

Gas-chromatography/mass spectrometry (GC-MS) Interpretation of EI spectra

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CCIC MSP

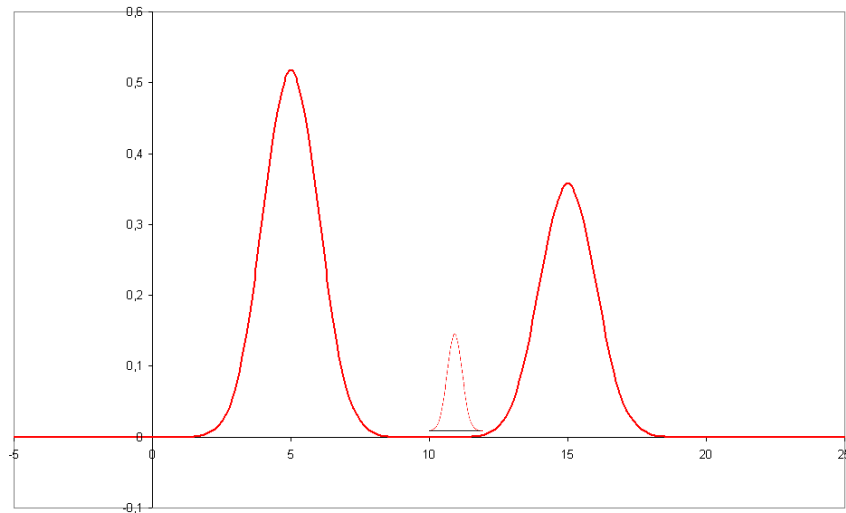
Mass Spec Summer Workshop

August 17, 2015

Gas Chromatography

Important goals in chromatography

- Achieve the best separation
 - Little band-broadening – narrow chromatogram peaks – efficient column
- “Dynamic range”
 - Separate and detect the “small” in the close vicinity of the “big”
- Reproducibility
 - Stable peak positions, retention times



Even with the best column **diffusion** always plays a role!

Parameters to control diffusion

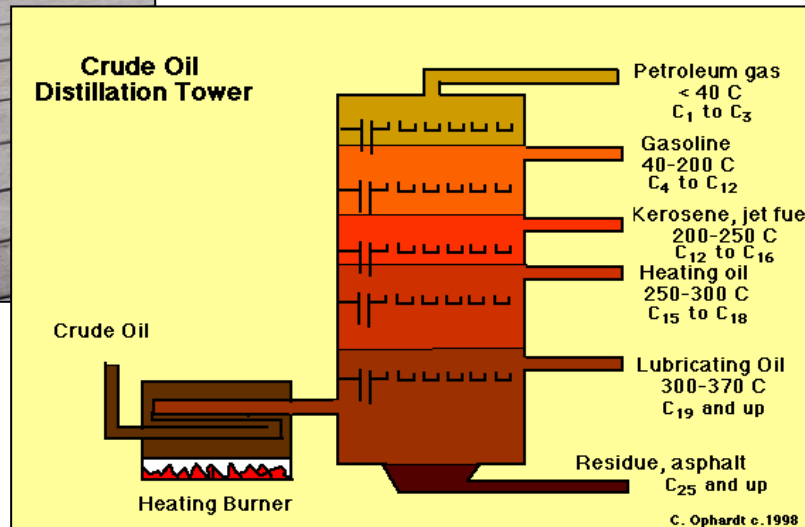
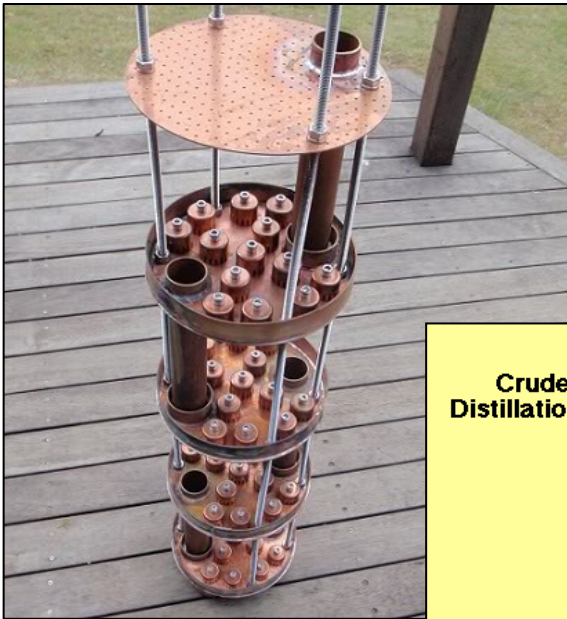
Particle size (Column type)

Flow rate

The Van Deemter Equation

$$HETP = A + (B/u) + (C_s + C_m) \times u$$

HETP = height equivalent to a theoretical plate
-a measure of the resolving power of the column



$$H = L/N$$

The Van Deemter Equation

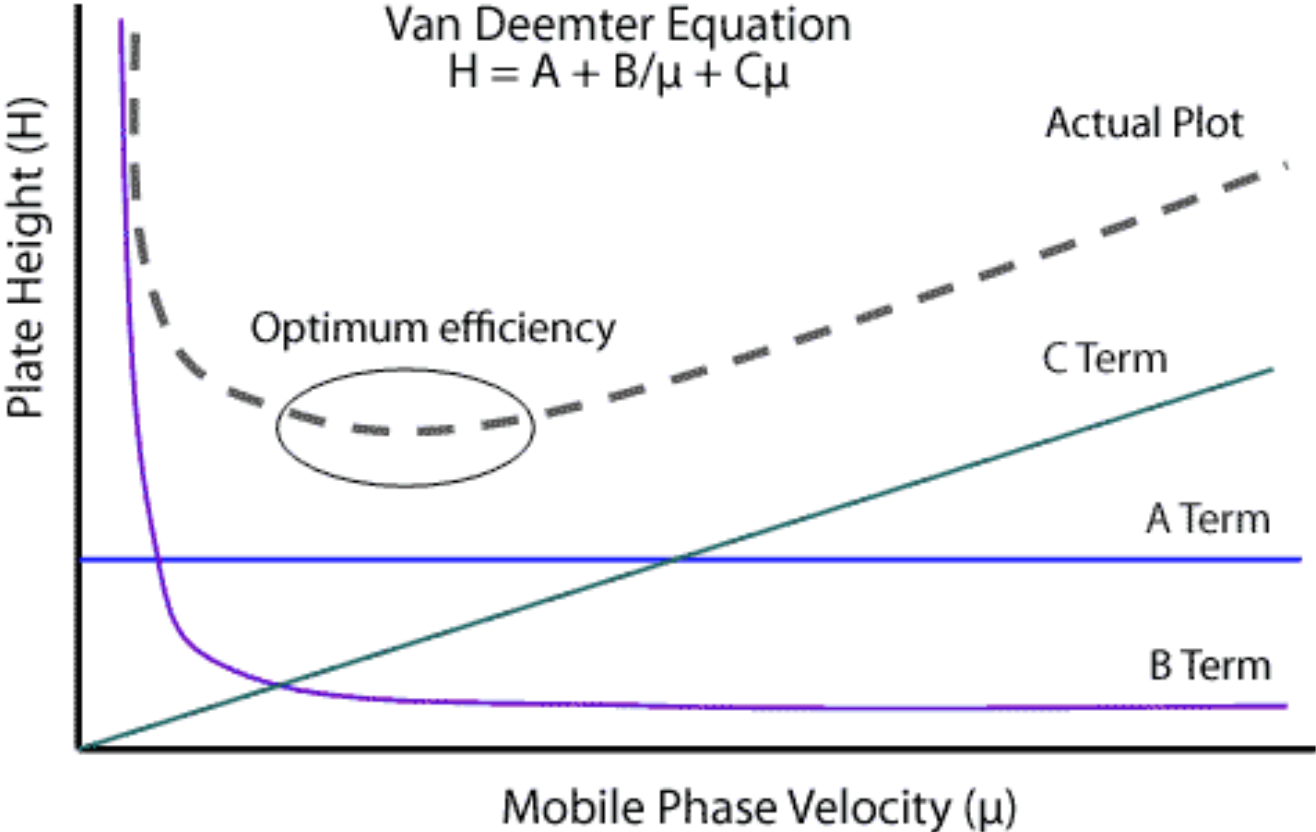
$$HETP = A + (B/u) + (C_s + C_m) \times u$$

- [HETP](#) = height equivalent to a theoretical plate, a measure of the resolving power of the column [m]
(Height = Length/number of plates=L/N)
- A = [Eddy-diffusion](#) parameter, related to channeling through a non-ideal packing [m]
- B = [diffusion coefficient](#) of the eluting particles in the **longitudinal** direction, resulting in [dispersion](#) [m² s⁻¹]
- C = Resistance to [mass transfer coefficient](#) of the analyte between mobile [m] and stationary phase [s]
- u = [Linear Velocity](#) [m s⁻¹]

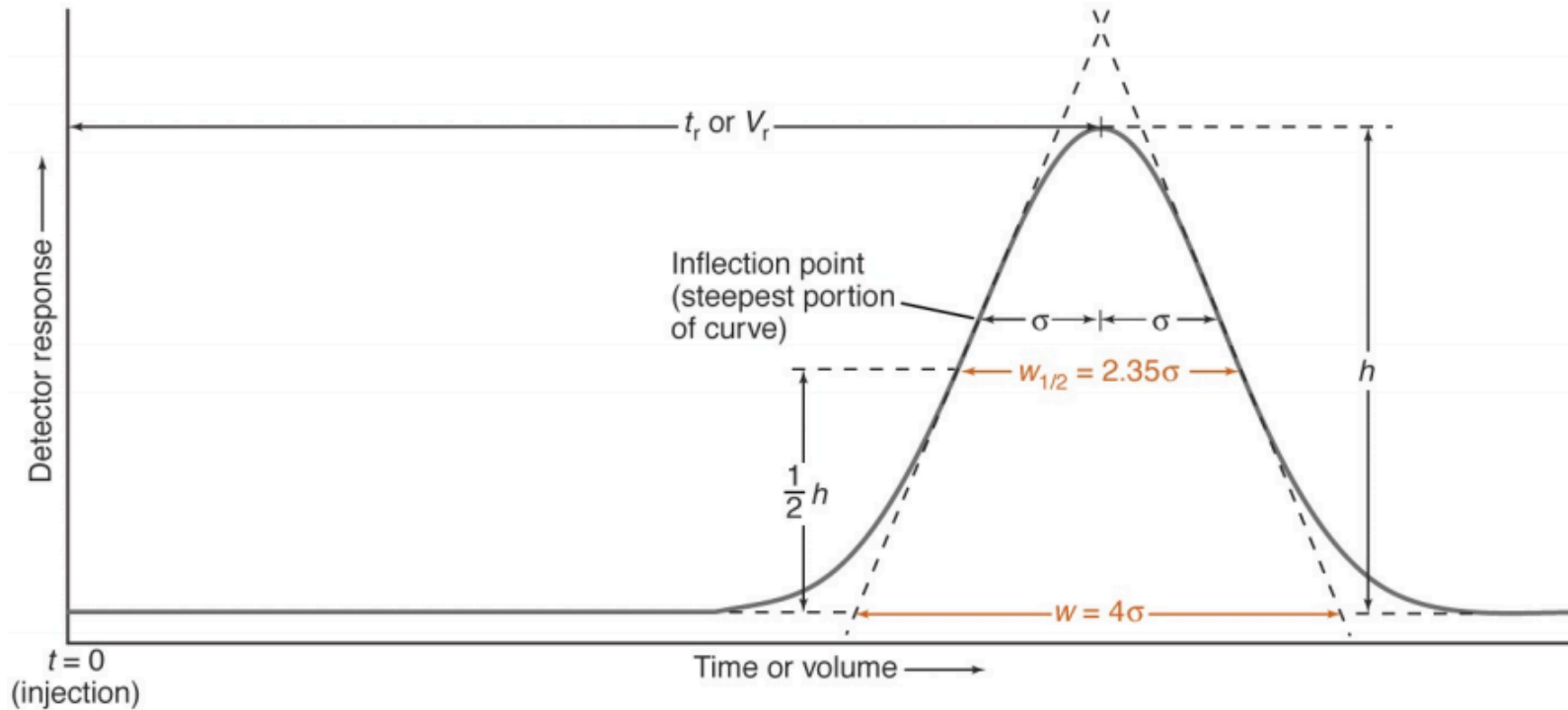
Original paper: Van Deemter JJ, Zuiderweg FJ and Klinkenberg A (1956). "Longitudinal diffusion and resistance to mass transfer as causes of non ideality in chromatography". *Chem. Eng. Sc.* 5: 271–289

Youtube: https://www.youtube.com/watch?v=8i_4-OMCANE

The Van Deemter Curve



Resolution



Solute moving through a column spreads into a Gaussian shape with standard deviation σ . Common Measures of breadth are:

- 1) The width $w_{1/2}$ measured at half-height
- 2) The width w at the baseline between tangents drawn to the steepest parts of the peak (inflection points).

Derive Van Deemter for Resolution

$$HETP = L/N$$

$$N = L/H \longrightarrow \text{substitute } H = \sigma^2/L$$

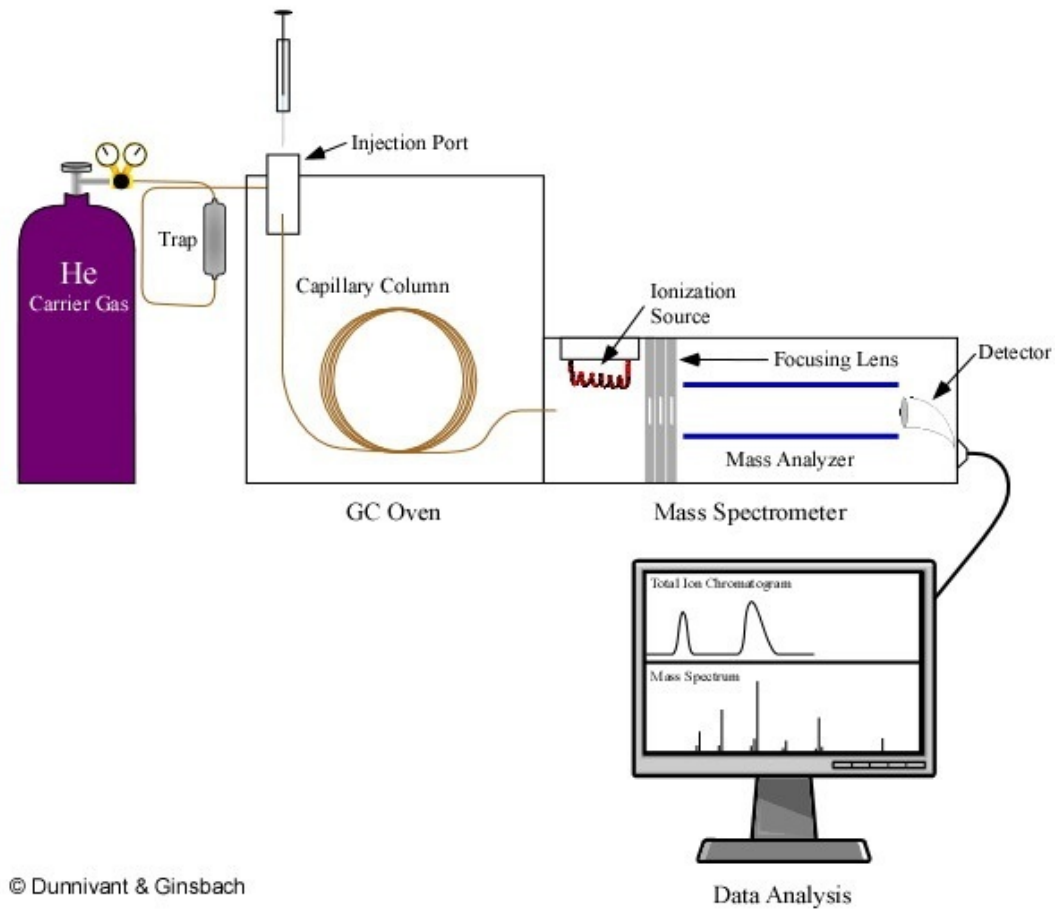
$$N = L^2/\sigma^2 \longrightarrow \text{convert length to time (utility)}$$

$$N = (t_r)^2/(\sigma)^2 \longrightarrow \text{relate } \sigma \text{ to } w_{1/2} (2.35\sigma) \text{ and } w (4\sigma)$$

$$N = 16t_r^2/w^2$$

$$N = 5.55t_r^2/w_{1/2}^2$$

GC coupled to Mass Spectrometry (MS)



© Dumivant & Ginsbach

Autosampler



MS Analyzer:

-**Quadrupole**

-Ion trap

-Time of flight (TOF)

-Orbitrap

GC oven

-**GC Column**

GC controller

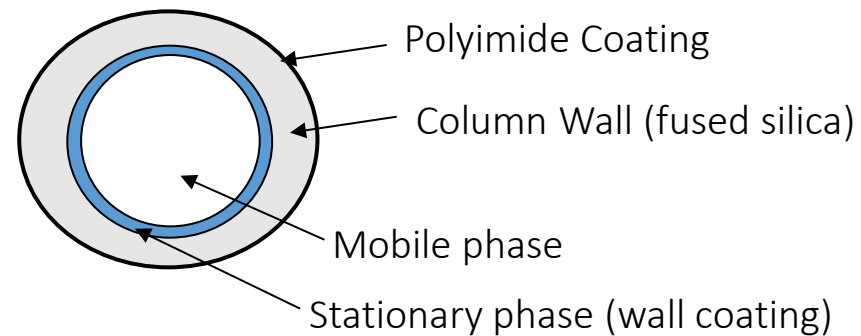
GC Columns

- Two Common Formats
 - Packed columns (most common with bonded liquid coating)
 - Open tubular (typically long columns with small diameters)

