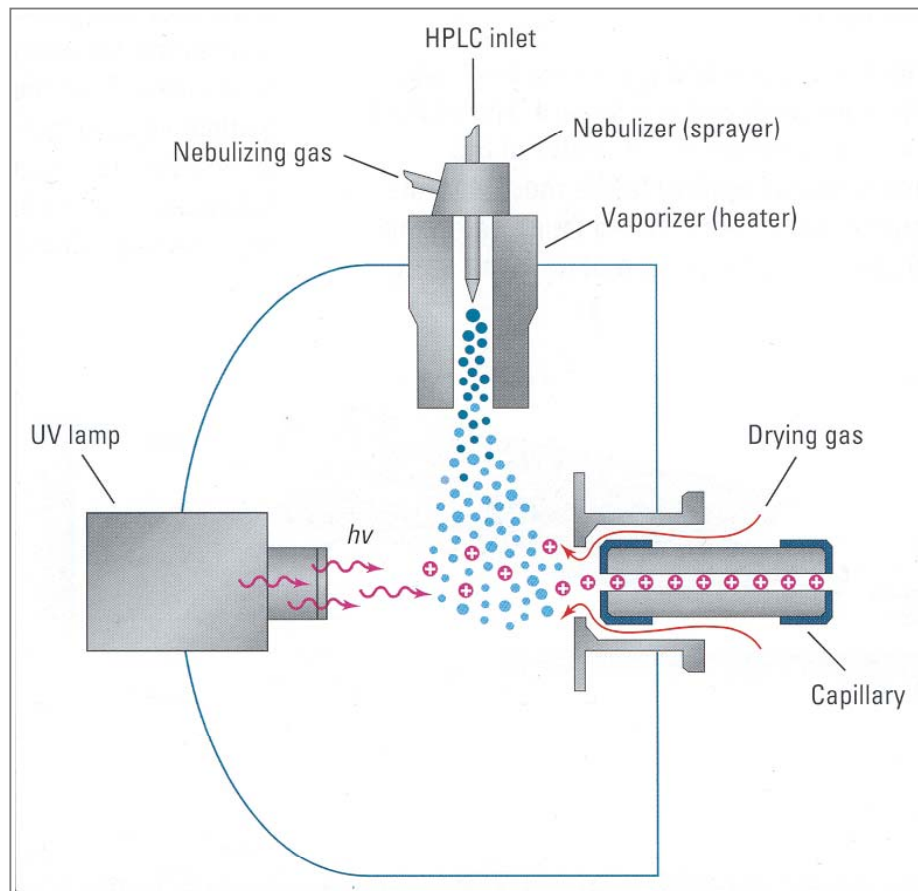


## Desorption of ions from solution



Source: "Basics of LC/MS"  
Agilent Technologies, 2002,  
[www.agilent.com/chem](http://www.agilent.com/chem)

# Atmospheric Pressure Photoionization (APPI)



Source: "Basics of LC/MS"  
Agilent Technologies, 2002

## APPI Ion Source

- Discharge lamp generates photons in narrow range ionization energies
- Ions in solution unnecessary; ions formed in gas phase
- Post-column dopant (toluene, acetone) aid analyte ionization

# Single quadrupole mass analyzer

## GCMS

- Very stable
- Standard calibration curves comparable over 3-month period
- High sensitivity for ppb & ppt marker concentration

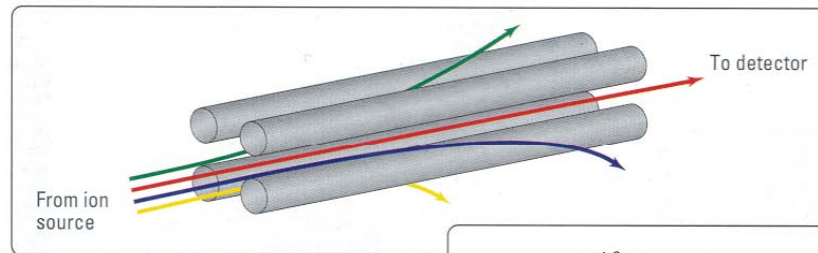


Figure 8. Quadrupole mass analyzer

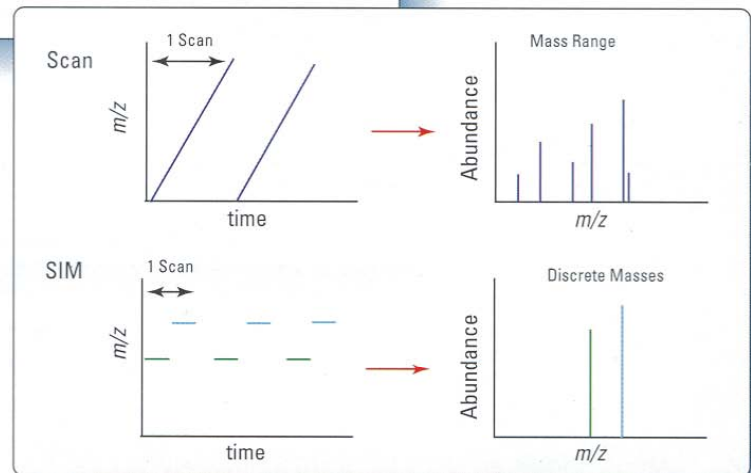


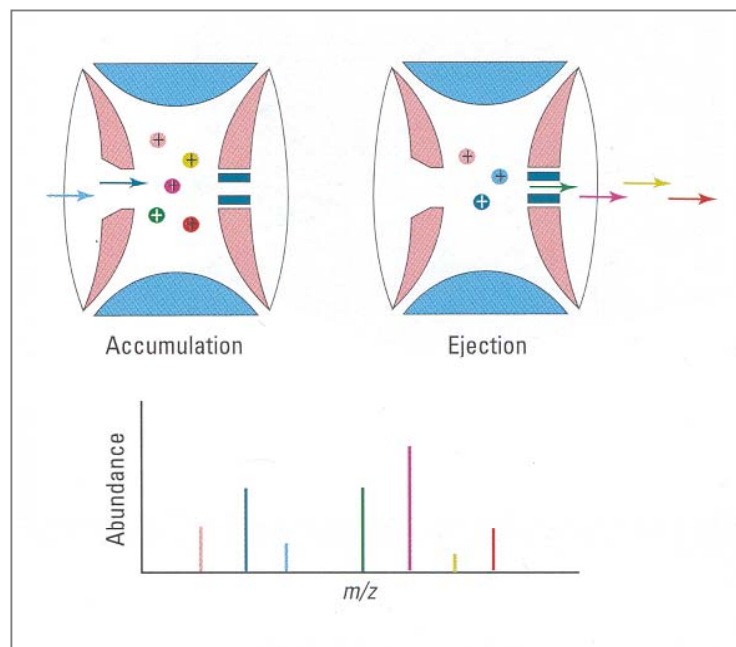
Figure 9. The quadrupole mass analyzer can scan over a range of mass-to-charge ratios or alternate between just a few

**LCMS...**  
**Do not know**

Source: "Basics of LC/MS"  
Agilent Technologies, 2002

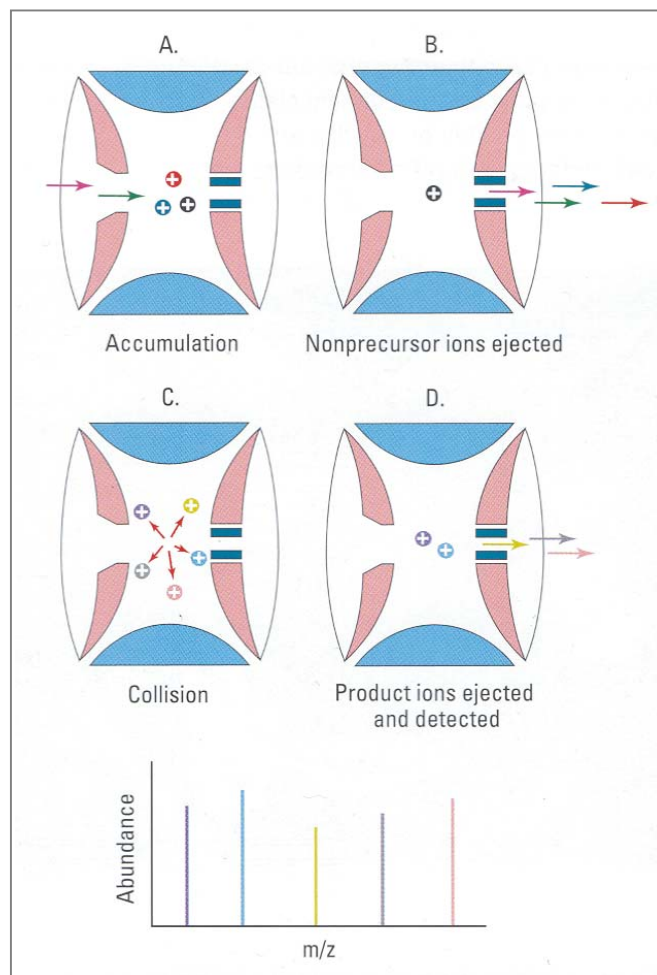
# Ion trap mass analyzer

## Single stage MS



Multiple stage MS in LC  
necessary for structural  
elucidation of target analyte

