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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 PM2.5 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 PM2.5 in the NY City Area (SOAP) **SOAP 2002-2003**

Sources of fine carbonaceous particles

Ambient concentrations TC, EC, OC

Ambient concentrations molecular markers

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PM-2.5 Collection

SOAP 2002-2003 network field program

Queen's College NY Supersite

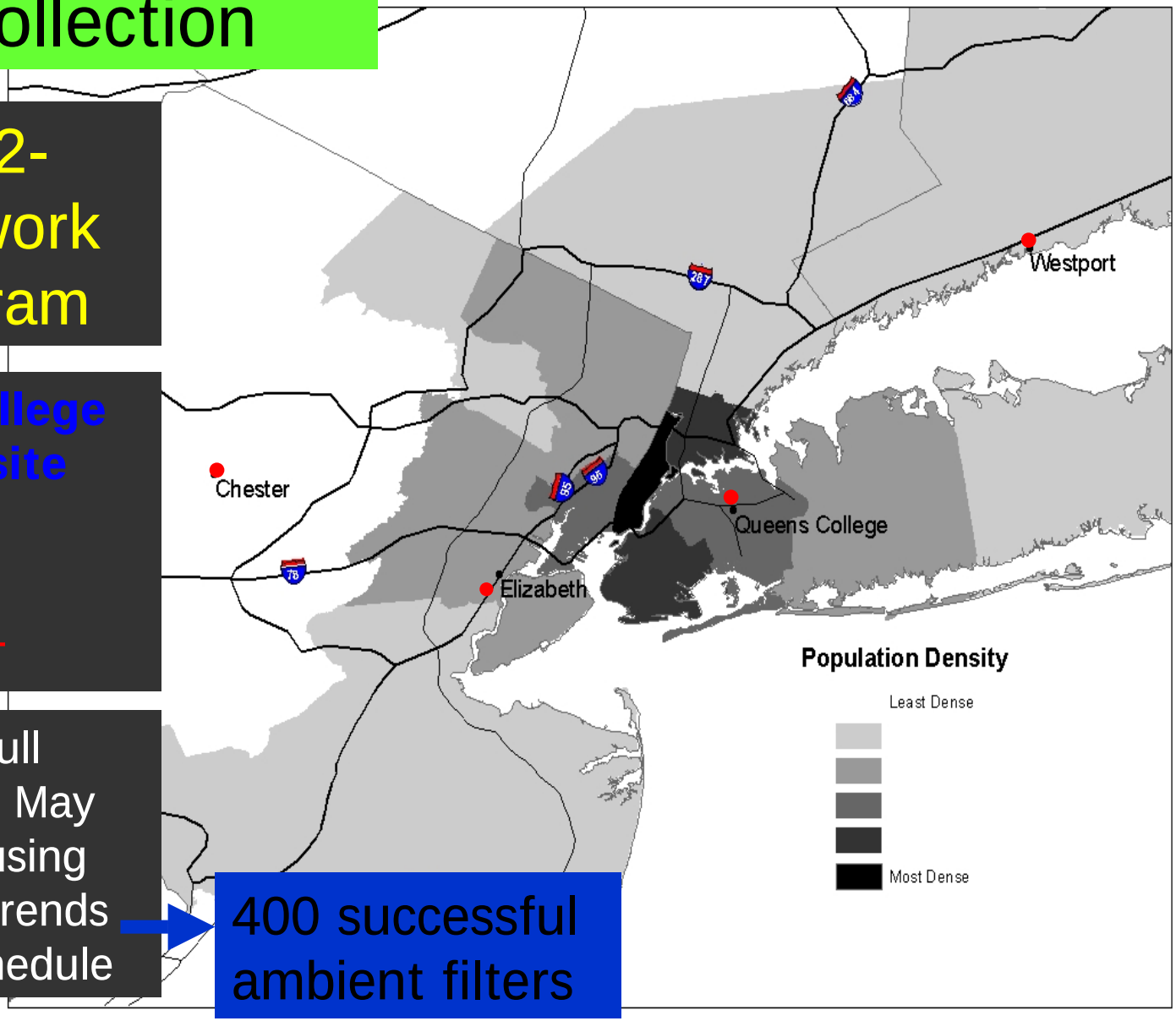
Elizabeth, NJ

Chester, NJ

Westport, CT

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

400 successful ambient filters



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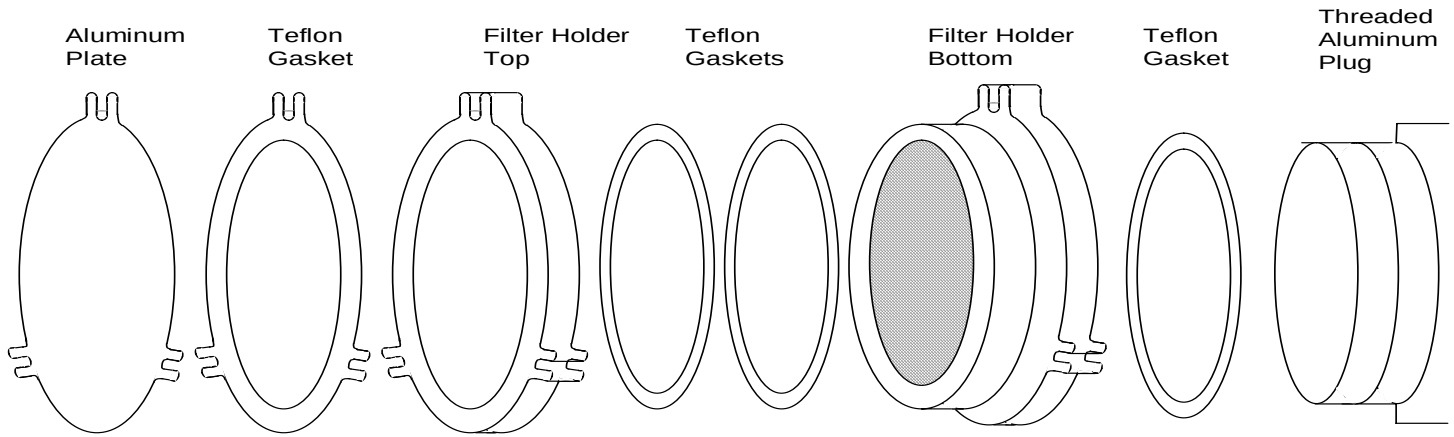
Fine Particle Collection