Packed Columns



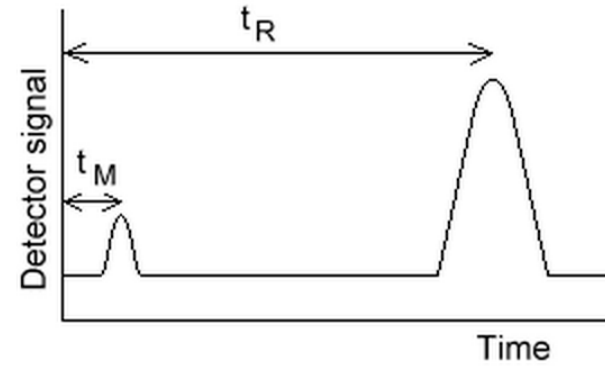
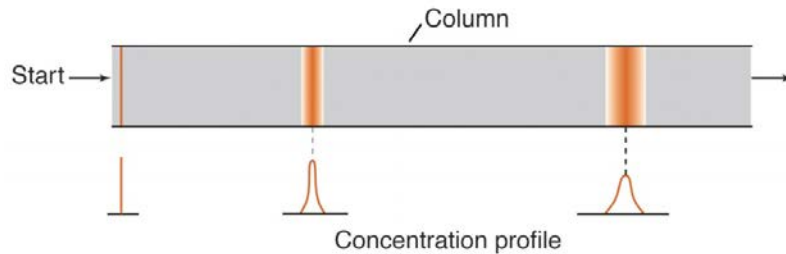
Open Tubular (end on, cross section view)



GC Columns

- Advantages of Open Tubular Columns
 - Best resolution (negligible A term, small C term in Van Deemter Equation)
 - More robust
 - Better sensitivity with many detectors (due to less band broadening vs. lower mass through column)
- Column Selection
 - High resolution (thin film, 0.25 mm diameter, 60 m) vs. higher capacity (thick film, 0.53 mm diameter)
 - Stationary phase based on polarity

GC Stationary Phase



Retention factor (k') describes the migration of the analyte on the column

$$k' = (t_R - t_M) / t_M$$

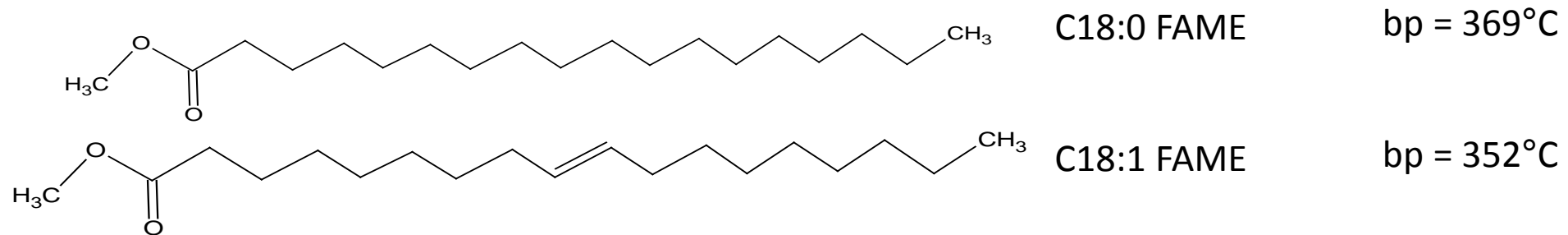
Selectivity factor (α) describes the separation of 2 species, A and B, on the column

$$\alpha = k'_B / k'_A$$

$$\text{Resolution (R)} = \underbrace{\frac{1}{4}}_{\text{efficiency}} \underbrace{\sqrt{N}}_{\text{selectivity}} \underbrace{(\alpha - 1/\alpha) (k'/k' + 1)}_{\text{retention}}$$

GC Adjustments

- k is adjusted by changing temperature (higher T means smaller k)
- Selection of stationary phase affects k and α values
 - The α values are adjusted by changing column (will work if there is a difference in solute polarity)
 - example: separation of saturated and unsaturated fatty acid methyl esters (FAMES).

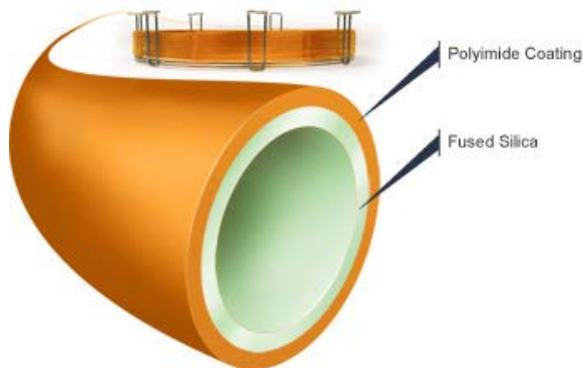


- Retention of C18:0 and C18:1 FAMES on RTX-5MS columns is very similar (due to similar boiling points)
 - Retention on more polar columns (RTX-50MS) is greater for the more polar unsaturated FAMES
- Main concerns of stationary phase are: polarity, functional groups, maximum operating temperature, and column bleed (loss of stationary phase)
- More polar columns suffer from lower maximum temperatures and greater column bleed-**derivatize?**
- Changing carrier gas has no effect on retention

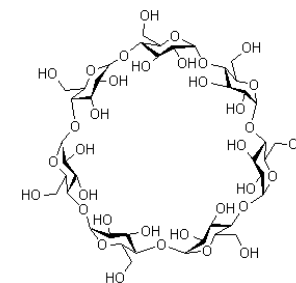
GC Column Options



Type	Functional Groups	Polarity
RTX-1MS	100% dimethyl	Non-polar
RTX-5MS	5% diphenyl/95% dimethyl	Low polarity
RTX-50MS	Phenyl methyl	More polar
Stabliwax-MS	PEG	High polarity



Chirality Columns

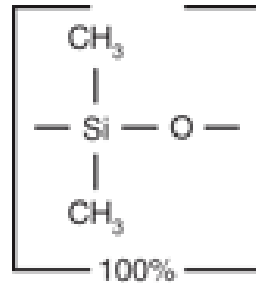


β -cyclodextrin

GC Column Options

RTX-1MS = NonPolar

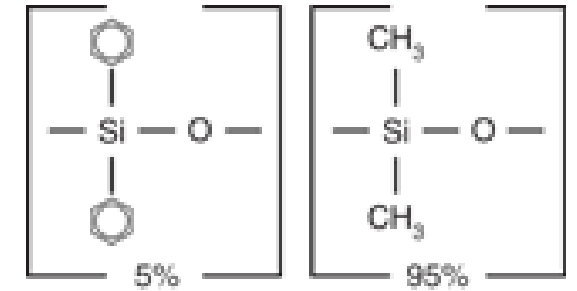
Saturated Hydrocarbons
Olefinic Hydrocarbons
Aromatic Hydrocarbons
Halocarbons
Mercaptans
Sulfides
CS₂



Long lifetime and very low bleed at high operating temperatures.
Temperature range: -60 °C to 350 °C

RTX-5MS = Low Polarity

Ethers
Ketones
Aldehydes
Esters
Tertiary amines
Nitro compounds without α -H atoms
Nitrile compounds without α -H atoms



Column specifically tested for low-bleed performance.
Temperature range: -60 °C to 350 °C.

GC Column Options

RTX-50MS = Medium Polarity

Alcohols

Carboxylic acids

Phenols

Primary and secondary amines

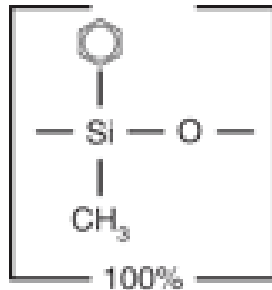
Oximes

Nitro compounds without α -H atoms

Nitrile compounds without α -H atoms

Low bleed

Temperature range: 40 °C to 320 °C.



stabilwax-5MS = High Polarity

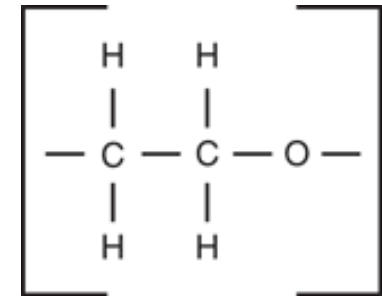
Polyhydroxyalcohols

Amino alcohols

Hydroxy acids

Polyprotic acids

Polyphenols

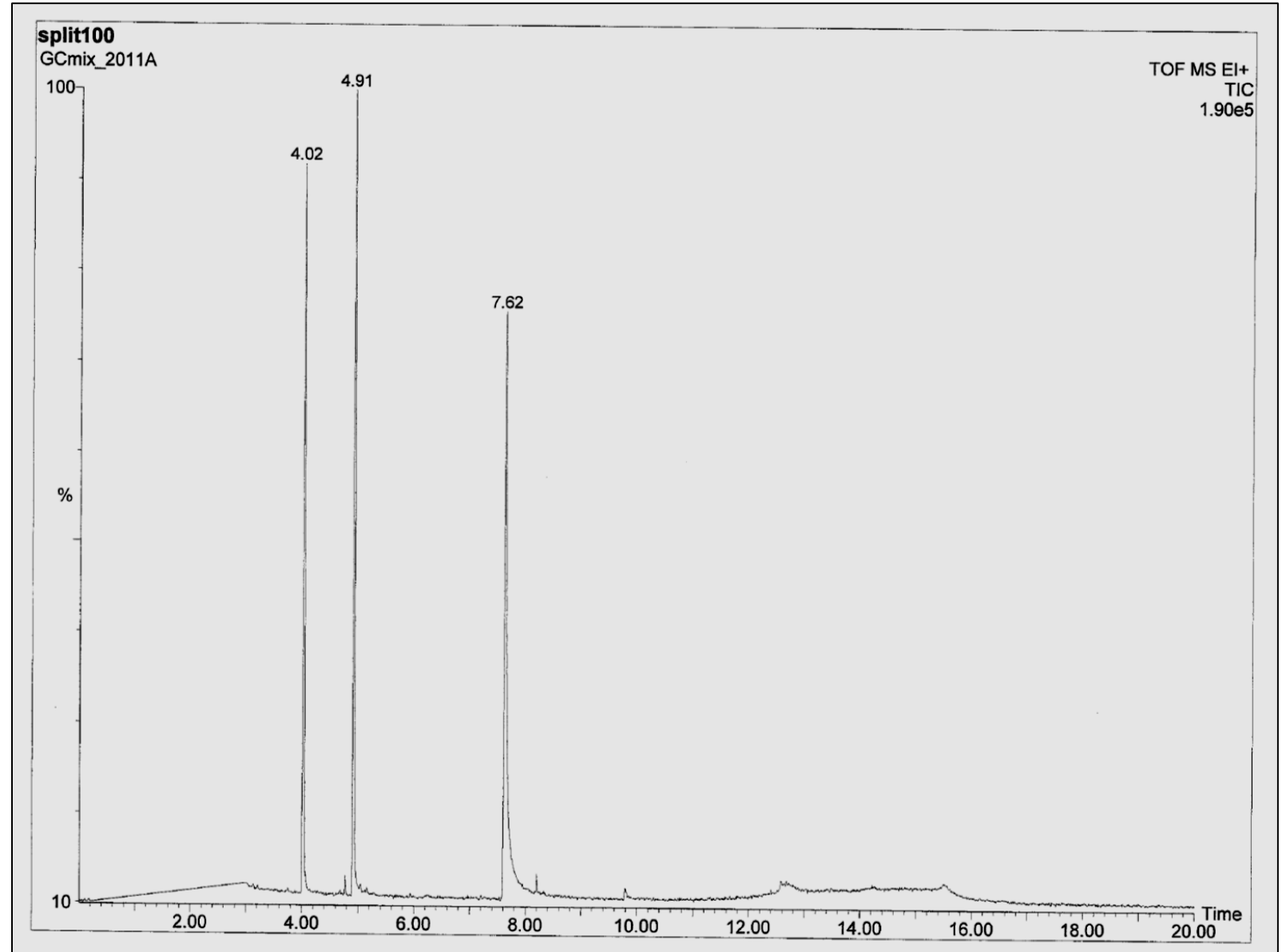


Low bleed but rugged enough to withstand repeated cycles without retention time shifting.

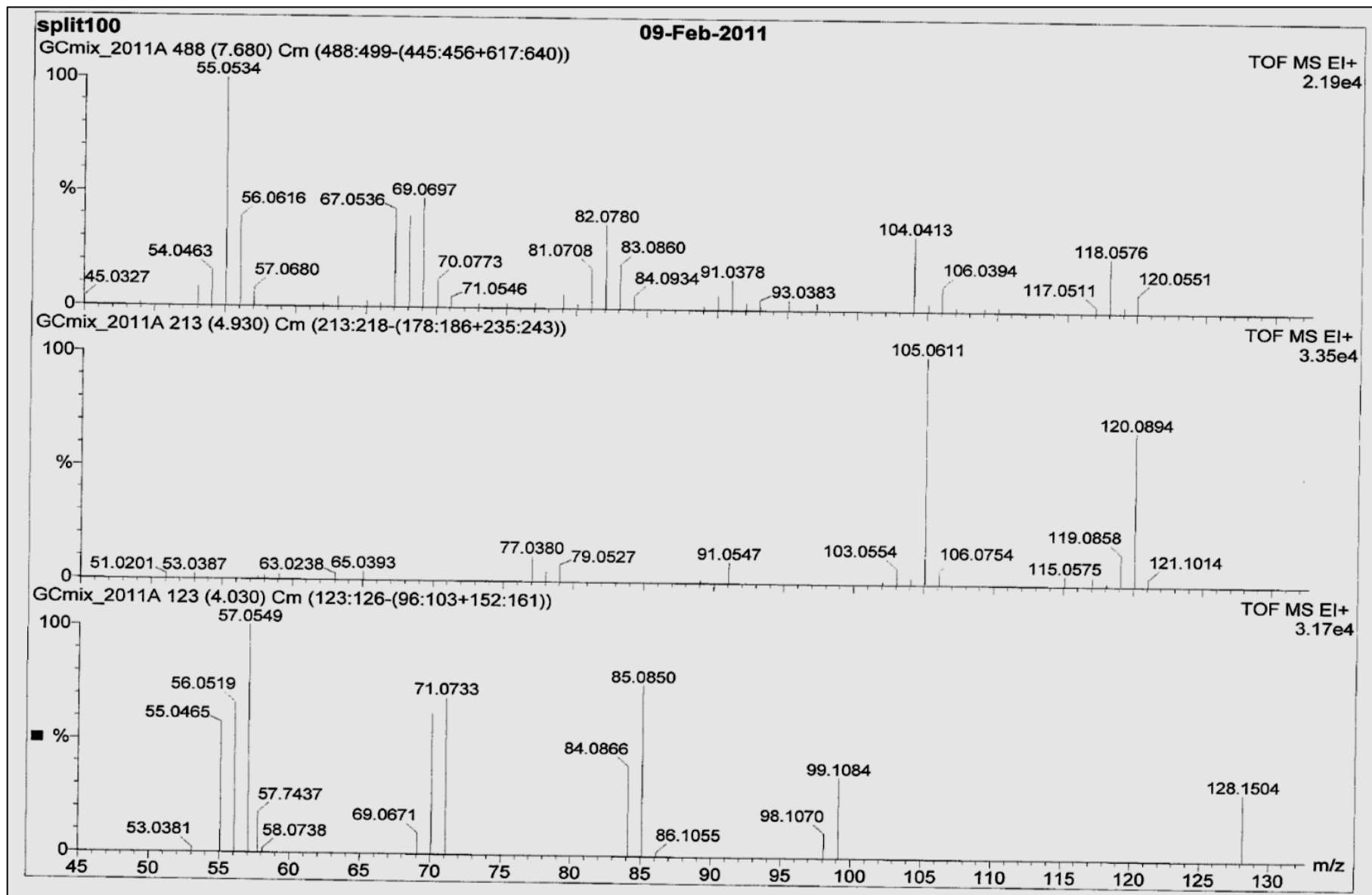
Sensitive to water and oxidation.

Temperature range: 40 °C to 250/260 °C.

GC-Chromatogram



El Spectrum



The Nitrogen Rule

- Compounds* that contain **even** number of N atoms have **even** number of *nominal* molecular weight
- Compounds* that contain **odd** number of N atoms have **odd** number of *nominal* molecular weight

But what about ***singly protonated*** molecules and ***accurate*** molecular weights??

* Common organic compounds

Ion Stabilities

- ***Even electron ions are more stable*** than odd electron (radical) ions

How about protonated molecules: even electron or not?

And how about ions formed by electron impact (EI) ionization?

Selected Isotope Ratios and ¹³C Contributions

Accurate elemental masses:

C: 12.000000

H: 1.007825

O: 15.9949

N: 14.003

Cl: 34.9688

Br: 78.9183

S: 31.9720

Table 2.1. Natural isotopic abundances of common elements.^a

Element	A		A + 1		A + 2		Element type
	Mass	Per cent	Mass	Per cent	Mass	Per cent	
H	1	100	2	0.015			"A"
C	12	100	13	1.1 ^b			"A + 1"
N	14	100	15	0.37			"A + 1"
O	16	100	17	0.04	18	0.20	"A + 2"
F	19	100					"A"
Si	28	100	29	5.1	30	3.4	"A + 2"
P	31	100					"A"
S	32	100	33	0.80	34	4.4	"A + 2"
Cl	35	100			37	32.5	"A + 2"
Br	79	100			81	98.0	"A + 2"
I	127	100					"A"

^aWapstra and Gove (1971).
^b1.1 ± 0.02, depending on source.