## $MS^n$ ....multiple stage







GCMS quadrupole –  
nonpolar compounds

2) Instruments  
must be stable

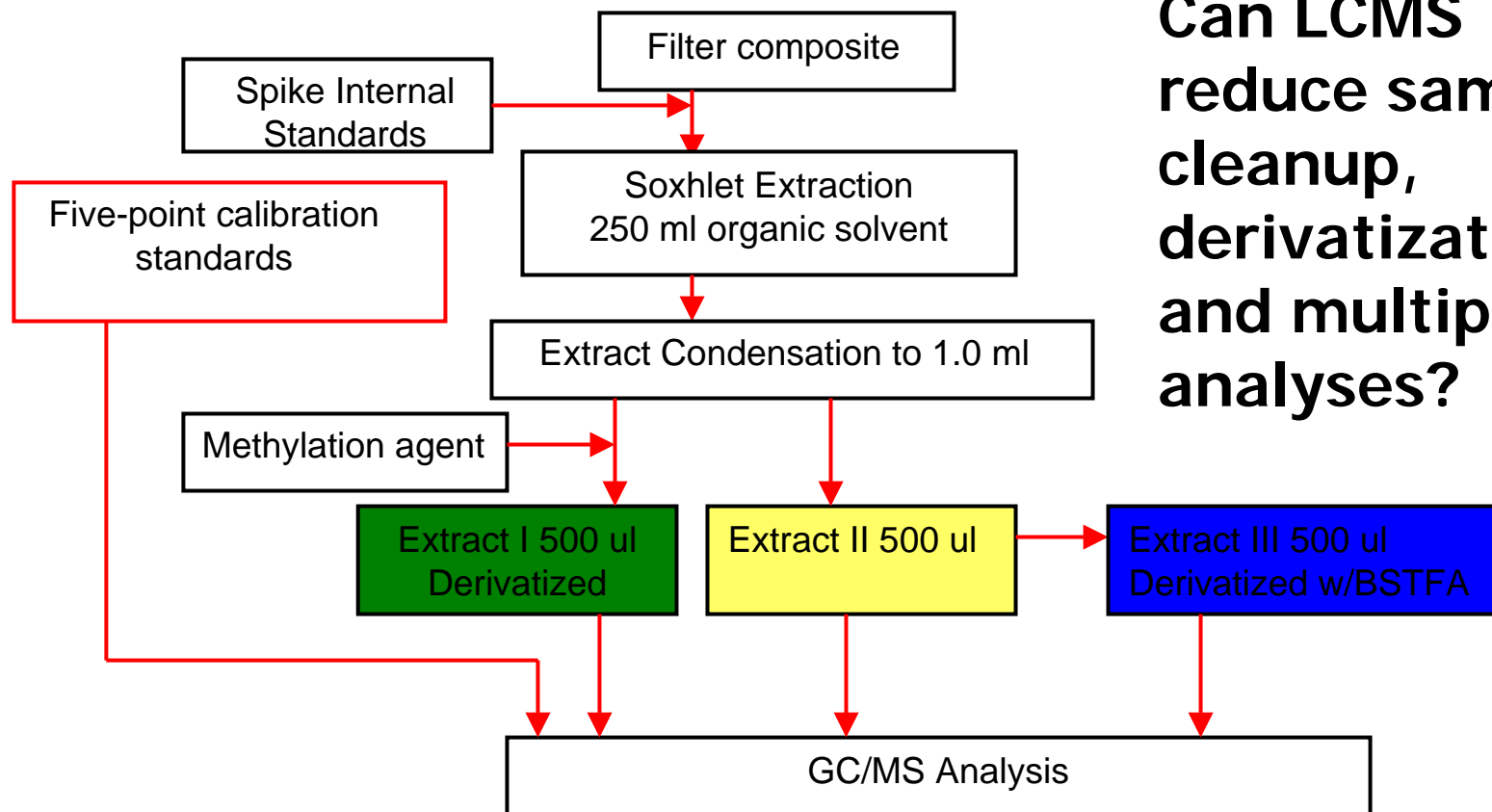
1) Molecular level  
instrumentation  
must  
accommodate  
complex mixtures



LCMS ion trap – polar compounds

# Analytical protocol GCMS markers

**Can LCMS  
reduce sample  
cleanup,  
derivatization  
and multiple  
analyses?**



**Extract I: Organic acids**

**Extract II: Neutral compounds**

**Extract III: Polar compounds**

# Reproducibility of five-point RRF over 3-month analysis period by GC/MS .... is LCMS better?

Source: Li et al., 2005, AWMA Conf. Proceedings

| Molecular Markers  | Retention Time (minute) | RRF         |             | %SD         |
|--|-------------------------|-------------|-------------|-------------|
|  |                         | Nov, 2002   | Feb, 2003   |             |
| n-Pentacosane (C25)                                      | 33.2                    | 1.11        | 1.13        | 1.41        |
| n-Hexacosane (C26)                                       | 35.1                    | 1.03        | 0.99        | 2.83        |
| n-Heptacosane (C27)                                      | 37.0                    | 0.93        | 0.94        | 0.71        |
| n-Octacosane (C28)                                       | 38.8                    | 0.82        | 0.84        | 1.41        |
| n-Nonacosane (C29)                                       | 40.6                    | 0.81        | 0.81        | 0.00        |
| n-Triacontane (C30)                                      | 42.3                    | 0.8         | 0.86        | 4.24        |
| n-Hentriacontane (C31)                                   | 44.0                    | 0.52        | 0.57        | 3.54        |
| n-Dotriacontane (C32)                                    | 45.9                    | 0.22        | 0.28        | 4.24        |
| benzo[b]fluoranthene                                     | 43.6                    | 0.62        | 0.70        | 5.66        |
| benzo[k]fluoranthene                                     | 43.7                    | 0.70        | 0.65        | 3.54        |
| benzo[e]pyrene   | 45.1                    | 0.71        | 0.73        | 1.41        |
| <b>17<math>\alpha</math>,21<math>\beta</math>,hopane</b> | <b>43.6</b>             | <b>1.29</b> | <b>1.20</b> | <b>6.36</b> |
| Dodecanoic acid (C12)                                    | 11.9                    | 1.10        | 0.77        | *23.33      |
| Palmitic acid (C16)                                      | 22.2                    | 1.21        | 0.76        | *31.82      |
| Tetracosanoic acid (C24)                                 | 37.6                    | 0.61        | 0.32        | *20.51      |

%SD=100  $\times$  (standard deviation/arithmetic mean)

# Experiments comparing and establishing optimum source conditions

|                      | Smart Parameter Settings / Mode  | APPI (dopant)          |                   | APPI (no dopant)       |                    | ESI               |                    | Total runs  |                 |                 |
|----------------------|----------------------------------|------------------------|-------------------|------------------------|--------------------|-------------------|--------------------|-------------|-----------------|-----------------|
|                      |                                  | Scan                   | Iso/Frag          | Scan                   | Iso/Frag           | Scan              | Iso/Frag           |             |                 |                 |
| System Blanks        | High energy/<br>Larger Molecules | 2/21/07 24 runs        | NA                | 2/21/07 24 runs        | NA                 | 2/27/07 24 runs   | NA                 | 120         |                 |                 |
|                      |                                  | 2/22/07 24 runs        |                   | 2/22/07 24 runs        |                    | 2/27/07 24 runs   |                    |             |                 |                 |
|                      | <b>48 RUNS</b>                   | <b>48 RUNS</b>         |                   | <b>24 RUNS</b>         |                    |                   |                    |             |                 |                 |
|                      | Low energy/<br>Smaller Molecules | 2/22/07 24 runs        |                   | NA                     |                    | 2/22/07 24 runs   |                    |             | NA              | 2/27/07 24 runs |
| 2/21/07 24 + 24 runs |                                  | 2/21/07 24 + 24 runs   | 2/27/07 24 runs   |                        |                    |                   |                    |             |                 |                 |
| <b>72 RUNS</b>       | <b>72 RUNS</b>                   | <b>24 RUNS</b>         |                   |                        |                    |                   |                    |             |                 |                 |
|                      |                                  |                        |                   |                        |                    |                   |                    |             |                 |                 |
| Diacids              | High energy/<br>Larger Molecules | 2/21/07 90 runs        | 2/2/2007 360 runs | 2/21/07 90 runs        | 1/31/2007 360 runs | 2/27/07 90 runs   | 2/16/2007 360 runs | 1350        |                 |                 |
|                      |                                  | <b>90 RUNS</b>         | <b>360 RUNS</b>   | <b>90 RUNS</b>         | <b>360 RUNS</b>    | <b>90 RUNS</b>    | <b>360 RUNS</b>    |             |                 |                 |
|                      | Low energy/<br>Smaller Molecules | 2/21/07 90 + 6 runs    | 2/22/07 48 runs   | 2/21/07 90 + 6 runs    | 2/22/07 48 runs    | 2/27/07 90 runs   | 2/27/07 48 runs    |             | 426             |                 |
|                      |                                  | <b>96 RUNS</b>         | <b>48 RUNS</b>    | <b>96 RUNS</b>         | <b>48 RUNS</b>     | <b>90 RUNS</b>    | <b>48 RUNS</b>     |             |                 |                 |
|                      |                                  |                        |                   |                        |                    |                   |                    |             |                 |                 |
|                      |                                  |                        |                   |                        |                    |                   |                    |             |                 |                 |
| Oxoacids             | High energy/<br>Larger Molecules | 2/22/2007 12 runs      | 2/21/07 24 runs   | 2/22/2007 12 runs      | 2/21/07 24 runs    | 2/27/2007 12 runs | NA                 | 84          |                 |                 |
|                      |                                  | <b>12 RUNS</b>         | <b>24 RUNS</b>    | <b>12 RUNS</b>         | <b>24 RUNS</b>     | <b>12 RUNS</b>    |                    |             |                 |                 |
|                      | Low energy/<br>Smaller Molecules | 2/22/2007 12 + 12 runs | 2/22/07 48 runs   | 2/22/2007 12 + 12 runs | 2/22/07 48 runs    | 2/27/2007 12 runs |                    |             | 2/27/07 48 runs | 204             |
|                      |                                  | <b>24 RUNS</b>         | <b>48 RUNS</b>    | <b>24 RUNS</b>         | <b>48 RUNS</b>     | <b>12 RUNS</b>    |                    |             | <b>48 RUNS</b>  |                 |
|                      |                                  |                        |                   |                        |                    |                   |                    |             |                 |                 |
|                      |                                  |                        |                   |                        |                    |                   |                    |             |                 |                 |
|                      | Total runs                       | 342                    | 480               | 342                    | 480                | 252               | 456                | <b>2352</b> |                 |                 |

## Atmospheric Pressure Photoionization Mechanisms

For many compounds, APPI directly ionizes the target molecule, resulting in  $M^{\bullet+}$ . The ionized molecule may undergo further reactions, such as abstracting a hydrogen atom from the solvent, resulting in  $[M+H]^+$ . For PAHs, adding dopant resulted in the best sensitivity.

### Direct APPI



and under certain conditions ...



Analyte molecule **M** is ionized to molecular ion  $M^{\bullet+}$

Molecular ion  $M^{\bullet+}$  abstracts a hydrogen from ionized solvent

### Dopant APPI



Photoionizable dopant **D** is in excess & yields many  $D^+$  ions

$D^+$  ionizes analyte **M** by proton transfer

$D^+$  ionizes analyte **M** by electron transfer

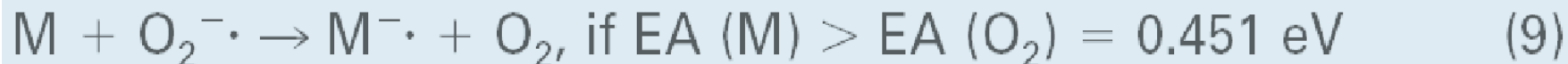
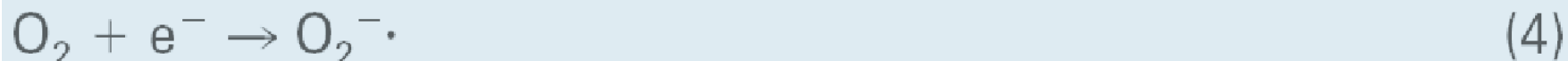
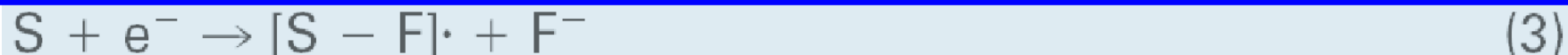
<http://www.chem.agilent.com/temp/radD52D3/00026439.pdf>

Analysis of Polyaromatic Hydrocarbons by Atmospheric Pressure Photoionization LC/MS

Patricia H. Cormia, Steven M. Fischer and Christine A. Miller, Agilent Technologies, Inc., Palo Alto, CA

