Chapter 8
Mass Spectrometry

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Mass Spectrometry

- Technique(s) used to measure the masses of ions and their abundances in the gas phase >> molecular weight and structures of compounds

- Consists of following sub-steps
  1. Generation of gas phase molecules (and molecular fragments and atoms) and their ionization
  2. Separation based upon mass (m) to charge (z) ratio (m/z)
  3. Detection

- Hardware
  1. Mass (Ion) source
  2. Analyzer (Filter)
  3. Detector

Overview

https://www.youtube.com/watch?v=NuIH9-6Fm6U

Fragmentation

https://www.youtube.com/watch?v=stIwRio9FeM

More

https://www.youtube.com/watch?v=2oPUyIbPxLo

Hardware

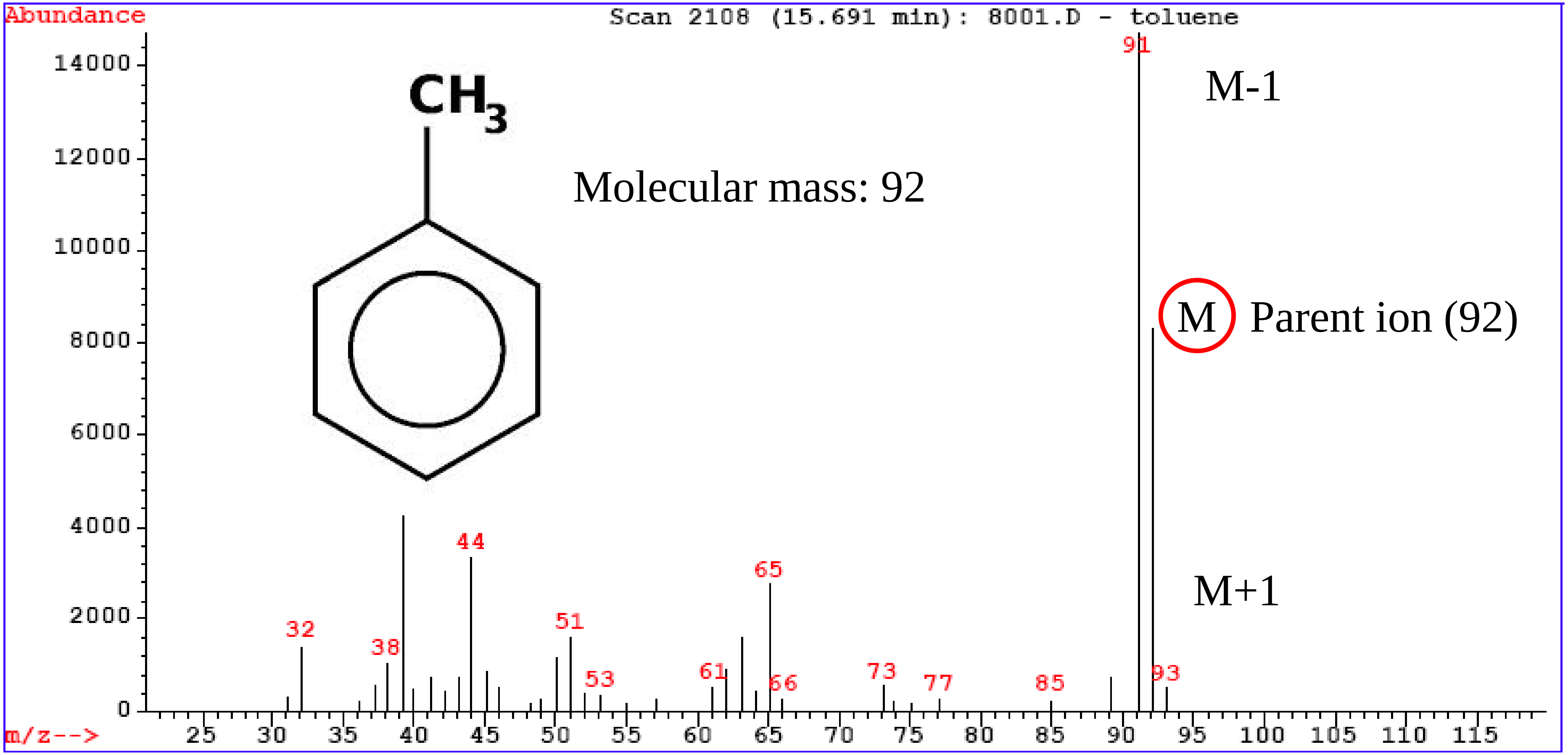
- Mass source (ion source):
  1. Molecules are introduced as a gas, liquid, or solid
  2. Vaporization (liquid and solid)
  3. Ionized (several methods)
  4. Accelerated to analyzer

- Analyzer (filter): several methods
  1. Separation by mass (m/z)
  2. Separation by time (from source to detector)

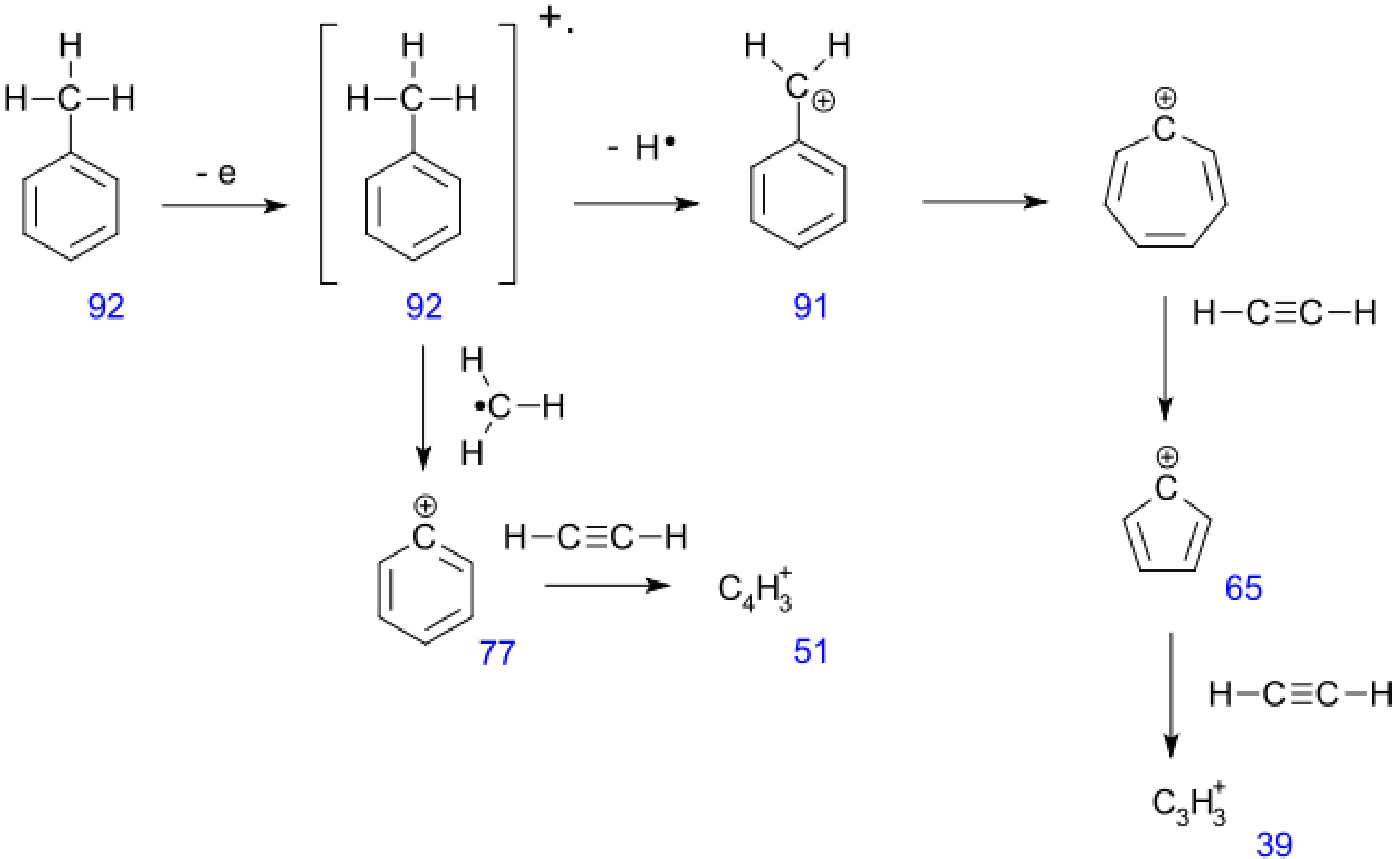
- Detector: count # of ions from analyzer

  Ion multiplier: amplifies current similar to photomultiplier

Presentation of Mass Spectrum



How Molecules are Fragmented

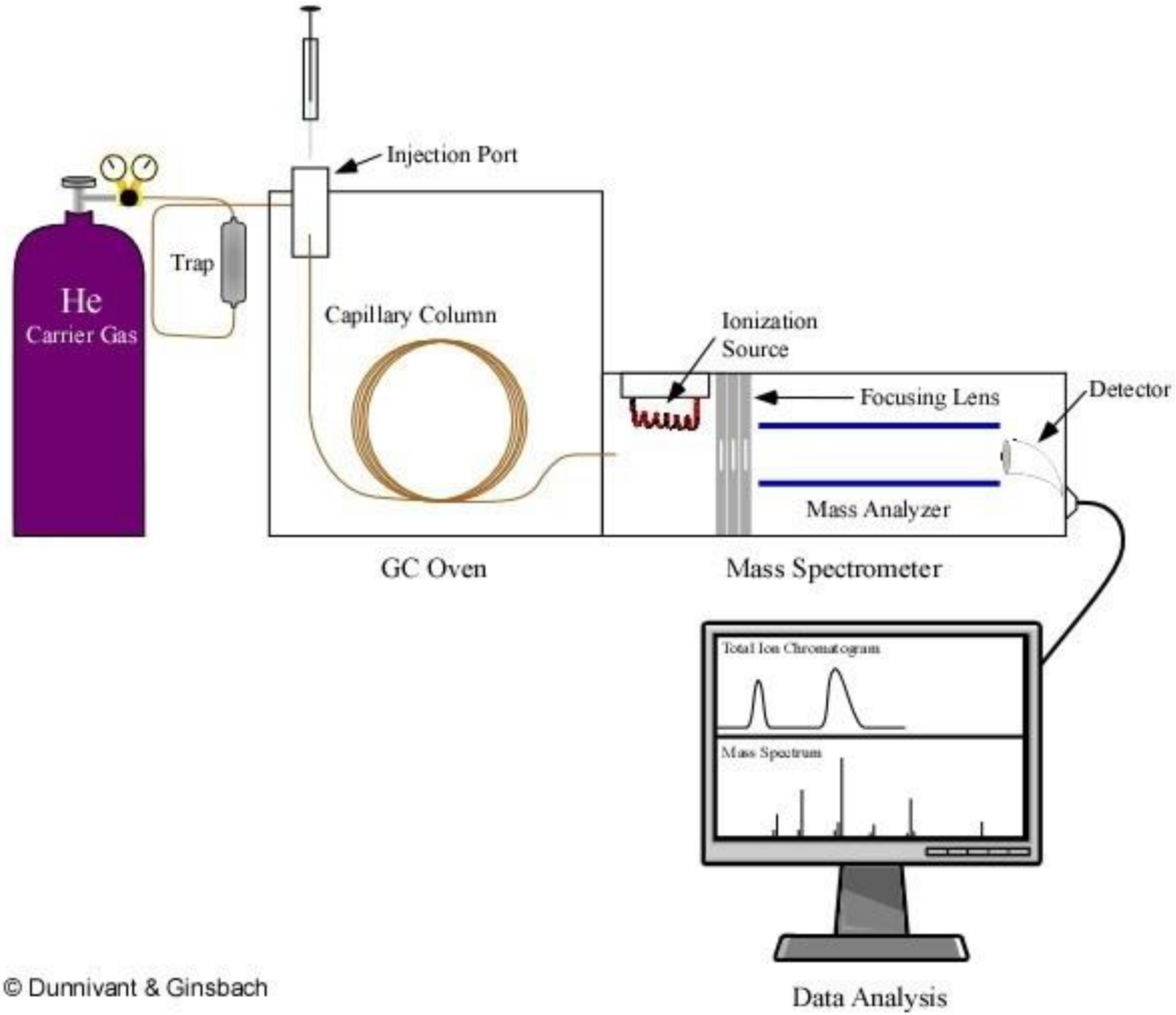


Sample Introduction

- Direct Introduction:
  1. Syringe: Gas (or liquid) samples
  2. Probe tip: Deposited solid samples