Table 2.2. Isotopic contributions for carbon and hydrogen.
 If the abundance of the peak A is 100 (after correction for isotopic contributions to it), then its isotopic contributions will be:

	(A + 1)	(A + 2)		(A + 1)	(A + 2)	(A + 3)
C ₁	1.1	0.00	C ₁₆	18	1.5	0.1
C ₂	2.2	0.01	C ₁₇	19	1.7	0.1
C ₃	3.3	0.04	C ₁₈	20	1.9	0.1
C ₄	4.4	0.07	C ₁₉	21	2.1	0.1
C ₅	5.5	0.12	C ₂₀	22	2.3	0.2
C ₆	6.6	0.18	C ₂₂	24	2.8	0.2
C ₇	7.7	0.25	C ₂₄	26	3.3	0.3
C ₈	8.8	0.34	C ₂₆	29	3.9	0.3
C ₉	9.9	0.44	C ₂₈	31	4.5	0.4
C ₁₀	11.0	0.54	C ₃₀	33	5.2	0.5
C ₁₁	12.1	0.67	C ₃₅	39	7.2	0.9
C ₁₂	13.2	0.80	C ₄₀	44	9.4	1.3
C ₁₃	14.3	0.94	C ₅₀	55	15	1.3
C ₁₄	15.4	1.1	C ₆₀	66	21	4.6
C ₁₅	16.5	1.3	C ₁₀₀	110	60	22

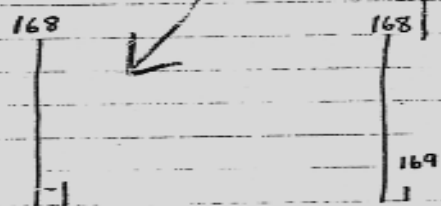
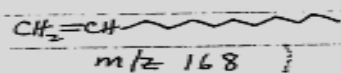
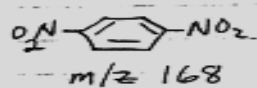
For each additional element present, add *per atom*:
 (A + 1): N, 0.37; O, 0.04; Si, 5.1; S, 0.80.
 (A + 2): O, 0.20; Si, 3.4; S, 4.4; Cl, 32.5; Br, 98.0.
 Typical values for (A + 4): C₂₅, 0.02; C₄₀, 0.13; C₁₀₀, 5.7.

Use of Isotope Ratios to Distinguish Structures

Isotope ratios in molecular ion region provide information on molecular formula

e.g.

Skoog + Leary p 450



How large is $(M+1)^+$? $(M+2)^+$?

^{13}C	$6 \times 1.08 = 6.48\%$
^2H	$4 \times 0.015 = 0.06$
^{15}N	$2 \times 0.37 = 0.74$
^{17}O	$4 \times 0.04 = 0.16$
	$(M+1)^+/M = 7.44\%$

^{13}C	$12 \times 1.08 = 12.96\%$
^2H	$24 \times 0.015 = 0.36$
	13.32

What are M , $M+1$, $M+2$, ... for C_{60}^+ (buckminsterfullerene)?

work

Calculate the abundance ratio $\frac{[M+2H]^{++}}{[M+1+2H]^{++}}$ for polyalanine H-(NH-CH(CH3)-CO)n-OH with $n=5$ and $n=50$. What resolution

Increasing ^{13}C contribution in polyalanines

Page: 1

[Theoretical Ion Distribution]
Molecular Formula : C15 H29 O6 N5
(m/z 375.2118, MW 375.4252, U.S. 4.0)
Base Peak : 375.2118, Averaged MW : 375.4263 (a), 375.4269 (w)

m/z	INT.
375.2118	100.0000
376.2146	19.1839
377.2168	2.9467
378.2192	0.3302
379.2215	0.0310
380.2238	0.0025
381.2261	0.0002

$n = 5$

[Theoretical Ion Distribution]
Molecular Formula : C90 H129 O26 N25
(m/z 1975.9541, MW 1977.1662, U.S. 39.0)
Base Peak : 1976.9570, Averaged MW : 1977.1722 (a), 1977.1729 (w)

m/z	INT.
1975.9541	89.1183
1976.9570	100.0000
1977.9597	60.2390
1978.9624	25.6258
1979.9651	8.5827
1980.9677	2.3982
1981.9702	0.5794
1982.9727	0.1240
1983.9753	0.0239
1984.9778	0.0042
1985.9802	0.0007
1986.9827	0.0001

$n = 25$

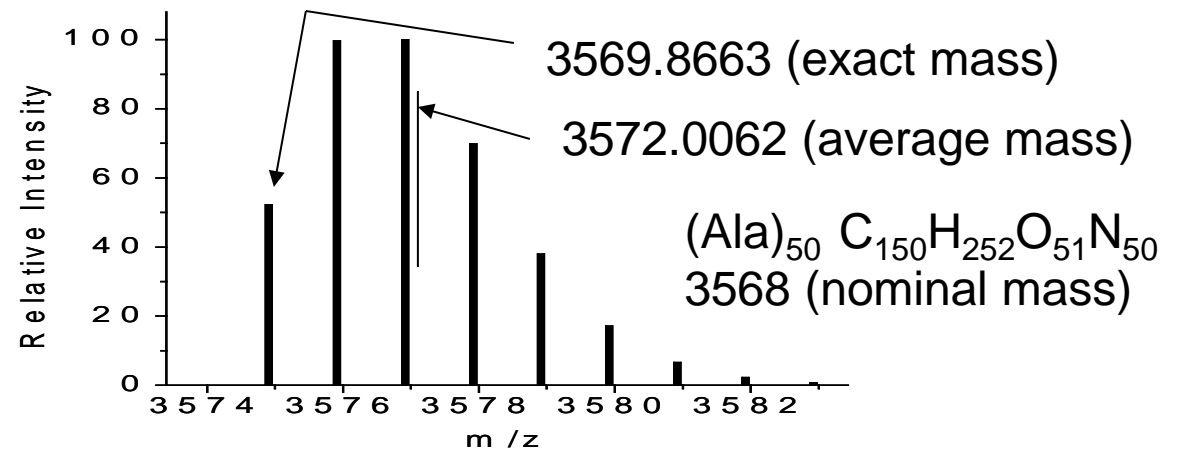
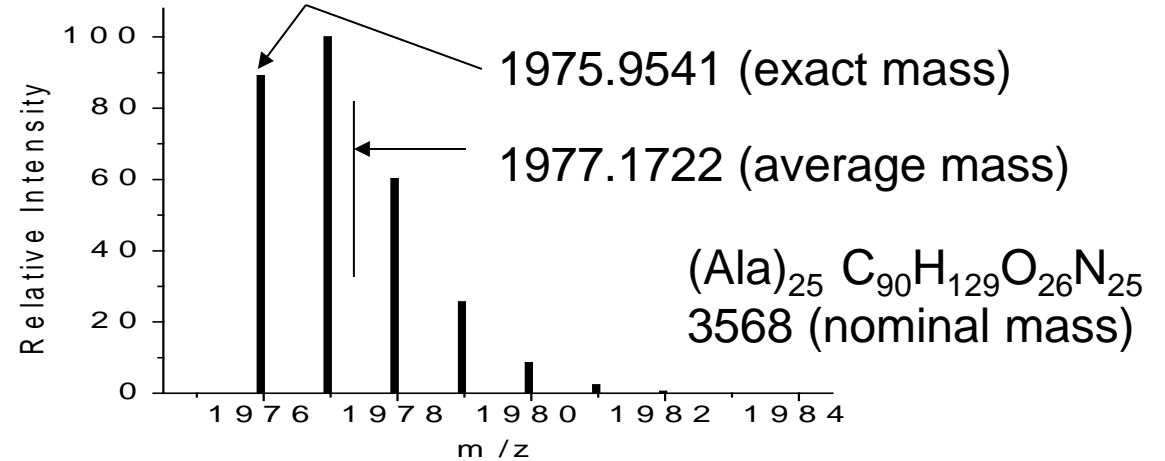
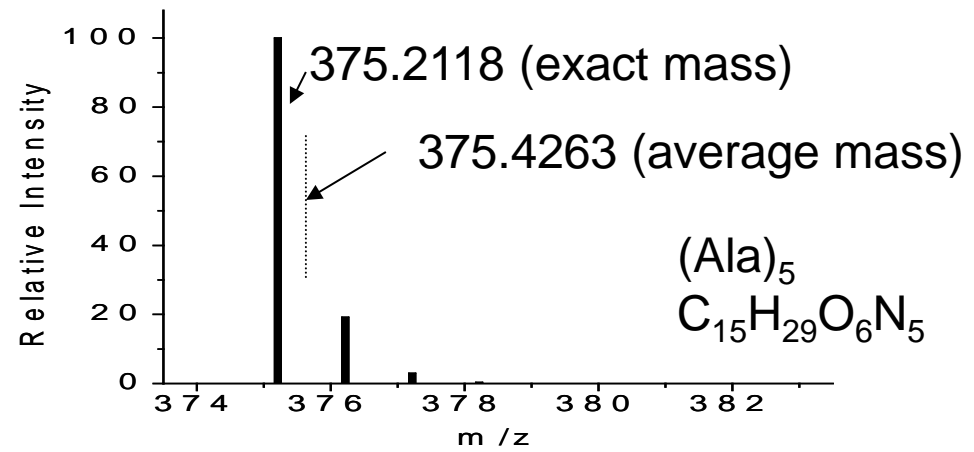
[Theoretical Ion Distribution]
Molecular Formula : C150 H257 O51 N50
(m/z 3574.9054, MW 3576.9950, U.S. 47.5)
Base Peak : 3576.9109, Averaged MW : 3577.0061 (a), 3577.0067 (w)

m/z	INT.
3574.9054	52.1735
3575.9082	99.6516
3576.9109	100.0000
3577.9136	69.8217
3578.9163	37.9680
3579.9189	17.0842
3580.9214	6.6049
3581.9240	2.2507
3582.9265	0.6886
3583.9290	0.1917
3584.9315	0.0491
3585.9340	0.0117
3586.9364	0.0026
3587.9389	0.0005
3588.9413	0.0001

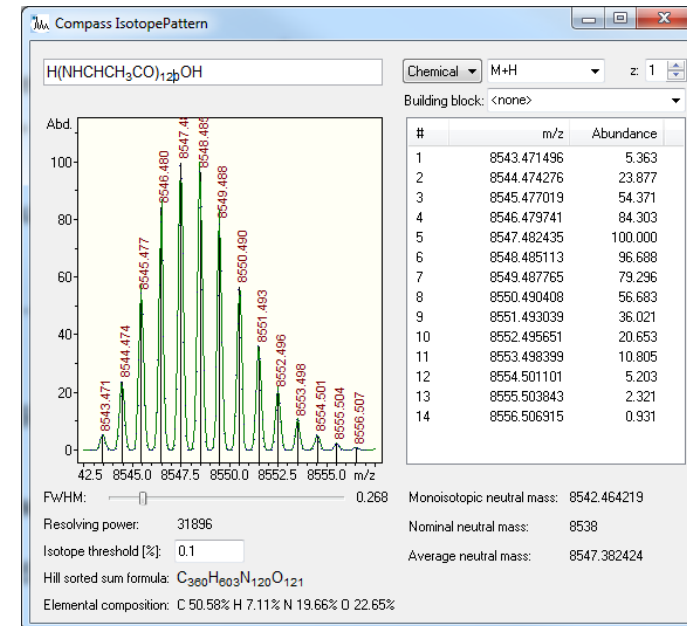
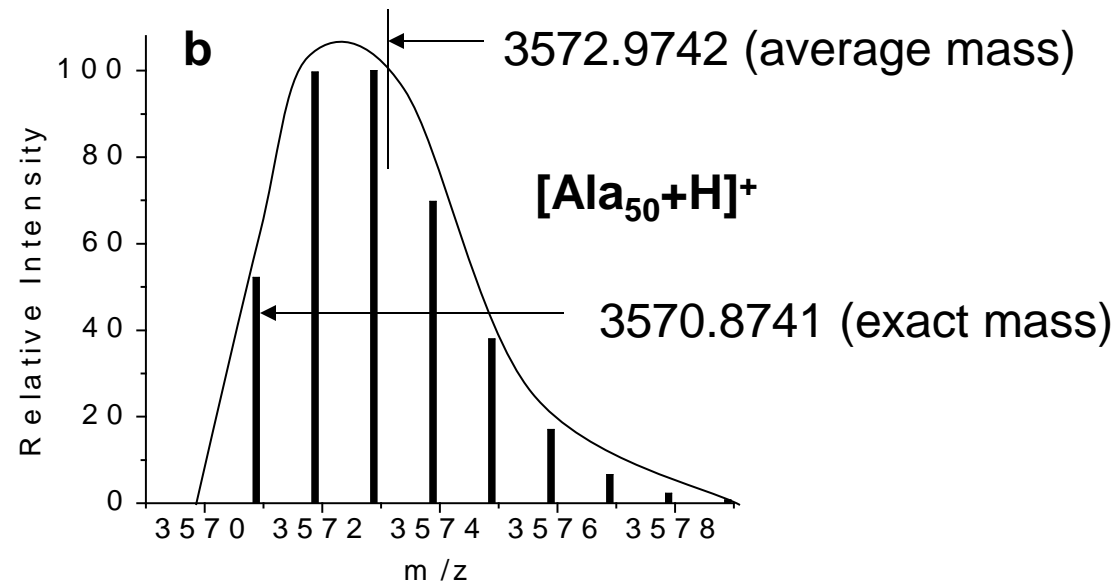
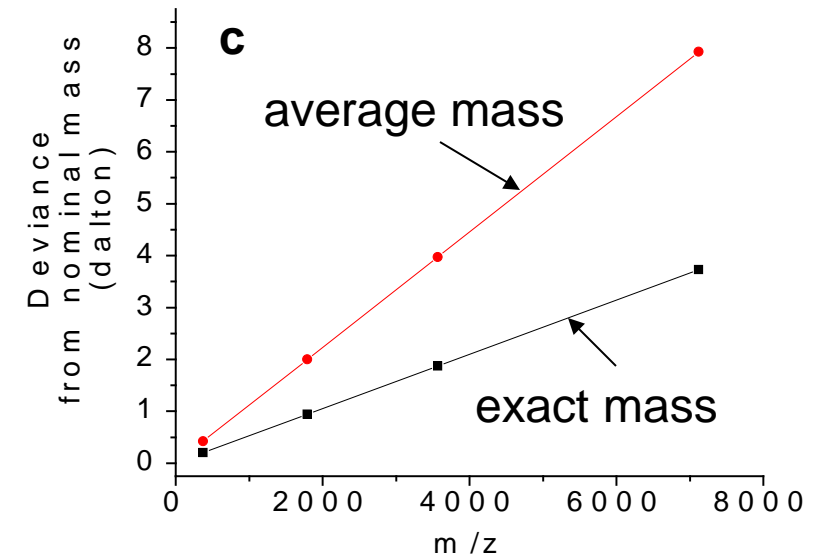
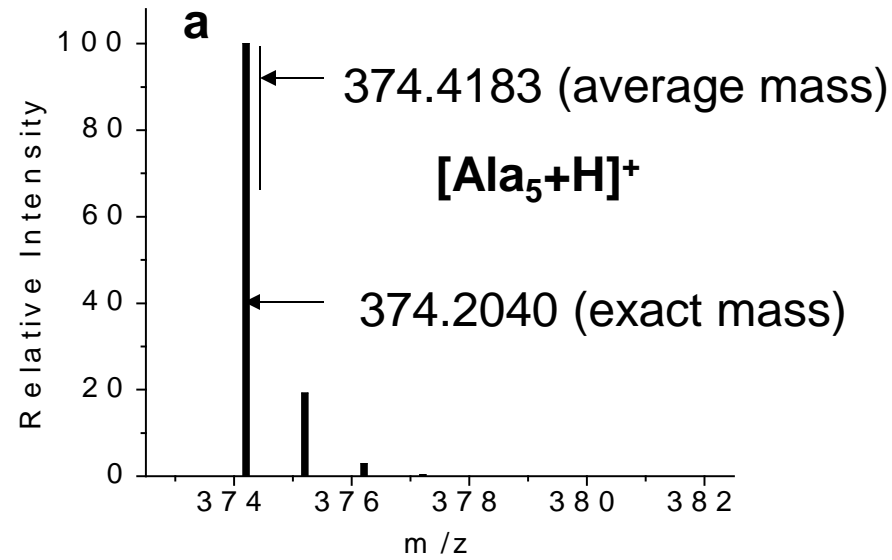
$n = 50$

$$\text{H} - \left(\text{NH} - \overset{\text{CH}_3}{\underset{|}{\text{C}}} - \overset{\text{O}}{\underset{||}{\text{C}}} \right)_n \text{OH} + 2\text{H}^+$$