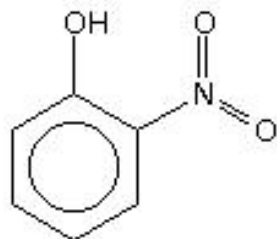
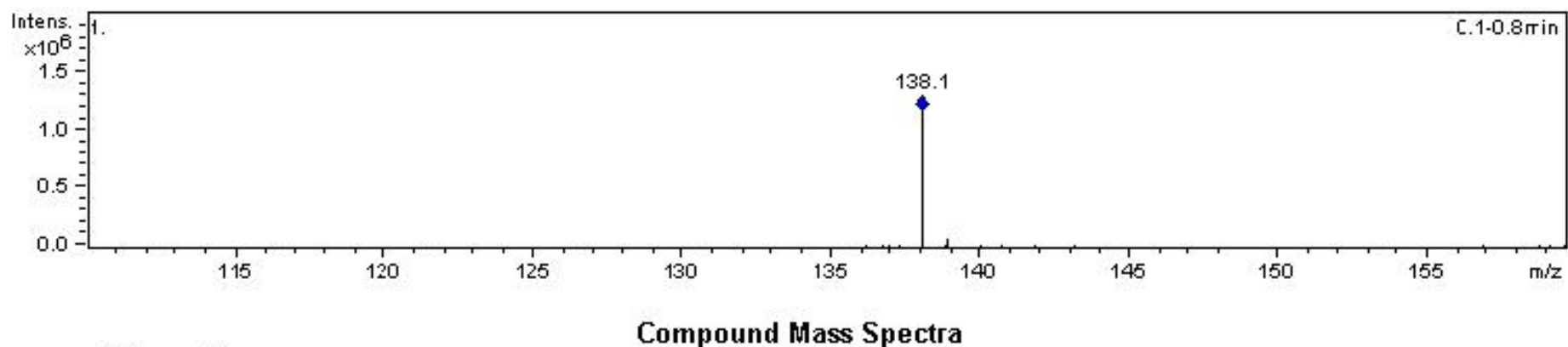
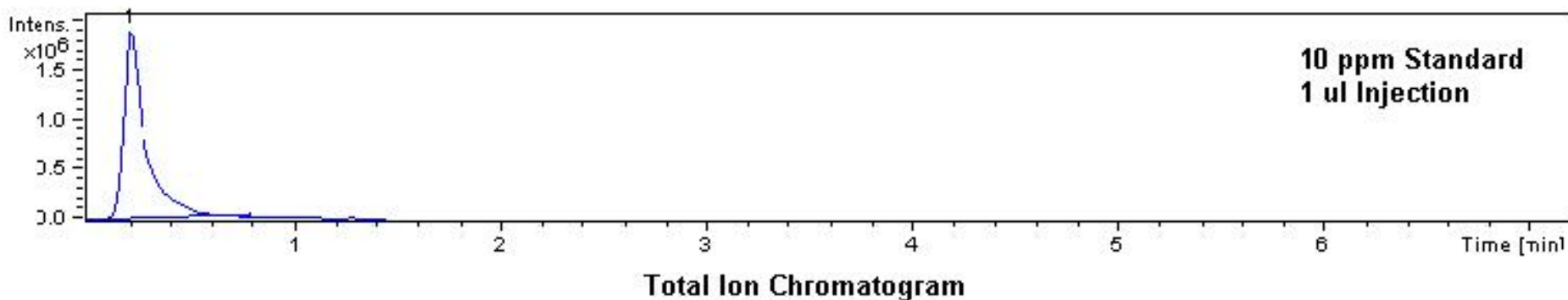


## The reactions in negative ion APPI



Source: Kauppila et al. J. Am Soc Spectrometry 2004, 15, 203-211

## 2-Nitrophenol LC/MS Ion Trap: Atmospheric Pressure Photolysis Negative Mode with 10% Acetone Dopant



2-nitrophenol

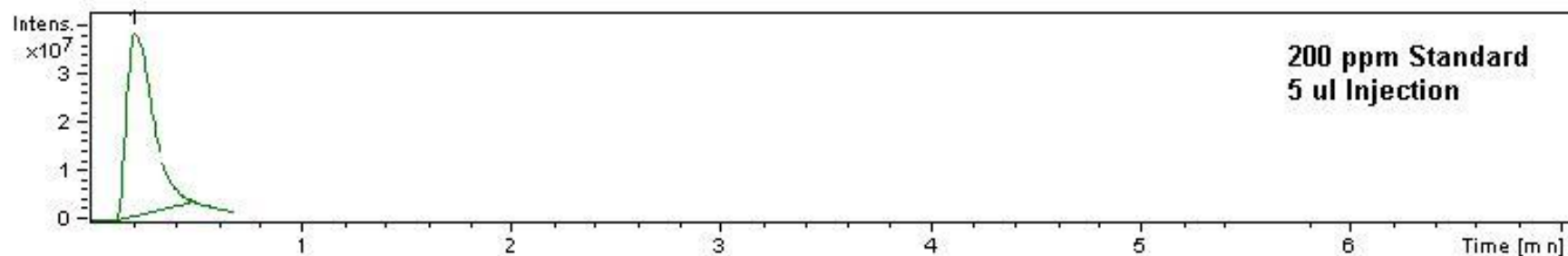
Formula: C<sub>6</sub>H<sub>5</sub>NO<sub>3</sub>

Molecular Weight: 139.11

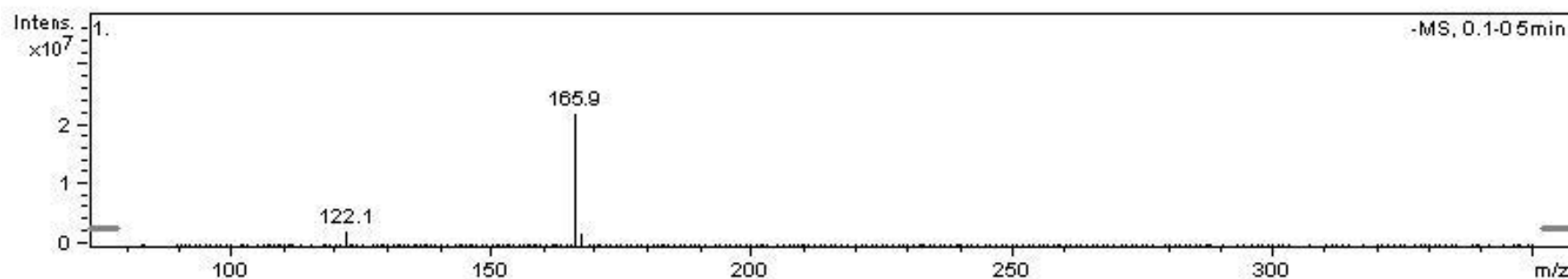
CAS Registry Number: 88-75-5

|   | m/z   | I       |
|---|-------|---------|
| 1 | 138.1 | 1144872 |
| 2 | 138.9 | 64077   |
| 3 | 138.8 | 16512   |
| 4 | 140.0 | 10838   |
| 5 | 136.6 | 334     |

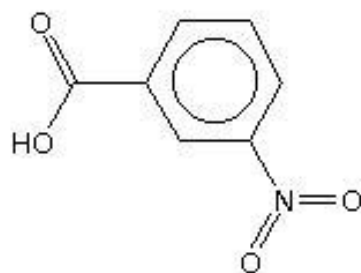
### 3-Nitrobenzoic Acid LC/MS Ion Trap: Atmospheric Pressure Photoionization Negative Mode with 10% Acetone Dopant



Total Ion Chromatogram



Compound Mass Spectra



3-Nitrobenzoic acid

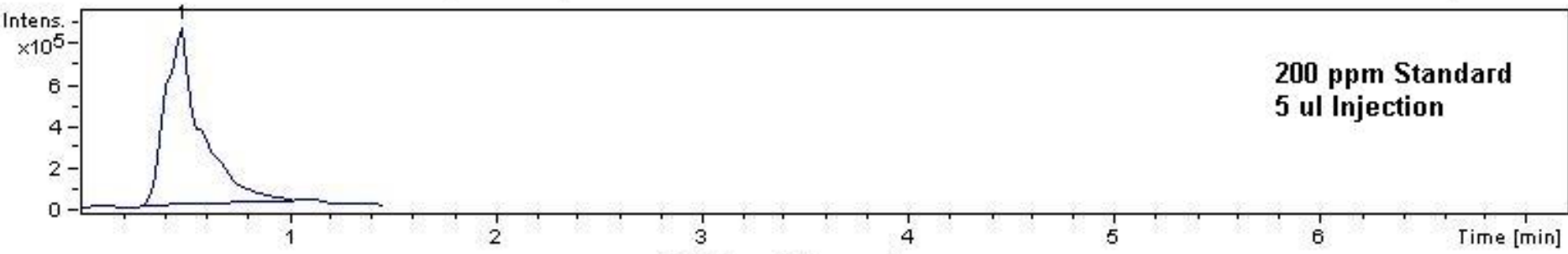
Formula: C<sub>7</sub>H<sub>5</sub>NO<sub>4</sub>

Molecular Weight: 167.12

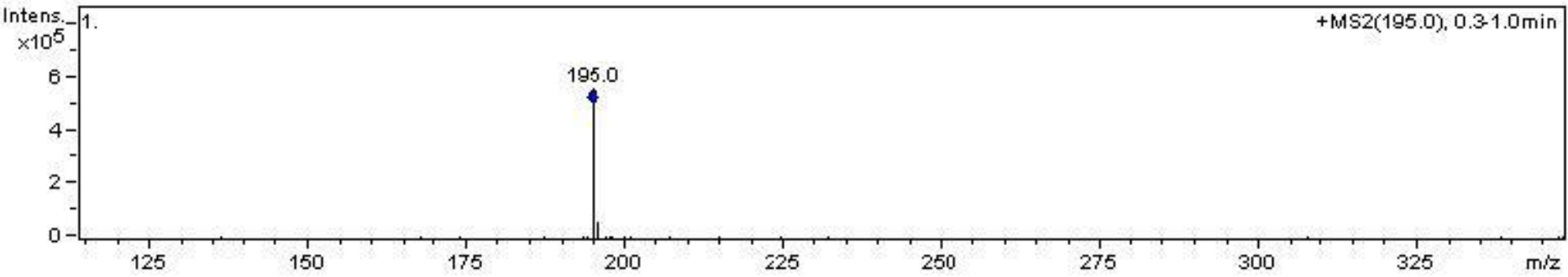
CAS Registry Number: 121-92-6

| # | m/z   | I        |
|---|-------|----------|
| 1 | 165.9 | 21847882 |
| 2 | 122.1 | 2114604  |
| 3 | 166.8 | 1802433  |
| 4 | 92.2  | 279171   |
| 5 | 167.8 | 215004   |

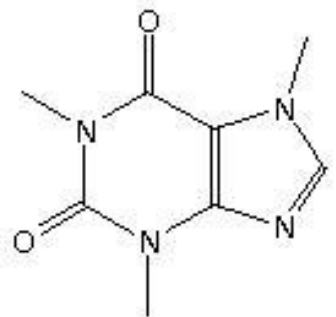
# Caffeine LC/MS Ion Trap: Atmospheric Pressure Photolization Positive Mode with 10% Acetone Dopant