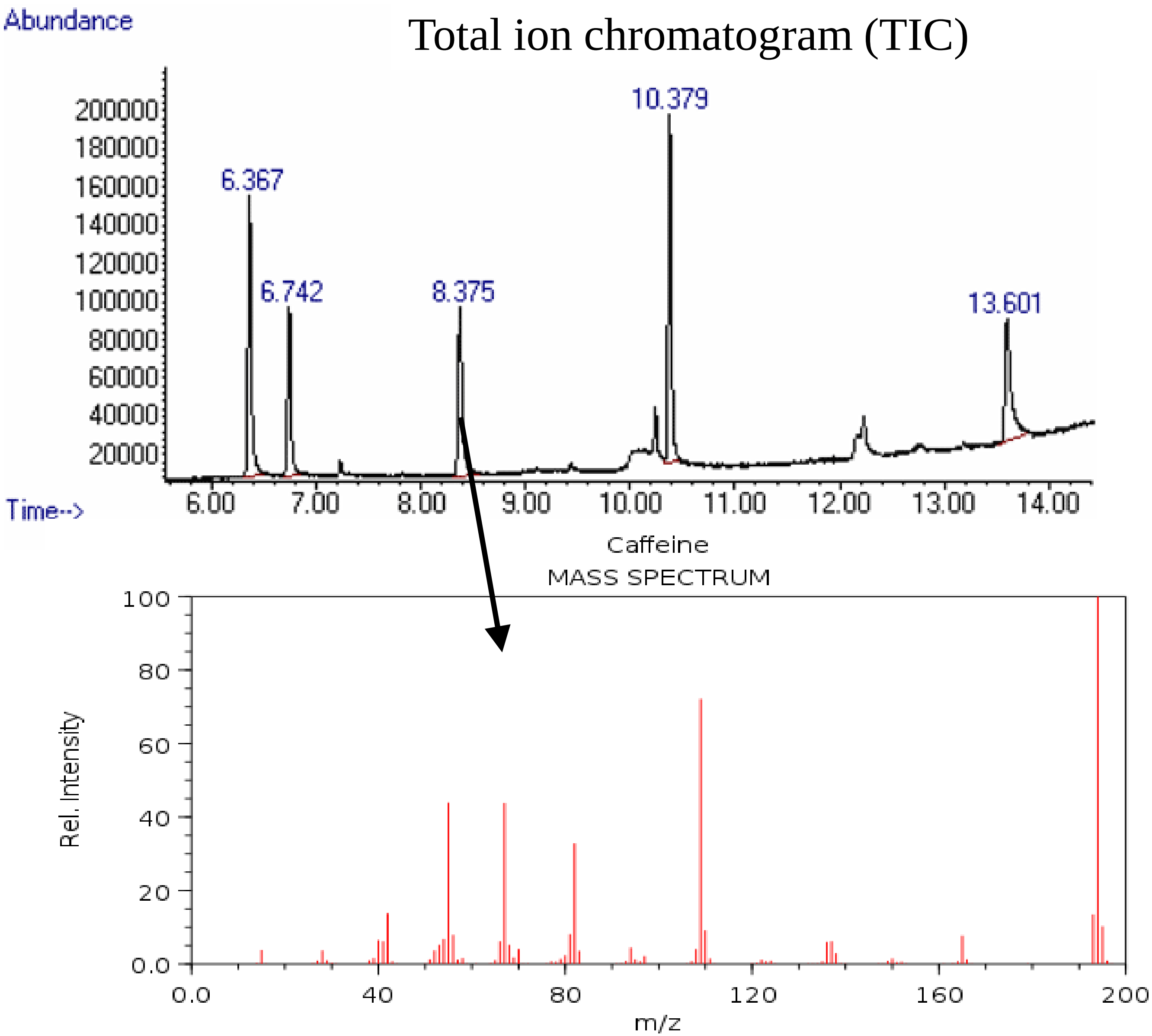
- Introduction via hypernated techniques
  1. GC/MS: GC capillary is directed connected to ionization chamber (protic solvent should be avoided)
  2. LC/MS: Micro-column (short column) to reduce flow rate (water is poisonous to MS)

GC/MS Interface



Typical Data from GC/MS

Total ion chromatogram (TIC)

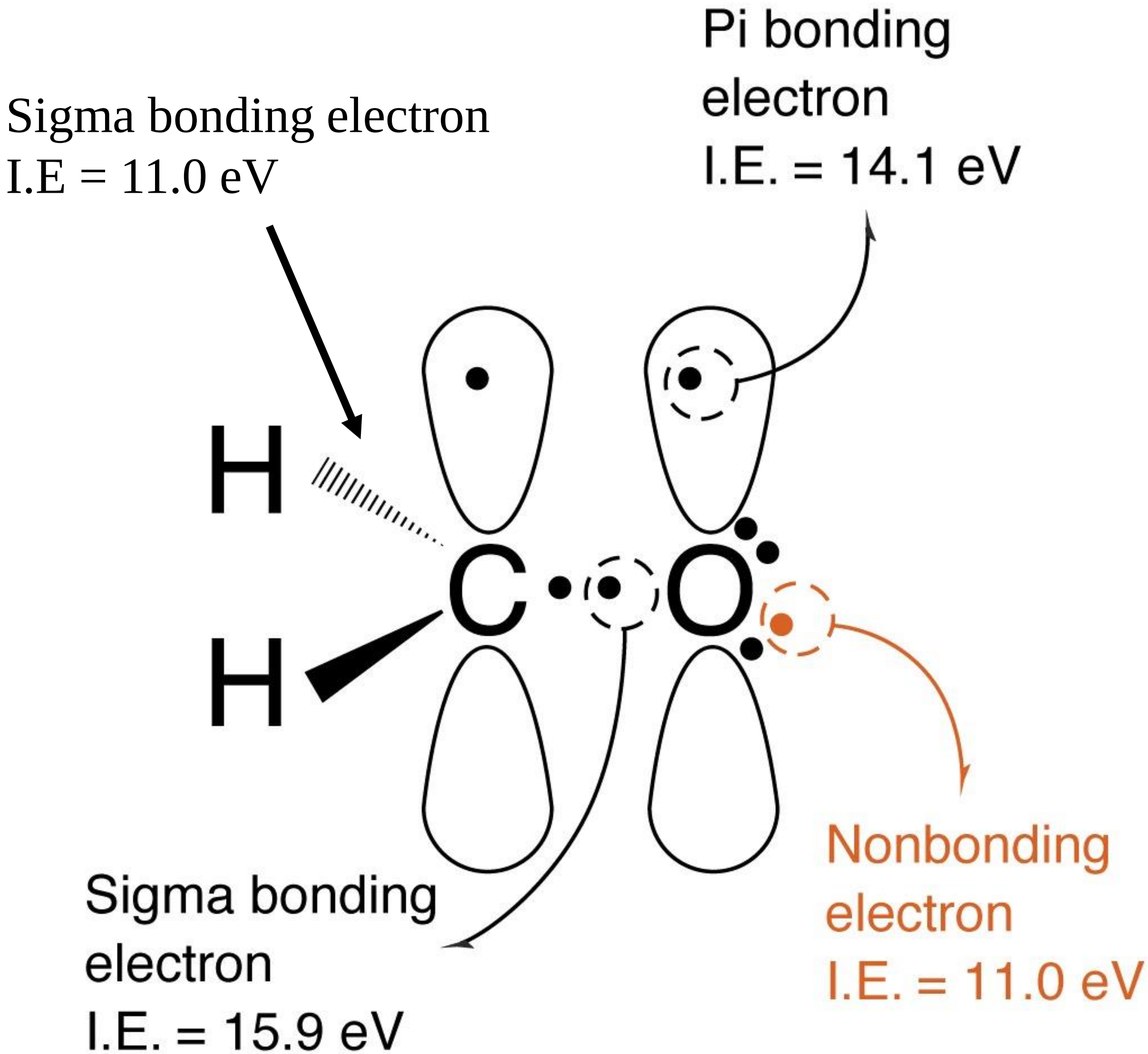


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Similar to chromatograms

Structural information

How to Fragment to Ions

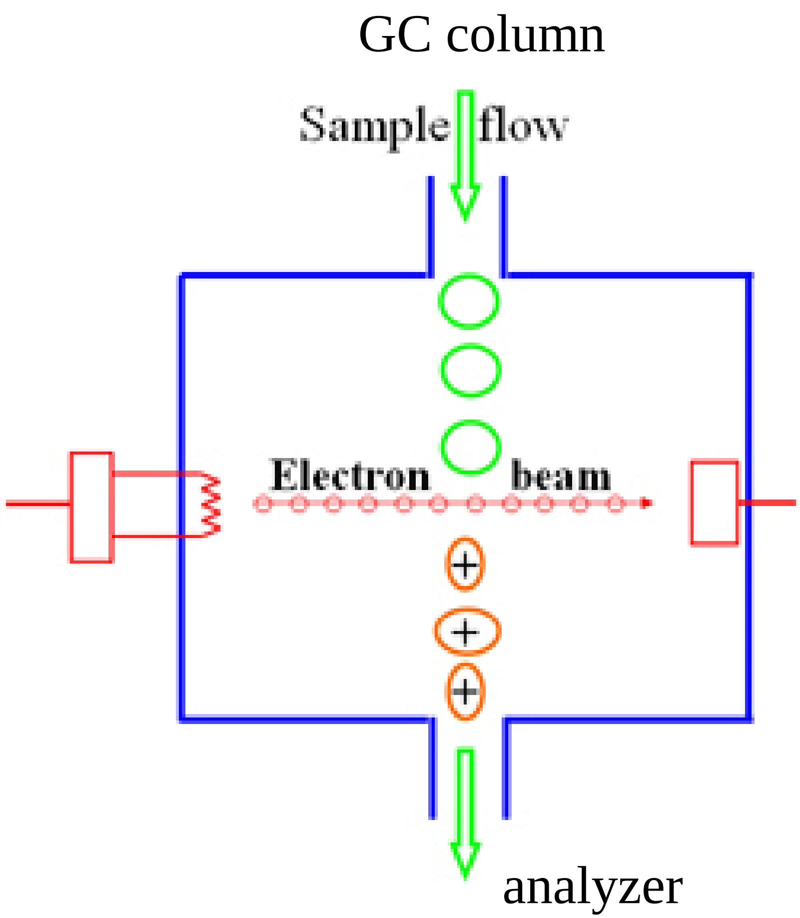


Typical Ionization Methods

- GC-MS
  - EI (electron ionization)
  - CI (chemical ionization)

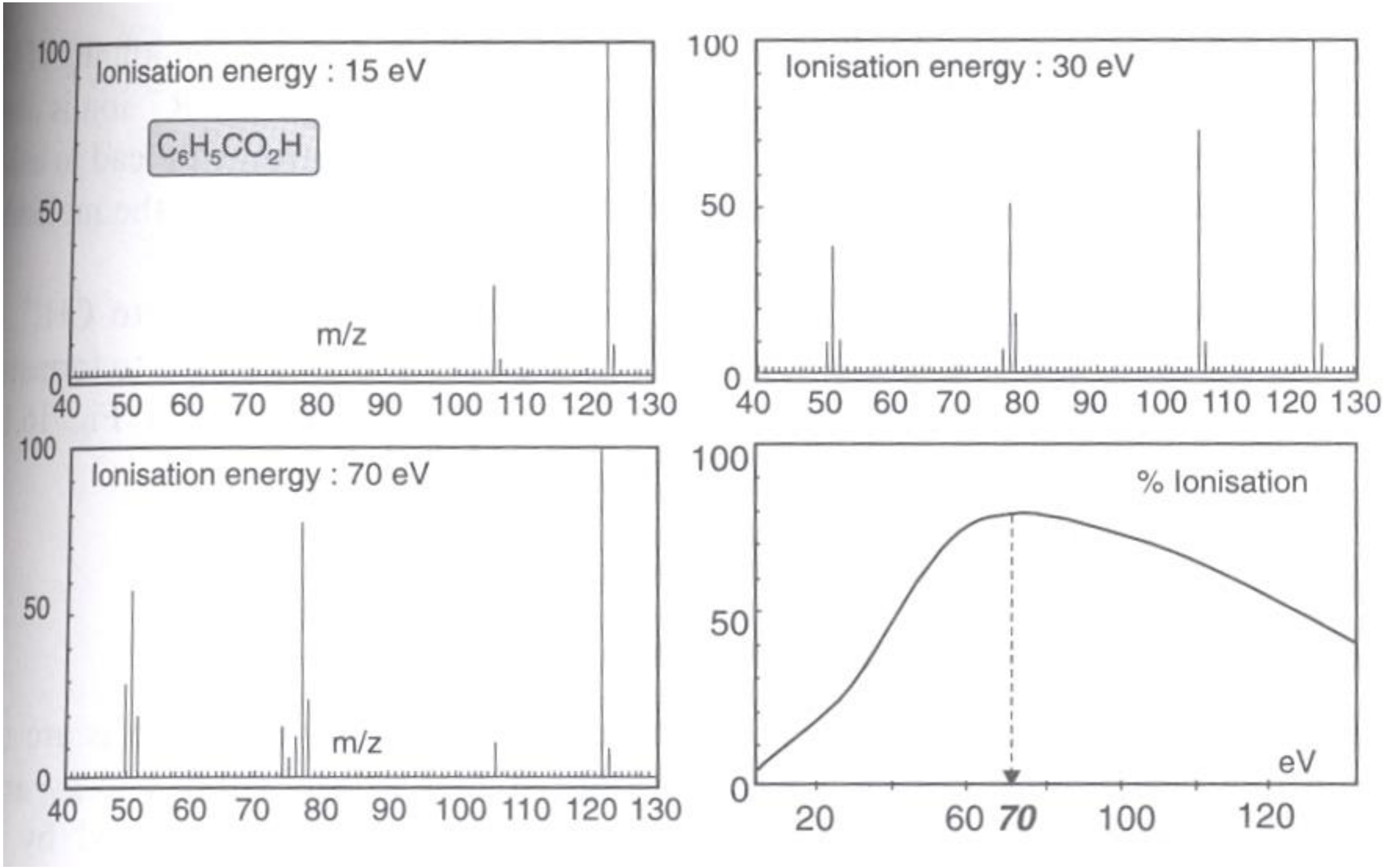
Electron Ionization (EI)