Increasing ^{13}C contribution in polyananines

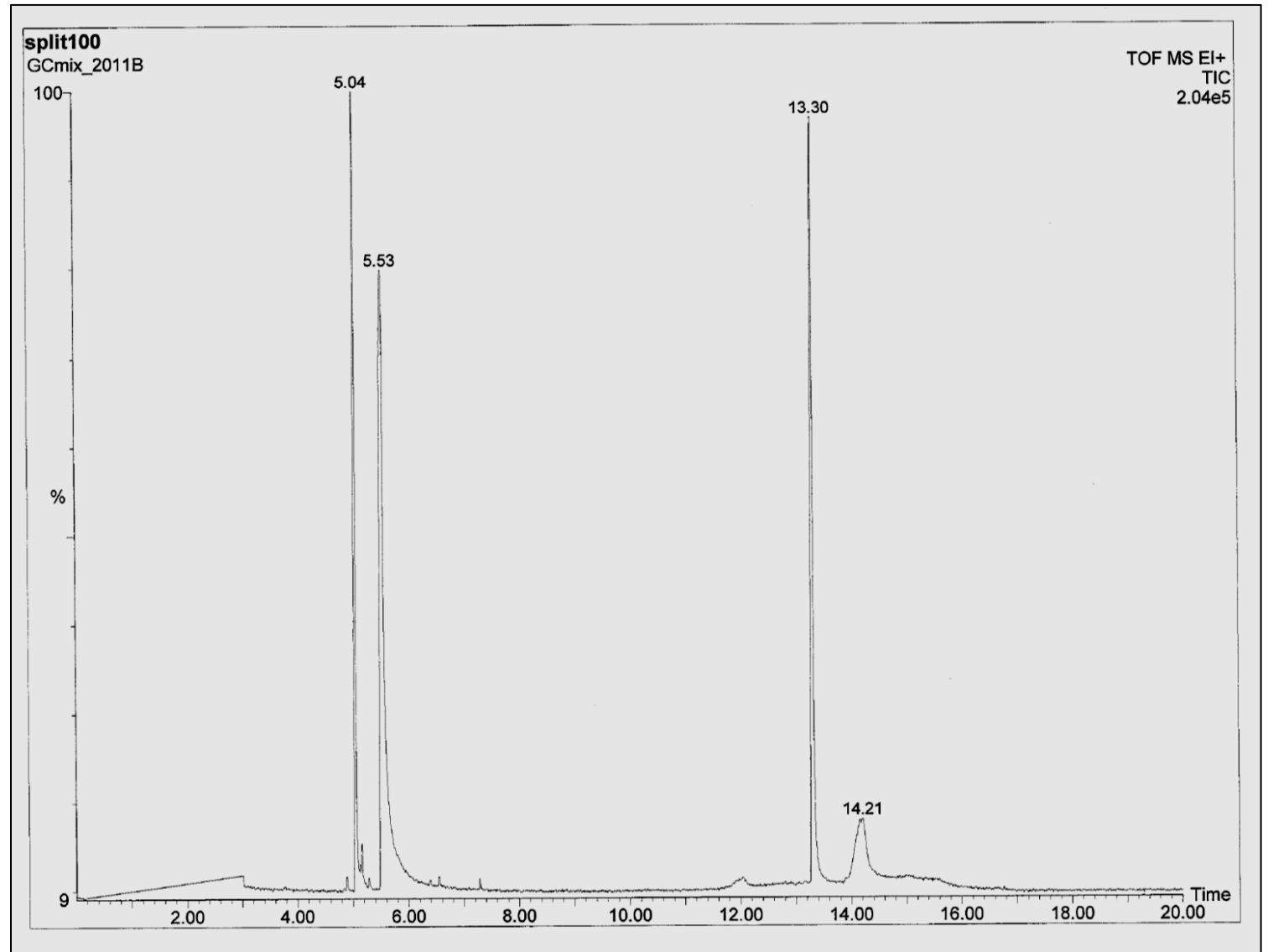


Increasing ^{13}C contribution in polyananines

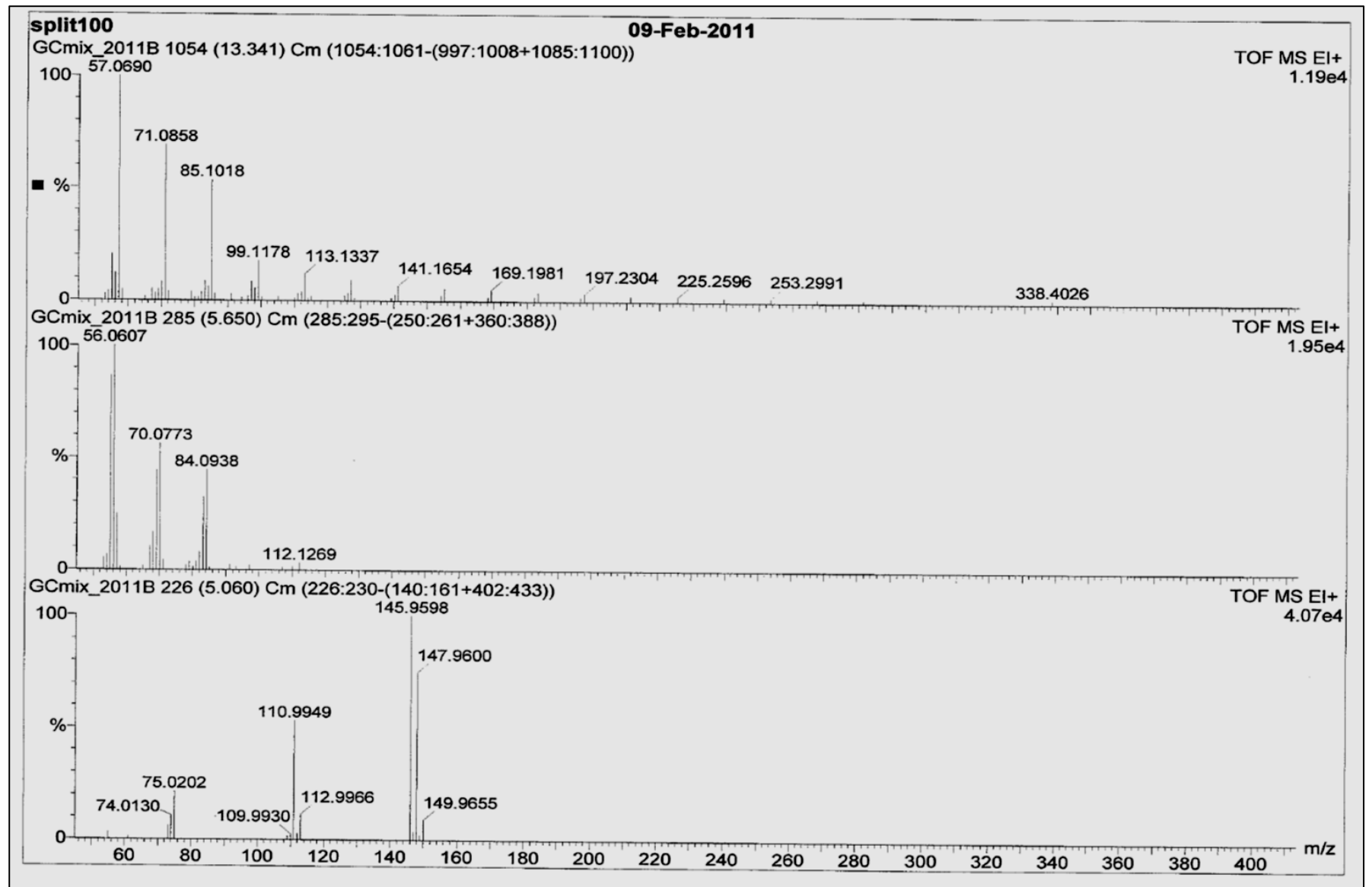


$[\text{Ala}_{120}+\text{H}]^+$

GC Chromatogram- an example for you

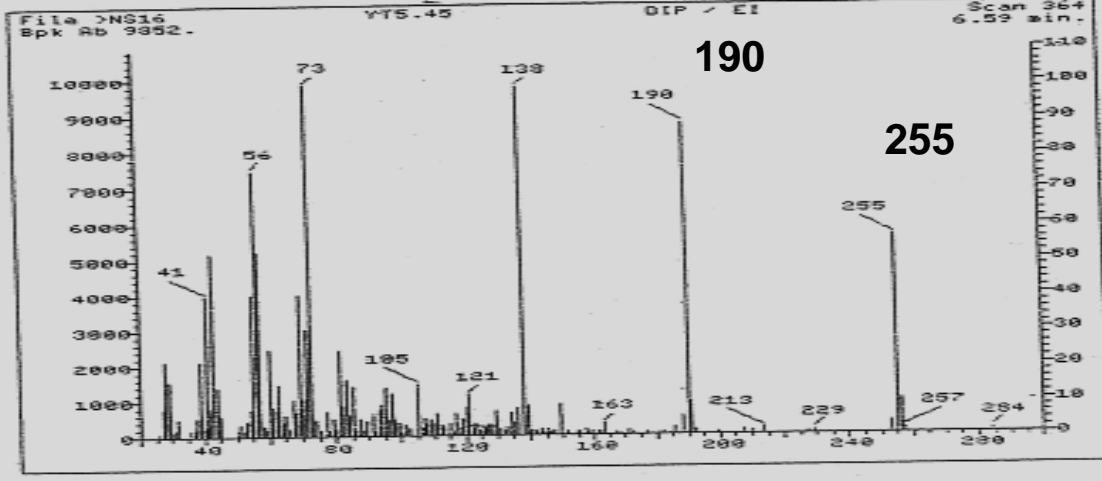


El Spectrum- give the top and bottom a try

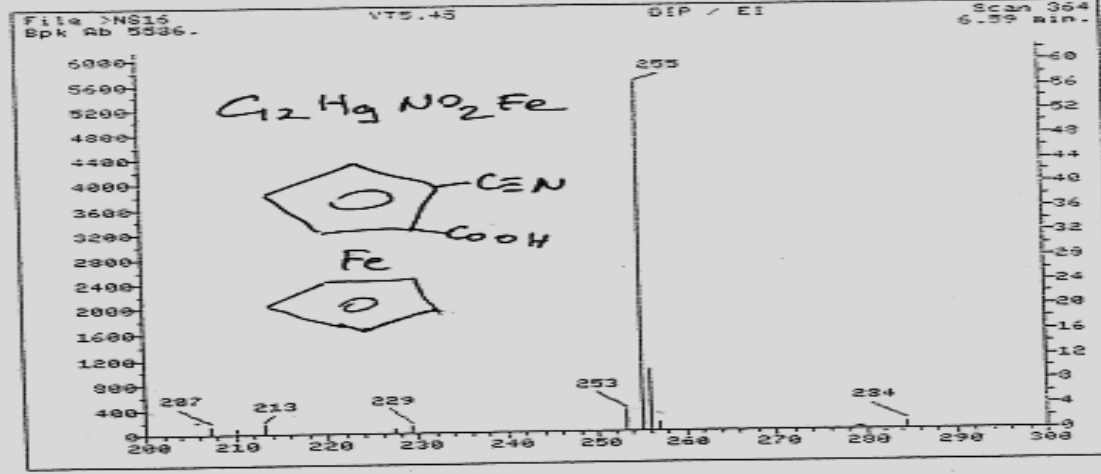


Characteristic Isotope Distribution of Selected Transition Metal Elements

m/z	INT.	Mo	Sn	Re	Cu	Fe
1.9068	61.5002	*****	*****	*****	*****	*****
3.9051	38.3340	*****	*****	*****	*****	*****
4.9058	65.9760	*****	*****	*****	*****	*****
5.9047	69.1256	*****	*****	*****	*****	*****
6.9060	39.5773	*****	*****	*****	*****	*****
17.9054	100.0000	*****	*****	*****	*****	*****
39.9075	39.9088	*****	*****	*****	*****	*****
m/z	INT.					
111.9048	2.9764	**	**	*****	*****	*****
113.9028	1.9945	*	*	*****	*****	*****
114.9033	1.1046	*	*	*****	*****	*****
115.9017	44.5842	*****	*****	*****	*****	*****
116.9030	23.5655	*****	*****	*****	*****	*****
117.9016	74.3173	*****	*****	*****	*****	*****
118.9033	26.3271	*****	*****	*****	*****	*****
119.9022	100.0000	*****	*****	*****	*****	*****
121.9034	14.2068	*****	*****	*****	*****	*****
123.9053	17.7662	*****	*****	*****	*****	*****
m/z	INT.					
184.9530	59.7444	*****	*****	*****	*****	*****
186.9558	100.0000	*****	*****	*****	*****	*****
m/z	INT.					
62.9296	100.0000	*****	*****	*****	*****	*****
64.9278	44.5713	*****	*****	*****	*****	*****
m/z	INT.					
53.9396	6.3236	****	****	*****	*****	*****
55.9349	100.0000	*****	*****	*****	*****	*****
56.9354	2.3986	*	*	*****	*****	*****
57.9333	0.3053	*****	*****	*****	*****	*****
m/z	INT.					
1.9068	61.5002	*****	*****	*****	*****	*****
3.9051	38.3340	*****	*****	*****	*****	*****
4.9058	65.9760	*****	*****	*****	*****	*****
5.9047	69.1256	*****	*****	*****	*****	*****
6.9060	39.5773	*****	*****	*****	*****	*****
17.9054	100.0000	*****	*****	*****	*****	*****
39.9075	39.9088	*****	*****	*****	*****	*****
m/z	INT.					
111.9048	2.9764	**	**	*****	*****	*****
113.9028	1.9945	*	*	*****	*****	*****
114.9033	1.1046	*	*	*****	*****	*****
115.9017	44.5842	*****	*****	*****	*****	*****
116.9030	23.5655	*****	*****	*****	*****	*****
117.9016	74.3173	*****	*****	*****	*****	*****
118.9033	26.3271	*****	*****	*****	*****	*****
119.9022	100.0000	*****	*****	*****	*****	*****
121.9034	14.2068	*****	*****	*****	*****	*****
123.9053	17.7662	*****	*****	*****	*****	*****
m/z	INT.					
184.9530	59.7444	*****	*****	*****	*****	*****
186.9558	100.0000	*****	*****	*****	*****	*****
m/z	INT.					
62.9296	100.0000	*****	*****	*****	*****	*****
64.9278	44.5713	*****	*****	*****	*****	*****
m/z	INT.					
53.9396	6.3236	****	****	*****	*****	*****
55.9349	100.0000	*****	*****	*****	*****	*****
56.9354	2.3986	*	*	*****	*****	*****
57.9333	0.3053	*****	*****	*****	*****	*****



Origin of m/z 190?



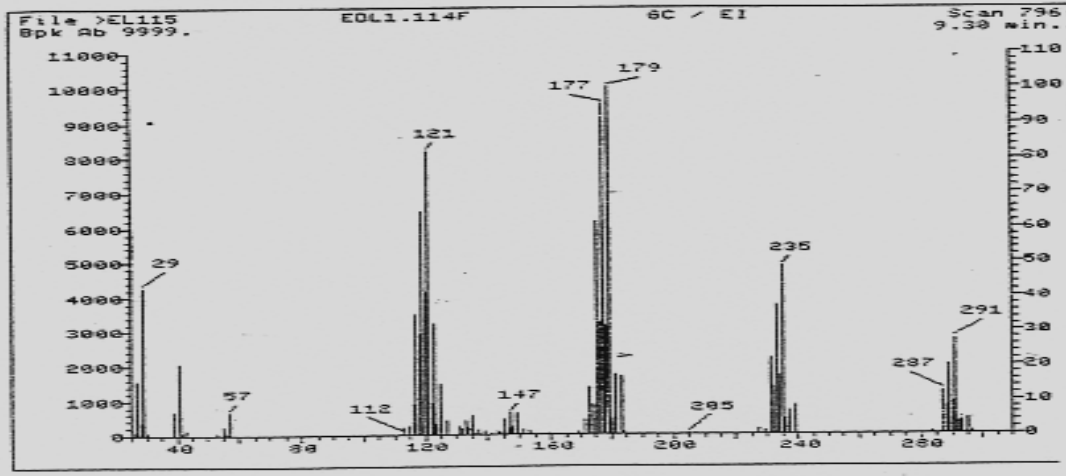
Theoretical Ion Distribution]

Molecular Formula : $C_{12}H_9NO_2Fe$

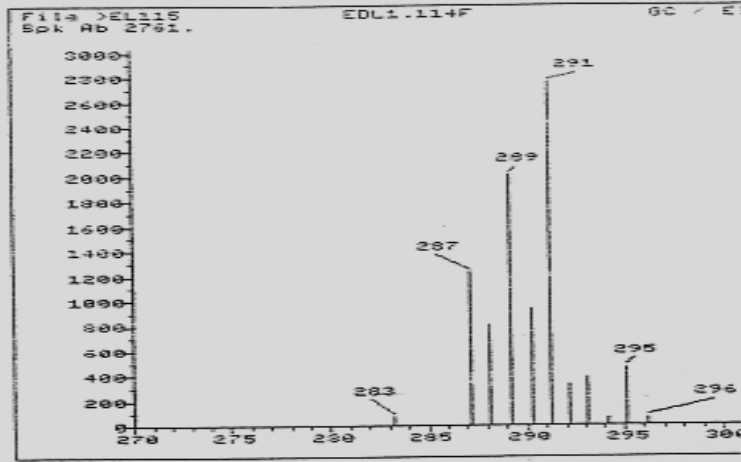
(m/z 254.9983, MW 255.0560, U.S. 9.5)

base Peak : 254.9983, Averaged MW : 255.0564(a), 255.0580(w)

m/z	INT.
253.0029	6.3184 ****
254.0062	0.8799 *
254.9983	100.0000 *****
256.0011	16.3163 *****
257.0025	1.9336 *
258.0044	0.1643
259.0063	0.0110
260.0082	0.0006



Metal
element?