Total Ion Chromatogram



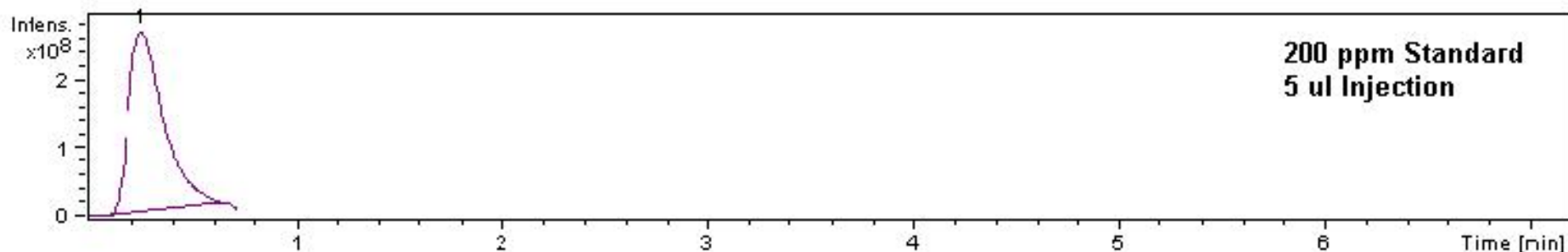
Compound Mass Spectra



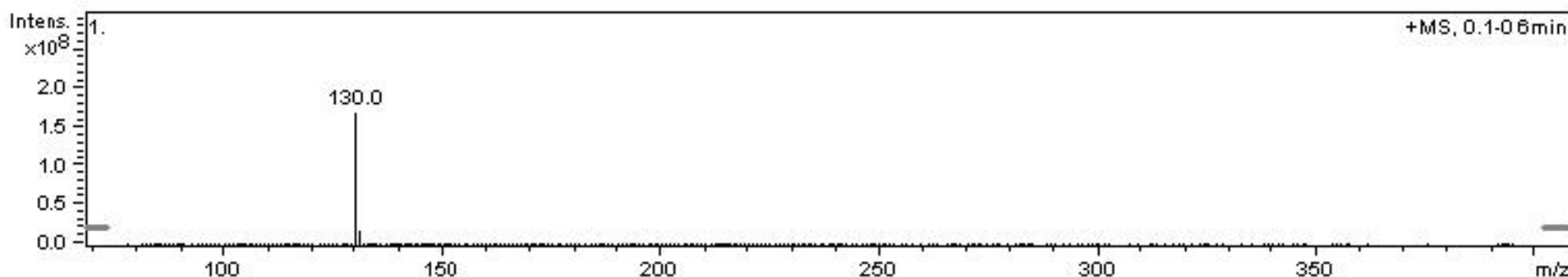
Caffeine  
Formula: C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>  
Molecular Weight: 194.19  
CAS Registry Number: 58-08-2

| # | m/z   | I      |
|---|-------|--------|
| 1 | 195.0 | 489694 |
| 2 | 196.0 | 53114  |
| 3 | 197.0 | 5715   |
| 4 | 193.1 | 2931   |
| 5 | 194.0 | 2676   |

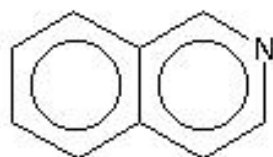
# Isoquinoline LC/MS Ion Trap: Atmospheric Pressure Photolization Positive Mode with 10% Acetone Dopant



Total Ion Chromatogram



Compound Mass Spectra



Isoquinoline

Formula: C<sub>9</sub>H<sub>7</sub>N

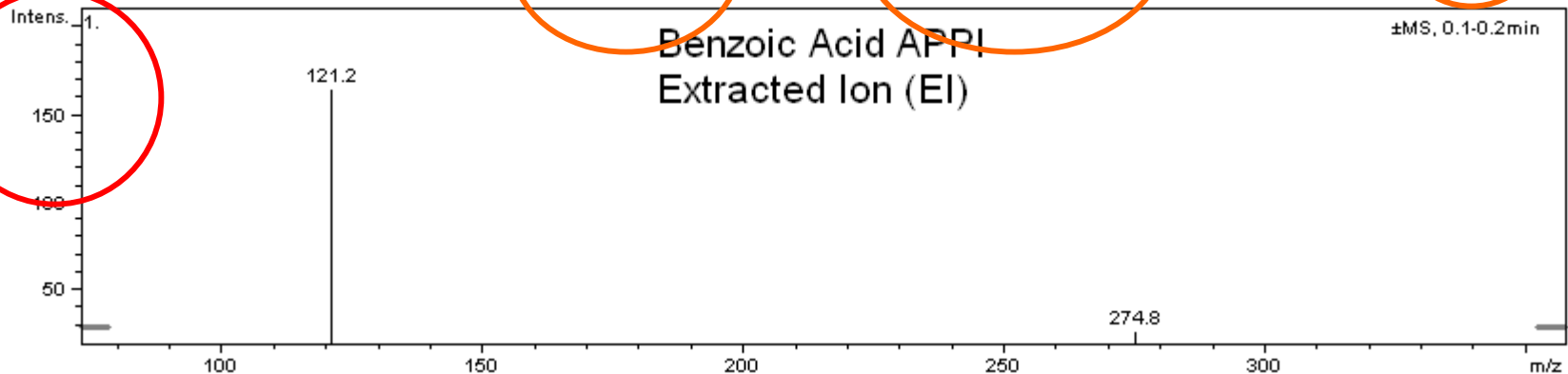
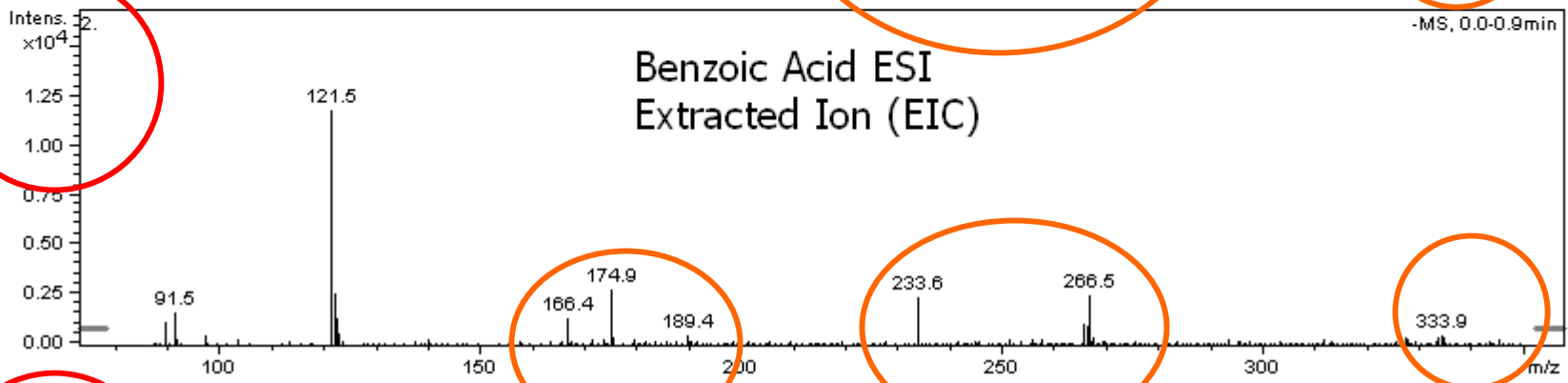
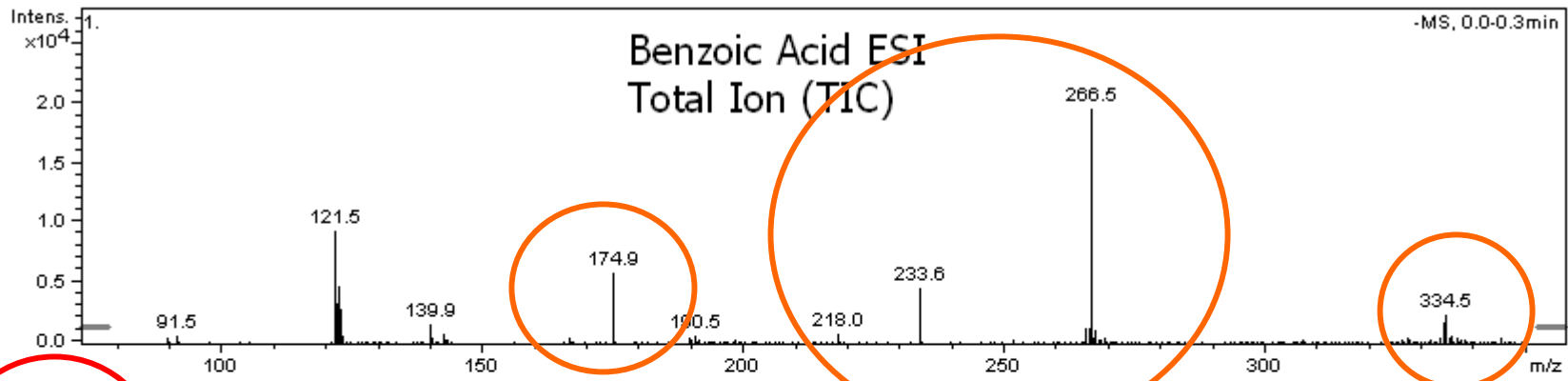
Molecular Weight: 129.16

CAS Registry Number: 119-65-3

| # | m/z   | I         |
|---|-------|-----------|
| 1 | 130.0 | 168823648 |
| 2 | 131.0 | 17127998  |
| 3 | 144.0 | 1698470   |
| 4 | 132.0 | 758232    |
| 5 | 136.0 | 730664    |