- Ionization via collision of sample molecules with electrons
- Electrons are produced by thermo ionic process (~70 eV)
- Ionization efficiency: ~1/10000 (~0.01%)



Effects of EI on Fragmentation

$C_6H_5CO_2H$ (Benzoic acid, MW 122.12)



Chemical Ionization (CI)

- Ionization via collision of sample molecules ionized reagent gases with hydrogen (CH_4, NH_3, etc)
- Soft ionization (high concentration of M+1)

Primary reactions :

$$CH_4 + e^- \longrightarrow CH4]^{+\bullet} + 2\,e^- \quad \textit{(Ionisation)}$$

Secondary reactions :

$$CH_4]^{+\bullet} \longrightarrow CH_3]^+ + H^\bullet$$

$$CH_4]^{+\bullet} + CH_4 \longrightarrow CH_5]^+ + CH_3^\bullet \quad \textit{(Autoprotonation)}$$

$$CH_3]^+ + CH_4 \longrightarrow C_2H_5]^+ + H_2$$

Collisions with M :

$$CH_5]^+ + M \longrightarrow MH]^+ + CH_4 \quad \text{(ion at M+1)}$$

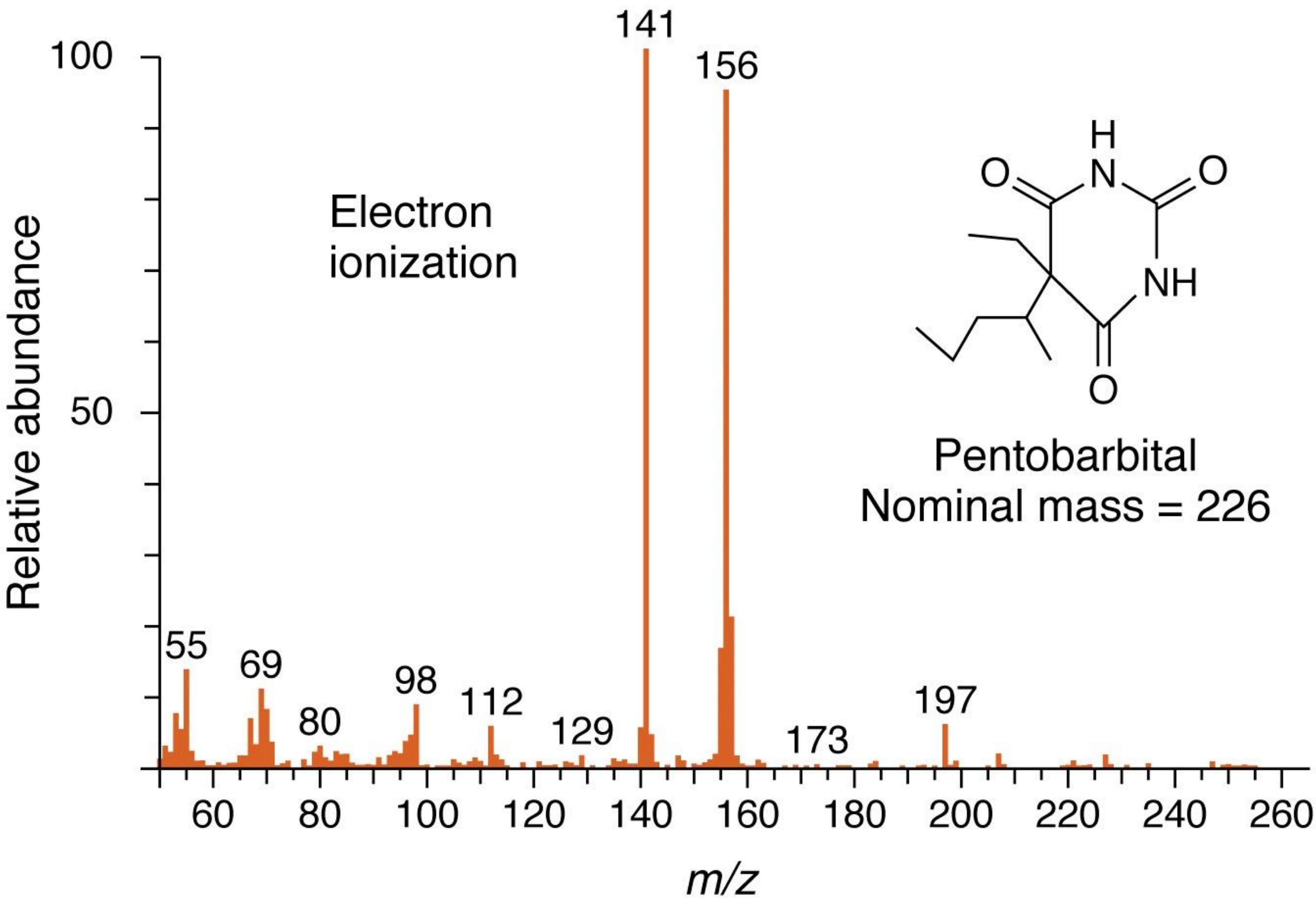
$$C_2H_5]^+ + M \longrightarrow MC_2H_5]^+ \quad \text{(ion at M+29)}$$

If M is of the type RH :

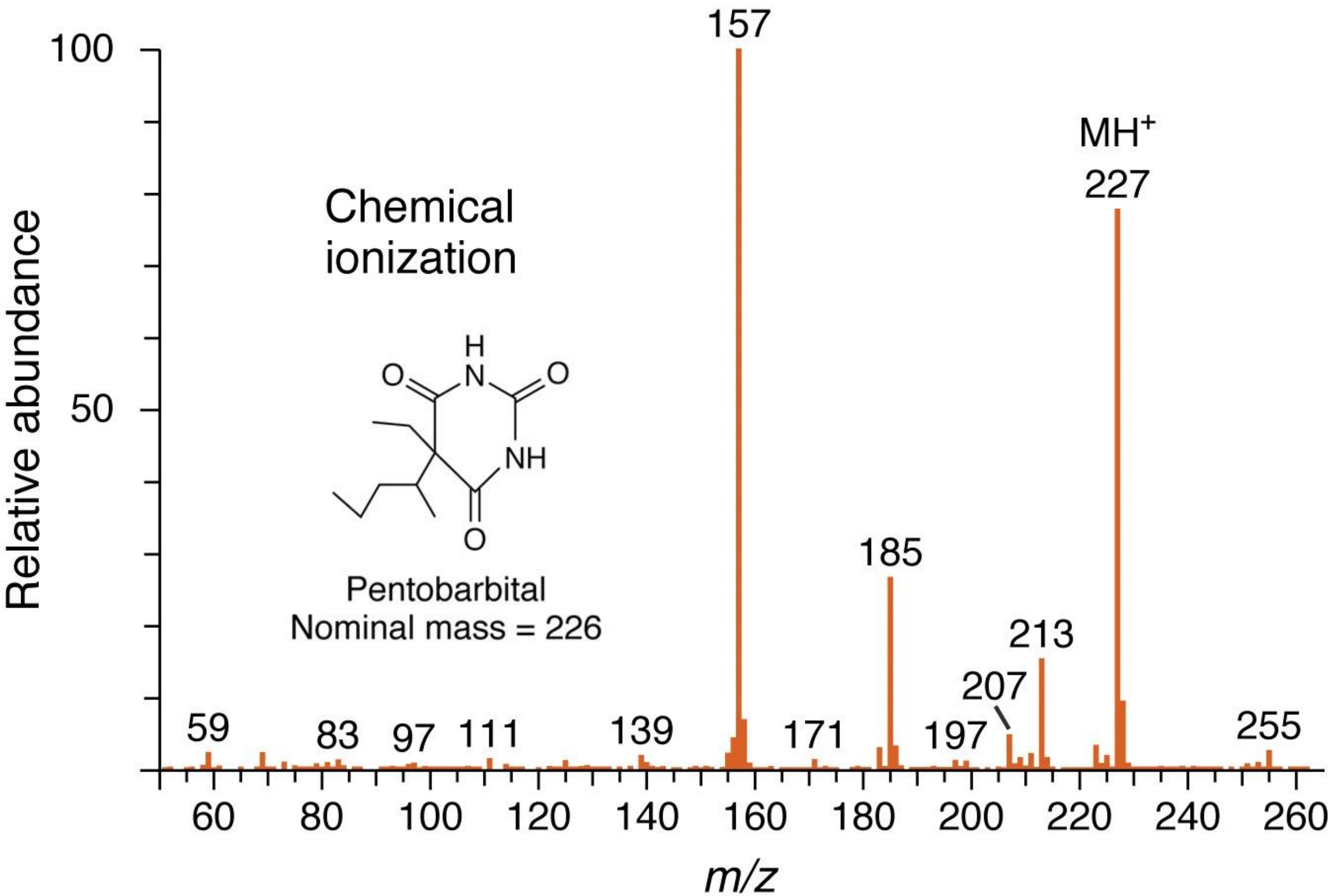
$$CH_5]^+ + RH \longrightarrow R^+ + CH_4 + H_2 \quad \text{(ion at M-1)}$$

If it is a tert-butyl cation :

$$(CH_3)_3C]^+ + M \longrightarrow MH]^+ + CH_2{=}C(CH_3)_2$$



141
156
100
50
Relative abundance
Electron
ionization
Pentobarbital
Nominal mass = 226
H
N
O
O
NH
O
55
69
80
98
112
129
173
197
60
80
100
120
140
160
180
200
220
240
260
m/z



Chemical
ionization
Pentobarbital
Nominal mass = 226
MH+
227
157
185
213
207
197
171
139
111
97
83
59
255
Relative abundance
100
50
60
80
100
120
140
160
180
200
220
240
260
m/z
H
N
O
O
NH
O

Ion Analyzers

- Make use of m/z (mass/charge ratio) of ions and their speeds
- Magnetic analyzer (EB type)
- Time of flight (TOF) analyzer
- Quadrupole analyzer
- Ion traps (Orbitrap)