(Theoretical Ion Distribution)

Molecular Formula : C12 H27 Sn

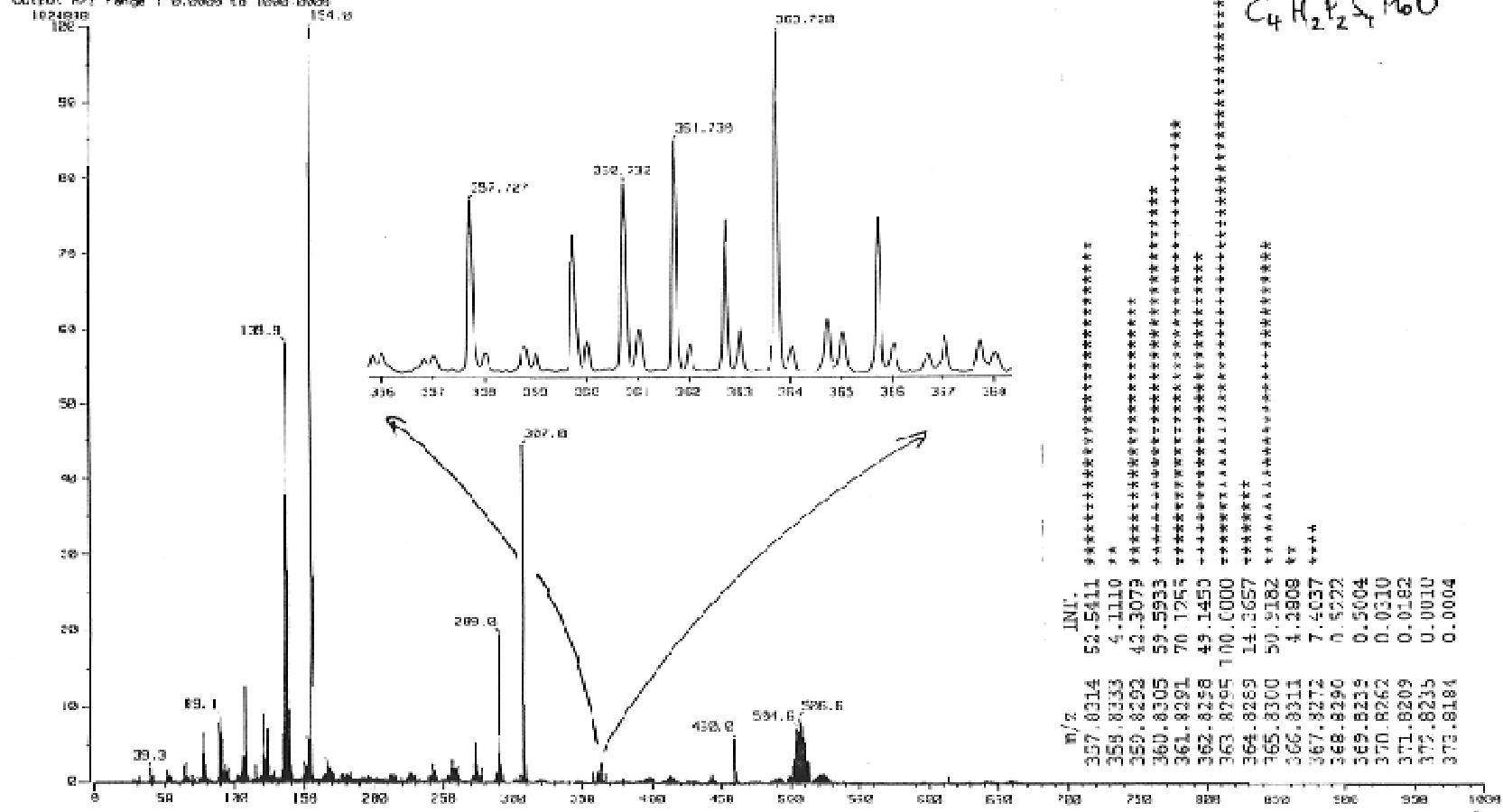
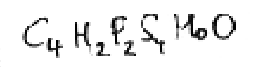
(m/z 291.1135, MW 290.0564,

Base Peak : 291.1137, Averaged MW : 290.0580(a),

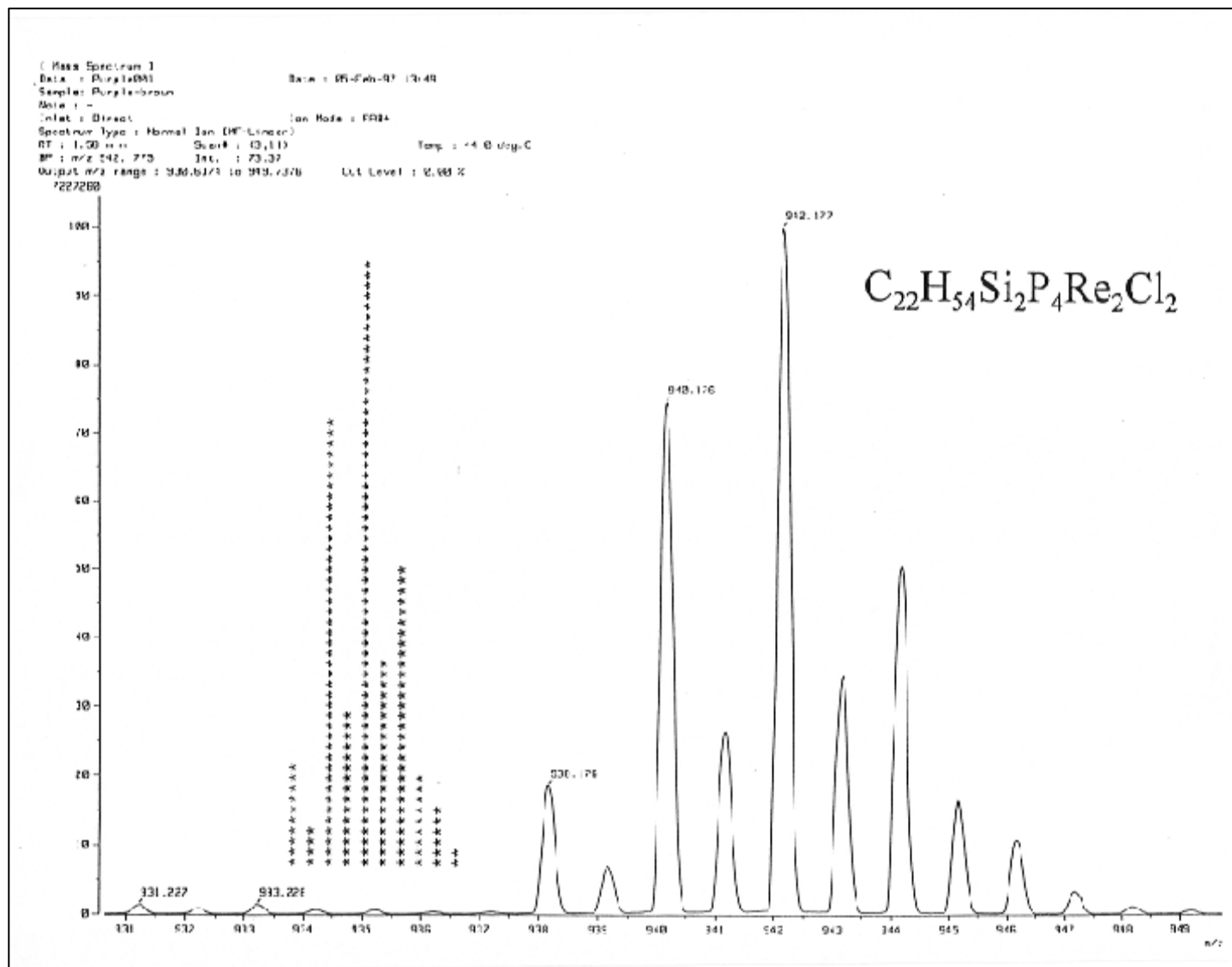
m/z	INT.
283.1161	2.8543 **
284.1195	0.3925
285.1142	1.9376 *
286.1152	1.3233 *
287.1130	42.9182 *****
288.1147	28.4887 *****
289.1131	74.7503 *****
290.1151	35.2596 *****
291.1137	100.0000 *****
292.1170	13.4321 *****
293.1150	14.4689 *****
294.1183	1.9061 *
295.1166	17.1572 *****
296.1200	2.3476 *

Mass Spectrum 3
 Date : 11/01/97 08:00
 Sample: P1012a
 Note: P1012a.mw08 Pex=10000
 Inlet: Direct Ion Mode: FID
 Spectrum Type: Normal Ion (HF-Linear)
 RT: 0.39 min Scan#: 11,4
 BF: m/z: 153.3589 Int.: 43.3
 Output m/z range: 0.0000 to 1000.0000
 Temp: 55.1 deg.C

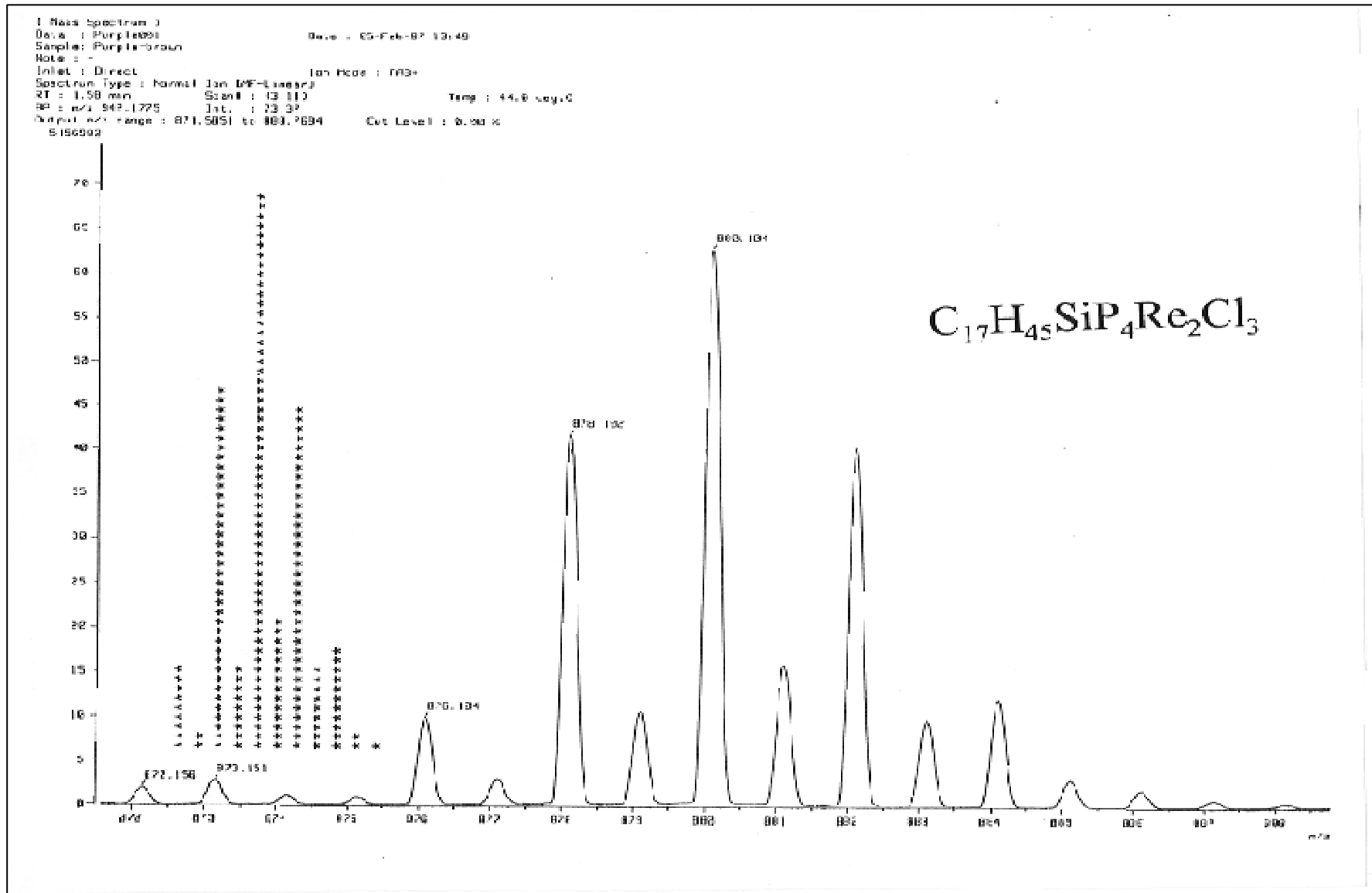
Transition Metal?



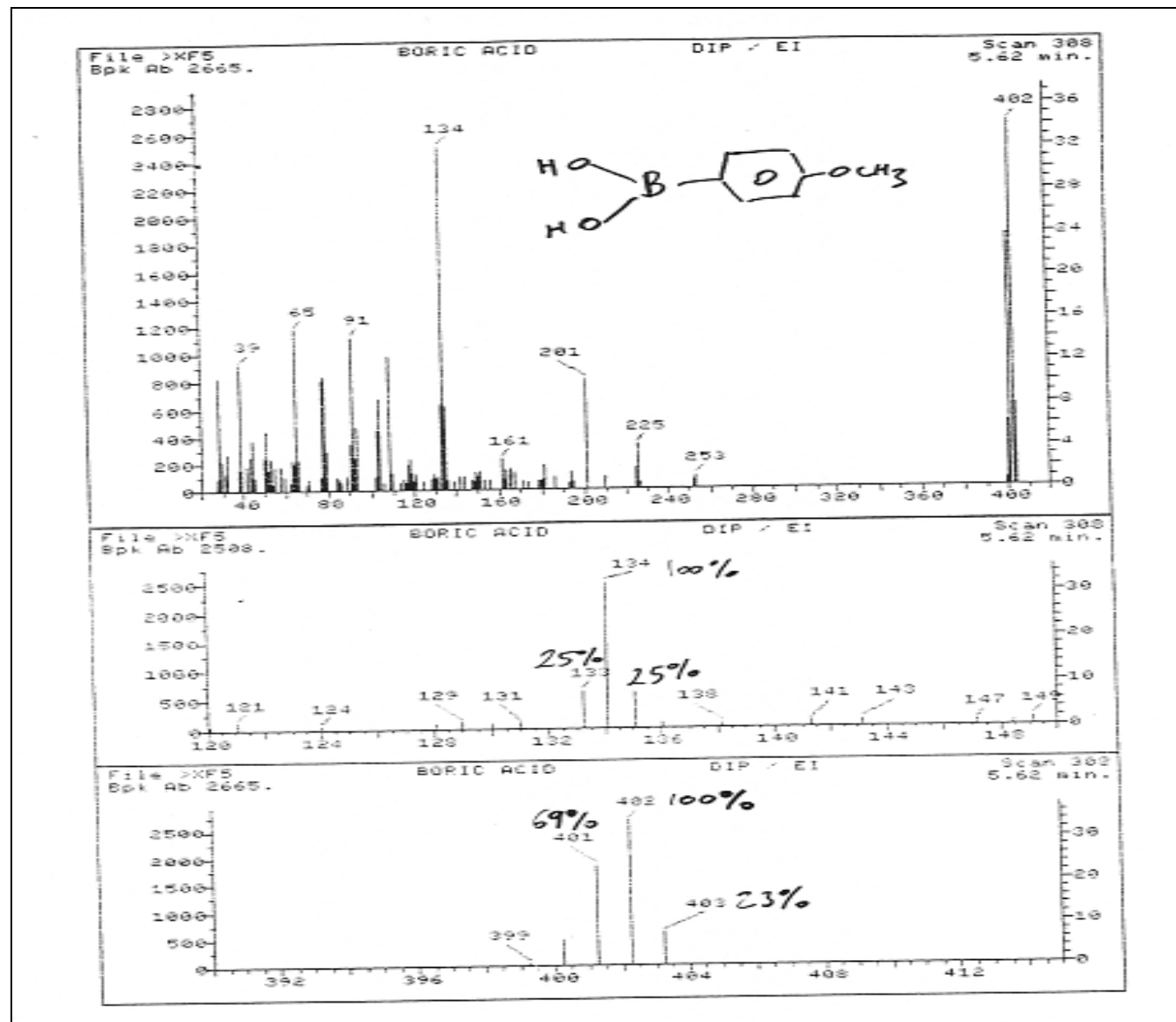
Isotope Ratios to Identify Chemical Compositions...No Accurate Mass!



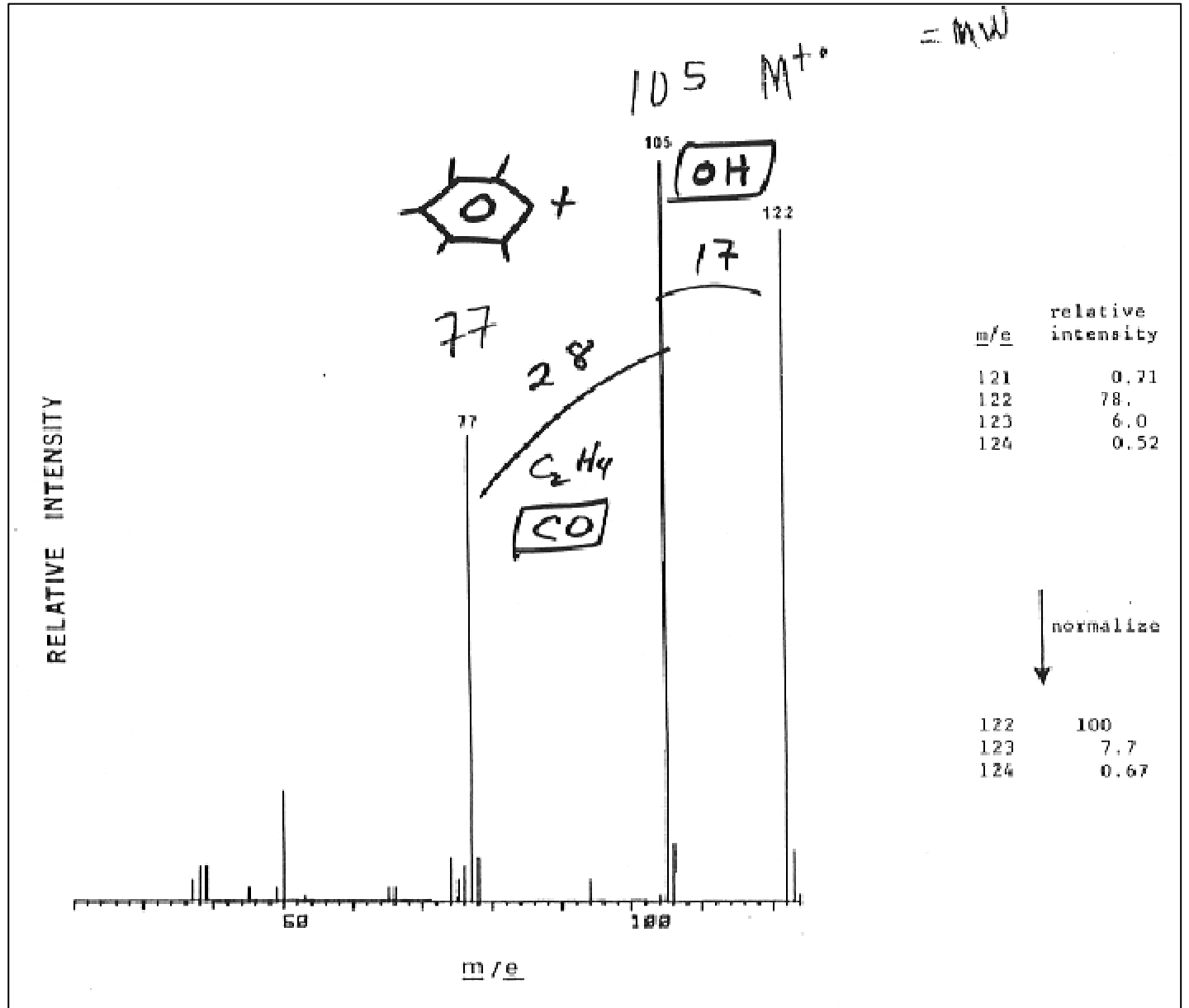
Isotope Ratios to Identify Chemical Compositions...No Accurate Mass!



Isotope Ratios to Identify Chemical Compositions...No Accurate Mass!