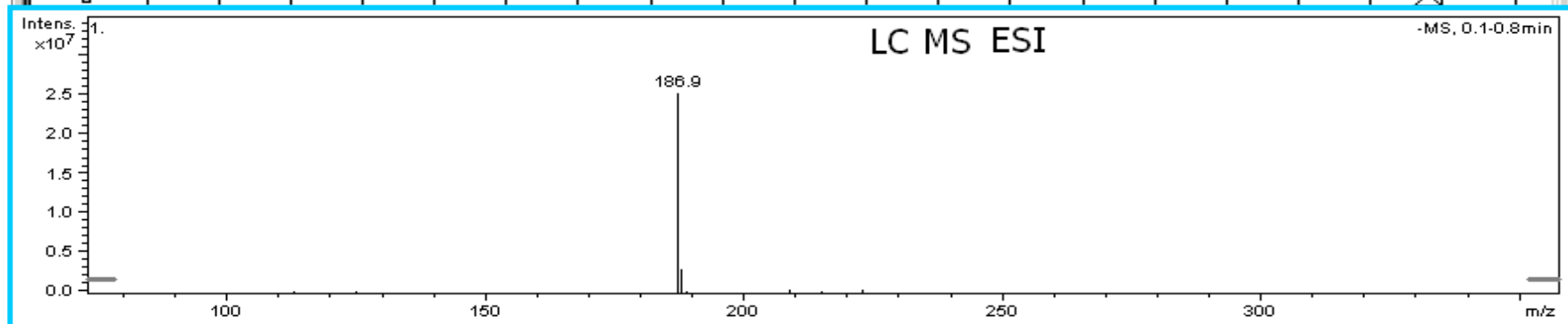
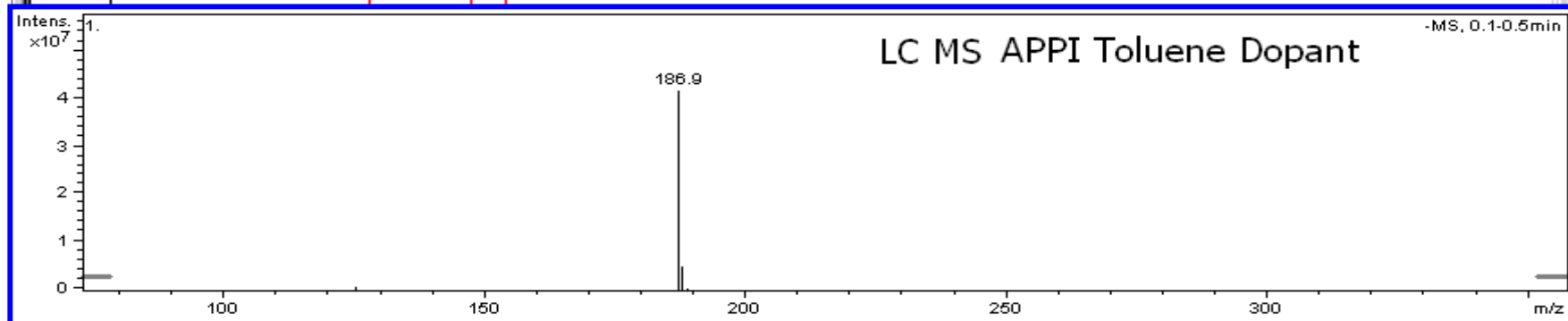
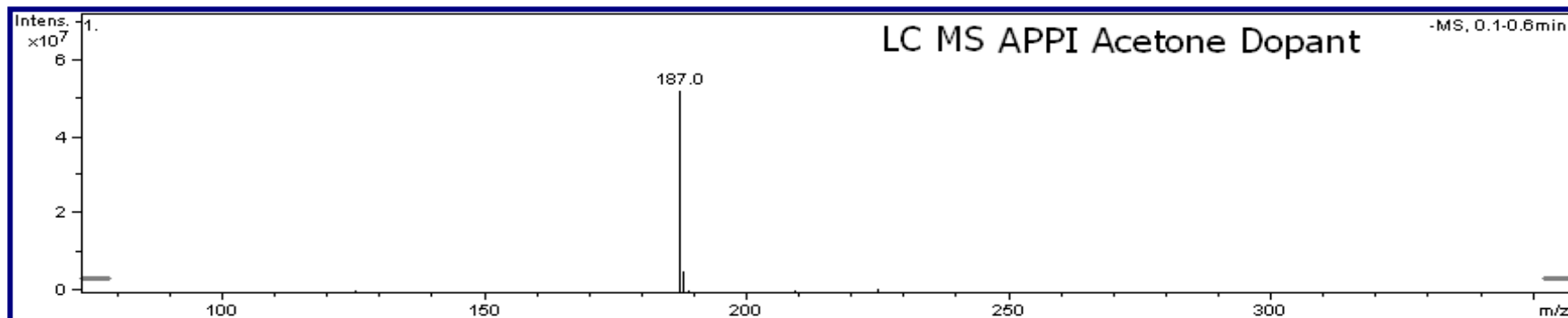


# Example of LCMS sources for detecting molecular markers



# Ion spectra for azelaic acid

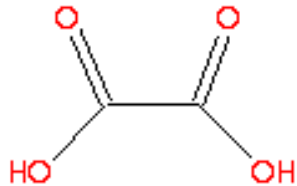
MW 188



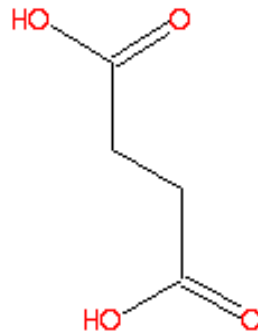
# Not all acids conform to a clear molecular ion or M-1 spectra

Strong or reactive acids form dimers in the APPI source as adduct ions with mobile phase and/or dopant molecules

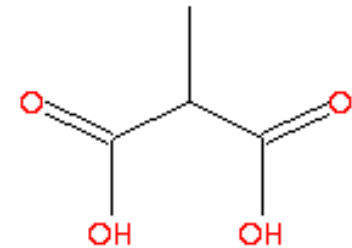
Found commonly with aliphatic acids where carbon chains  $< C3$



Oxalic acid

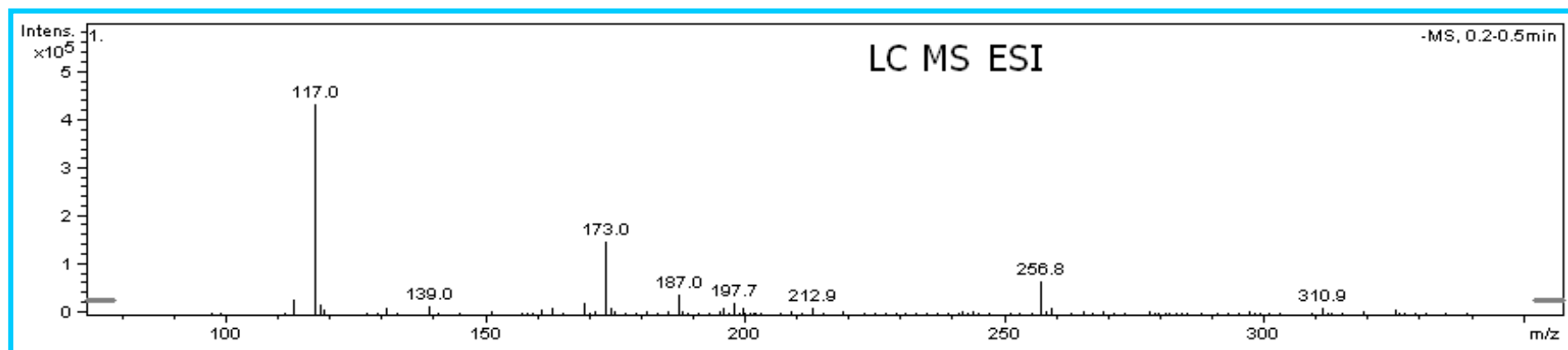
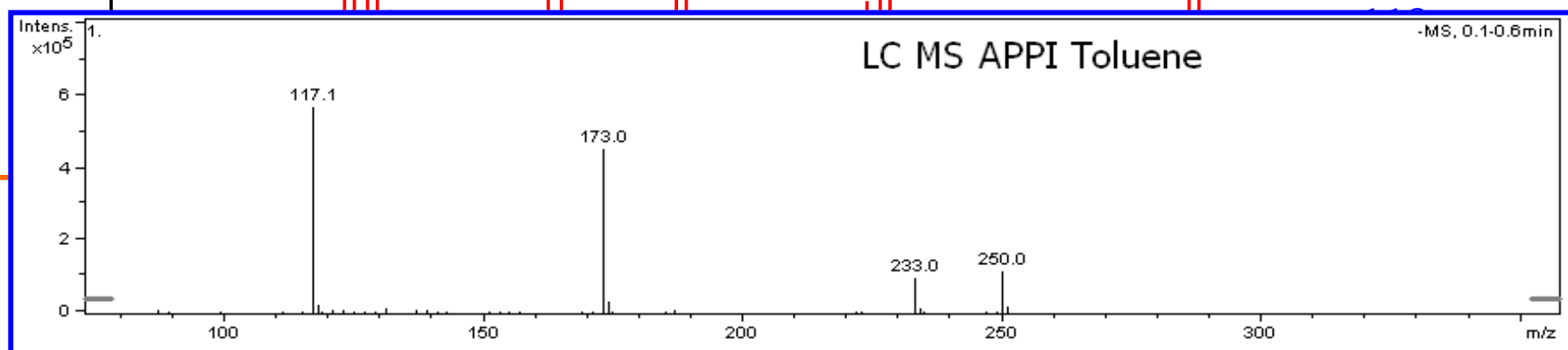
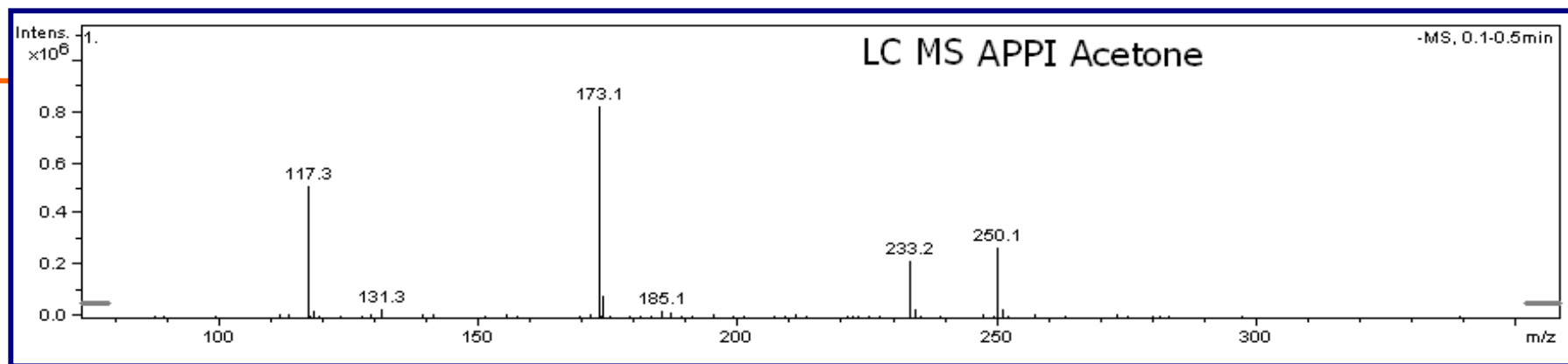