Time-of-Flight

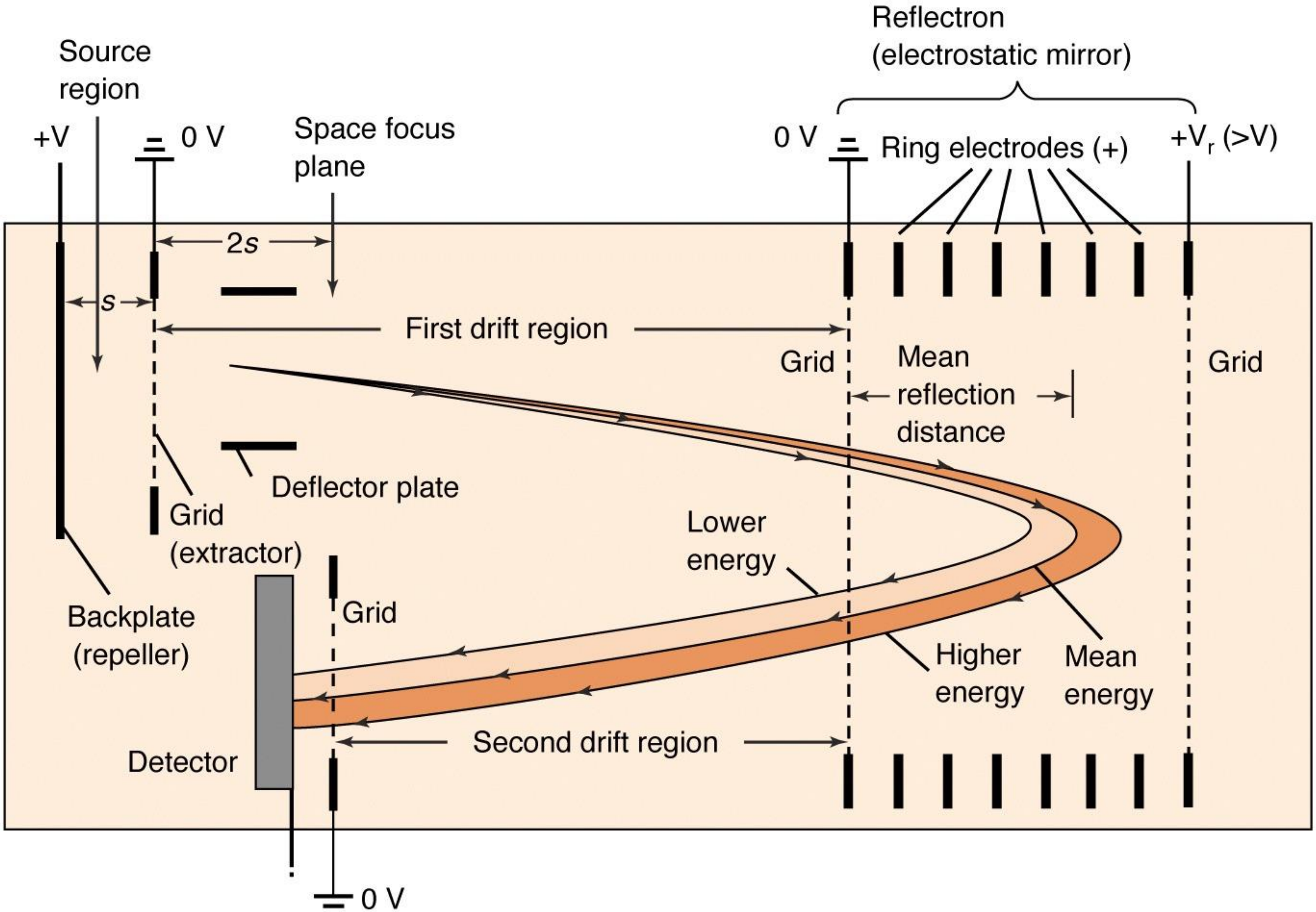
V

Energy gain: $\boldsymbol{E = zV}$ Kinetic energy $\frac{mv^2}{2}$

$$\frac{mv^2}{2} = zV, \text{or } v^2 = \frac{2zV}{m}$$

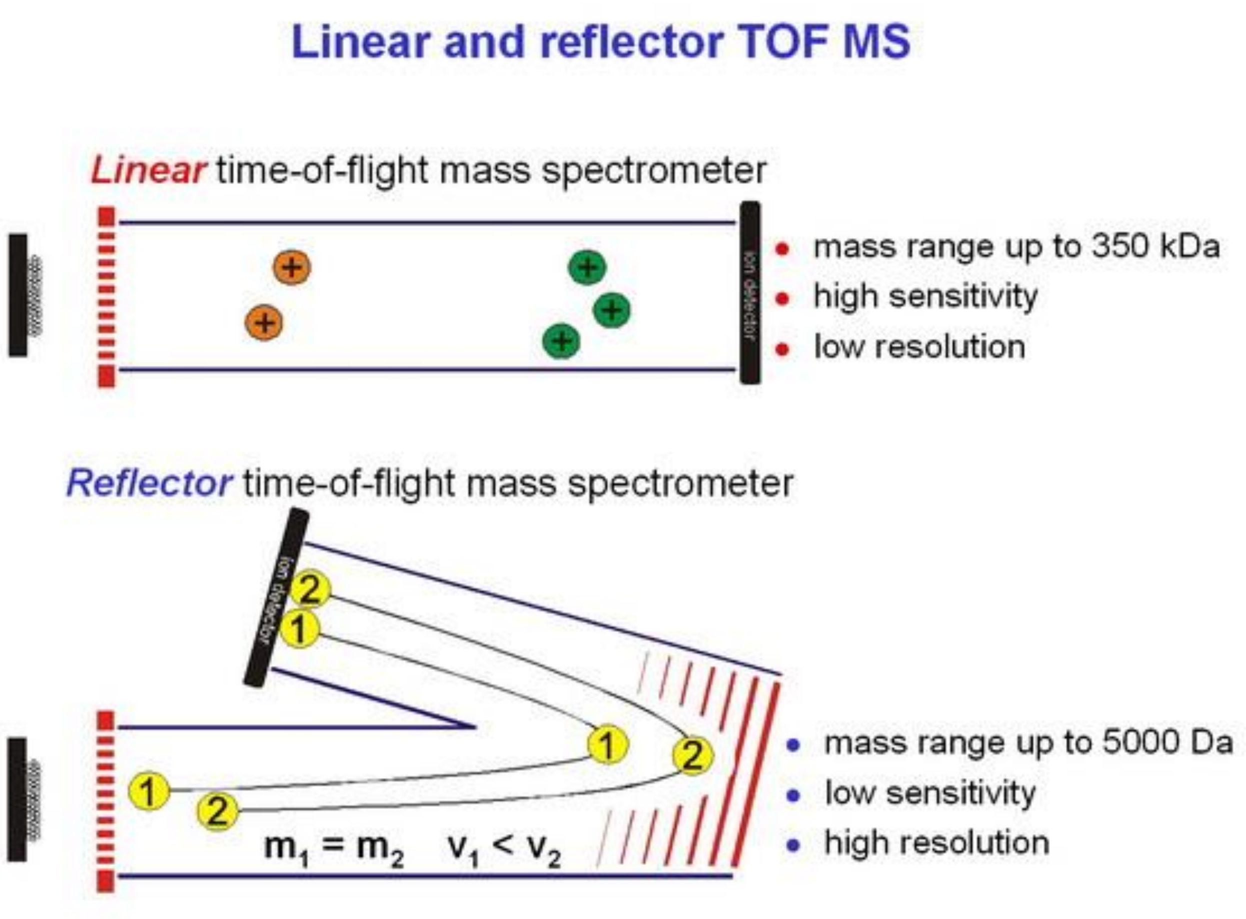
$$v = \sqrt{\frac{2zV}{m}}$$

$$time = \frac{length}{v} = length \times \sqrt{\frac{m}{2zV}} = const \times \sqrt{\frac{m}{z}}$$


Reflectron
(electrostatic mirror)
Source
region
+V
0 V
Space focus
plane
0 V
Ring electrodes (+)
$+V_r$ (>V)
2s
s
First drift region
Grid
Mean
reflection
distance
Grid
Deflector plate
Grid
(extractor)
Lower
energy
Backplate
(repeller)
Grid
Higher
energy
Mean
energy
Second drift region
Detector
0 V

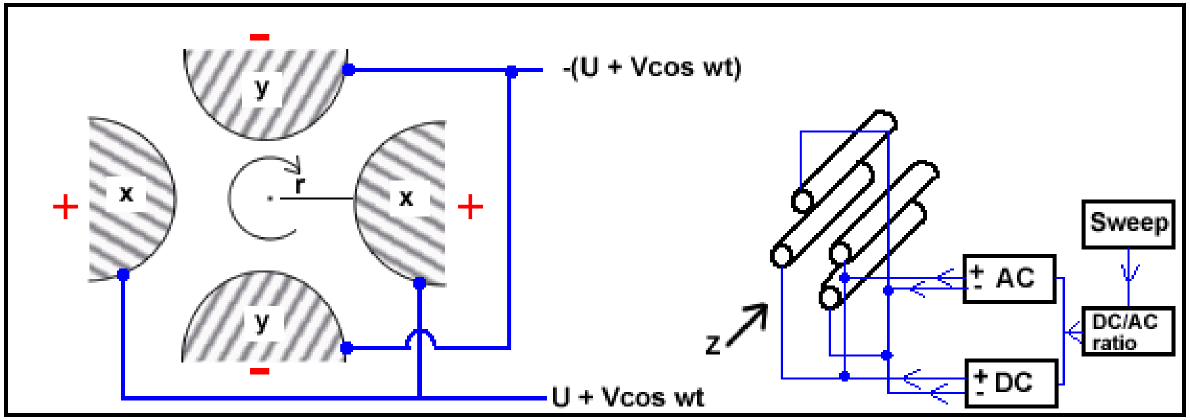
Time of Flight (TOF) Analyzer

- Ions should have same kinetic energy ($E = \frac{1}{2}mv^2$)
- Lighter ions travel fast than heavier ones
- Ions > 300 kD (proteins)

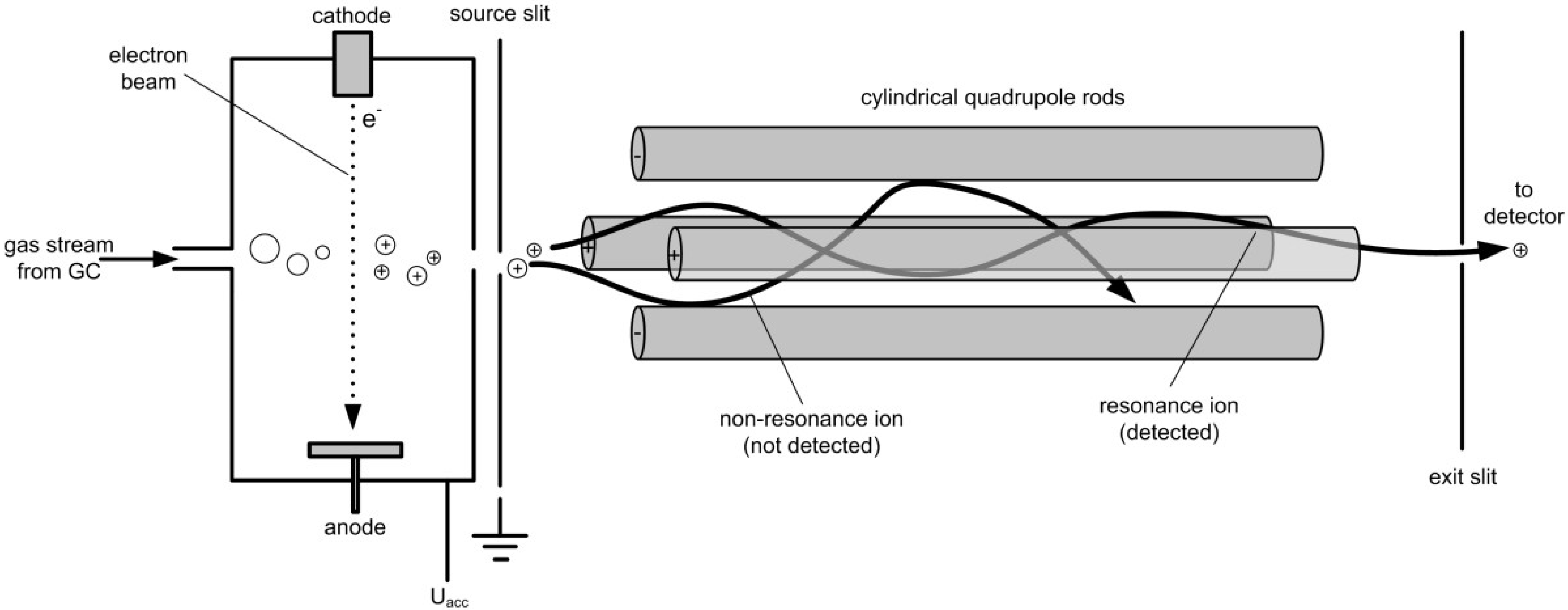


Quadrupole Analyzer

- Commonly account in GC/MS or LC/MS
- Positive ions enter quadrupole,
  - it will move along O-z direction
  - Two positive electrode: focusing by repulsion
  - Two negative electrode: defocusing by attraction