Tisch 2 or 4 Channel Sampler

Quartz fiber filter collection substrate, 102mm

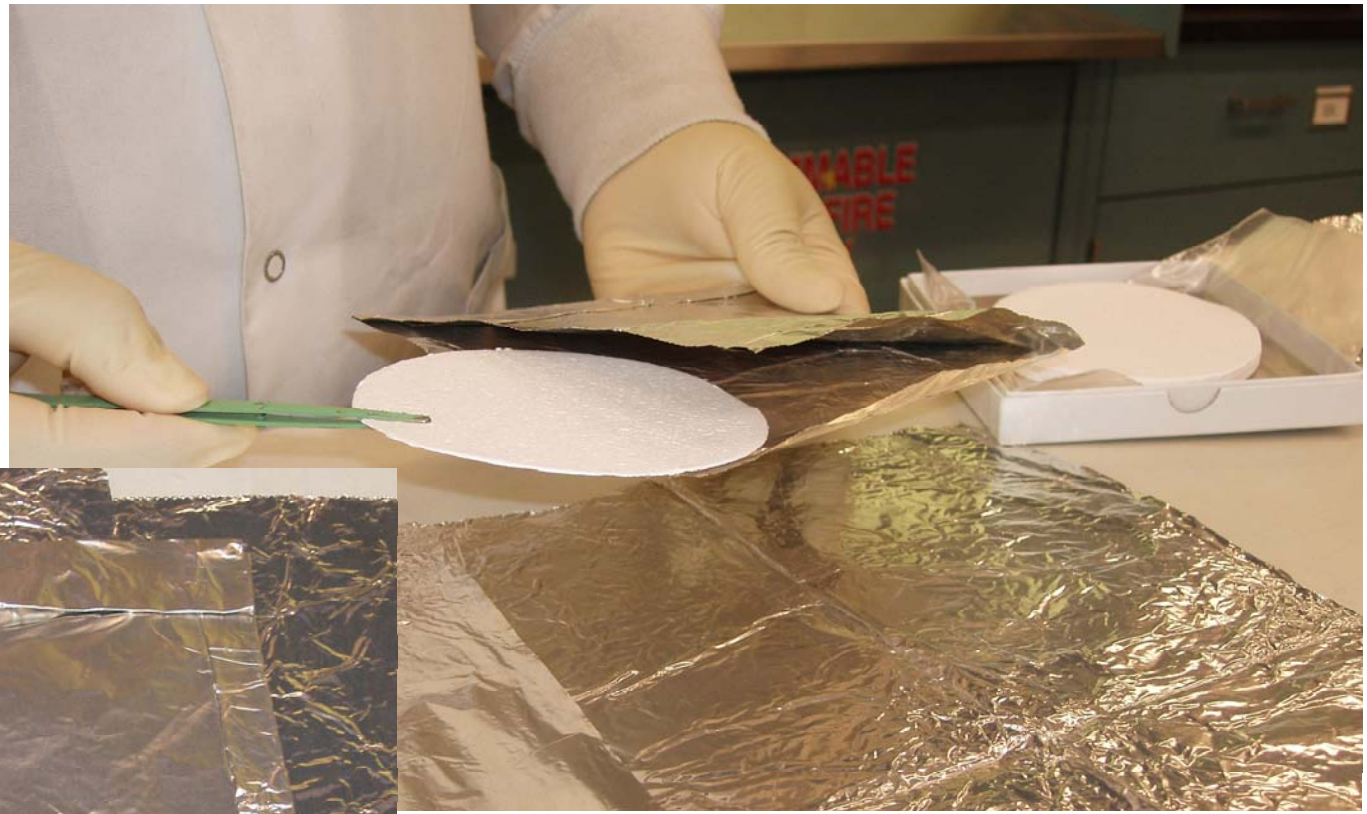
24 hr, 113 lpm

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



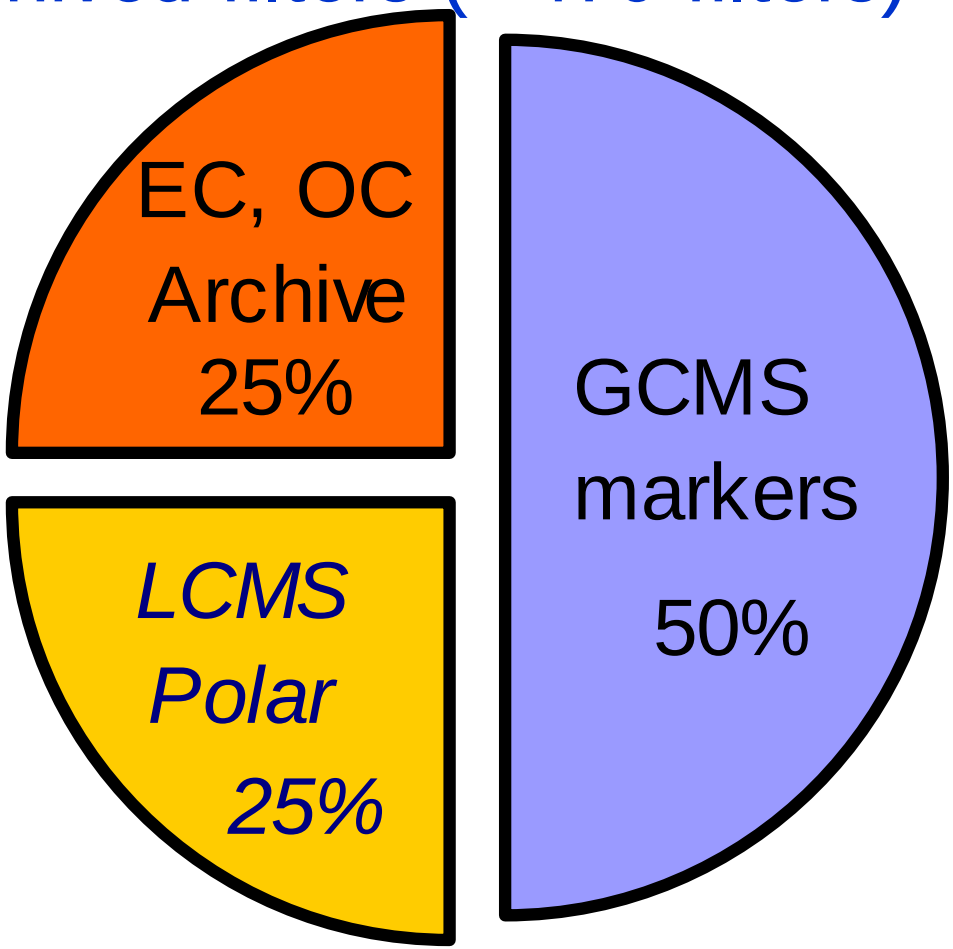
Shipping Module for Filter Holder

Reducing carbon background...



… filter handling, preparation & storage steps critical

EC, OC and TC filter mass loadings (μg/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

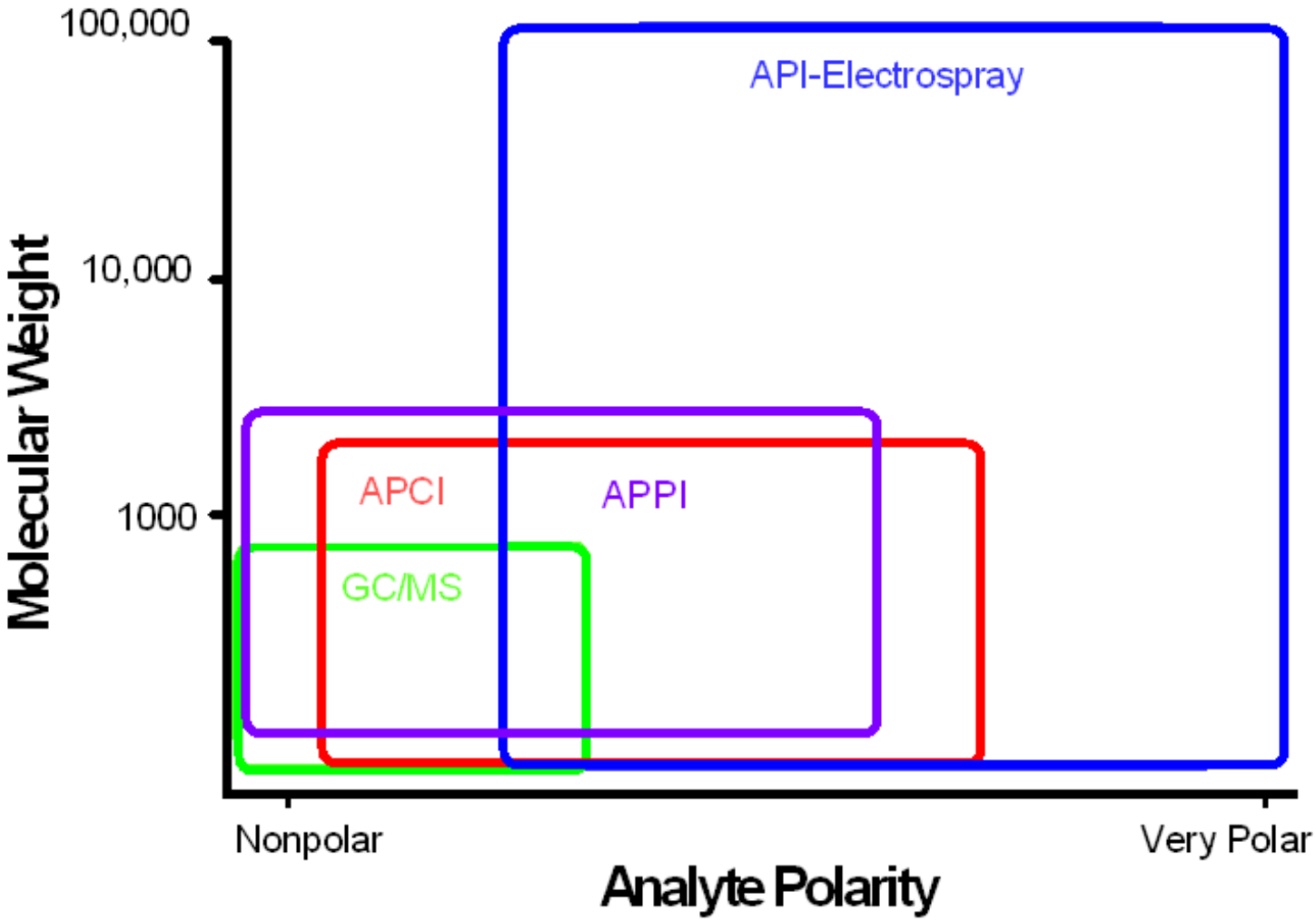
Target Compound Classes

- 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

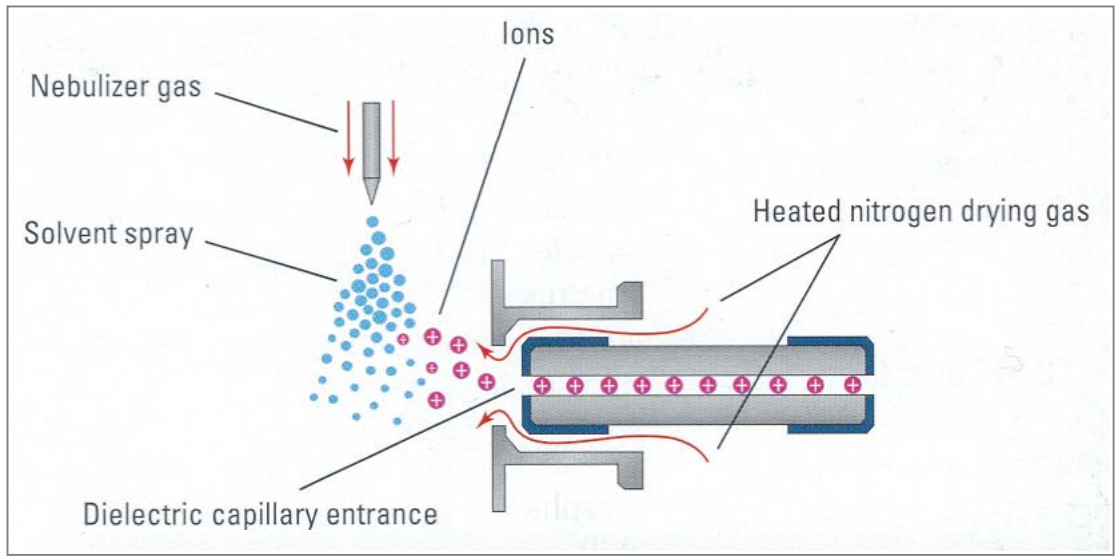
- Analyte concentration sufficient for quantitative analysis (multi-level standard response curves)
- Maximize ionization through careful evaluation of solvents, buffers and modifiers (pK_a of compound must be known; mobile phase pH must be 1.5 units above or below compound pH_a)
- Minimize presence 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

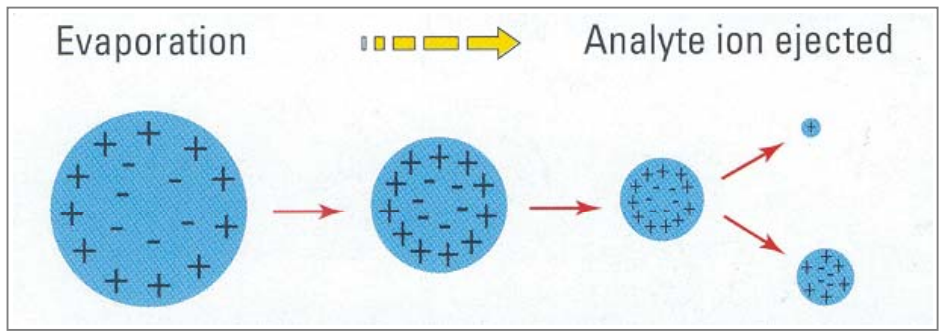
Electrospray Ionization (ESI)

Electrospray Ion Source

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

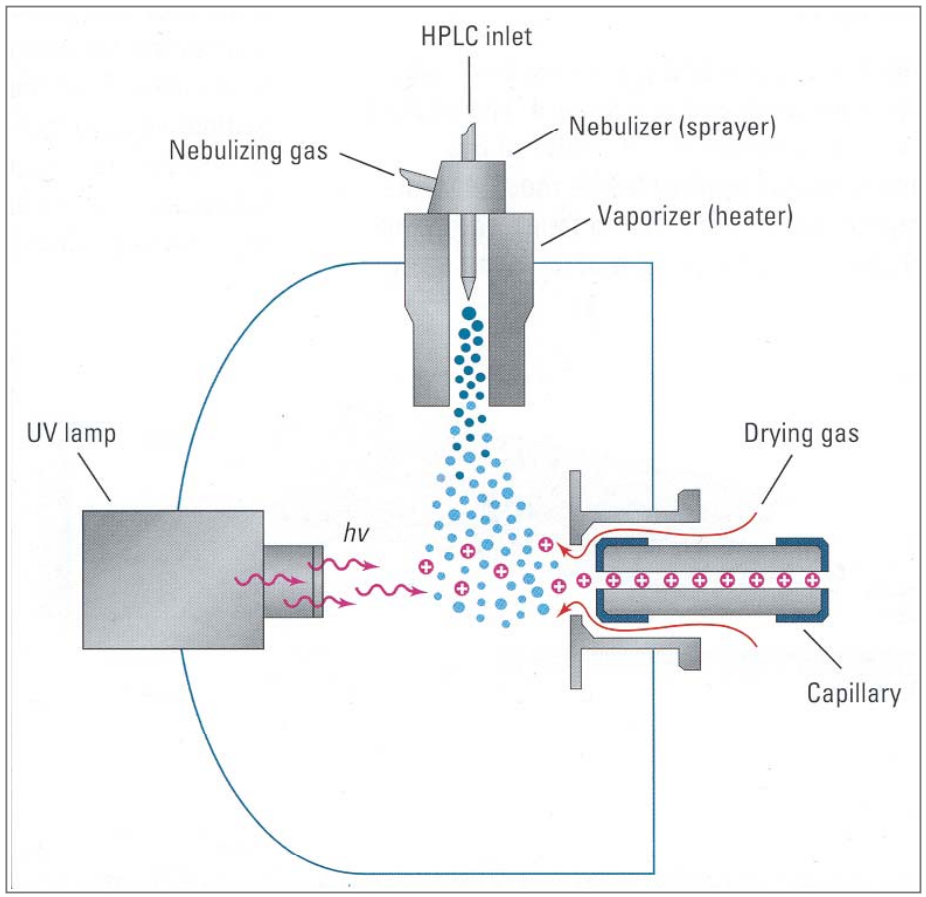


Desorption of ions from solution



Source: "Basics of LC/MS" Agilent Technologies, 2002, www.agilent.con/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