Succinic acid



Methyl malonic acid

# Methyl Malonic Acid MW 118



# Do ESI and APPI produce the same spectra for compounds of atmospheric significance?

**61 standard compounds evaluated by LCMS ESI and APPI analysis**

| Neutral Compounds          |     |            | Organic Acids            |     |          | Organic Bases             |     |            |
|----------------------------|-----|------------|--------------------------|-----|----------|---------------------------|-----|------------|
| Name                       | MW  | Formula    | Name                     | MW  | Formula  | Name                      | MW  | Formula    |
| Salicylaldehyde            | 122 | C7H6O2     | Oxalic acid              | 90  | C2H2O4   | Pyridine                  | 79  | C5H5N      |
| Naphthalene                | 128 | C10H8      | Fumaric Acid             | 116 | C4H4O4   | 1,6-Diaminohexane         | 116 | C6H16N2    |
| Naphthalene (d8)           | 136 | C10D8      | Maleic Acid              | 116 | C4H4O5   | Isoquinoline              | 129 | C9H7N      |
| 4-hydroxy-1-naphthaldehyde | 172 | C11H8O2    | Methyl Malonic acid      | 118 | C4H6O4   | Quinoline                 | 129 | C9H7N      |
| Phenanthrene               | 178 | C14H10     | Succinic Acid            | 118 | C4H6O4   | 3-Methylindole            | 131 | C9H9N      |
| Fructose                   | 180 | C6H12O6    | Benzoic Acid             | 122 | C7H6O2   | 4-Nitrophenol             | 139 | C6H5NO3    |
| Glucose                    | 180 | C6H12O6    | Glutaric Acid            | 132 | C5H8O4   | 3-methylisoquinoline      | 143 | C10H9N     |
| Phenanthrene-D10           | 188 | C14D10     | Salicylic Acid           | 138 | C7H6O3   | 2-Methylthia-naphthalene  | 148 | C9H8S      |
| Formaldehyde, DNPH         | 210 | C7H6N4O4   | Adipic Acid              | 146 | C6H10O4  | Carbazole                 | 167 | C12H9N     |
| Acetaldehyde, DNPH         | 224 | C8H8N4O4   | Terephthalaldehydic Acid | 150 | C8H6O3   | 9-methylcarbazole         | 181 | C14H13N    |
| Acrolein-DNPH              | 236 | C9H8N4O4   | 4-Hydroxysalicylic acid  | 154 | C7H6O4   | Dibenzothiophene          | 184 | C12H8S     |
| Acetone, DNPH              | 238 | C9H10N4O4  | 1,3-naphthalenediol      | 160 | C10H8O2  | Caffeine                  | 194 | C8H10N4O2  |
| Propionaldehyde, DNPH      | 238 | C9H10N4O4  | 1,4-naphthalenediol      | 160 | C10H8O2  | 9-ethylcarbazole          | 195 | C13H11N    |
| Crotonaldehyde, DNPH       | 250 | C10H10N4O4 | 2,3-naphthalenediol      | 160 | C10H8O2  | 4-methyldibenzo-thiophene | 198 | C13H10S    |
| Methacrolein-DNPH          | 250 | C10H10N4O4 | Sodium Salicylate        | 160 | NaC7H5O3 | Reserpine                 | 609 | C33H40N2O9 |
| 2-Butanone-DNPH            | 252 | C10H12N4O4 | Isophthalic Acid         | 166 | C8H6O4   |                           |     |            |
| Benzo[b]fluoranthene       | 252 | C20H12     | Phthalic Acid            | 166 | C8H6O4   |                           |     |            |
| Butyraldehyde, DNPH        | 252 | C10H12N4O4 | Terephthalic Acid        | 166 | C8H6O4   |                           |     |            |
| Isovaleraldehyde, DNPH     | 266 | C11H14N4O4 | 3-Nitrobenzoic Acid      | 167 | C7H5NO4  |                           |     |            |
| Valeraldehyde-DNPH         | 266 | C11H14N4O4 | 2-naphthoic acid         | 172 | C11H8O2  |                           |     |            |
| Hexaldehyde-DNPH           | 280 | C12H16N4O4 | Suberic Acid             | 174 | C8H14O4  |                           |     |            |
| Benzaldehyde, DNPH         | 286 | C13H10N4O4 | Azelaic Acid             | 188 | C9H16O4  |                           |     |            |
| m-Tolualdehyde-DNPH        | 300 | C14H12N4O4 | Phenol-D5                | 100 | C6D6O    |                           |     |            |



# Oxalic acid standard mass spectra

## ESI ions

| Acid        | MW    | Amp | File       |     | 1     | 2     | 3     | 4     | 5     |
|-------------|-------|-----|------------|-----|-------|-------|-------|-------|-------|
| Oxalic Acid | 90.03 | 0.4 | SOAP000001 | m/z | 88.9  | 61.3  | 89.9  | 403.6 | 583.1 |
|             |       |     |            |     | 31757 | 905   | 831   | 528   | 383   |
| Oxalic Acid | 90.03 | 0.4 | SOAP000002 | m/z | 88.9  | 234   | 89.9  | 665.6 | 407   |
|             |       |     |            |     | 28221 | 1095  | 830   | 828   | 819   |
| Oxalic Acid | 90.03 | 0.4 | SOAP000003 | m/z | 88.9  | 651.1 | 511.1 | 89.9  | 161.2 |
|             |       |     |            |     | 31603 | 2548  | 1476  | 758   | 731   |
| Oxalic Acid | 90.03 | 0.4 | SOAP000004 | m/z | 89.0  | 90.0  | 473.5 | 61.2  | 124.9 |
|             |       |     |            |     | 34866 | 1172  | 1160  | 945   | 892   |
| Oxalic Acid | 90.03 | 0.4 | SOAP000005 | m/z | 88.9  | 453.6 | 90    | 244.7 | 369.7 |
|             |       |     |            |     | 27982 | 4310  | 864   | 857   | 748   |
| Oxalic Acid | 90.03 | 0.4 | SOAP000006 | m/z | 88.9  | 513.7 | 89.9  | 61.2  | 604.3 |
|             |       |     |            |     | 29680 | 3432  | 1423  | 853   | 636   |

**Solvent-ion, oligomers formed in ESI source**

**Inconsistent ions formed**

## APPI ions

| Acid        | MW    | Amp | File       |     | 1      | 2    | 3    | 4    | 5    |
|-------------|-------|-----|------------|-----|--------|------|------|------|------|
| Oxalic Acid | 90.03 | 0.4 | SOAP000001 | m/z | 88.7   | 89.6 | 90.6 | 86.8 | 61   |
|             |       |     |            |     | 123730 | 4874 | 3196 | 2988 | 1048 |
| Oxalic Acid | 90.03 | 0.4 | SOAP000002 | m/z | 88.7   | 89.6 | 90.6 | 86.8 | 92.7 |
|             |       |     |            |     | 120600 | 5230 | 2795 | 2704 | 1212 |
| Oxalic Acid | 90.03 | 0.4 | SOAP000003 | m/z | 88.7   | 89.6 | 90.7 | 86.8 | 61   |
|             |       |     |            |     | 170510 | 6841 | 2844 | 1390 | 1244 |
| Oxalic Acid | 90.03 | 0.4 | SOAP000004 | m/z | 88.7   | 89.6 | 90.6 | 86.7 | 92.6 |
|             |       |     |            |     | 127166 | 5449 | 2390 | 2189 | 776  |
| Oxalic Acid | 90.03 | 0.4 | SOAP000005 | m/z | 88.7   | 89.6 | 90.6 | 86.8 | 61   |
|             |       |     |            |     | 121238 | 4807 | 2651 | 2019 | 1332 |
| Oxalic Acid | 90.03 | 0.4 | SOAP000006 | m/z | 88.7   | 89.6 | 90.6 | 86.8 | 61   |
|             |       |     |            |     | 121238 | 4807 | 2651 | 2019 | 1332 |

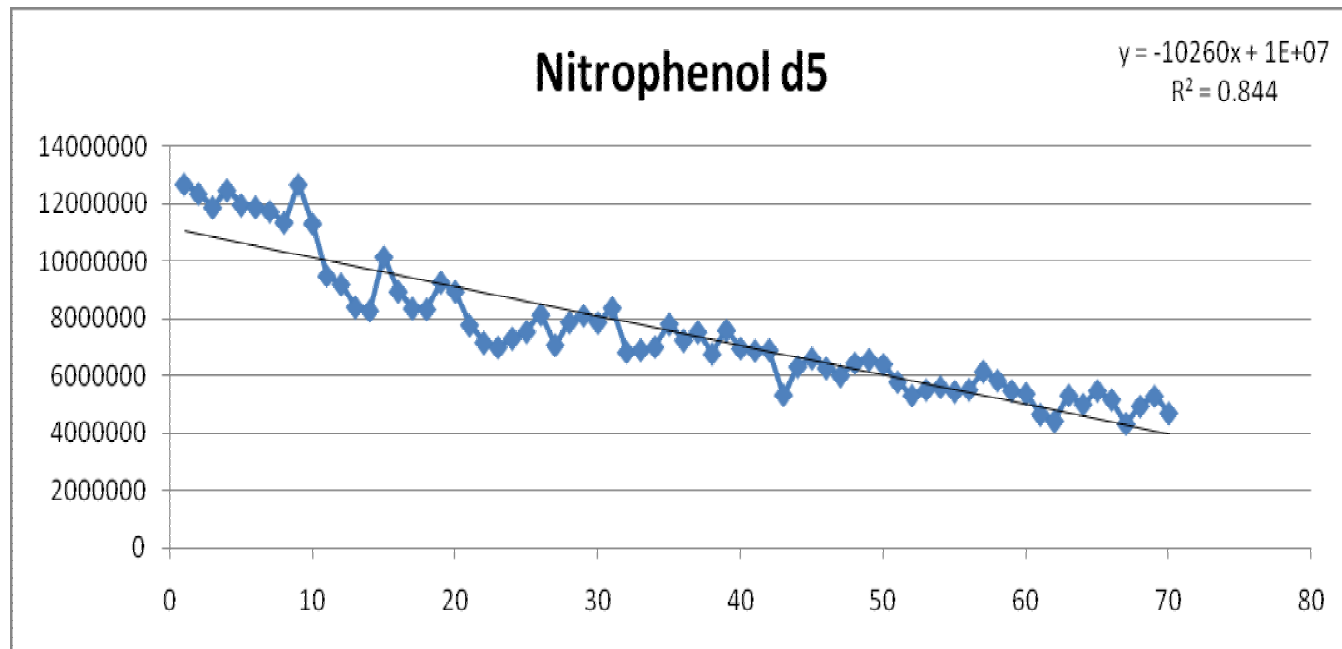
**NO solvent-ion, oligomers formed**

**Consistent order & ions formed**

**Higher response**

# Nitrophenol-d5 external standard results

Loss of response seen after 200 runs of nitrophenol-d5 despite adding a positive switch at end of run

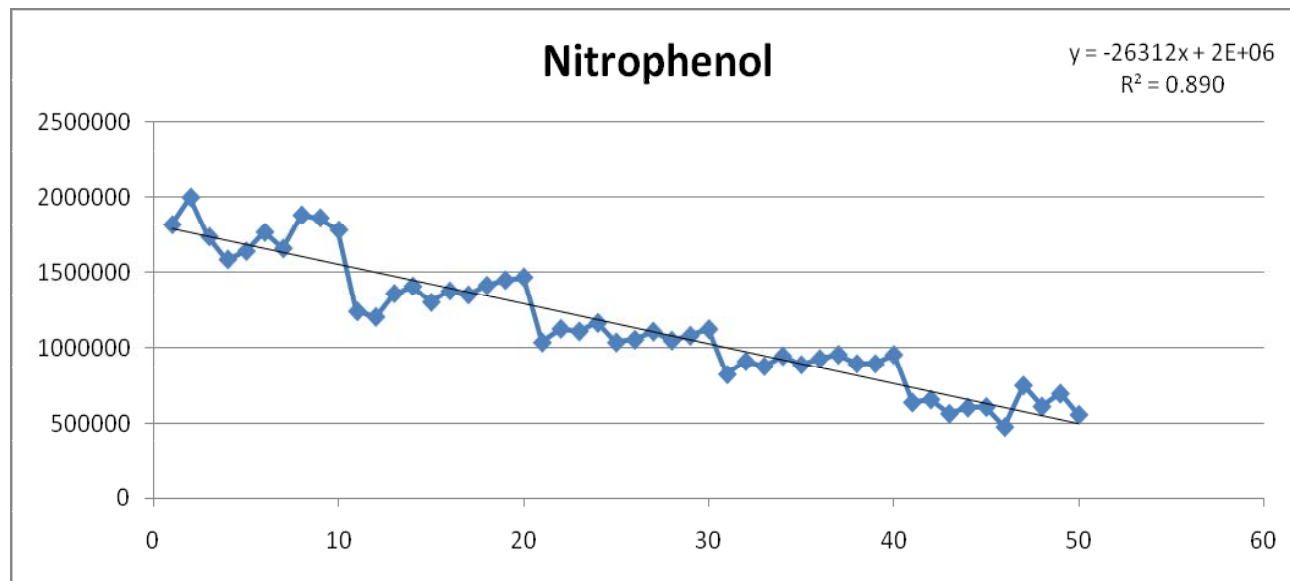


|      |          |              |          |
|------|----------|--------------|----------|
| Mean | 7532360  | Lowest Area  | 4318908  |
| STD  | 2272851  | Highest Area | 12699881 |
| %RSD | 30.17449 | % Difference | 65.99    |