Mass Selection by Changing Field Strength

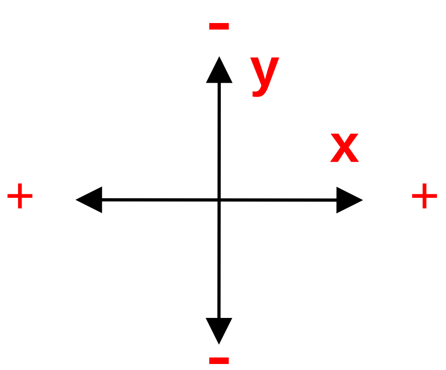


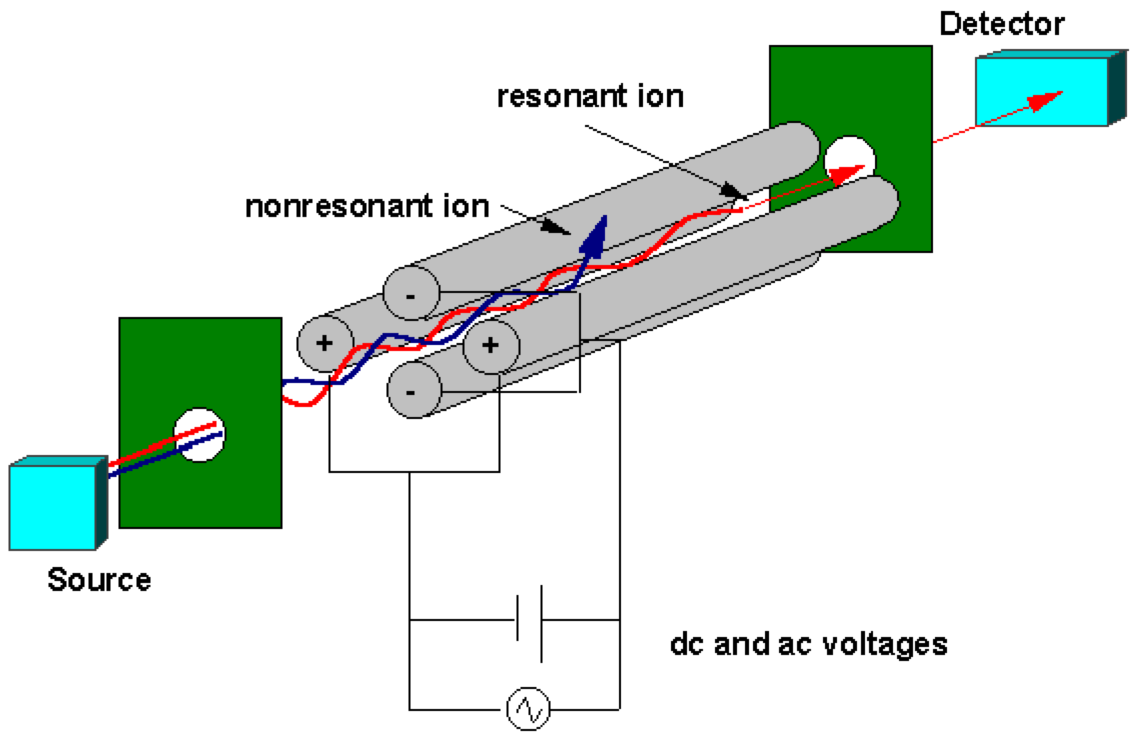
- For a give +/- potential, ions with specific mass can go to detectors and other can't
- Applied +/- potential to quadrupole can be changed
- This is why it is called mass selected detector (MSD) rather than mass spectrometer

Quadrupole Analyzer: Mass Selective Detector (MSD)

- Ions with zero velocity in the O-y direction: x-O-z plan
  1. Heavy ions: won't respond to variation of field (resonant)
  2. Light ions: will respond to variation of field and be lost (nonresonant)

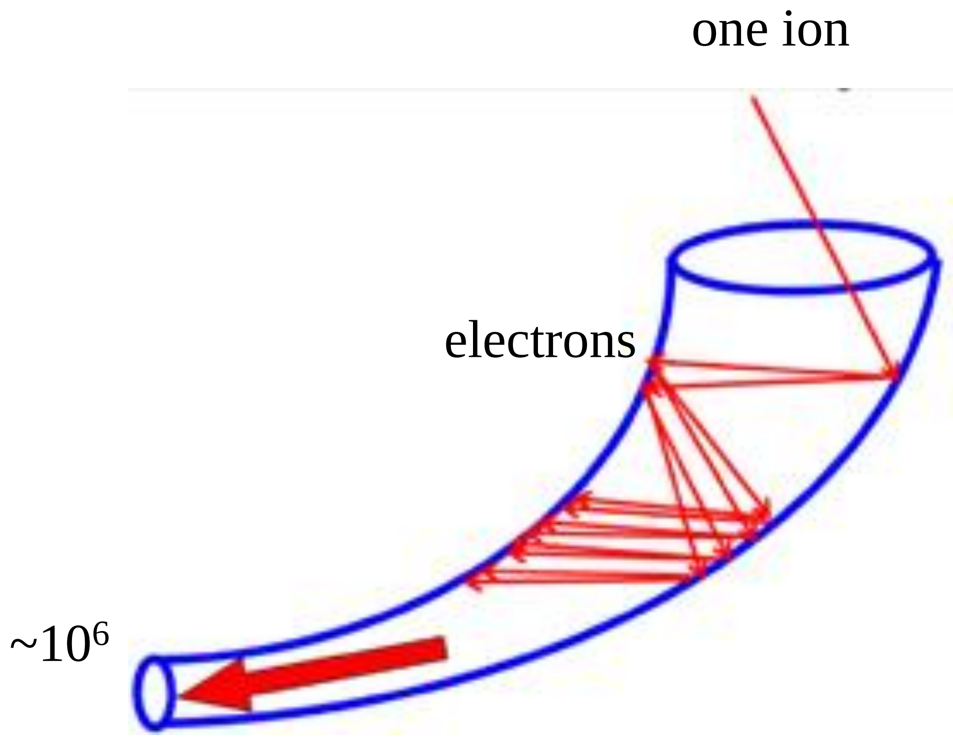
- Ions with zero velocity in the O-x direction: y-O-z plan
  1. Heavy ions: will respond to variation of field and be lost (nonresonant)
  2. Light ions: won't respond to variation of field (resonant)





Ion Detector

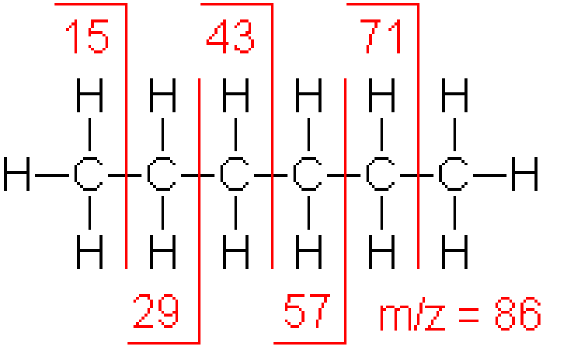
- Measurements of electrical charge (current) carried by ions
- Dynode

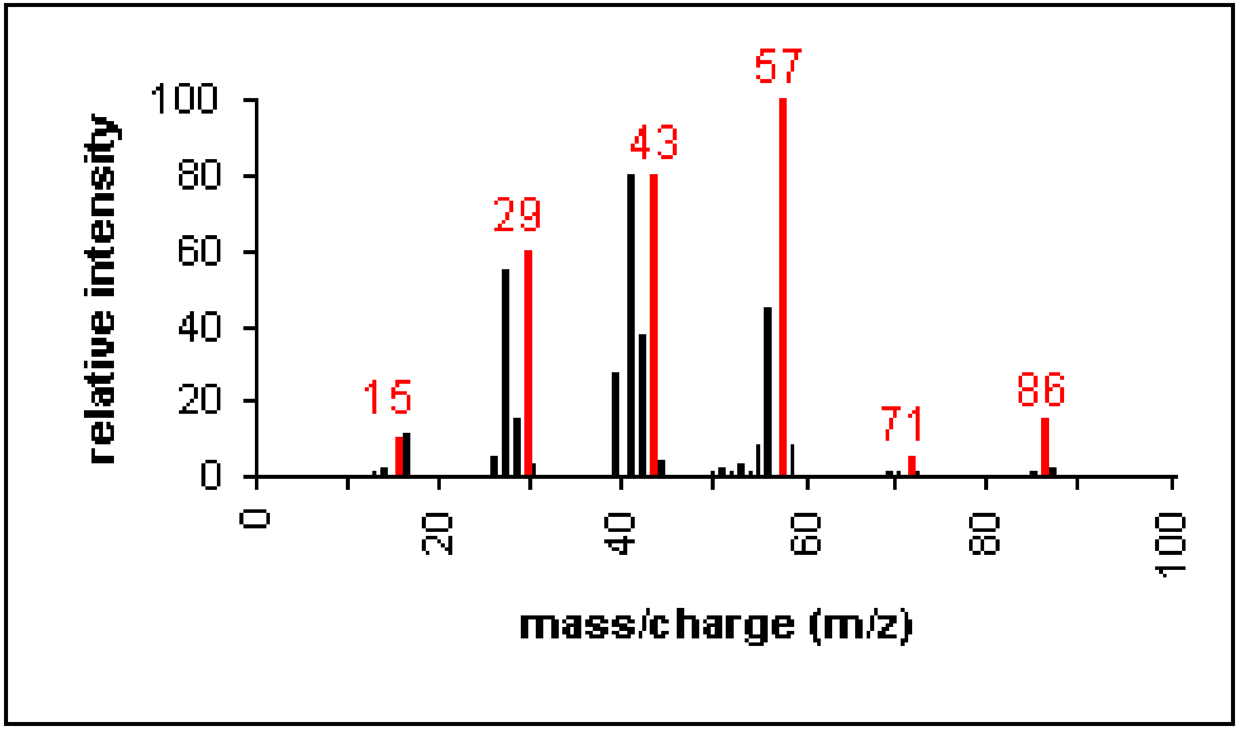


Alkane

- Peak at 15 (CH_3^+), 29 ($CH_3CH_2^+$), 43 ($CH_3CH_2CH_2^+$), 57 ($CH_3CH_2CH_2CH_2^+$), 71 ($CH_3CH_2CH_2CH_2CH_2^+$)
- Clusters of peaks 14 mass units apart (CH_2)

Hexane (C_6H_{14}) with MW = 86.18

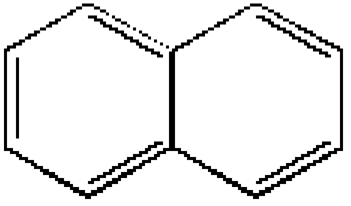




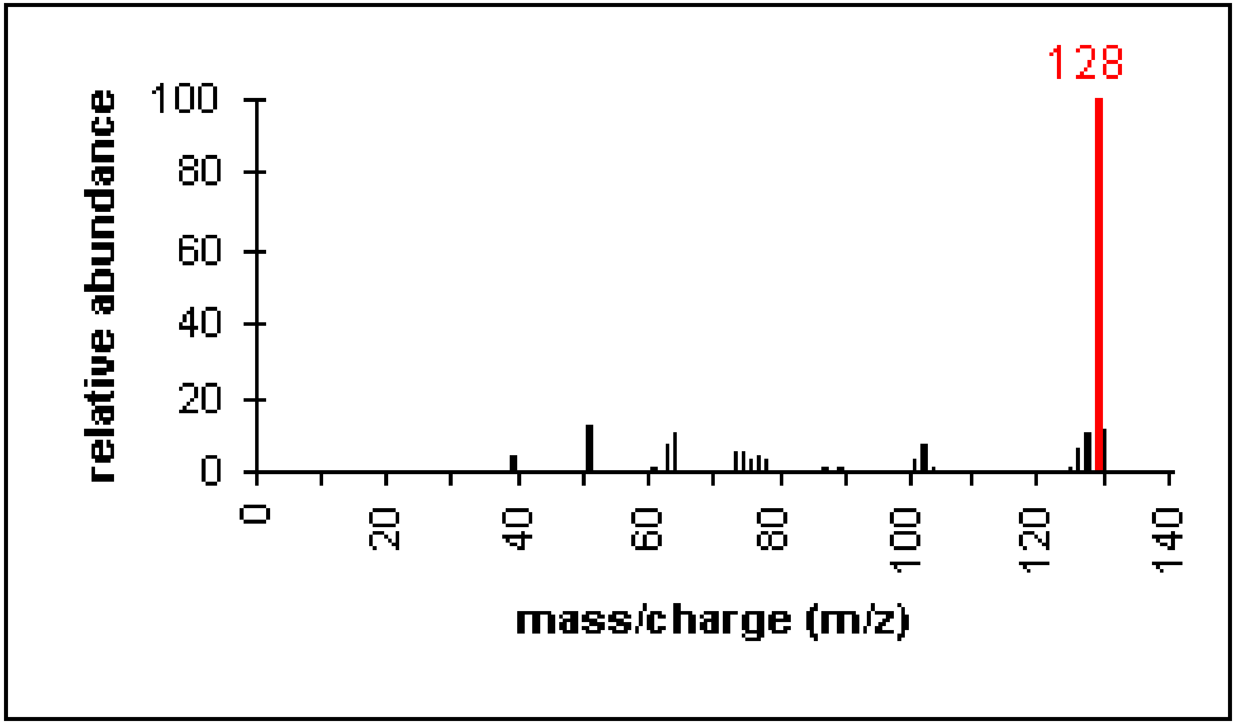
Aromatics

- Molecular ion peaks are base peaks due to the stable structure.