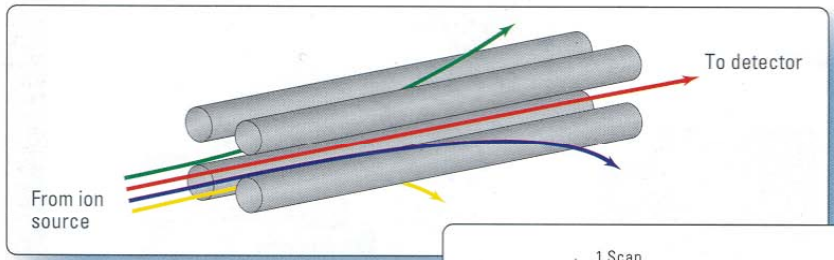


Figure 8. Quadrupole mass analyzer

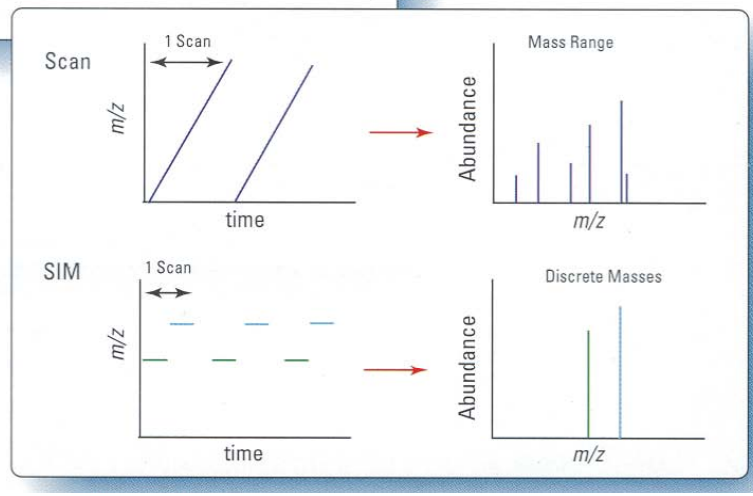


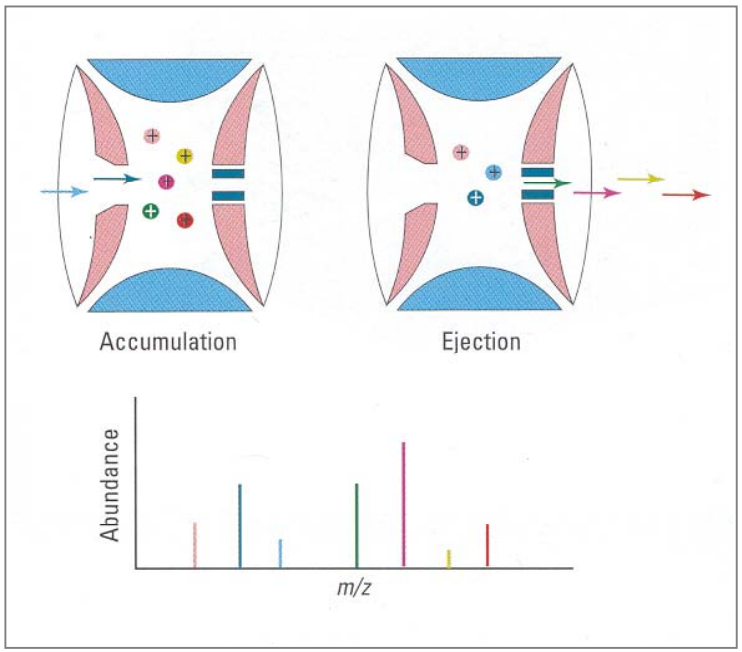
Figure 9. The quadrupole mass analyzer can scan over a range of mass-to-charge ratios or alternate between just a few

LCMS…
Do not know

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

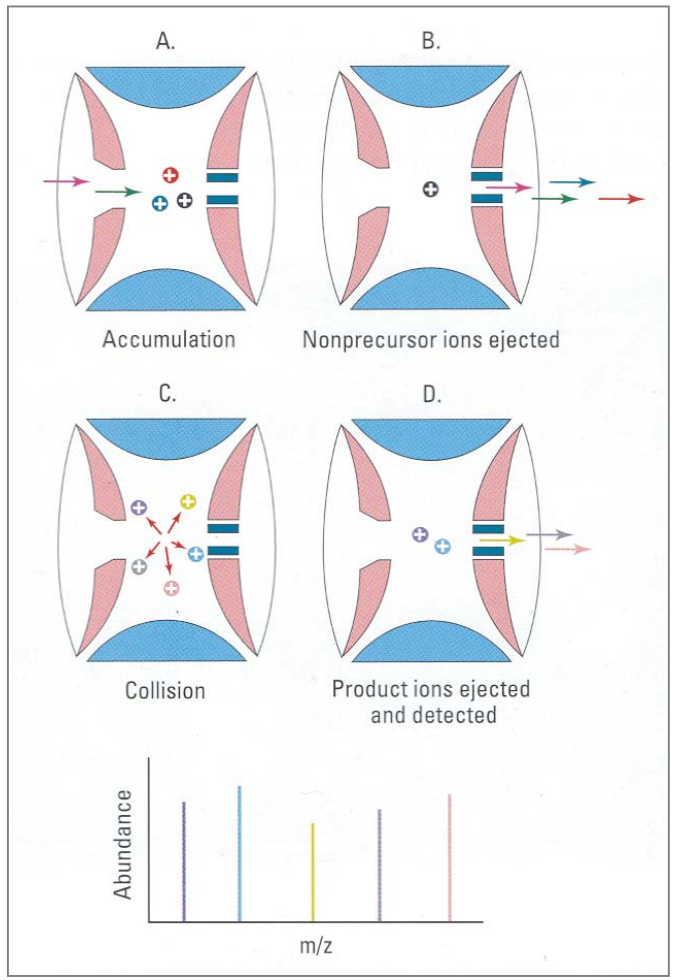
Ion trap mass analyzer

Single stage MS



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

MS^n ….multiple stage



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

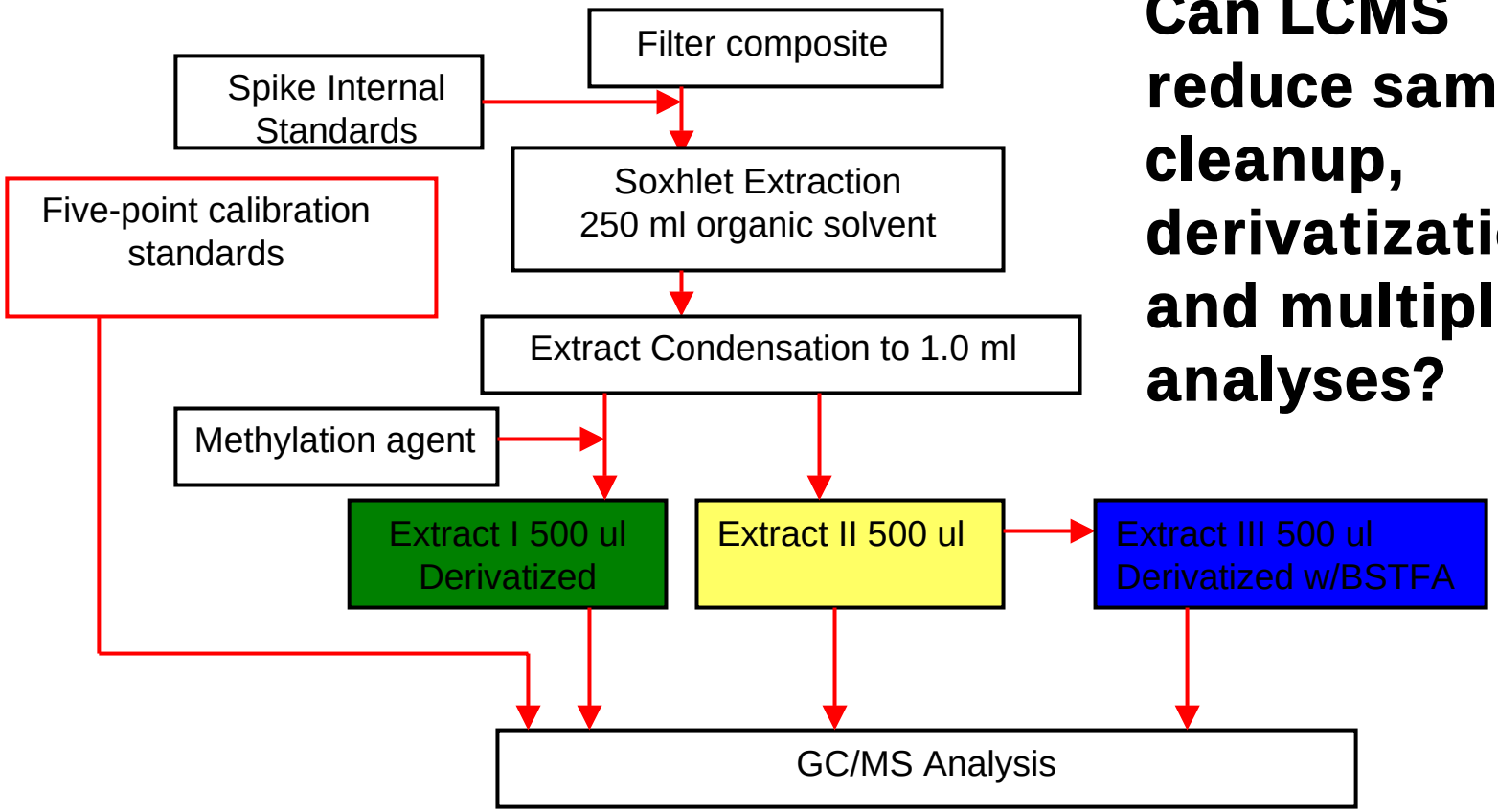
GCMS quadrupole – nonpolar compounds

1) Molecular level instrumentation must accommodate complex mixtures

2) Instruments must be stable

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

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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 **Nov, 2002**	RRF **Feb, 2003**	%SD
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
17α,21β,hopane	43.6	1.29	1.20	6.36
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