- Significant negative slope
- % RSD shows high variability in standard response over 200 injections (~2 days run)
- High/low area difference 66%

# Nitrophenol (10 ppm check standard)

Loss of response is seen after 200+ runs of the sequence despite adding a positive switch at end of run

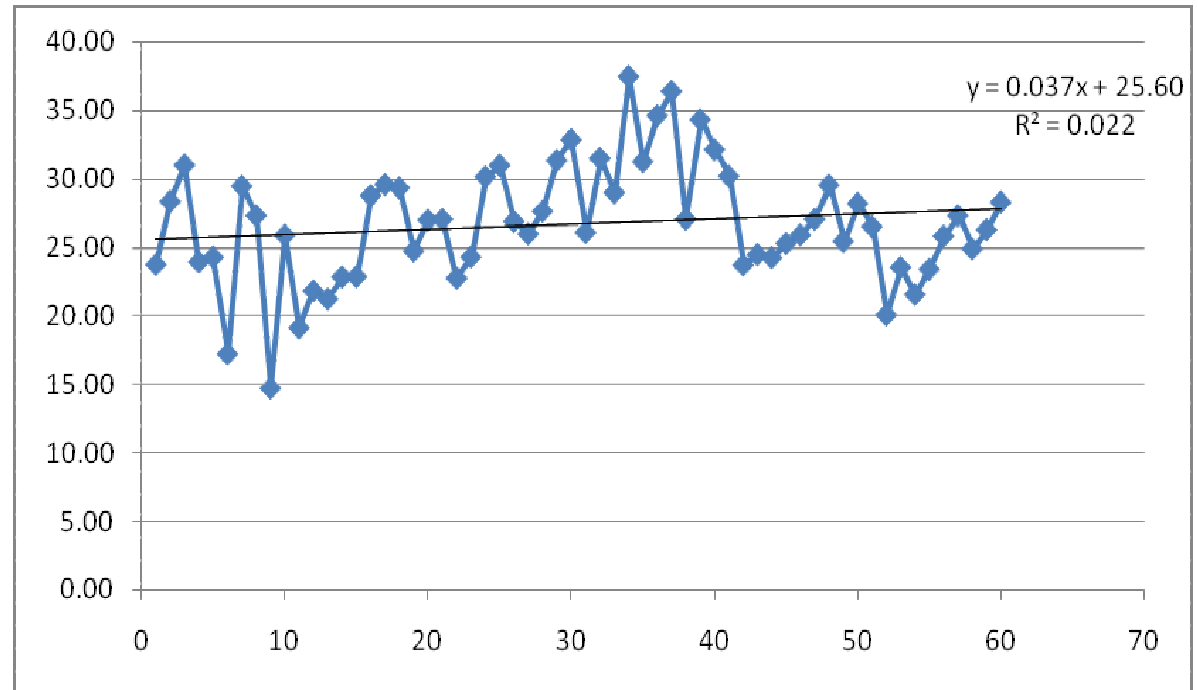


|             |          |                     |          |
|-------------|----------|---------------------|----------|
| <b>Mean</b> | 1146033  | <b>Lowest Area</b>  | 475277.5 |
| <b>STD</b>  | 406396.2 | <b>Highest Area</b> | 1998150  |
| <b>%RSD</b> | 35.46111 | <b>% Difference</b> | 76.21    |

- % difference and RSD's of experiments from 2006 and 2007 show same loss of area over a sample/standard sequence
- differences in the high/low areas range from 24-58%
- differences in RSD also range from 11-36%.

# Carbonyl and internal standards analysis

**Response factors for ISTD & Acrolein in CARB STD**

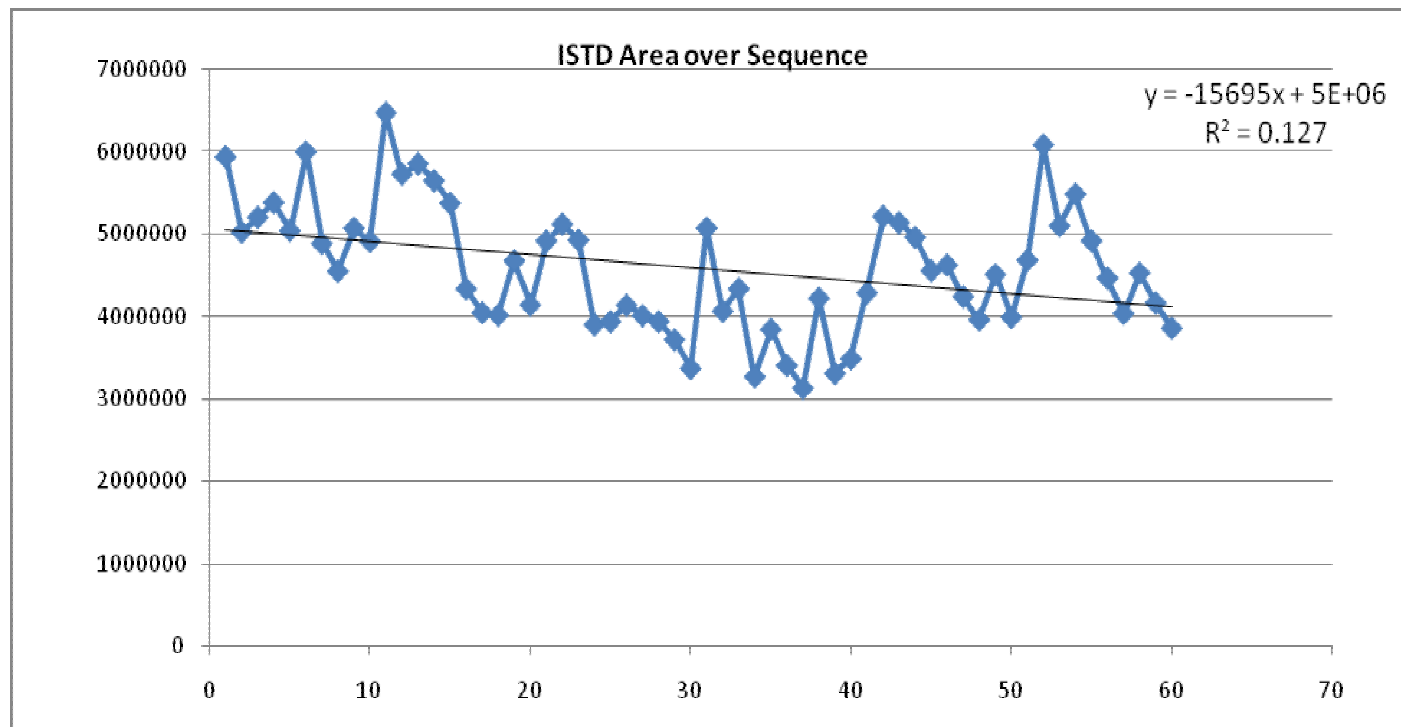


|                |          |                     |          |
|----------------|----------|---------------------|----------|
| <b>Mean Rf</b> | 26.74739 | <b>Lowest Rf</b>    | 14.74879 |
| <b>STD Rf</b>  | 4.339096 | <b>Highest Rf</b>   | 37.44239 |
| <b>%RSD Rf</b> | 16.2225  | <b>% Difference</b> | 60.61    |

Response factors determined by the calculation:

$$RRF = \left( \frac{\text{Area sample}}{\text{Area ISTD}} \right) \times \left( \frac{\text{Mass ISTD}}{\text{Mass sample}} \right)$$

# Internal STD areas over sequence



|                  |            |                          |            |
|------------------|------------|--------------------------|------------|
| <b>ISTD Mean</b> | 4589146.05 | <b>Lowest ISTD Area</b>  | 3133962.87 |
| <b>ISTD STD</b>  | 768455.85  | <b>Highest ISTD Area</b> | 6470433.03 |
| <b>ISTD %RSD</b> | 16.75      | <b>%Difference</b>       | 51.56      |

- Significant negative slope
- Large %RSD of 17%



# What we have learned...

- Every polar organic molecular marker of interest in CMB and source apportionment studies is more rapidly detected and reliably quantified by GCMS
- Compounds must be introduced as ions into the source (ESI) or be ionized within the source (ESI & APPI); sugars are difficult
- Ions interfere with target analytes; reduction of unnecessary compounds and ions necessary
- Every analyte must have an authentic standard, be run on a column, evaluated for characteristic spectrum
- Adducts & complexes readily formed in source with just the standard compound injected with ESI