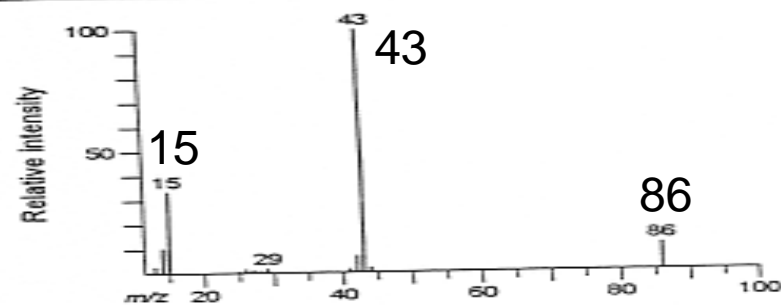
Renormalized Isotope Distribution in the M^+ Region



5.1 General appearance of the spectrum

Unknown 5.2

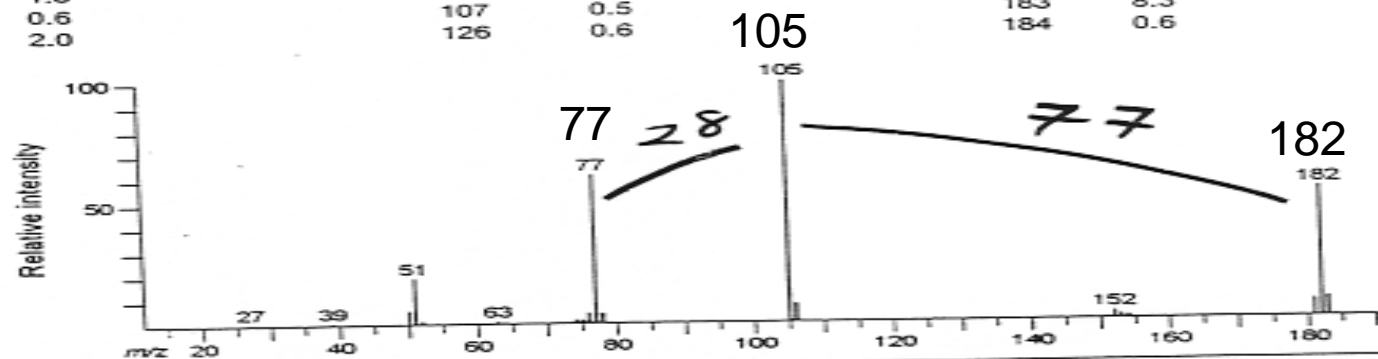
m/z	Int.
15	34.
16	0.5
27	1.4
28	1.0
29	2.0
41	1.8
42	7.2
43	100.
44	2.1
45	0.2
86	11.
87	0.4



Unknowns 5.3 and 5.4 are the spectra of larger molecules producing only a few prominent peaks. In evaluating the m/z 50 and 51 peaks of Unknown 5.3, don't forget that the importance of a peak decreases with decreasing mass, as well as with decreasing abundance.

Unknown 5.3

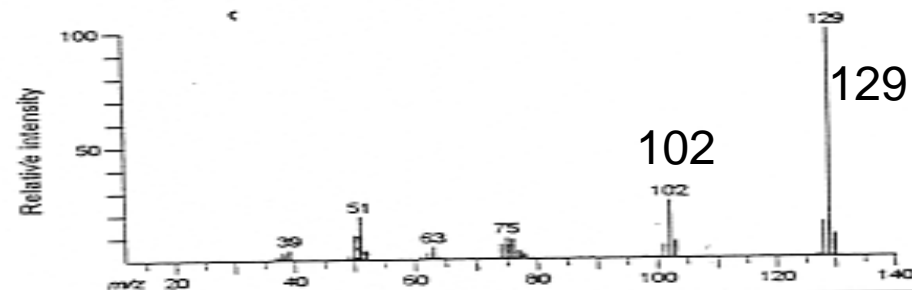
m/z	Int.	m/z	Int.	m/z	Int.
38	0.4	75	1.7	127	0.4
39	1.1	76	4.3	151	1.1
50	6.2	77	62.	152	3.4
51	19.	78	4.2	153	1.8
52	1.4	104	0.4	154	1.4
53	0.3	105	100.	181	7.4
63	1.3	106	7.8	182	55.
64	0.6	107	0.5	183	8.3
74	2.0	126	0.6	184	0.6



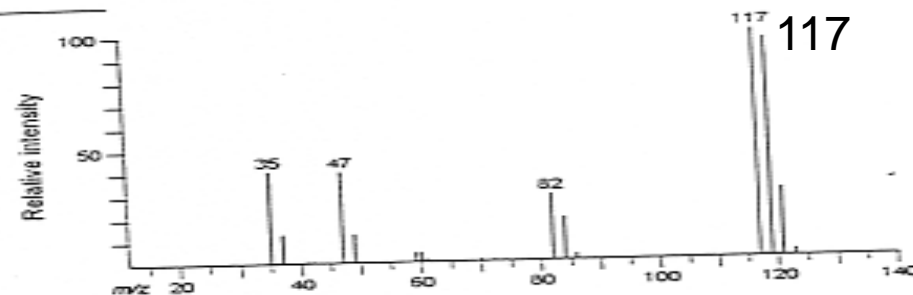
Try these!!

...and these!!

m/z	Int.	m/z	Int.	m/z	Int.
38	3.7	62	3.2	88	0.3
39	4.8	63	5.8	98	1.2
40	0.6	64	1.5	99	0.9
43	0.4	64.5	3.9	100	0.9
49	2.0	65	0.8	101	5.6
49.5	0.6	74	7.1	102	24.
50	12.	75	9.9	103	7.6
50.5	0.4	76	9.0	104	0.6
51	19.	77	3.8	127	1.8
51.5	1.0	78	2.5	128	16.
52	4.2	79	0.5	129	100.
53	0.4	81	0.4	130	10.
		87	0.9	131	0.5



m/z	Int.
35	41.
37	13.
41	1.2
42	0.8
47	40.
48	0.5
49	13.
58.5	4.7
59.5	4.5
60.5	1.4
70	1.4
72	0.9
82	29.
83	0.3
84	19.
85	0.2
86	2.9
117	100.
118	1.0
119	96.
120	1.0
121	30.
122	0.3
123	3.1



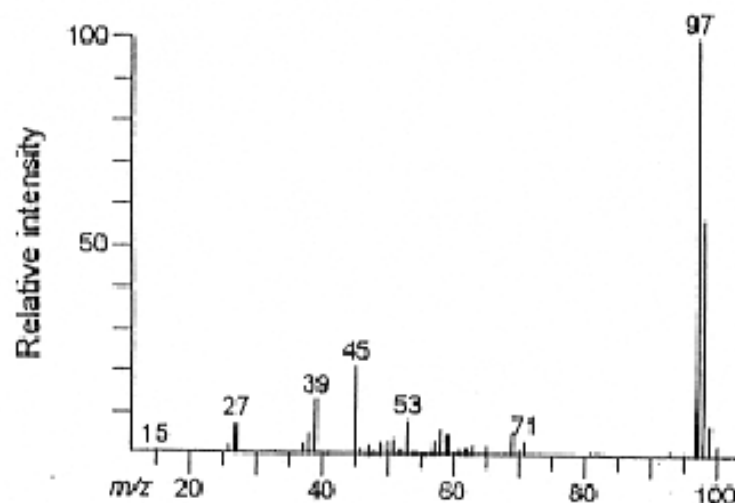
Halogen?

...and this!!

Unknown 4.3

m/z	Int.	m/z	Int.	m/z	Int.
15	1.1	52	1.4	70	1.3
26	3.3	53	8.7	71	3.8
27	8.0	54	0.3	72	0.5
37	4.1	57	3.9	81	0.9
38	4.9	58	6.6	82	1.0
39	13.	59	5.1	83	0.5
40	0.4	60	0.7	95	1.0
45	21.	61	1.6	96	0.6
46	0.9	62	1.9	97	100.
47	1.9	63	3.0	98	56.
48	0.8	64	0.5	99	7.6
49	3.1	65	2.4	100	2.4
50	3.6	68	0.7		
51	4.0	69	6.2		

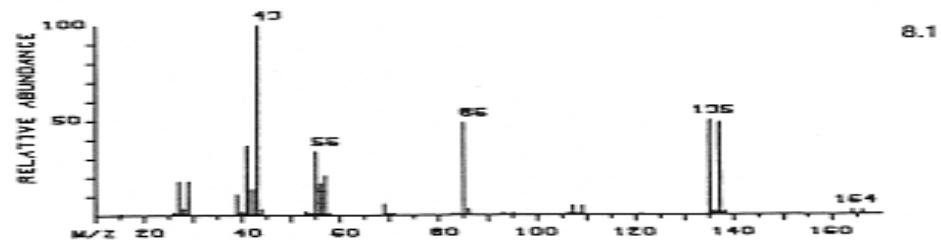
Use Isotope
Distribution in
the M^+ Region



...and these!!

Unknown 8.1. What is unusual about this ion series?

<i>m/z</i>	Rel. abund.	<i>m/z</i>	Rel. abund.	<i>m/z</i>	Rel. abund.
15	0.6	56	17.	106	0.6
27	18.	57	21.	107	5.0
28	3.5	58	0.9	108	0.7
29	18.	69	6.0	109	4.7
30	0.4	70	0.5	121	0.5
39	11.	71	0.5	123	0.4
40	2.1	83	0.7	135	50.
41	37.	84	0.6	136	2.2
42	14.	85	49.	137	49.
43	100.	86	3.2	138	2.1
44	3.4	93	1.2	164	2.2
55	34.	95	1.2	166	2.2

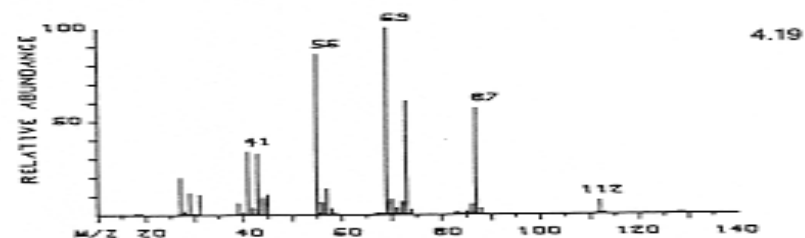


Unknown 4.19 involves some important points that have been covered previously. Be sure you understand its solution before proceeding. The utility of the *m/z* 96.5 peak formed by metastable ion decomposition will be discussed in Section 6.4.

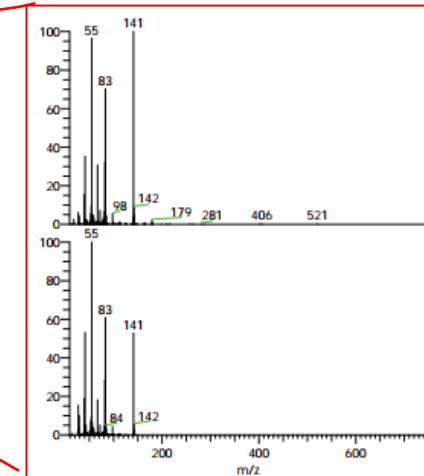
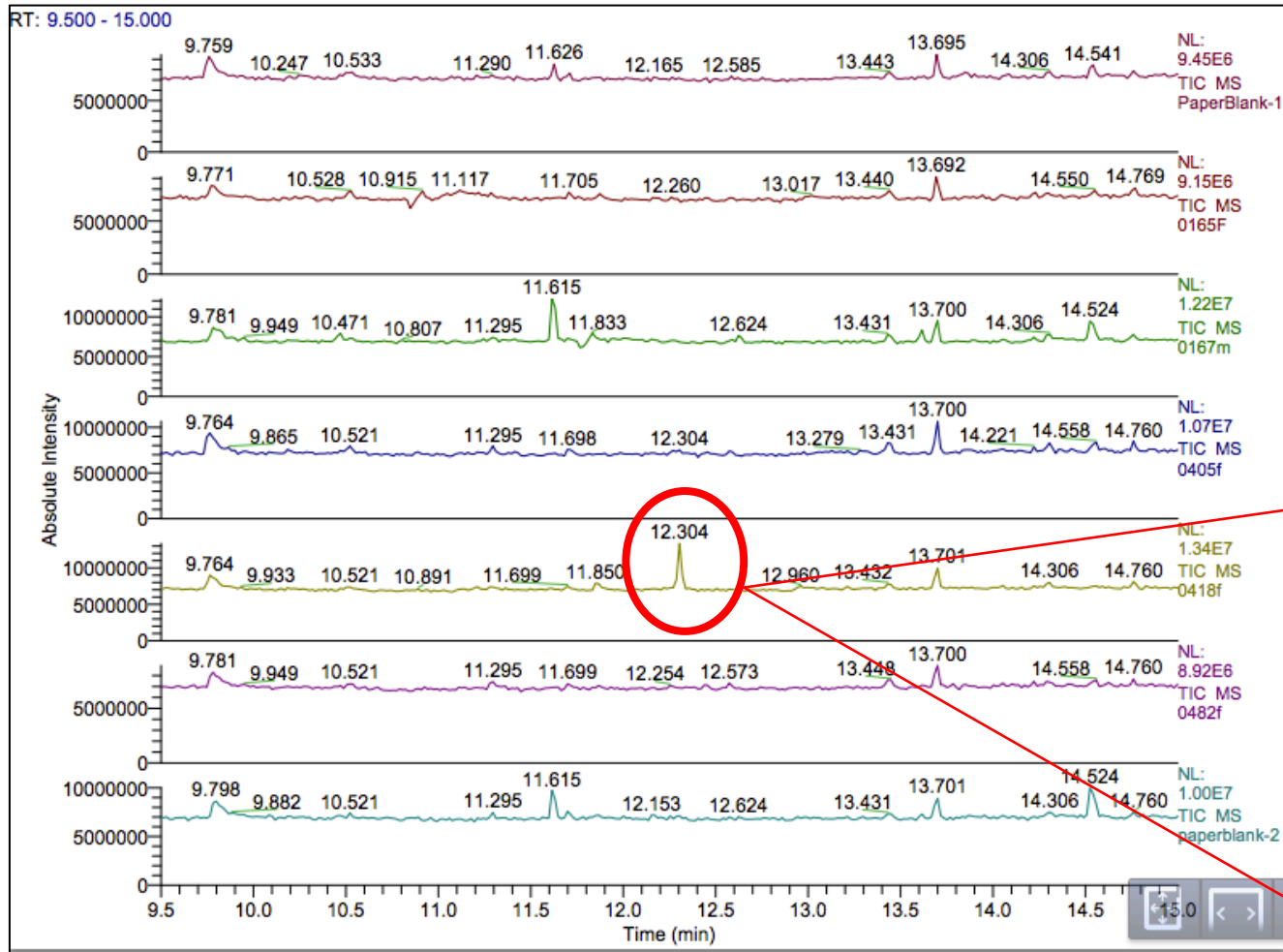
Unknown 4.19

<i>m/z</i>	Rel. abund.	<i>m/z</i>	Rel. abund.	<i>m/z</i>	Rel. abund.
15	0.7	45	11.	84	0.8
18	1.1	46	0.2	85	1.7
19	0.9	55	86.	86	5.6
27	20.	56	6.6	87	57.
28	2.0	57	14.	88	3.4
29	12.	58	3.6	96.5	0.1
30	0.6	59	1.0	112*	7.4
31	11.	69	100.	113	1.0
39	6.4	70	8.4	127	0.3
40	1.0	71	3.7	128	0.5
41	34.	72	7.1	129*	0.9
42	4.0	73	61.	130	0.1
43	33.	74	2.8		
44	9.2	83	1.6		

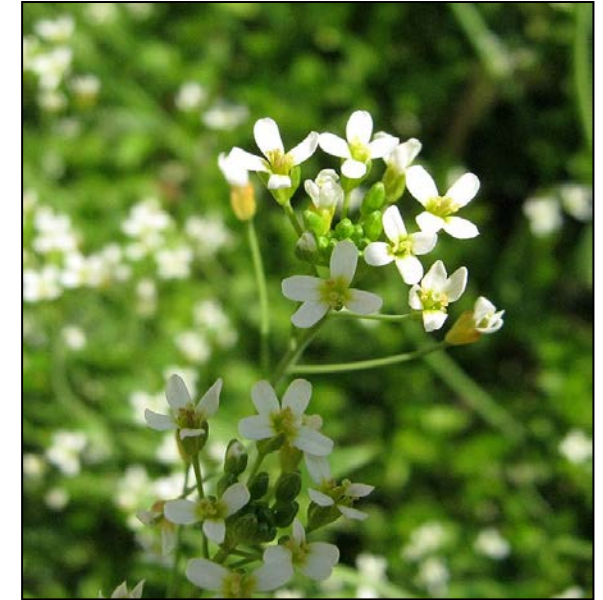
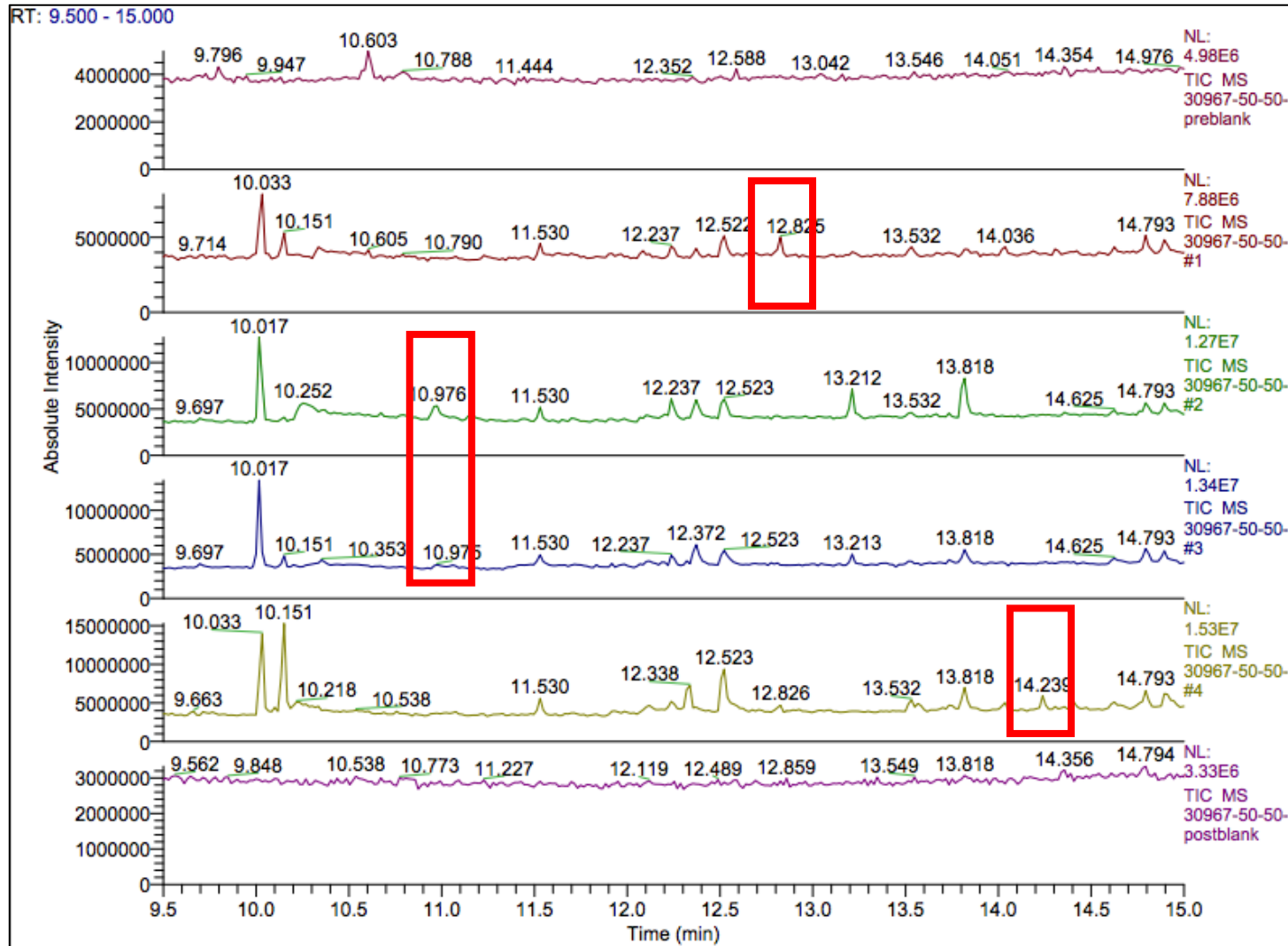
*The elemental compositions of the *m/z* 112 and 129 ions are C_6H_8 and C_6H_8O , respectively, by high-resolution mass spectrometry.