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

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Experiments comparing and establishing optimum source conditions

		APPI (dopant)		APPI (no dopant)		ESI		
	Smart Parameter Settings / **Mode**	**Scan**	**Iso/Frag**	**Scan**	**Iso/Frag**	**Scan**	**Iso/Frag**	Total runs
System Blanks	High energy/ Larger Molecules	2/21/07 24 runs 2/22/07 24 runs **48 RUNS**	NA	2/21/07 24 runs 2/22/07 24 runs **48 RUNS**	NA	2/27/07 24 runs **24 RUNS**	NA	120
	Low energy/ Smaller Molecules	2/22/07 24 runs 2/21/07 24 + 24 runs **72 RUNS**	NA	2/22/07 24 runs 2/21/07 24 + 24 runs **72 RUNS**	NA	2/27/07 24 runs **24 RUNS**	NA	168
Diacids	High energy/ Larger Molecules	2/21/07 90 runs **90 RUNS**	2/2/2007 360 runs **360 RUNS**	2/21/07 90 runs **90 RUNS**	1/31/2007 360 runs **360 RUNS**	2/27/07 90 runs **90 RUNS**	2/16/2007 360 runs **360 RUNS**	1350
	Low energy/ Smaller Molecules	2/21/07 90 + 6 runs **96 RUNS**	2/22/07 48 runs **48 RUNS**	2/21/07 90 + 6 runs **96 RUNS**	2/22/07 48 runs **48 RUNS**	2/27/07 90 runs **90 RUNS**	2/27/07 48 runs **48 RUNS**	426
Oxoacids	High energy/ Larger Molecules	2/22/2007 12 runs **12 RUNS**	2/21/07 24 runs **24 RUNS**	2/22/2007 12 runs **12 RUNS**	2/21/07 24 runs **24 RUNS**	2/27/2007 12 runs **12 RUNS**	NA	84
	Low energy/ Smaller Molecules	2/22/2007 12 + 12 runs **24 RUNS**	2/22/07 48 runs **48 RUNS**	2/22/2007 12 + 12 runs **24 RUNS**	2/22/07 48 runs **48 RUNS**	2/27/2007 12 runs **12 RUNS**	2/27/07 48 runs **48 RUNS**	204
	Total runs	342	480	342	480	252	456	**2352**

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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

$M + h\nu \rightarrow M^{\bullet+} + e^-$	Analyte molecule M is ionized to molecular ion $M^{\bullet+}$
and under certain conditions ...	
$M^{\bullet+} + [S+H]^+ \rightarrow [M+H]^+$	Molecular ion $M^{\bullet+}$ abstracts a hydrogen from ionized solvent

Dopant APPI

$D + h\nu \rightarrow D^+ + e^-$	Photoionizable dopant D is in excess & yields many D^+ ions
$D^+ + M \rightarrow \rightarrow [M+H]^+ + D[-H]$	D^+ ionizes analyte M by proton transfer
$D^+ + M \rightarrow \rightarrow M^{\bullet+} + D$	D^+ ionizes analyte M by electron transfer

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

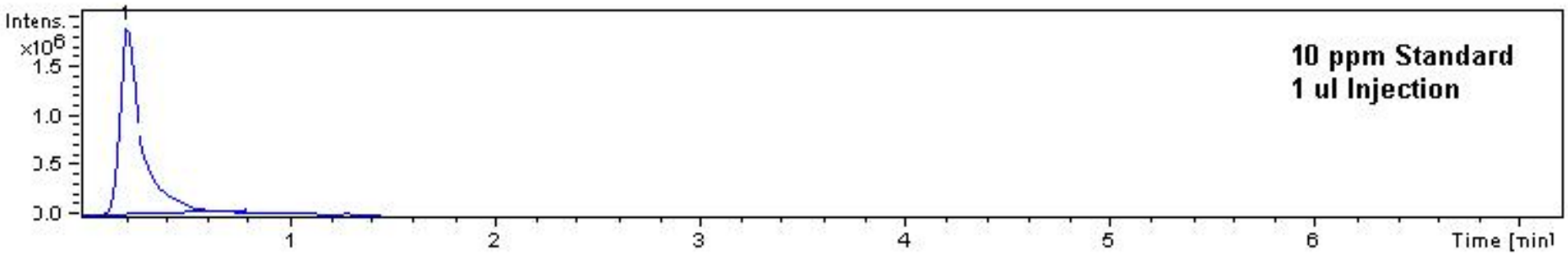
Analysis of Polyaromatic Hydrocarbons by Atmospheric Pressure Photoionization LC/MS
Patricia H. Cormia, Steven M. Fischer and Christine A. Miller, Agilent Technologies, Inc., Palo Alto, CA

The reactions in negative ion APPI

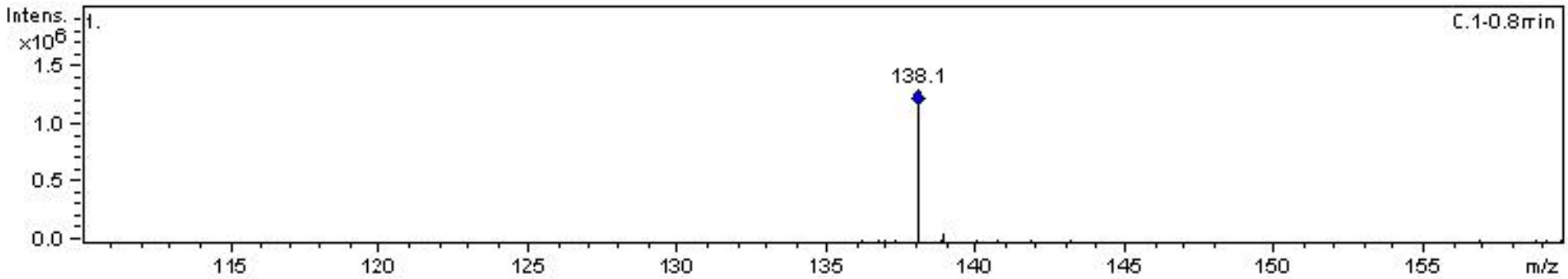
$D + h\nu \rightarrow D^{+}\cdot + e^{-}$	(1)
$S + e- \rightarrow S^{-}\cdot$	(2)
$S + e^{-} \rightarrow [S - F]\cdot + F^{-}$	(3)
$O_2 + e^{-} \rightarrow O_2^{-}\cdot$	(4)
$M + O_2^{-}\cdot \rightarrow [M - H]^{-} + HO_{2}\cdot$, if $\Delta_{acid}G\ (M) < \Delta_{acid}G\ (HO_{2}\cdot)$.	(5)
$S + O_2^{-}\cdot \rightarrow [S - H]^{-} + HO_{2}\cdot$, if $\Delta_{acid}G\ (S) < \Delta_{acid}G\ (HO_{2}\cdot)$.	(6)
$M + [S\text{-}H]^{-} \rightarrow [M - H]^{-} + S$, if $\Delta_{acid}G\ (M) < \Delta_{acid}G\ (S)$.	(7)
$M + e^{-} \rightarrow M^{-}\cdot$, if EA (M) > 0 eV	(8)
$M + O_2^{-}\cdot \rightarrow M^{-}\cdot + O_2$, if EA (M) > EA ($O_2$) = 0.451 eV	(9)
$M + O_2^{-}\cdot \rightarrow [M - X + O]^{-} + OX\cdot$, X = H, Cl, NO_2	(10)

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

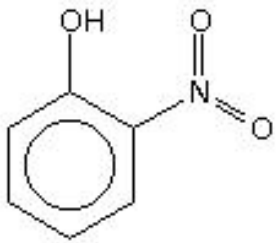
2-Nitrophenol LC/MS Ion Trap: Atmospheric Pressure Photolonization Negative Mode with 10% Acetone Dopant



Total Ion Chromatogram



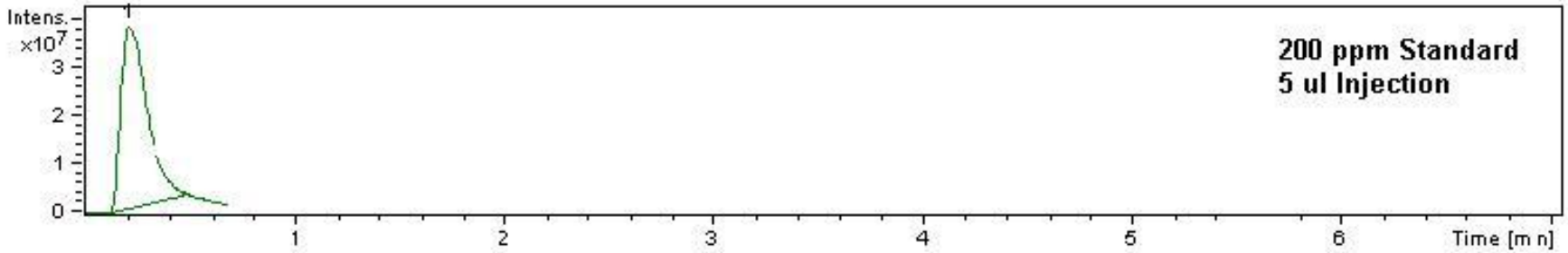
Compound Mass Spectra



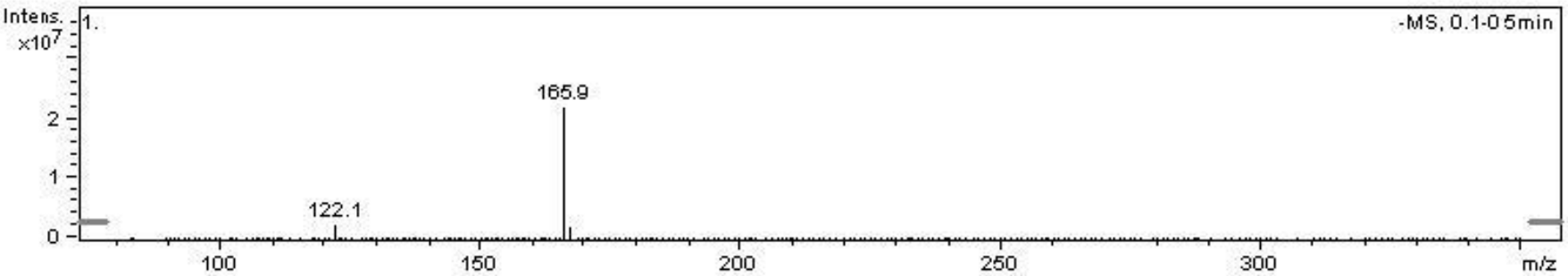
2-nitrophenol
Formula: C6H5NO3
Molecular Weight: 139.11
CAS Registry Number: 88-75-5