Naphthalene ($C_{10}H_8$)
MW = 128.17



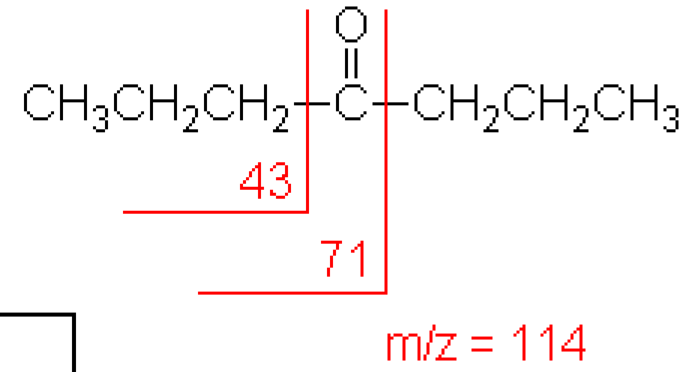
m/z = 128

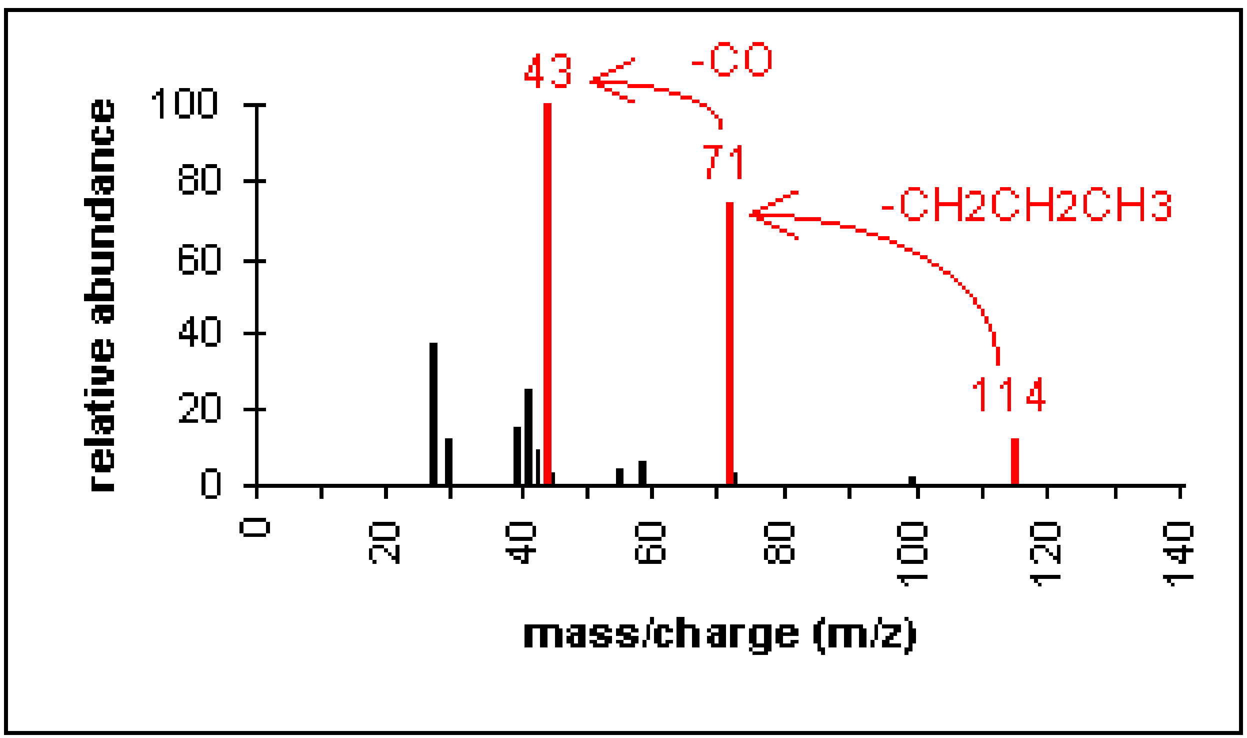


Ketones

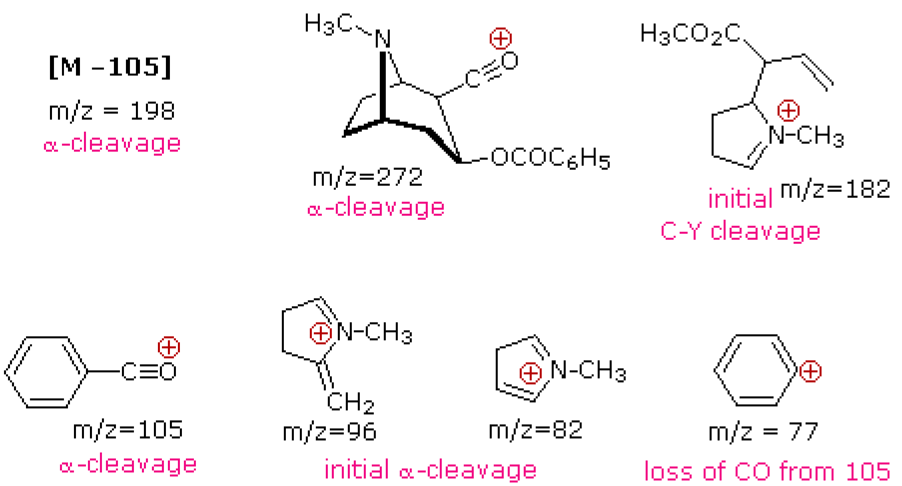
- The base peak is from the C-C cleavage adjacent to the C=O bond (α-cleavage)