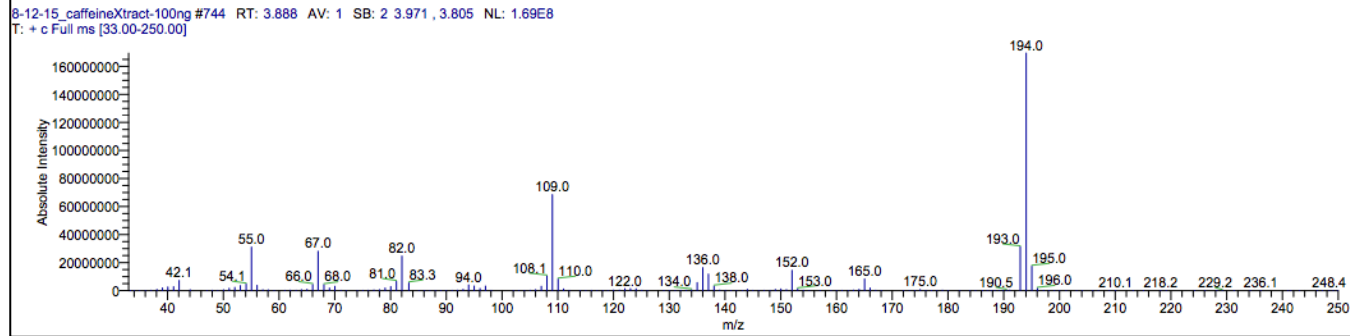
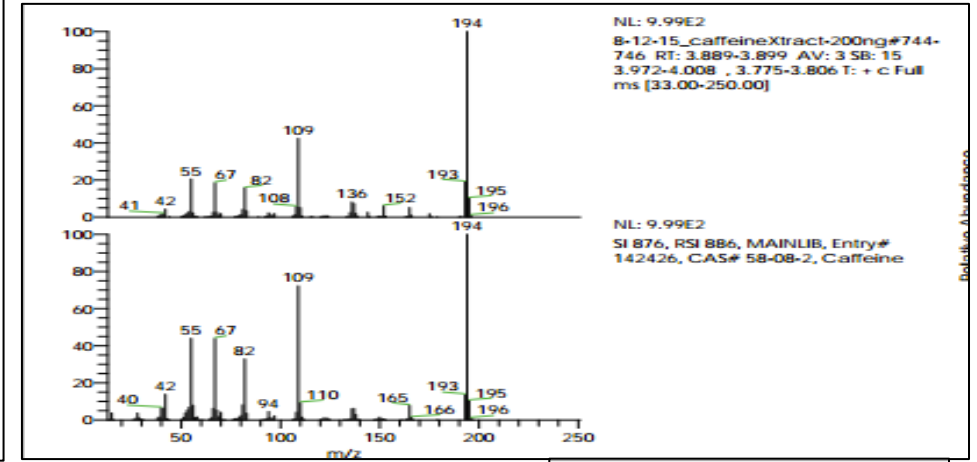
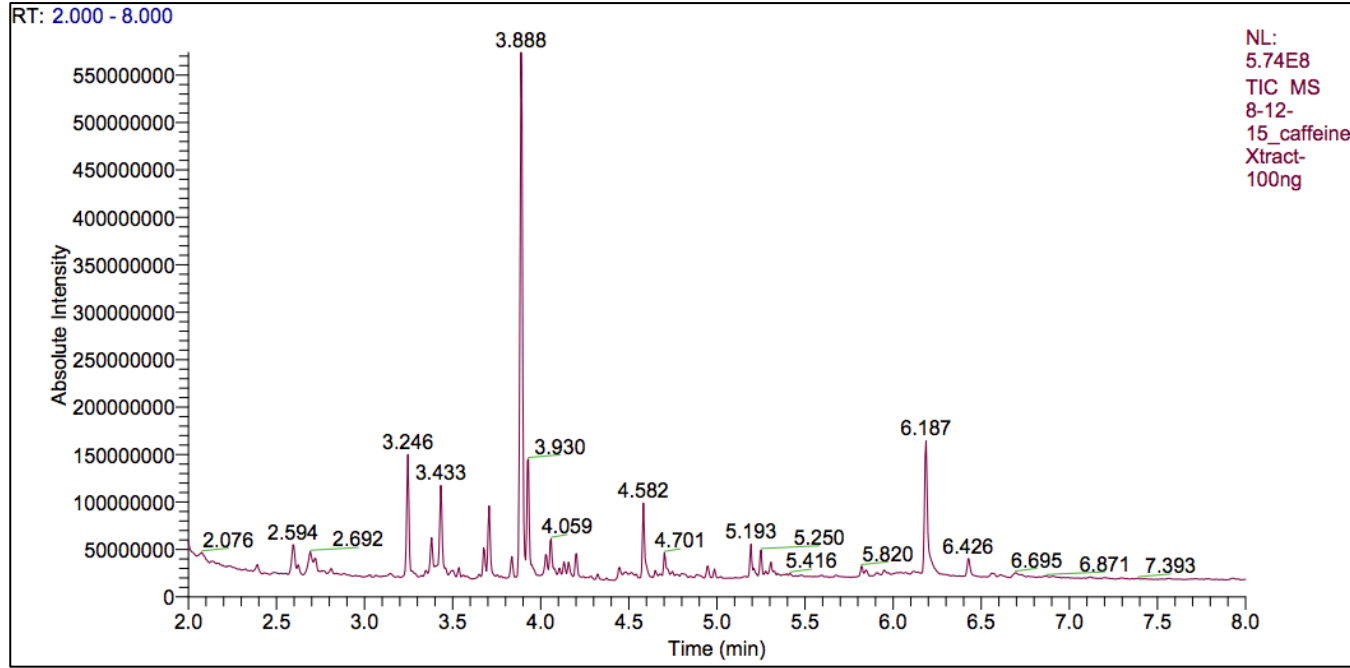
Untargeted GC-MS Analysis of Spider Silk Droppings -the hunt for hormones



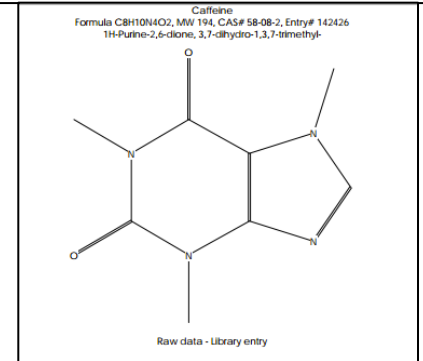
Untargeted GC-MS Analysis of Plants Exposed to Crude Oil



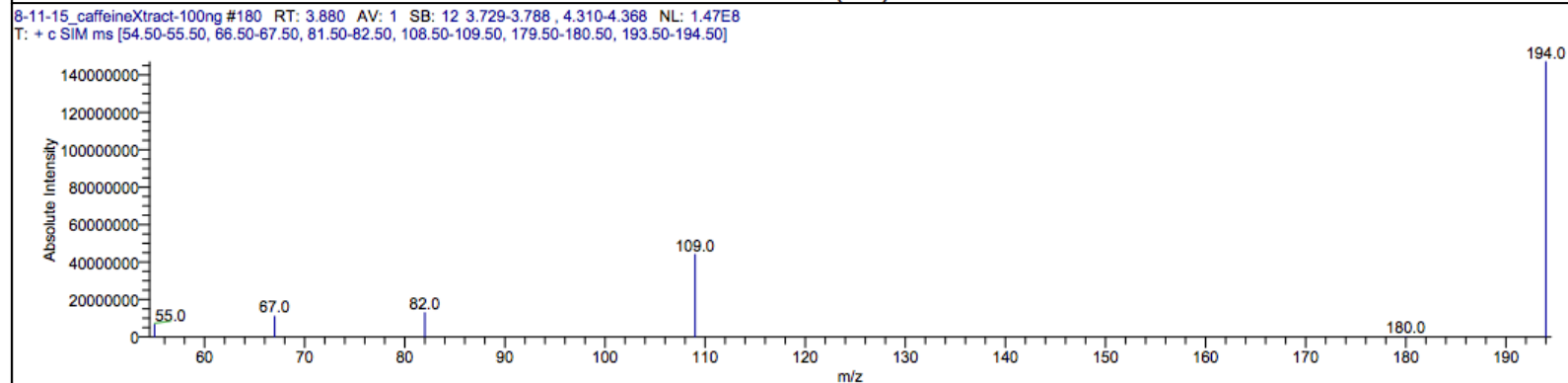
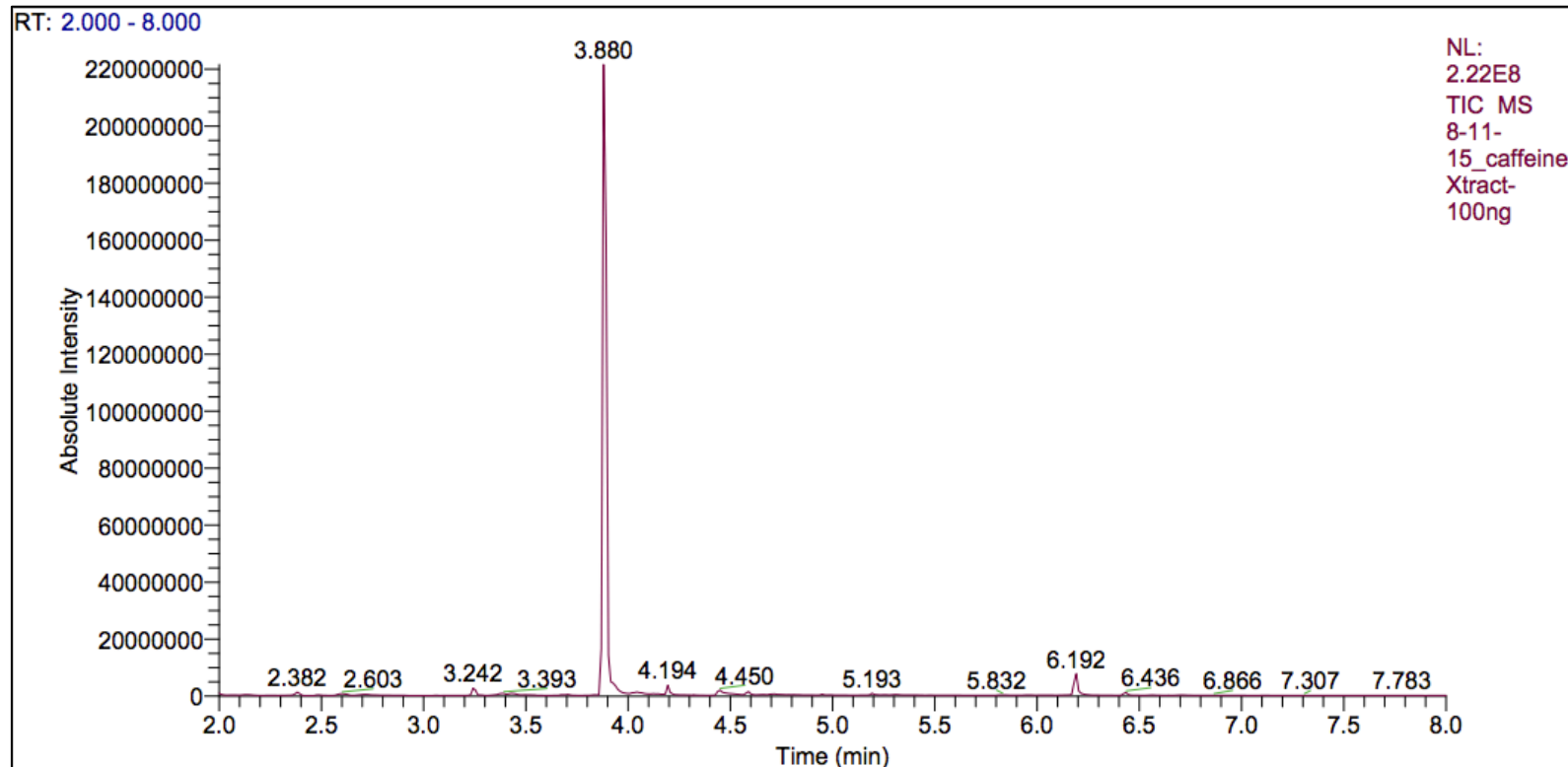
Targeted GC-MS Analysis of Caffeine in Urine-Full Scan



Hit	SI	RSI	Prob	Name	Library Name
1	876	886	95.38	Caffeine	MAINLIB
2	719	733	2.44	1,4-Dimethyl-4,5,7,8-tetrahydroimidazo[4,5-f]pyridine	MAINLIB
3	670	874	0.50	2-Fluorobenzylamine, N,N-dibutyl	MAINLIB
4	663	681	0.38	2-(1,3-Dimethyl-2,6-dioxo-1,2,3,6-tetrahydro	MAINLIB
5	656	707	0.29	6-Amino-1,3-dimethyl-1,6-dihydro-pyrrolo[3,2-b]pyridine	MAINLIB
6	633	640	0.10	Proxiphylline	MAINLIB
7	624	637	0.07	1(2H)-Pyridinecarboxaldehyde, 3,4-dihydro-	MAINLIB
8	622	631	0.07	2H-Pyrazol-3-ol, 5-(2,5-dimethylthiophen-3-yl)	MAINLIB
9	621	629	0.06	2-(1,3-Dimethyl-2,6-dioxo-1,2,3,6-tetrahydro	MAINLIB
10	620	630	0.06	Valerolactimether, (nb)-O-[(diethylboryloxy	MAINLIB



Targeted GC-MS Analysis of Caffeine in Urine-SIM



Quantitative GC-MS Analysis with Xcalibur

The screenshot displays the Xcalibur software interface. On the left, a 'Status' pane shows the 'Acquisition Queue' with a tree view of components: Run Manager (Ready To Download), DSG II (Ready to Download), TRACE GC Ultra (Ready to Download), and TriPlus Autosampler (Ready to Download). The main workspace features a workflow diagram with the following steps:

- Instrument Setup**: Represented by a keypad icon with 'ON-LINE' text. This step is circled in red.
- Sequence Setup**: Represented by an icon of four vials.
- Processing Setup**: Represented by an icon of a chromatogram.
- Results Review**: A central heading for the final stage, which includes three sub-components:
 - Qual Browser**: Represented by a molecular structure icon.
 - Quan Browser**: Represented by a balance scale icon.
 - Library Browser**: Represented by a chemical structure icon.

Arrows indicate the flow from Instrument Setup to Sequence Setup, then to Processing Setup, and finally to the Results Review section.

Xcalibur Method Setup-DSQ II

The screenshot displays the Xcalibur Method Setup software interface for a DSQ II instrument. The window title is "File DSQ II Help". The left sidebar contains three icons: "DSQ II" (circled in red), "TRACE GC Ultra", and "TriPlus Autosampler".

The main configuration area includes the following sections:

- Run parameters:** Includes "GC run time", "Probe run time", and "After" (10.00 minutes).
- Heated zones:** "Ion source (°C): 200".
- Acquisition options:** "Reagent gas" (Methane), "Acquire cal gas" (EI/NICI), "Acquire profile data", and "Acquisition threshold" (0).
- Segment 1:** A table with columns "Seg", "Start", and "Scan events". Row 1: "1", "0.00", "MS".
- Segment 1 parameters:** "Start time (min): 0.00", "Reagent Gas Flow (mL/min): 0.3", "Detector gain" (Use method: 3.00 x 10⁵, Multiplier voltage: 1601 V), "Scan mode" (Full Scan selected, SIM), "Mass range: 50 - 650", "Ions" (Positive selected, Negative), "Tune" (autotune), "Emission current" (Use tune file).
- Scan 1 parameters:** "Total scan time (s): 1.22", "Scan time (s): 1.22", "Rate" (Scans per second: 0.8170, Scan rate (amu/s): 500.0), "Mass defect: (mmu/100 amu): 0".