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

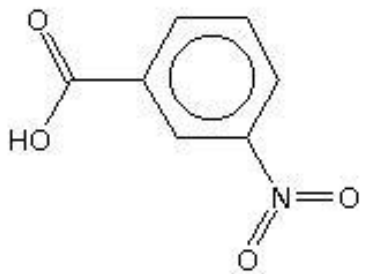
3-Nitrobenzoic Acid LC/MS Ion Trap: Atmospheric Pressure Photolonization Negative Mode with 10% Acetone Dopant



Total Ion Chromatogram



Compound Mass Spectra



3-Nitrobenzoic acid
Formula: C7H5NO4
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

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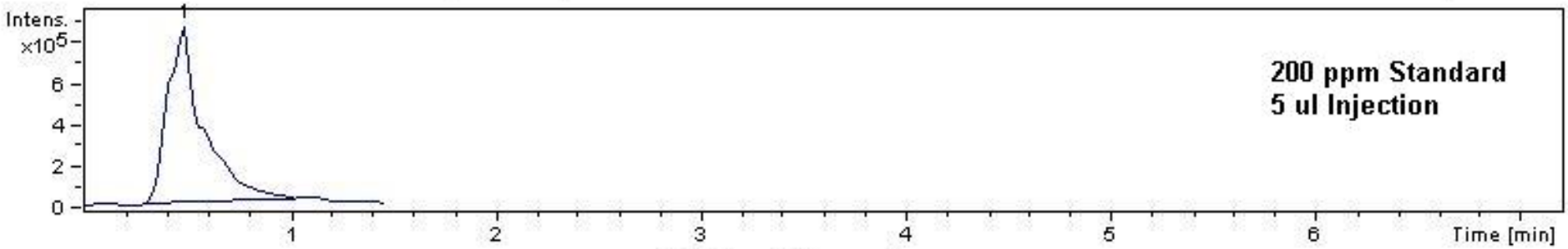
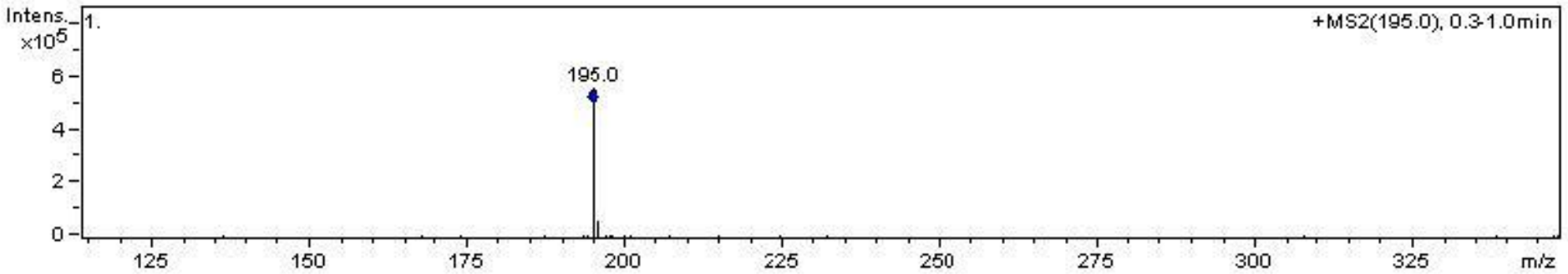
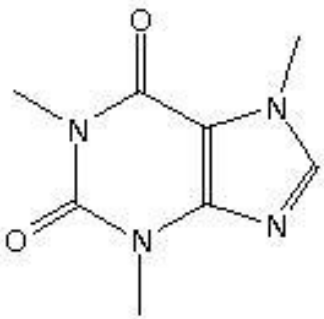
Caffeine LC/MS Ion Trap: Atmospheric Pressure Photolonization Positive Mode with 10% Acetone Dopant



Total Ion Chromatogram



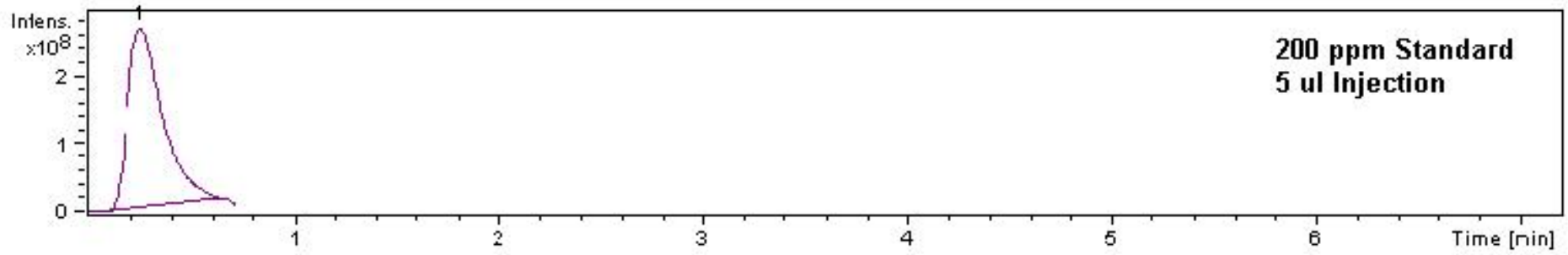
Compound Mass Spectra



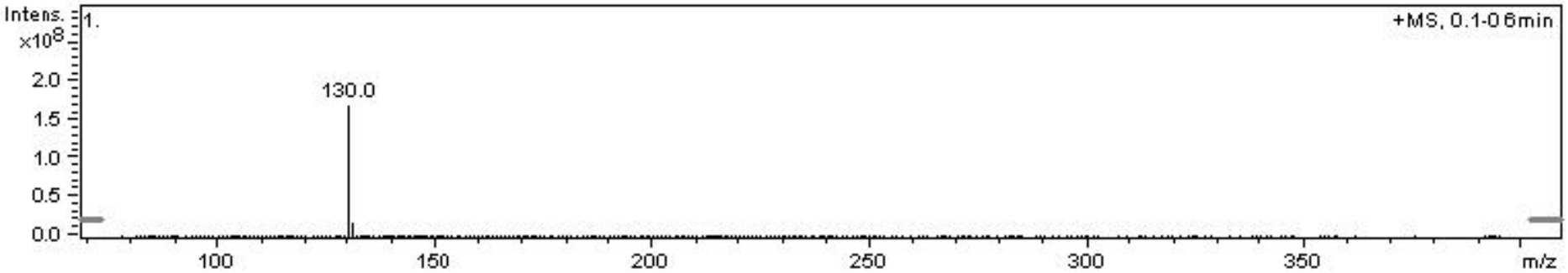
Caffeine
Formula: C8H10N4O2
Molecular Weight: 194.19
CAS Registry Number: 58-08-2

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

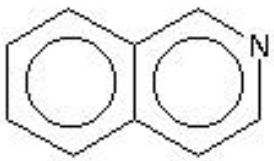
Isoquinoline LC/MS Ion Trap: Atmospheric Pressure Photolonization Positive Mode with 10% Acetone Dopant



Total Ion Chromatogram



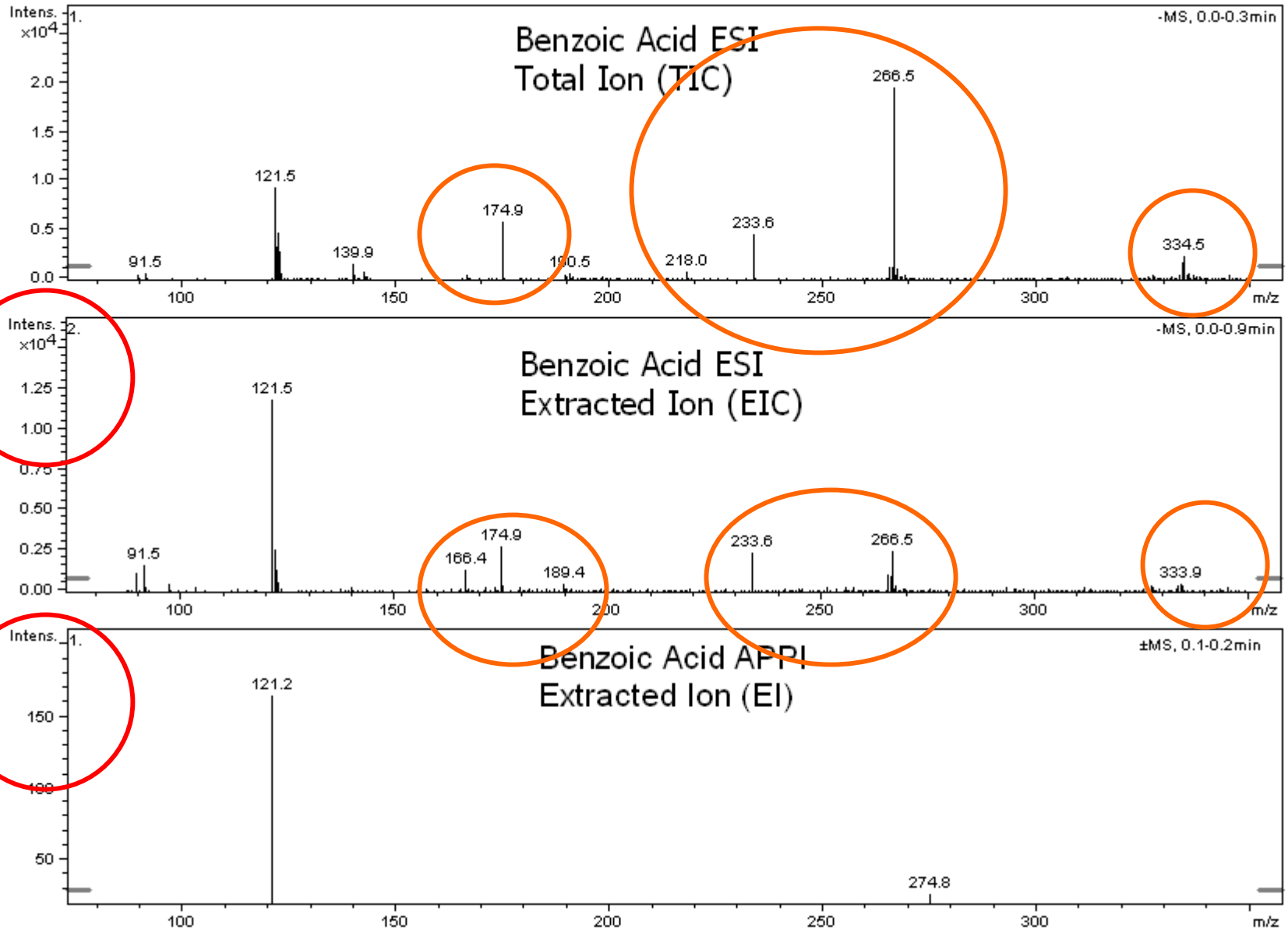
Compound Mass Spectra



Isoquinoline
Formula: C9H7N
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