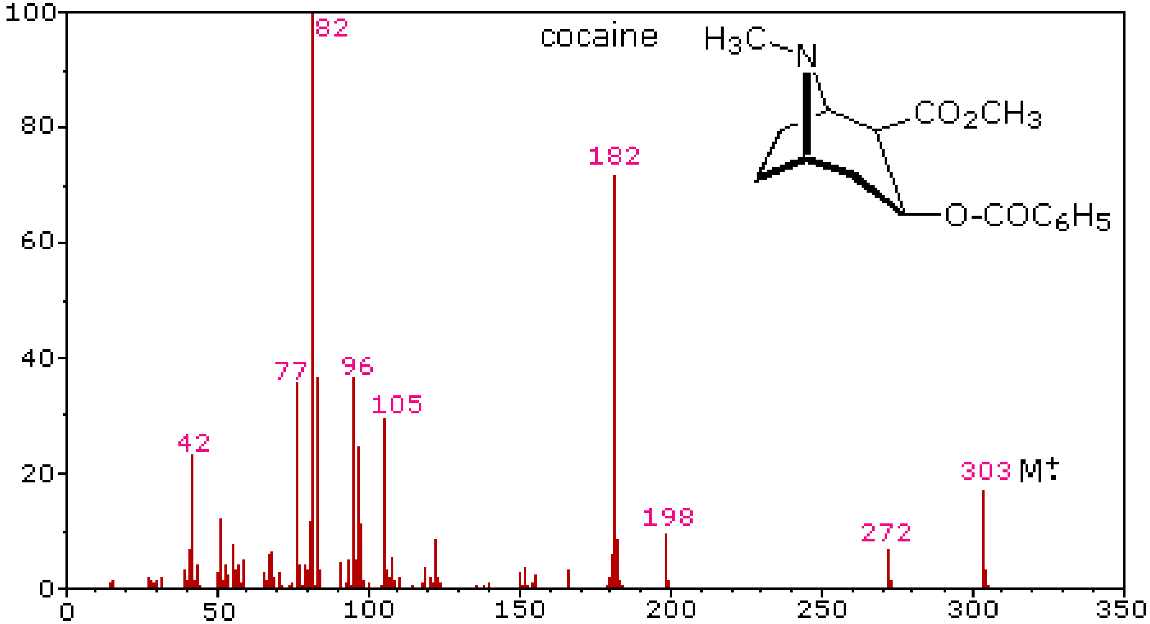
4-Heptanone ($C_7H_{14}O$)
MW = 114.19





Database is required to confirm the structure: NIST MS Library

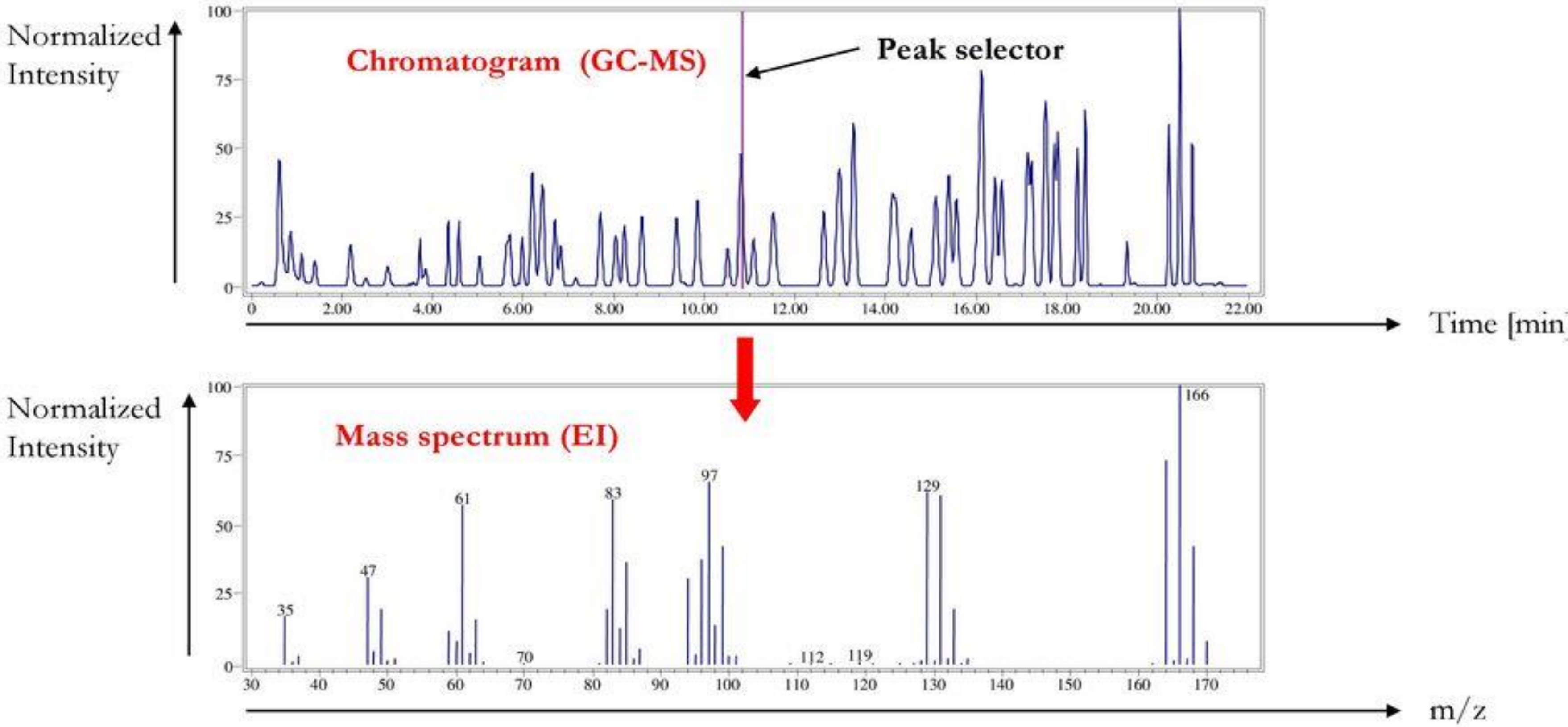




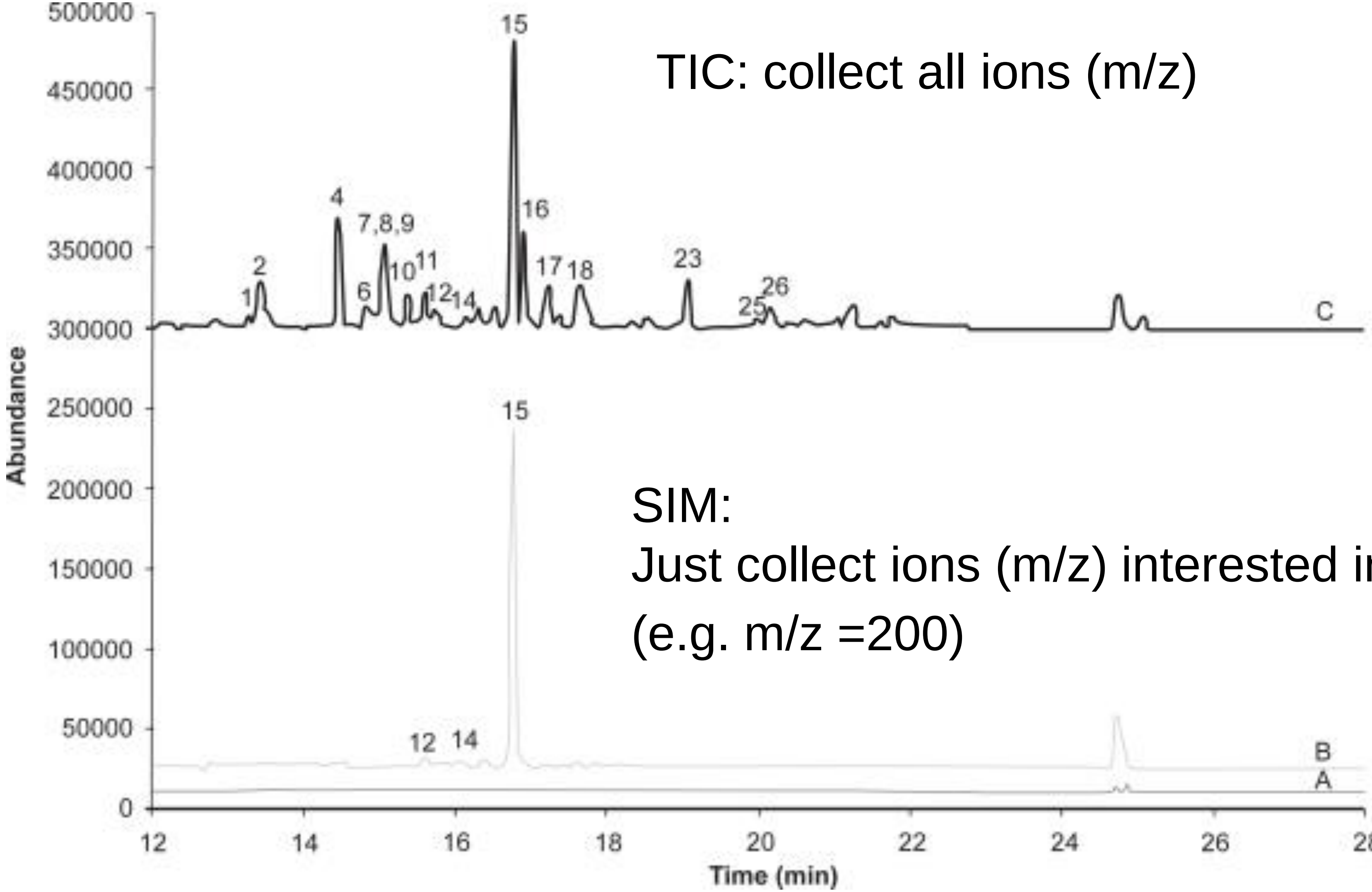
MW: 303

Detection

Total Ion Current (TIC) vs Spectrum



TIC vs SIM (Selected Ion Monitoring)



TIC: collect all ions (m/z)

SIM:
Just collect ions (m/z) interested in
(e.g. m/z =200)

Calibration of Mass Spectrometer

PFTBA (Perfluorotributylamine)

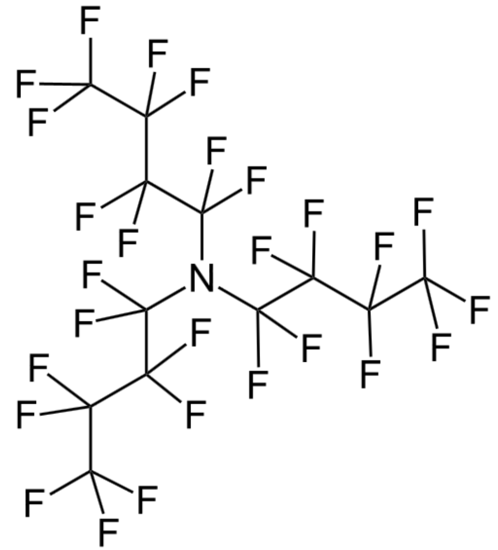
CF_3: 69

CF_3CF_2: 119

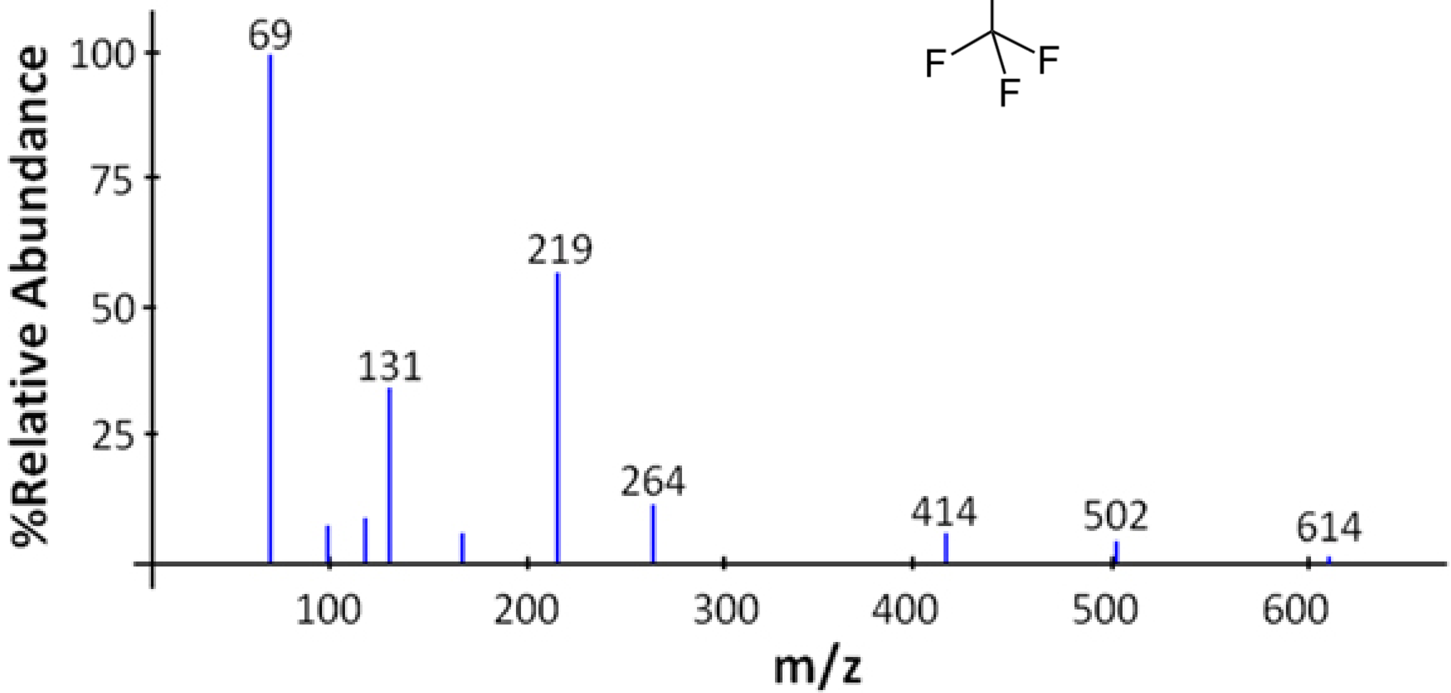
$CF_3CF_2CF_2$: 169

$CF_3CF_2CF_2CF_2$: 219

671-169: 502

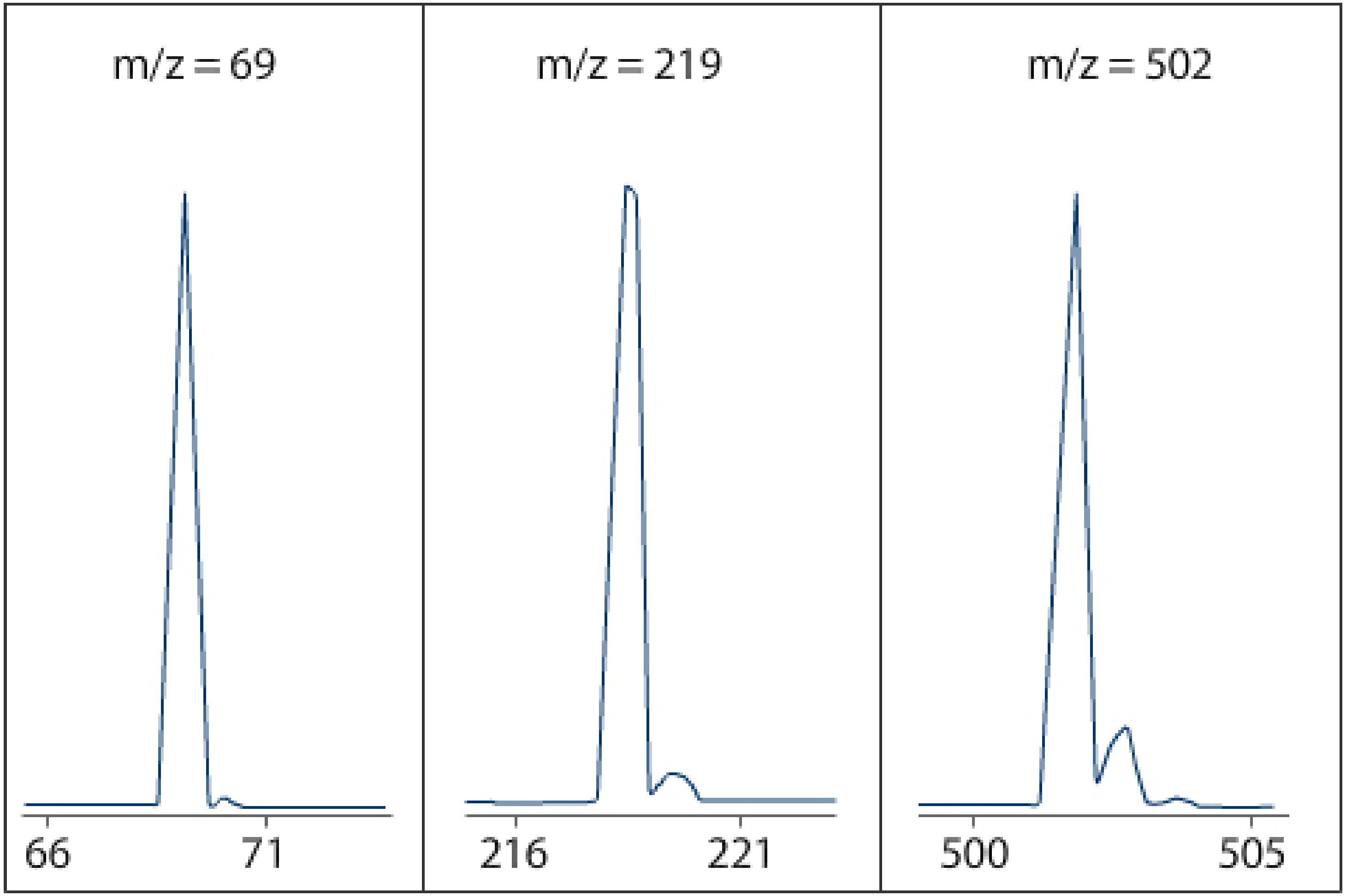


MW: 671



Tuning of Mass Spectrometer

Optimization of MS conditions (EI voltage, etc) using peak shapes, intensity of thee ions from PFTBA