# Part 2:

## Seasonal Abundance of Wood Smoke Markers and Cholesterol in Fine Particles from the New York Metropolitan Area

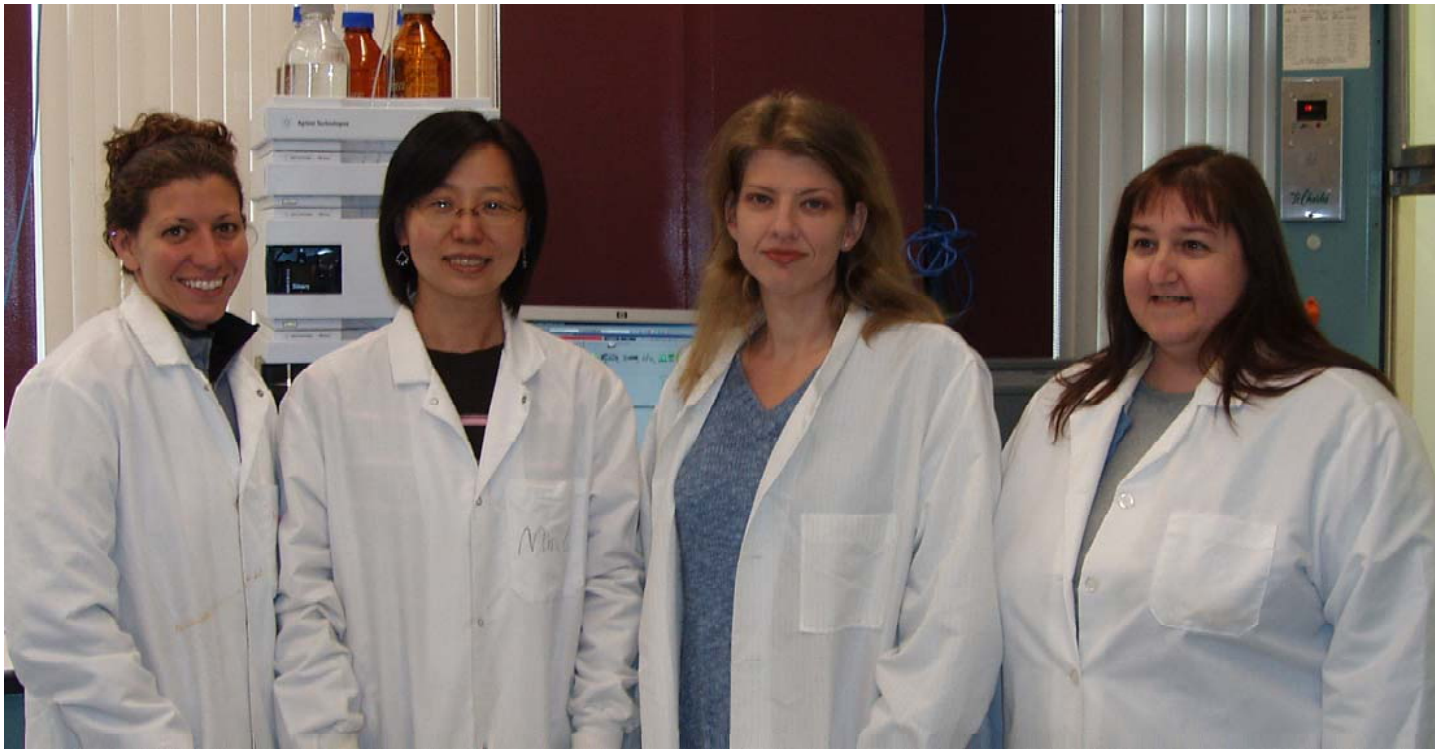
*Harmonie Hawley<sup>1</sup>, Min Li<sup>1</sup>, Monica Mazurek<sup>1</sup>, Steve McDow<sup>2</sup> and Claire Belisle<sup>1</sup>*

*<sup>1</sup>Civil & Environmental Engineering Department,  
School of Engineering, Rutgers, The State University  
of New Jersey*

*<sup>2</sup>Human Exposure and Atmospheric Sciences  
Division, National Exposure Research Laboratory,  
U.S. Environmental Protection Agency*

# Thanks To.....

U.S. EPA STAR Program "Polar Organic Fine Particles from the New York, New Jersey and Connecticut Regional Airshed" Grant #R832165



Research associates: [Patricia Atkins](#), [Min Li](#), [Claire Belisle](#)

Graduate research assistants: [Harmonie Hawley](#)

[Matt Ahearn](#)

[Rebecca Roy](#)

[Majad Ullah](#)

[Andrew Bausch](#)

# End of Presentation

## Thank you

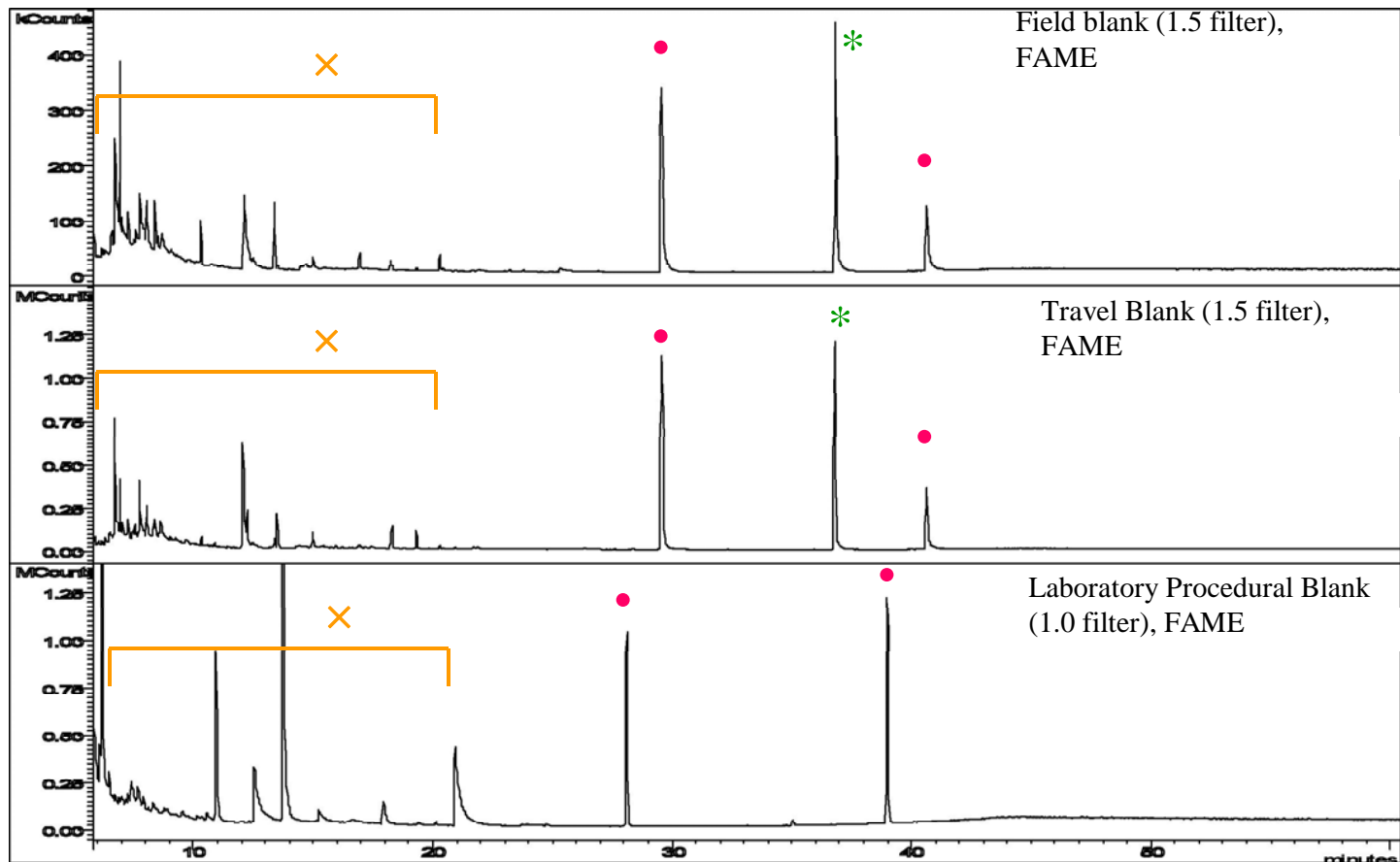
### *Contact Information*

Monica Mazurek, Assistant Professor  
Department of Civil and Environmental Engineering and  
Center for Advanced Infrastructure & Transportation (CAIT)  
School of Engineering  
100 Brett Road  
Rutgers, The State University of New Jersey  
Piscataway, NJ 08854-8058  
tel: 732-445-0579 ext. 128  
fax: 732-445-3325  
email: [mmazurek@rci.rutgers.edu](mailto:mmazurek@rci.rutgers.edu)

# Quality Control at the Molecular Level -- Blanks

Queens Winter Intensive

- C24D50, 30.4 minute
- C30D62, 41.4 minute
- \* Sampling artifact
- × Solvent artifact



# Comparison of area ratios of molecular marker quantitation ions to m/z to *n*-C24D50 internal standard m/z 92 for tracers present above the instrument detection levels for the Varian Saturn 3800 GCMS

| Molecular Marker                             | All SOAP Blanks Average Area Ratios (n=17) | All SOAP Blanks STD <sup>a</sup> | All SOAP Blanks RSD <sup>a</sup> | All SOAP Ambient Average Ratios (n=40) | Average Area Ratio All SOAP Ambient/Average Area Ratio All Blanks |
|--|--|----------------------------------|----------------------------------|--|---|
| <b><i>n</i>-Alkanes<sup>b</sup></b>          |  |                                  |                                  |  |   |
| <i>n</i> C25                                 | 0.00132                                    | 0.00096                          | 73                               | 0.05915                                | 45  |
| <i>n</i> C26                                 | 0.00106                                    | 0.00094                          | 89                               | 0.04065                                | 38  |
| <i>n</i> C27                                 | 0.00138                                    | 0.00096                          | 69                               | 0.05508                                | 40  |
| <i>n</i> C28                                 | 0.00136                                    | 0.00083                          | 61                               | 0.02696                                | 20  |
| <i>n</i> C29                                 | 0.00162                                    | 0.00052                          | 32                               | 0.08041                                | 50  |
| <i>n</i> C30                                 | 0.00159                                    | 0.00077                          | 49                               | 0.03071                                | 19  |
| <i>n</i> C31                                 | 0.00137                                    | 0.00054                          | 40                               | 0.05120                                | 37  |
| <i>n</i> C32                                 | 0.00092                                    | 0.00057                          | 62                               | 0.01108                                | 12  |
|  |  |                                  |                                  |  |   |
| <b>Mono and Di Acids as FAME<sup>b</sup></b> |  |                                  |                                  |  |   |
| C12 FAME                                     | 0.01004                                    | 0.00762                          | 76                               | 25.30060                               | 6   |
| Phthalic                                     | 0.07454                                    | 0.11694                          | 157                              | 52.35560                               | 3   |
| C14 FAME                                     | 0.01318                                    | 0.00700                          | 53                               | 17.70418                               | 7   |
| C16 FAME                                     | 0.06717                                    | 0.03072                          | 46                               | 15.28006                               | 7   |
| C18 FAME                                     | 0.06410                                    | 0.03290                          | 51                               | 17.14010                               | 4   |

<sup>a</sup>Relative Standard Deviation (RSD) calculated as coefficient of variation \*100 = (STD/Mean)\*100

<sup>b</sup>LOD expressed as area ratios to the internal standard *n*-C24D50 were: hopanes, 0.00073; *n*-alkanes, 0.00025; PAH, 0.00210; diacids and *n*-alkanoic acids, 0.00720

<sup>c</sup>Not determined (ND)

# Initial suite SOAP molecular markers

## Alkanes

n-pentacosane  
n-hexacosane  
n-heptacosane  
n-octacosane  
n-nonacosane  
n-triacontane  
n-hentriacontane  
n-dotriacontane  
anteiso-triacontane  
iso-hentriacontane  
anteiso-hentriacontane  
iso-dotriacontane  
anteiso-dotriacontane  
iso-tritriacontane  
phytane  
pristane

## PAHs

benzo[b]fluoranthene  
benzo[k]fluoranthene  
benzo[e]pyrene  
indeno[1,2,3-cd]pyrene  
indeno[1,2,3-cd]fluoranthene  
retene  
coronene

## Acids

21 n-alkanoic acids  
(with  $C_{10}$  to  $C_{30}$ )  
10 aliphatic dicarboxylic acids  
( $C_3$  to  $C_{10}$ )  
1 aromatic polycarboxylic acid  
cis-9-n-octadecenoic acid

## Other

9 hopanes  
nonanal  
levoglucosan  
galactosan  
mannosan  
cholesterol  
7H-benz[de]anthracen-7-one  
benz[a]anthracene-7,12-dione

Authentic  
standards for 63  
marker cmpds  
measured in  
ambient  
composites