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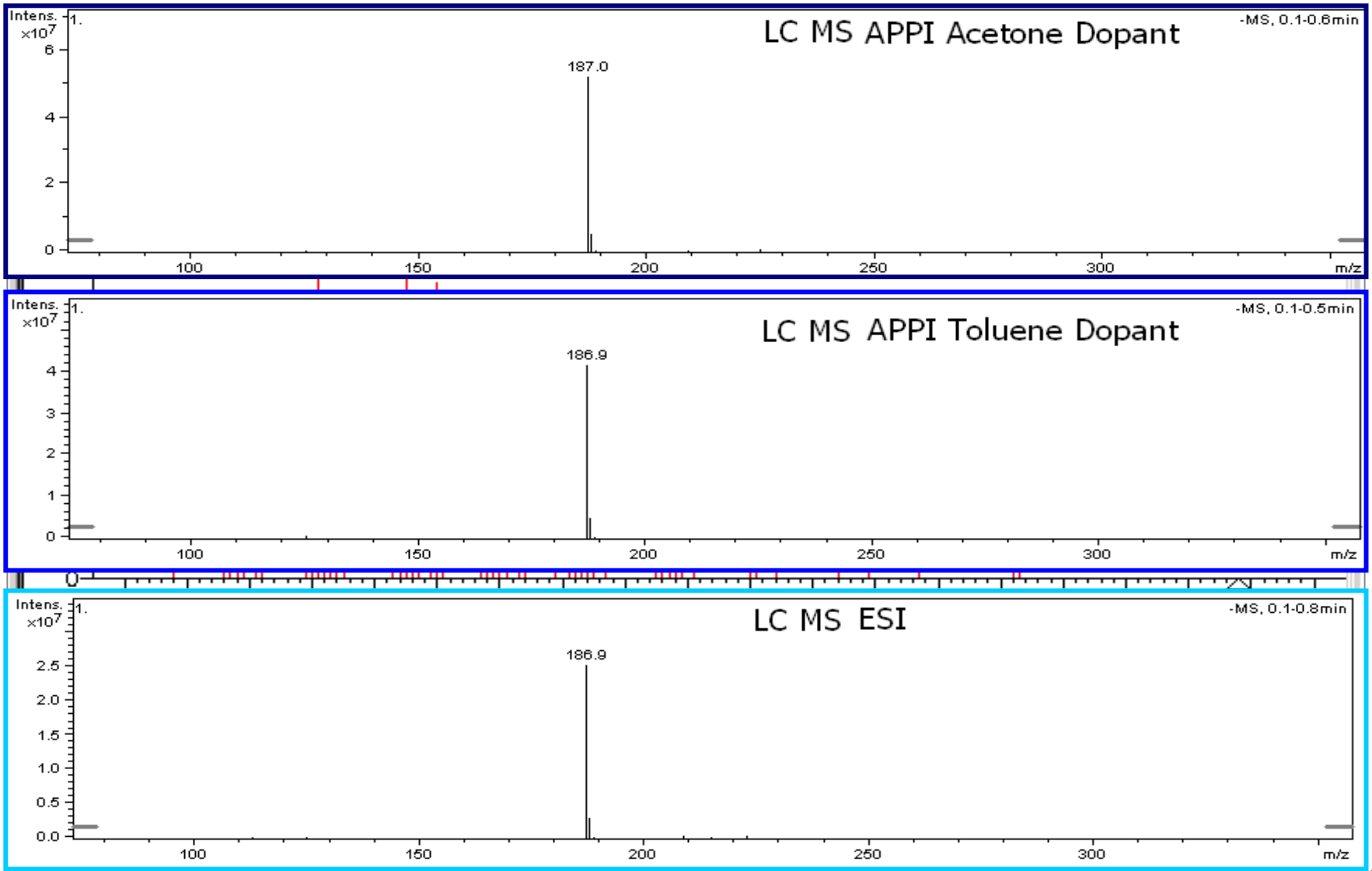
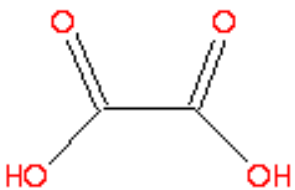
Ion spectra for azelaic acid

MW 188

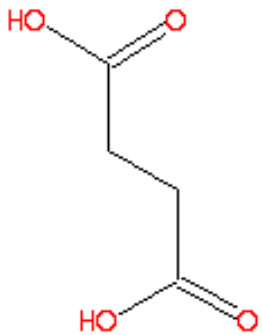


Not all acids conform to a clear molecular ion or M-1 spectra

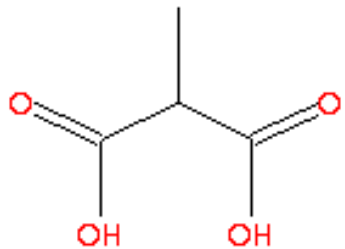
- Strong or reactive acids form dimers in the APPI source as adduct ions with mobile phase and/or dopant molecules
- Found commonly with aliphatic acids where carbon chains <C3



Oxalic acid

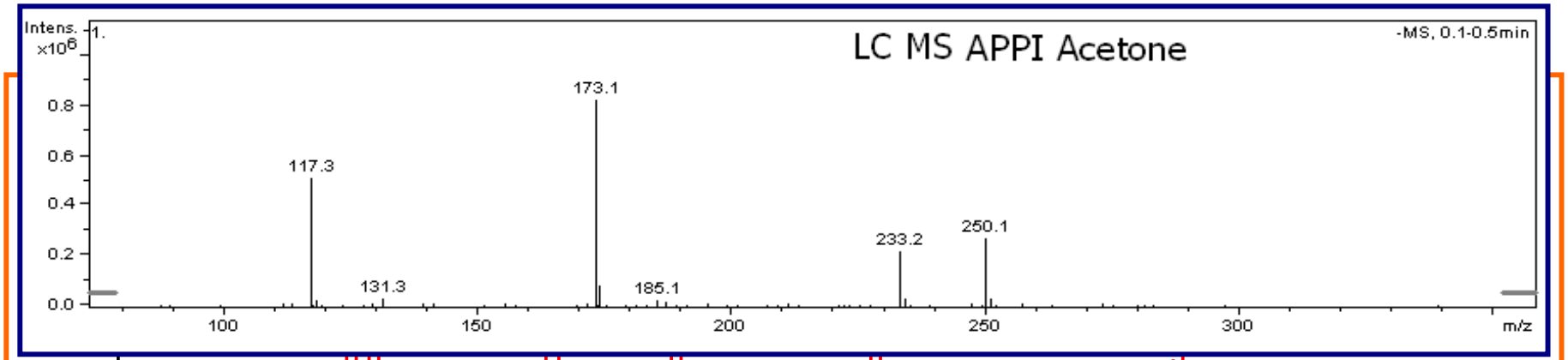


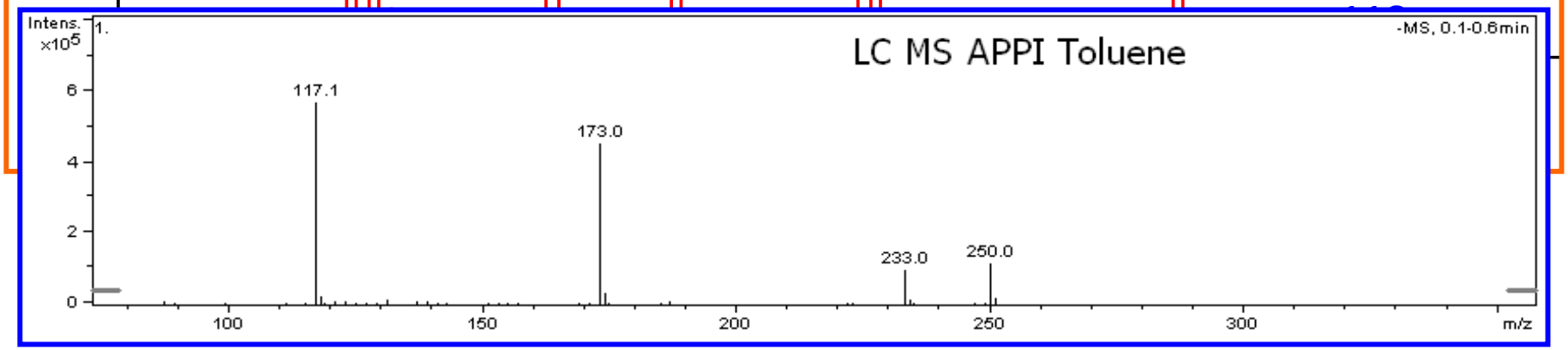
Succinic acid

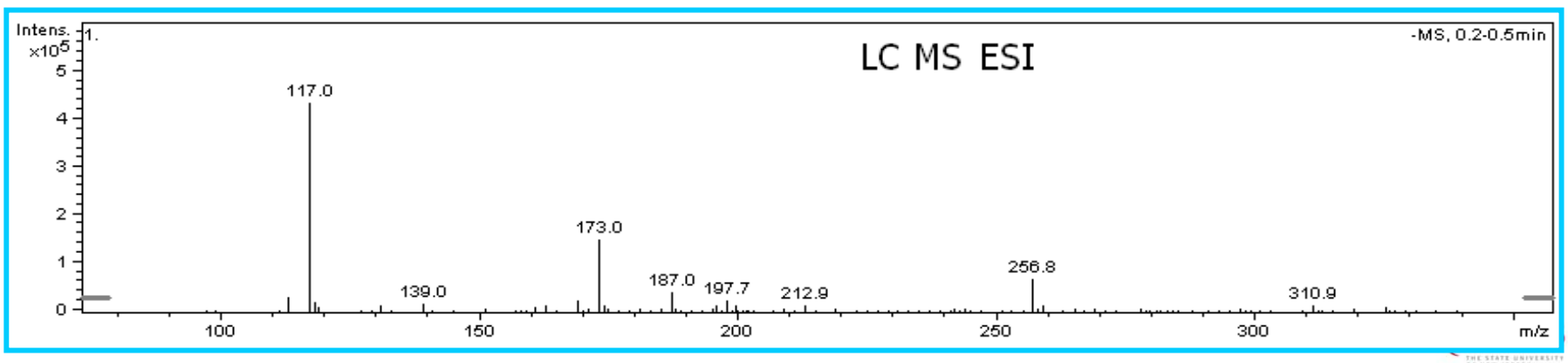


Methyl malonic acid

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**
Salicyaldehyde	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
				I	31757	905	831	528	383
Oxalic Acid	90.03	0.4	SOAP000002	m/z	**88.9**	**234**	89.9	665.6	407
				I	28221	1095	830	828	819
Oxalic Acid	90.03	0.4	SOAP000003	m/z	**88.9**	**651.1**	**511.1**	89.9	161.2
				I	31603	2548	1476	758	731
Oxalic Acid	90.03	0.4	SOAP000004	m/z	**89.0**	**90.0**	**473.5**	61.2	124.9
				I	34866	1172	1160	945	892
Oxalic Acid	90.03	0.4	SOAP000005	m/z	**88.9**	**453.6**	90	244.7	369.7
				I	27982	4310	864	857	748
Oxalic Acid	90.03	0.4	SOAP000006	m/z	**88.9**	**513.7**	**89.9**	61.2	604.3
				I	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
				I	123730	4874	3196	2988	1048
Oxalic Acid	90.03	0.4	SOAP000002	m/z	88.7	89.6	90.6	86.8	92.7
				I	120600	5230	2795	2704	1212
Oxalic Acid	90.03	0.4	SOAP000003	m/z	88.7	89.6	90.7	86.8	61
				I	170510	6841	2844	1390	1244
Oxalic Acid	90.03	0.4	SOAP000004	m/z	88.7	89.6	90.6	86.7	92.6
				I	127166	5449	2390	2189	776
Oxalic Acid	90.03	0.4	SOAP000005	m/z	88.7	89.6	90.6	86.8	61
				I	121238	4807	2651	2019	1332
Oxalic Acid	90.03	0.4	SOAP000006	m/z	88.7	89.6	90.6	86.8	61
				I	121238	4807	2651	2019	1332