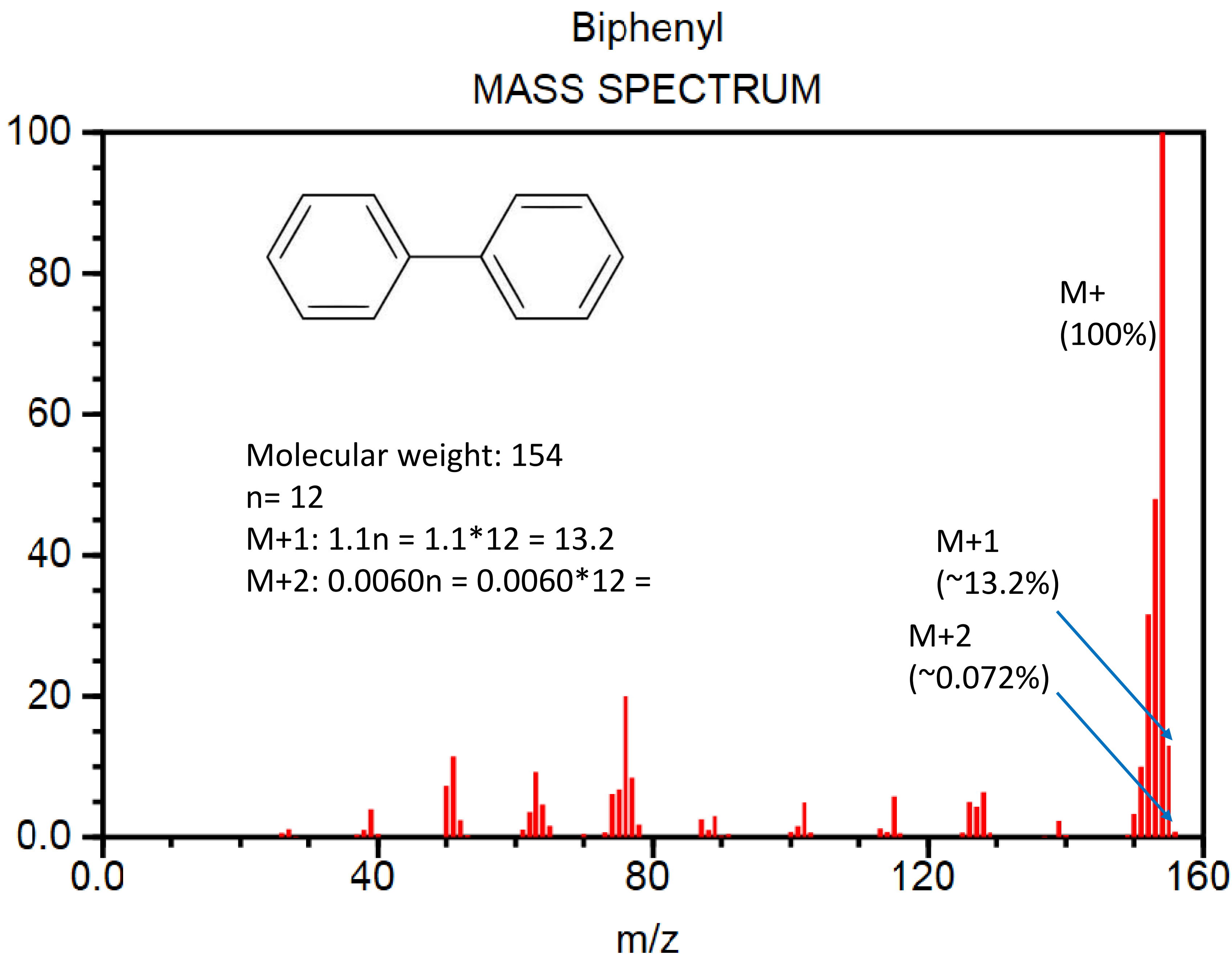


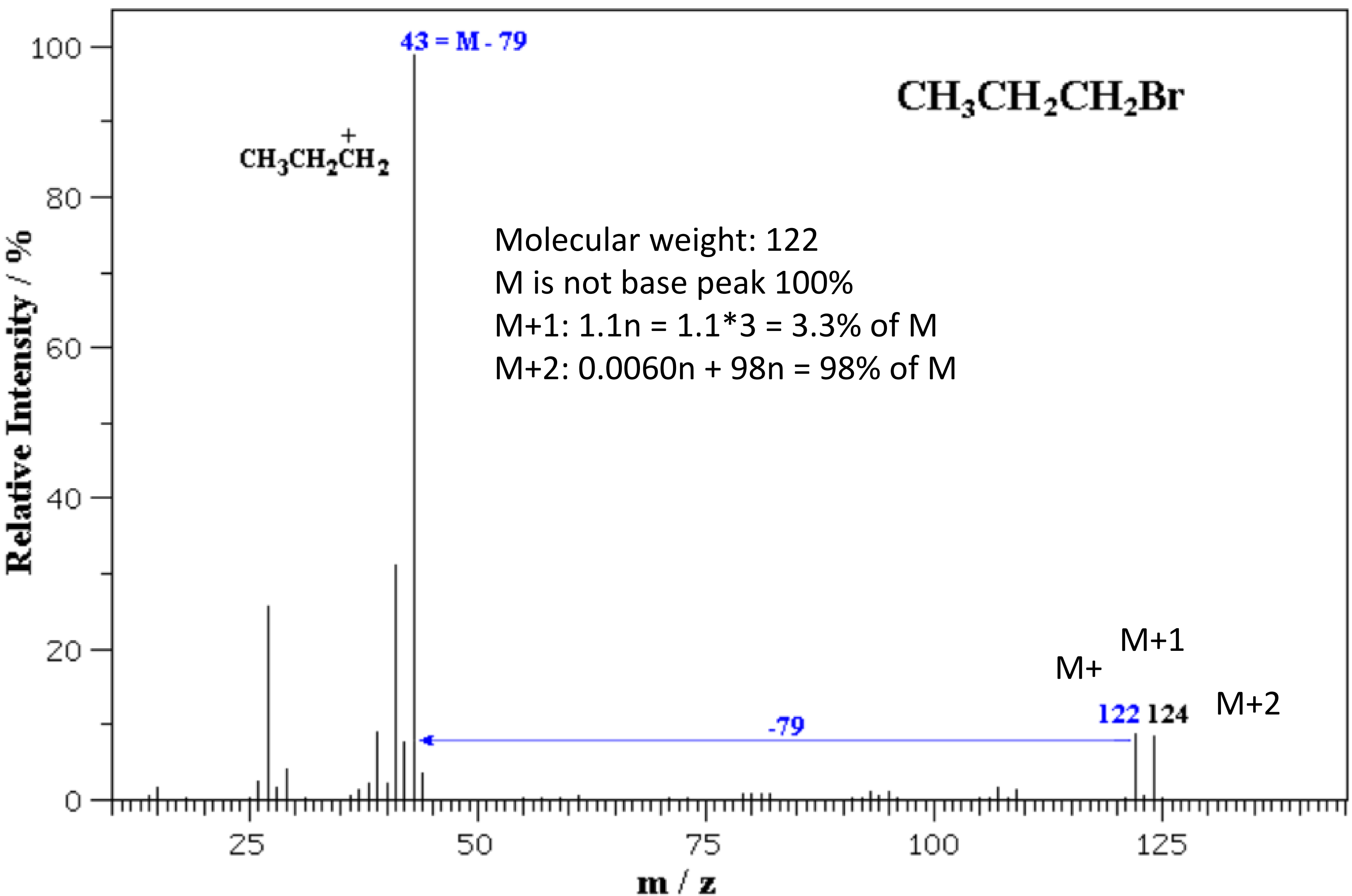
Isotope Effects (M+1, M+2 Peaks)

- H, C, N, O, Si, S, Cl, Br, etc
- Atomic weight is average
- MS spec shows

Table1

Type	Element	Symbol	Integer Mass[1]	Exact Mass[2]	Percent Abundance	X+1 Factor[3]	X+2 Factor[4]
X	Hydrogen	H	1	1.0078	99.99		
		D or ^{2}H	2	2.0141	0.01		
X+1	Carbon	^{12}C	12	12.0000	98.91		
		^{13}C	13	13.0034	1.1	$1.1n_C$	$0.0060n_{C2}$
X+1	Nitrogen	^{14}N	14	14.0031	99.6		
		^{15}N	15	15.0001	0.4	$0.37n_N$	
X+2	Oxygen	^{16}O	16	15.9949	99.76		
		^{17}O	17	16.9991	0.04	$0.04n_O$	
		^{18}O	18	17.9992	0.20		$0.20n_O$
X	Fluorine	F	19	18.9984	100		
X+2	Silicon	^{28}Si	28	27.9769	92.2		
		^{29}Si	29	28.9765	4.7	$5.1n_{Si}$	
		^{30}Si	30	29.9738	3.1		$3.4n_{Si}$
X	Sodium	Na	23	22.9898	100		
X	Phosphorus	P	31	30.9738	100		
X+2	Sulfur	^{32}S	32	31.9721	95.02		
		^{33}S	33	32.9715	0.76	$0.8n_S$	
		^{34}S	34	33.9679	4.22		$4.4n_S$
X+2	Chlorine	^{35}Cl	35	34.9689	75.77		
		^{37}Cl	37	36.9659	24.23		$32.5n_{Cl}$
X+2	Potassium	^{39}K	39	38.9637	93.26		
		^{40}K	40	39.9640	0.013	$0.012n_K$	
		^{41}K	41	40.9618	6.74		$7.22n_K$
X+2	Bromine	^{79}Br	79	78.9183	50.5		
		^{81}Br	81	80.9163	49.5		$98.0n_{Br}$
X	Iodine	I	127	126.9045	100		


Biphenyl
MASS SPECTRUM
Molecular weight: 154
n= 12
M+1: 1.1n = 1.1*12 = 13.2
M+2: 0.0060n = 0.0060*12 =
M+
(100%)
M+1
(~13.2%)
M+2
(~0.072%)
100
80
60
40
20
0.0
0.0
40
80
120
160
m/z



43 = M - 79
CH3CH2CH2Br
CH3CH2CH2+
Molecular weight: 122
M is not base peak 100%
M+1: 1.1n = 1.1*3 = 3.3% of M
M+2: 0.0060n + 98n = 98% of M
M+1
M+
M+2
122
124
-79
Relative Intensity / %
m / z
100
80
60
40
20
0
25
50
75
100
125

Exercise

2,4-Dichlorophenoxyacetic acid, methyl ester

$C_9H_8Cl_2O_3$

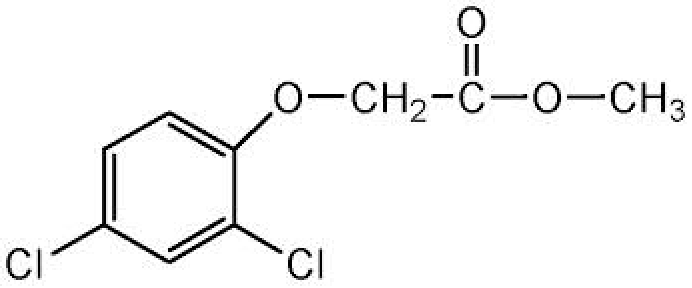
MW: 235.06

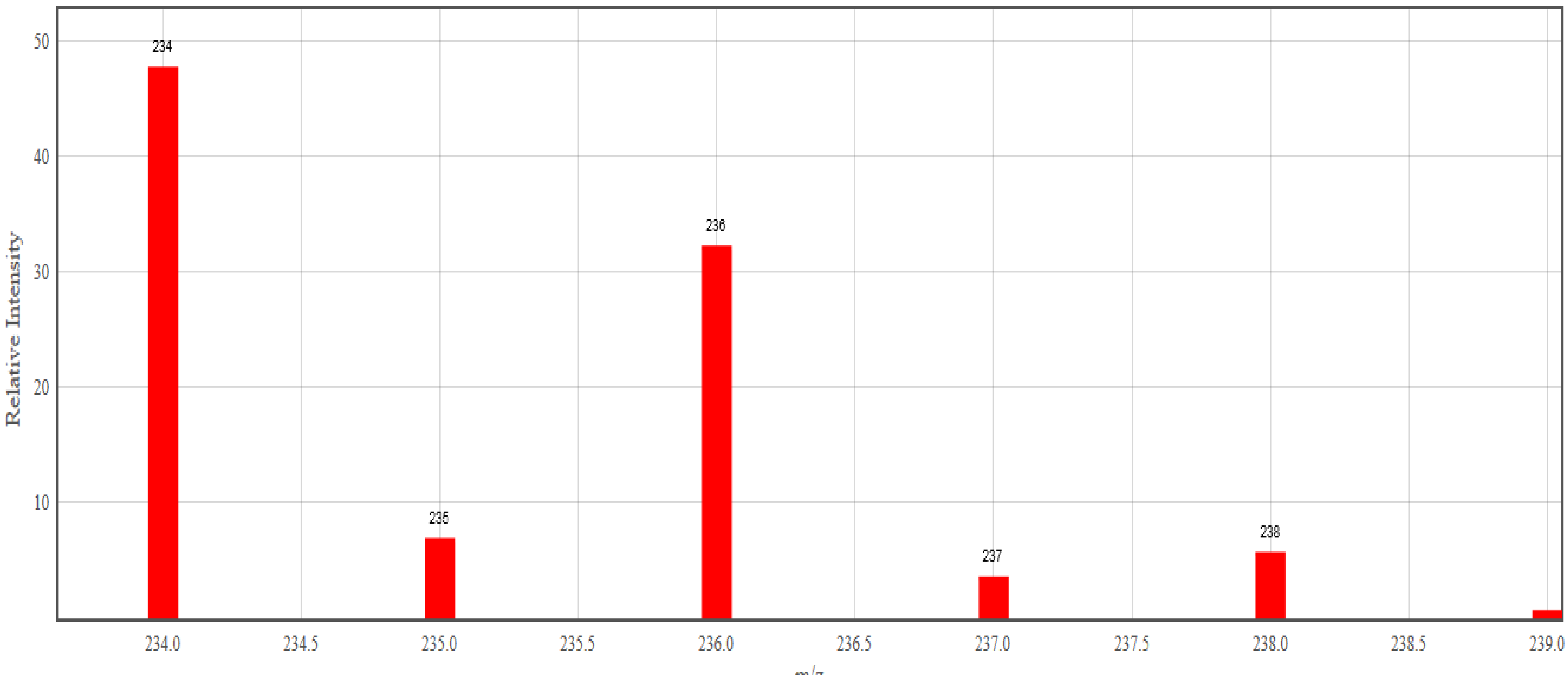
M: 234

M+1: 235

M+2: 236

M+3: 237





Relative Intensity
50
40
30
20
10
234
235
236
237
238
234.0
234.5
235.0
235.5
236.0
236.5
237.0
237.5
238.0
238.5
239.0