Two red circles highlight the "DSQ II" icon in the sidebar and the "Full Scan" radio button in the Scan 1 section.

Xcalibur Method Setup-Trace GC Ultra

The screenshot shows the TRACE software interface for method setup. The left sidebar contains icons for DSO II, TRACE GC Ultra (circled in red), and TriPlus Autosampler. The main window displays a temperature profile graph and various method parameters.

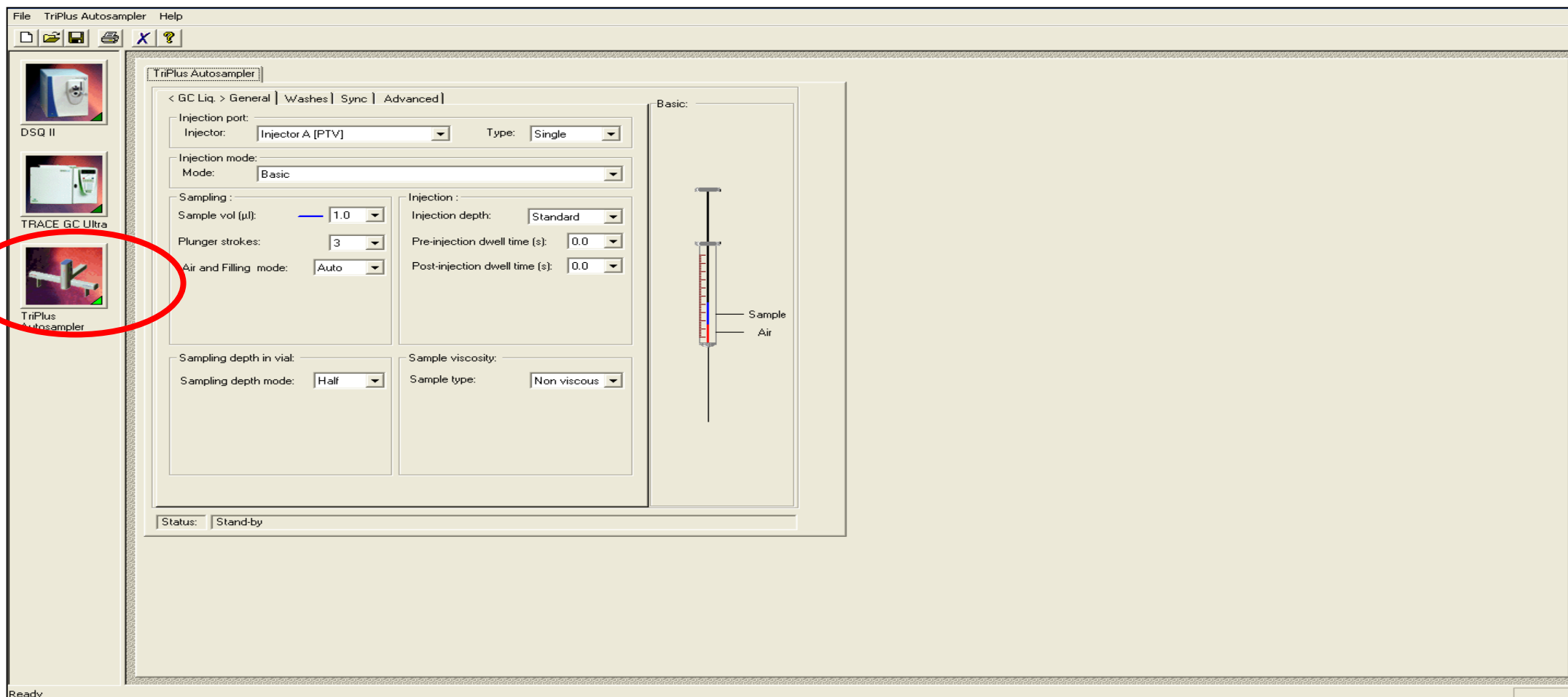
Temperature Profile Graph:

Time (min)	Temperature (°C)
0.00	40
1.00	40
2.00	50
3.00	50

Method Parameters:

Parameter	Value
Initial Temp (°C)	40
Ramp 1 Rate (°C/min)	10.0
Ramp 1 Temp (°C)	50
Hold Time (minutes)	1.00
Post Run Conditions Temperature (°C)	0
Post Run Conditions Time (min)	0
Pressure Left (psi)	0.5
Pressure Right (psi)	0.5
Acquisition Time (min)	3.00
Oven Run-Time (min)	3.00
Specific Time (min)	10.00
Oven Max Temp (°C)	350
Prep Run Timeout (min)	10.00
Equilibration Time (min)	0.50

Xcalibur Method Setup-Autosampler



Xcalibur Processing Method Setup

The screenshot displays the Xcalibur software interface. On the left, a 'Status' pane shows an 'Acquisition Queue' with a tree view containing 'Run Manager', 'DSQ II', 'TRACE GC Ultra', and 'TriPlus Autosampler', each with a 'Ready to Download' sub-item. The main workspace features a central navigation menu with icons for 'Instrument Setup', 'Sequence Setup', 'Processing Setup', 'Qual Browser', 'Quan Browser', and 'Library Browser'. The 'Processing Setup' icon is highlighted with a red circle. A 'Results Review' banner is visible in the background of the main workspace. The top of the window includes a menu bar (File, Actions, View, Tools, GoTo, Help) and a toolbar with 'ONLINE' status, a keyboard icon, and control buttons for play, stop, and help.

Xcalibur Processing Method Setup-Identification

The screenshot displays the Xcalibur software interface for method setup. The 'Identification' tab is active, and the 'Name' field is set to 'acetic_acid'. The 'Detector type' is 'MS' and 'Peak Detect' is 'ICIS'. The 'Filter' is '+ c Full ms [30.00-150.00]'. The 'Retention time' is '4.080' with a 'Window (sec)' of '20.000'. The 'Mass (m/z)' is '60.0'. The 'Keys' field is empty. The 'Components' list on the right includes 'acetic_acid', 'propanoic_acid', 'butyric_acid', and '4_methyl_valeric_'. The bottom section shows two chromatograms: a total ion chromatogram (TIC) on the left and a mass spectrum on the right. The TIC shows a peak at RT: 3.598 - 4.598 SM: 90. The mass spectrum shows a peak at RT: 4.088 AV: 1 NL: 1.33E7. The mass spectrum plot has a y-axis from 0 to 1,200,000 and an x-axis from 40 to 140. The TIC plot has a y-axis from 0 to 5,000,000 and an x-axis from 3.6 to 4.5. The software title bar is 'C:\Xcalibur...400' and the system tray shows '6/9/2015 1:03:45 PM'.

File View Zoom Options GoTo Help

Identification Detection Calibration Levels System Suitability Peak Purity

Name:

Detector type: Peak Detect:

Filter:

Trace:

Mass (m/z):

Retention time
Expected (min): Window (sec):
 Use as RT reference View width (min):
 Adjust using:

Keys:

OK Cancel Save As Default Help

Components
acetic_acid
propanoic_acid
butyric_acid
4_methyl_valeric_

C:\Xcalibur...400 6/9/2015 1:03:45 PM

RT: 3.598 - 4.598 SM: 90

NL: 5.52E6
m/z= 59.5-60.5 F: +
c Full ms
[30.00-
150.00] MS
ICIS 400

400 #527 RT: 4.088 AV: 1 NL: 1.33E7
F: + c Full ms [30.00-150.00]

Ready NUM

Xcalibur Processing Method Setup-Detection

File View Zoom Options GoTo Help

Identification Detection Calibration Levels System Suitability Peak Purity

ICIS Peak Integration

Smoothing points: 9

Baseline window: 40

Area noise factor: 5

Peak noise factor: 10

Constrain peak width

Peak height (±): 5.0

Tailing factor: 1.0

ICIS Peak Detection

Spectrum

Highest peak

Nearest BT

Minimum peak height (S/N): 3.0

Ion ratio confirmation

Enable

Ion ratio using: Area

	m/z	Target Ratio (%)	Window (±%)
1	43.0	100.00	20.00
2	45.0	90.00	20.00
3	60.0	75.00	20.00

Window %

Relative

Absolute

Qualifier ion coelution: 0.025 min

OK Cancel Save As Default Advanced... Flags... Help

Components

- acetic_acid
- propanoic_acid
- butyric_acid
- 4_methyl_valeric_

C:\Xcalibur...M00 6/9/2015 1:03:45 PM

RT: 3.588 - 4.688 SM: 90

NL: 5.52E6
m/z= 59.5-60.5 F: +
e Full ms [30.00-150.00] MS
ICIS 400

400 #527 RT: 4.088 AV: 1 NL: 1.33E7
F: + e Full ms [30.00-150.00]

Ready NUM

Xcalibur Processing Data

The screenshot displays the Xcalibur software interface. At the top, there is a menu bar with 'File', 'Actions', 'View', 'Tools', 'GoTo', and 'Help'. Below the menu bar is a toolbar with icons for 'ONLINE', a printer, a play button, a stop button, and a help icon. On the left side, there is a 'Status' window with a tree view under 'Acquisition Queue'. The tree view shows a hierarchy of folders and items, including 'Run Manager', 'DSQ II', 'TRACE GC Ultra', and 'TriPlus Autosampler', each with a sub-item 'Ready to Download'. The main area of the interface is a large grey panel. In the center of this panel is a workflow diagram. The diagram consists of six icons arranged in two rows. The top row contains 'Instrument Setup' (a keypad icon), 'Sequence Setup' (a vial rack icon), and 'Processing Setup' (a gear icon). The bottom row contains 'Qual Browser' (a chromatogram icon), 'Quan Browser' (a balance scale icon), and 'Library Browser' (a chemical structure icon). The 'Sequence Setup' icon is circled in red. The text 'Results Review' is written in a large, light blue font across the bottom of the workflow diagram.

File Actions View Tools GoTo Help

ONLINE

Status Acquisition Queue

- Run Manager
 - Ready To Download
 - Sequence:
 - Sample Name:
 - Working On:
 - Position:
 - Raw File:
 - Inst. Method:
- DSQ II
 - Ready to Download
- TRACE GC Ultra
 - Ready to Download
- TriPlus Autosampler
 - Ready to Download

ONLINE

ON-LINE

Instrument Setup

Sequence Setup

Processing Setup

Results Review

Qual Browser

Quan Browser

Library Browser

Xcalibur Processing Data

File Edit Change Actions View GoTo Help

Status: Acquisition Queue

- Run Manager
 - Ready To Download
 - Sequence:
 - Sample Name:
 - Working Dir:
 - Position:
 - Raw File:
 - Inst. Method:
- DSQ II
 - Initializing
- TRACE GC Ultra
 - Ready to Download
- TriPlus Autosampler
 - Initializing

Sample	Type	File Name	Path	Inst Meth	Proc Meth	Level	Position	Inj Vol
1	Blank	blank-1	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	1	1.00
2	Std Bracket	50	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	50	2	1.00
3	Blank	blank-2	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	3	1.00
4	Std Bracket	100	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	100	3	1.00
5	Blank	blank-3	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	4	1.00
6	Std Bracket	200	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	200	4	1.00
7	Blank	blank-4	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	5	1.00
8	Std Bracket	400-1	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	400	5	1.00
9	Blank	blank-5	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	6	1.00
10	Std Bracket	800	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	800	6	1.00
11	Blank	blank-6	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	7	1.00
12	Std Bracket	1000	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1000	7	1.00
13	Blank	blank-7	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	8	1.00
14	Unknown	CSD6M1-1	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	8	1.00
15	Blank	BLANK-8	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	8	1.00
16	Unknown	CSD6M1-2	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	8	1.00
17	Blank	BLANK-9	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	9	1.00
18	Unknown	HCCD6M8E2-1	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	9	1.00
19	Blank	BLANK-10	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	9	1.00
20	Unknown	HCCD6M8E2-2	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	9	1.00
21	Blank	BLANK-11	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
22	Unknown	CD6M8-1	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
23	Blank	BLANK-12	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
24	Unknown	CD6M8-2	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
25	Blank	BLANK-13	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
26	Unknown	SDRD6M2-1	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
27	Blank	BLANK-14	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
28	Unknown	SDRD6M2-2	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
29	Blank	BLANK-15	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
30	Unknown	HCCD6M1E2-1	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
31	Blank	BLANK-16	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
32	Unknown	HCCD6M1E2-2	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
33	Blank	BLANK-17	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
34	Unknown	CSD6M13-1	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
35	Blank	BLANK-18	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
36	Unknown	CSD6M13-2	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
37	Blank	BLANK-19	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
38	Unknown	SDRD12M12-1	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
39	Blank	BLANK-20	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
40	Unknown	SDRD12M12-2	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
41	Blank	BLANK-21	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
42	Unknown	HCCD12M4E2-1	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
43	Blank	BLANK-22	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00
44	Unknown	HCCD12M4E2-2	C:\XCALIBUR\DATA\Ross Maltz\06-12-15 Double	C:\Xcalibur\Methods\Ross Maltz\SCFA-split10	C:\Xcalibur\Metho	1	10	1.00

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Xcalibur Exported Results

061215 part 4 out 4 SCFA reprocessed_6-16-15 DA column [Compatibility Mode] - Microsoft Excel

Component Name	Curve Index	Weighting Index	Origin Index	Equation	Exp Amnt	Calc Amnt	Units	Level	%RSD-AMT	Peak Status	Response	Response Type	Equation	Area
acetic_acid	Linear	1/X^2	Ignore	$Y = 1.19048e+006+26002.9 \cdot X$ R ² = 0.9990										
Filename	Sample Type	Sample Name	Sample ID	Exp Amnt	Calc Amnt	Units	Level	%RSD-AMT	Peak Status	Response	Response Type	Equation	Area	
blank-1	Blank Sample		1	NA	0.126		NA	NA	Response Low	1193759.63	Area	$Y = 1.19048e+006+26002.9 \cdot X$	1193759.63	
50	Std Bracket Sample		1	50.000	50.889		2%	50		2513742.63	Area		2513742.63	
blank-2	Blank Sample		1	NA	2.029		NA	NA	Response Low	1243244.11	Area		1243244.11	
100	Std Bracket Sample		1	100.000	96.686		-3%	100		3704599.48	Area		3704599.48	
blank-3	Blank Sample		1	NA	-3.176		NA	NA	Response Low	1107888.44	Area		1107888.44	
200	Std Bracket Sample		1	200.000	199.071		0%	200		6366891.71	Area		6366891.71	
blank-4	Blank Sample		1	NA	-1.368		NA	NA	Response Low	1154914.03	Area		1154914.03	
400-1	Std Bracket Sample		1	400.000	394.692		-1%	400		11453610.16	Area		11453610.16	
blank-5	Blank Sample		1	NA	4.786		NA	NA	Response Low	1314922.08	Area		1314922.08	
800	Std Bracket Sample		1	800.000	796.467		0%	800		21900893.22	Area		21900893.22	
blank-6	Blank Sample		1	NA	1.378		NA	NA	Response Low	1226315.42	Area		1226315.42	
1000	Std Bracket Sample		1	1000.000	1037.689		4%	1000		28173372.27	Area		28173372.27	
blank-7	Blank Sample		1	NA	0.311		NA	NA	Response Low	1198579.96	Area		1198579.96	
CSD6M1-1	Unknown Sample		1	NA	1955.253		NA	NA	Response High	52032639.92	Area		52032639.92	
BLANK-8	Blank Sample		1	NA	4.177		NA	NA	Response Low	1299093.24	Area		1299093.24	
CSD6M1-2	Unknown Sample		1	NA	1984.652		NA	NA	Response High	52797120.53	Area		52797120.53	
BLANK-9	Blank Sample		1	NA	7.115		NA	NA	Response Low	1375498.66	Area		1375498.66	
HCCD6M8E2-1	Unknown Sample		1	NA	486.468		NA	NA		13640033.24	Area		13640033.24	
BLANK-10	Blank Sample		1	NA	2.256		NA	NA	Response Low	1249137.03	Area		1249137.03	
HCCD6M8E2-2	Unknown Sample		1	NA	490.771		NA	NA		13951942.18	Area		13951942.18	
BLANK-11	Blank Sample		1	NA	-0.563		NA	NA	Response Low	1175851.30	Area		1175851.30	
CD6M8-1	Unknown Sample		1	NA	484.574		NA	NA		13790780.25	Area		13790780.25	
BLANK-12	Blank Sample		1	NA	-1.252		NA	NA	Response Low	1157933.64	Area		1157933.64	
CD6M8-2	Unknown Sample		1	NA	484.446		NA	NA		13787451.85	Area		13787451.85	
BLANK-13	Blank Sample		1	NA	3.608		NA	NA	Response Low	1284291.10	Area		1284291.10	
SDRD6M2-1	Unknown Sample		1	NA	539.168		NA	NA		15210399.88	Area		15210399.88	
BLANK-14	Blank Sample		1	NA	3.234		NA	NA	Response Low	1274575.02	Area		1274575.02	
SDRD6M2-2	Unknown Sample		1	NA	543.429		NA	NA		15321189.47	Area		15321189.47	
BLANK-15	Blank Sample		1	NA	-0.559		NA	NA	Response Low	1175945.14	Area		1175945.14	
HCCD6M1E2-1	Unknown Sample		1	NA	678.802		NA	NA		18841264.82	Area		18841264.82	
BLANK-16	Blank Sample		1	NA	-2.110		NA	NA	Response Low	1135603.93	Area		1135603.93	
HCCD6M1E2-2	Unknown Sample		1	NA	686.767		NA	NA		19048399.63	Area		19048399.63	
BLANK-17	Blank Sample		1	NA	6.542		NA	NA	Response Low	1360601.75	Area		1360601.75	
CSD6M13-1	Unknown Sample		1	NA	662.769		NA	NA		18424378.73	Area		18424378.73	
BLANK-18	Blank Sample		1	NA	3.586		NA	NA	Response Low	1283721.00	Area		1283721.00	

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