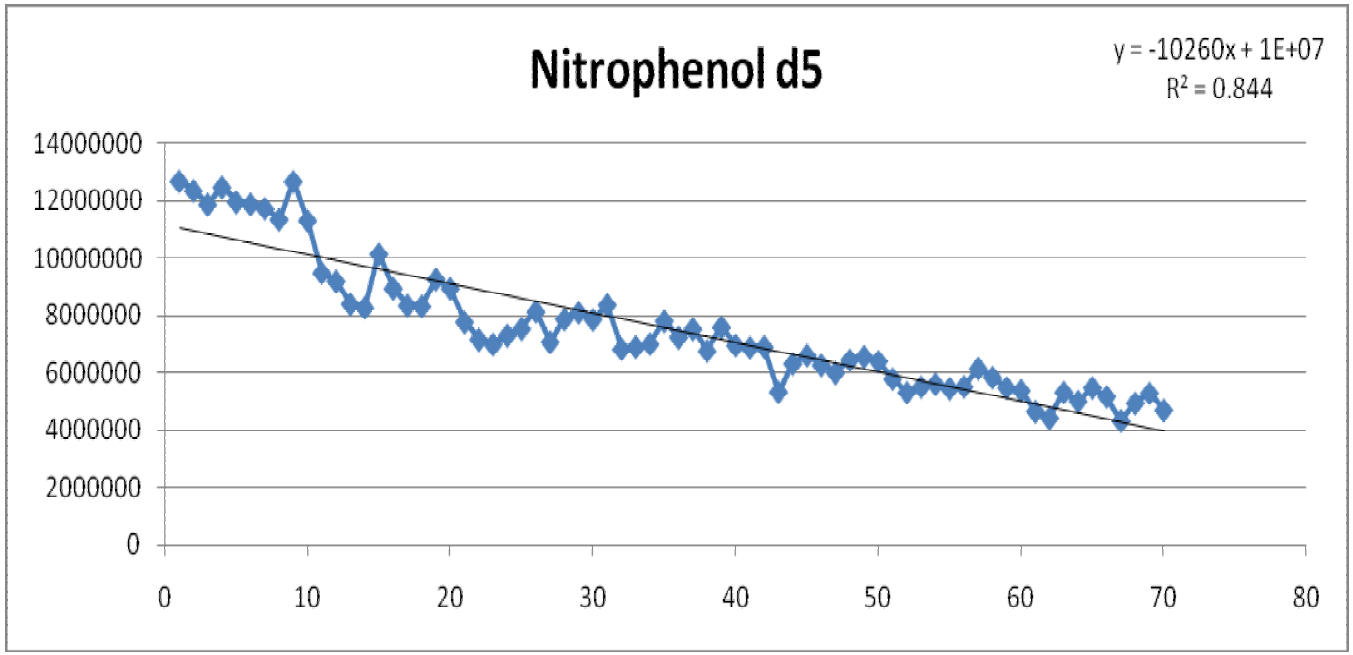
NO solvent-ion, oligomers formed

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%

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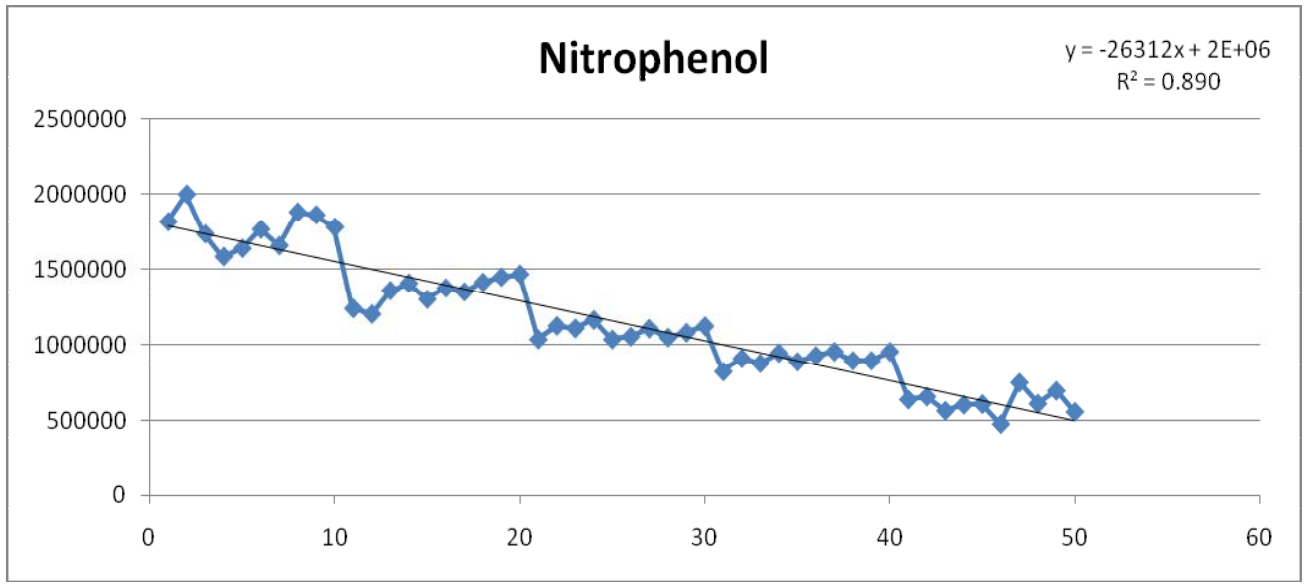
Nitrophenol (10 ppm check standard)

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



Mean	1146033	**Lowest Area**	475277.5
STD	406396.2	**Highest Area**	1998150
%RSD	35.46111	**% Difference**	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%.

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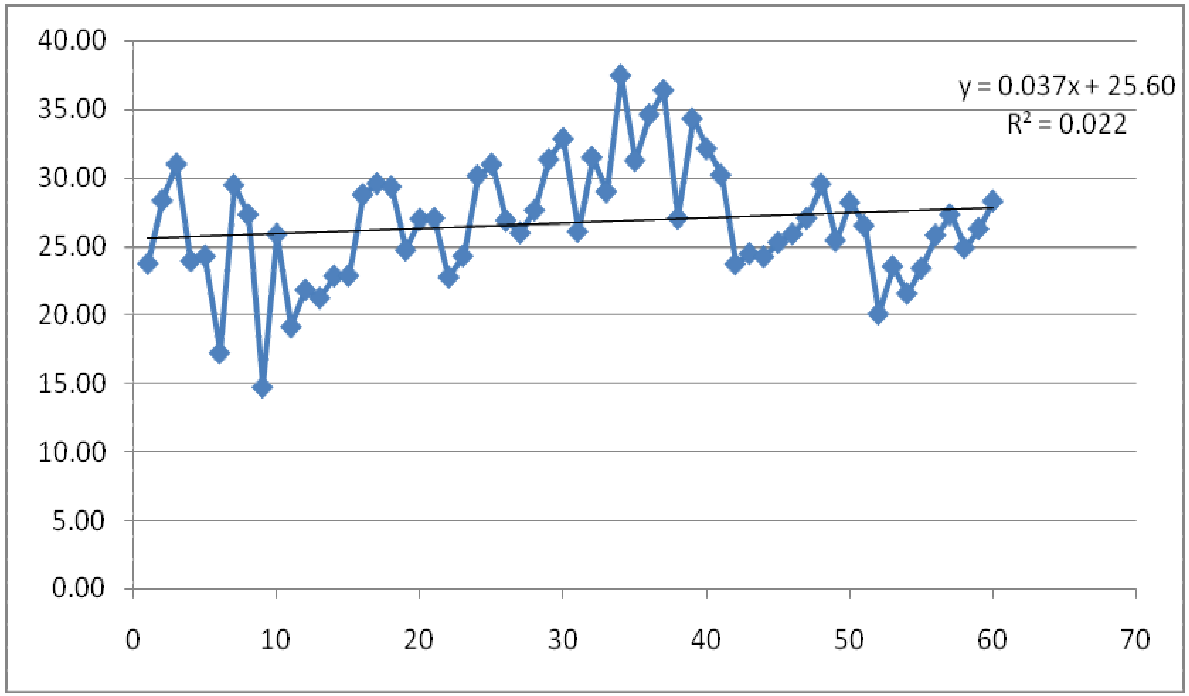
Carbonyl and internal standards analysis

Response factors for ISTD & Acrolein in CARB STD

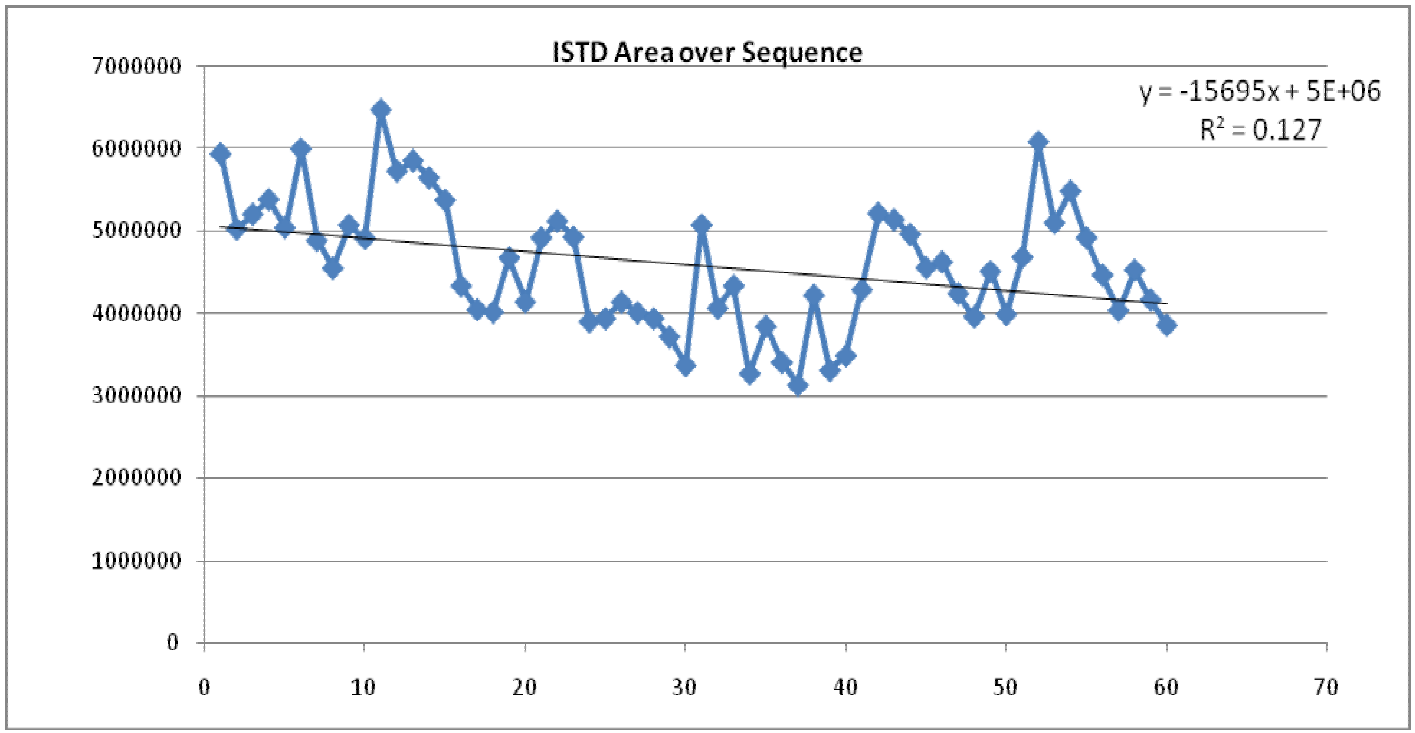


Mean Rf	26.74739	**Lowest Rf**	14.74879
STD Rf	4.339096	**Highest Rf**	37.44239
%RSD Rf	16.2225	**% Difference**	60.61

Response factors determined by the calculation:

RRF = (Area sample/Area ISTD) x (Mass ISTD/Mass sample)

Internal STD areas over sequence



ISTD Mean	4589146.05	**Lowest ISTD Area**	3133962.87
ISTD STD	768455.85	**Highest ISTD Area**	6470433.03
ISTD %RSD	16.75	**% Difference**	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[1], Min Li [1], Monica Mazurek[1], Steve McDow [2] and Claire Belisle [1]

[1]Civil & Environmental Engineering Department, School of Engineering, Rutgers, The State University of New Jersey

[2]Human Exposure and Atmospheric Sciences Division, National Exposure Research Laboratory, U.S. Environmental Protection Agency

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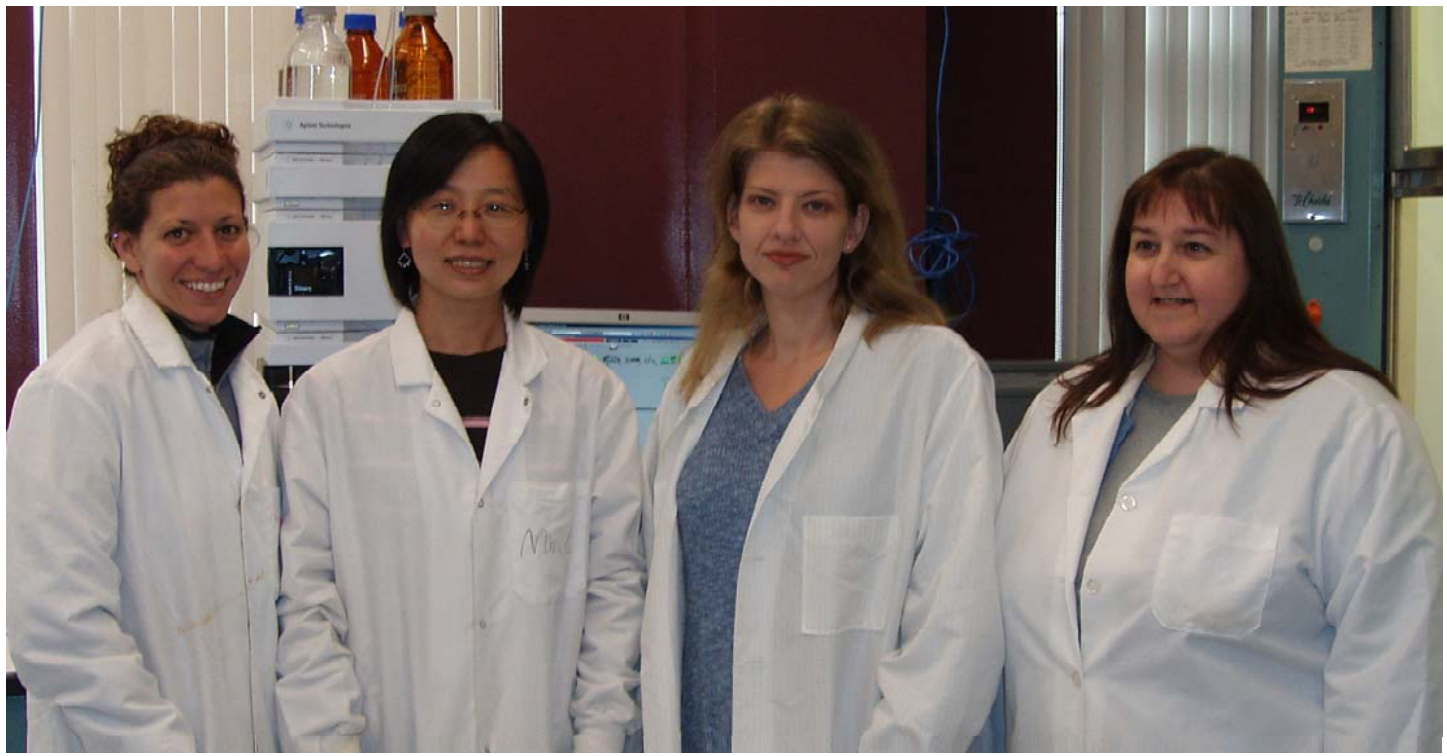
Thanks To.....

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

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End of Presentation

Thank you

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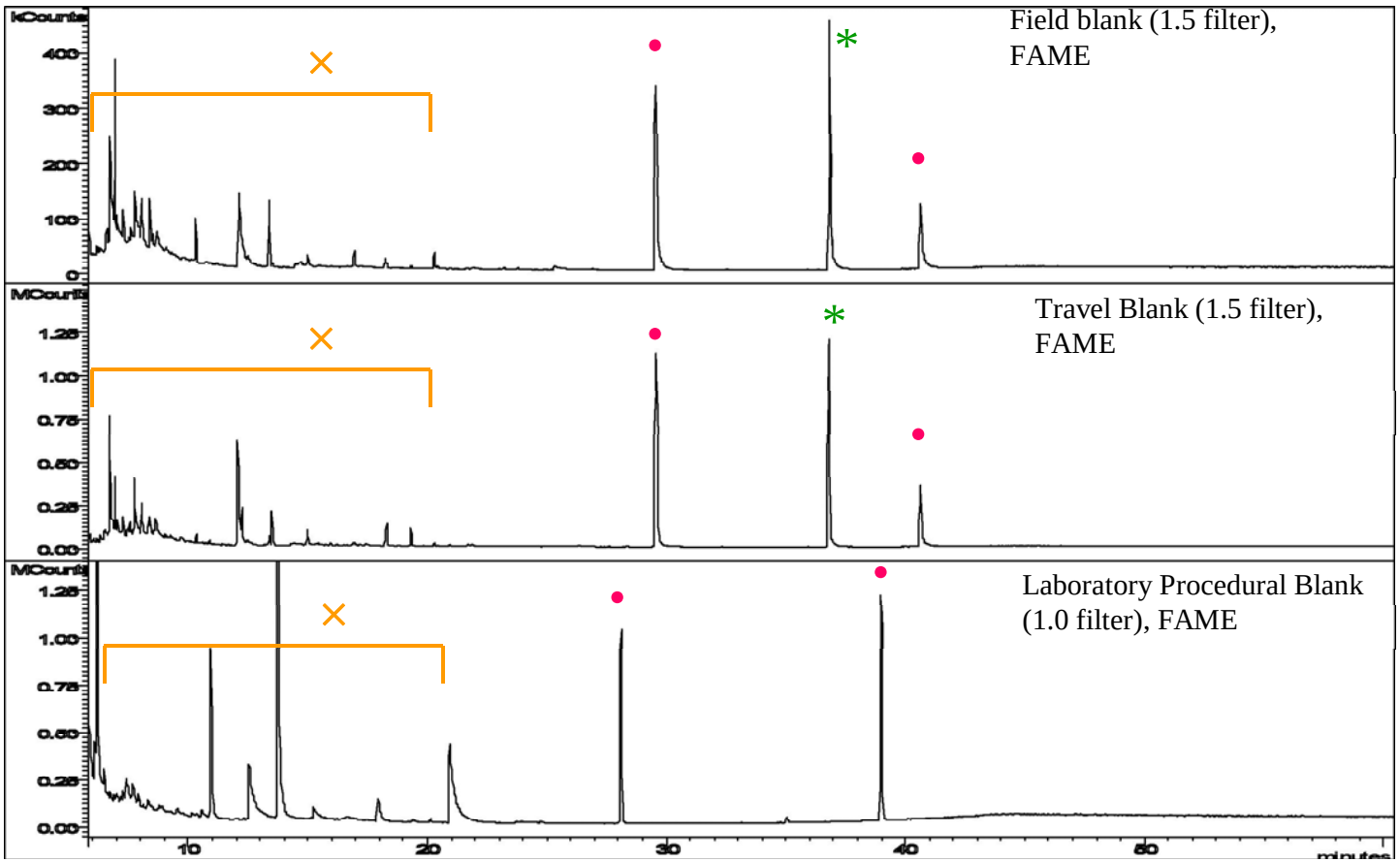
Quality Control at the Molecular Level -- Blanks

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[a]	All SOAP Blanks RSD[a]	All SOAP Ambient Average Ratios (n=40)	Average Area Ratio All SOAP Ambient/Average Area Ratio All Blanks
***n*-Alkanes**[b]					
*n*C25	0.00132	0.00096	73	0.05915	45
*n*C26	0.00106	0.00094	89	0.04065	38
*n*C27	0.00138	0.00096	69	0.05508	40
*n*C28	0.00136	0.00083	61	0.02696	20
*n*C29	0.00162	0.00052	32	0.08041	50
*n*C30	0.00159	0.00077	49	0.03071	19
*n*C31	0.00137	0.00054	40	0.05120	37
*n*C32	0.00092	0.00057	62	0.01108	12
Mono and Di Acids as FAME[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

[a]Relative Standard Deviation (RSD) calculated as coefficient of variation *100 = (STD/Mean)*100)

[b]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

[c]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

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