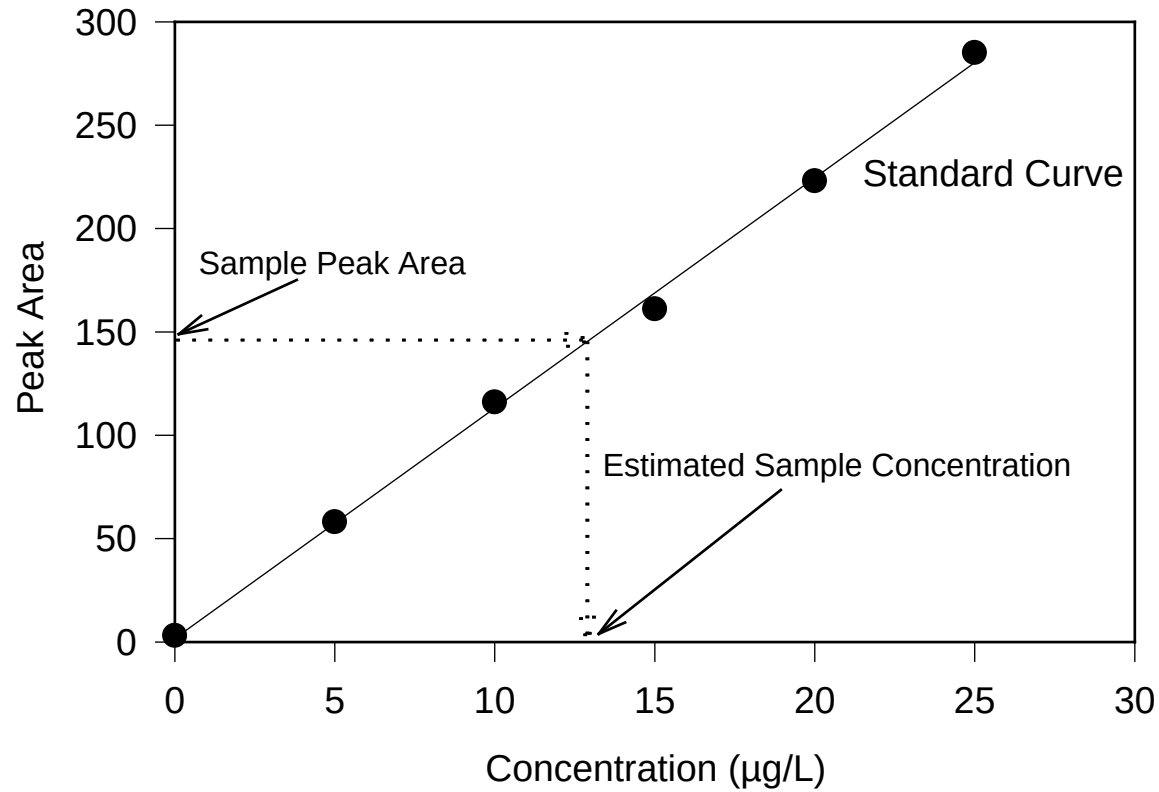


CEE 772: Instrumental Methods in Environmental Analysis Lecture #19

Mass Spectrometry: Basics
(Skoog, Chapt. 11, 26, 27, 28, pp.253-271, 674-693 718-721, 738-739)

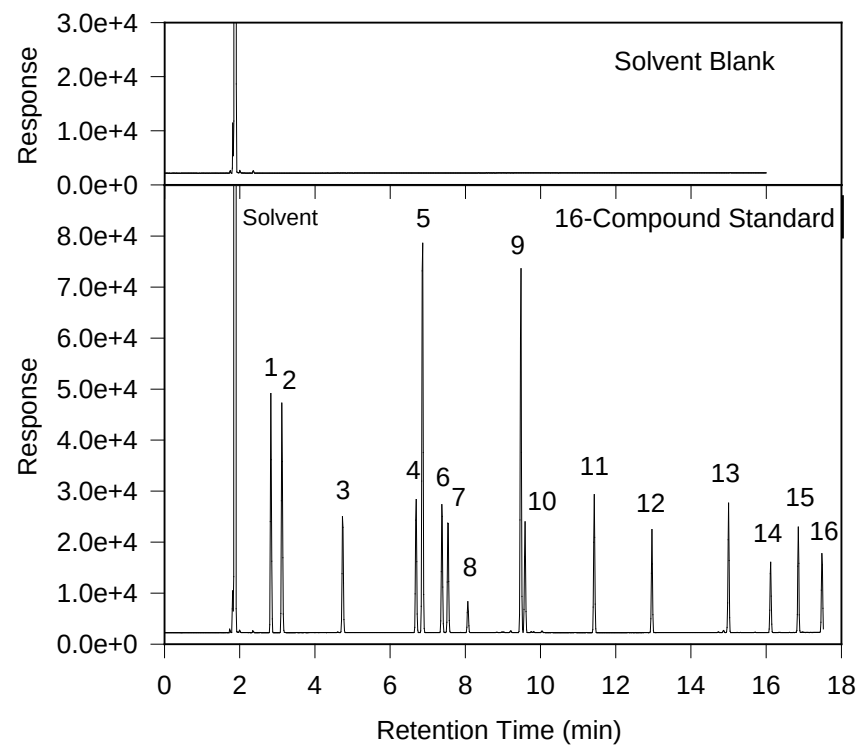
(Harris, Chapt. 23, 24 & 25)
(641-664, 699-706; 742-749)

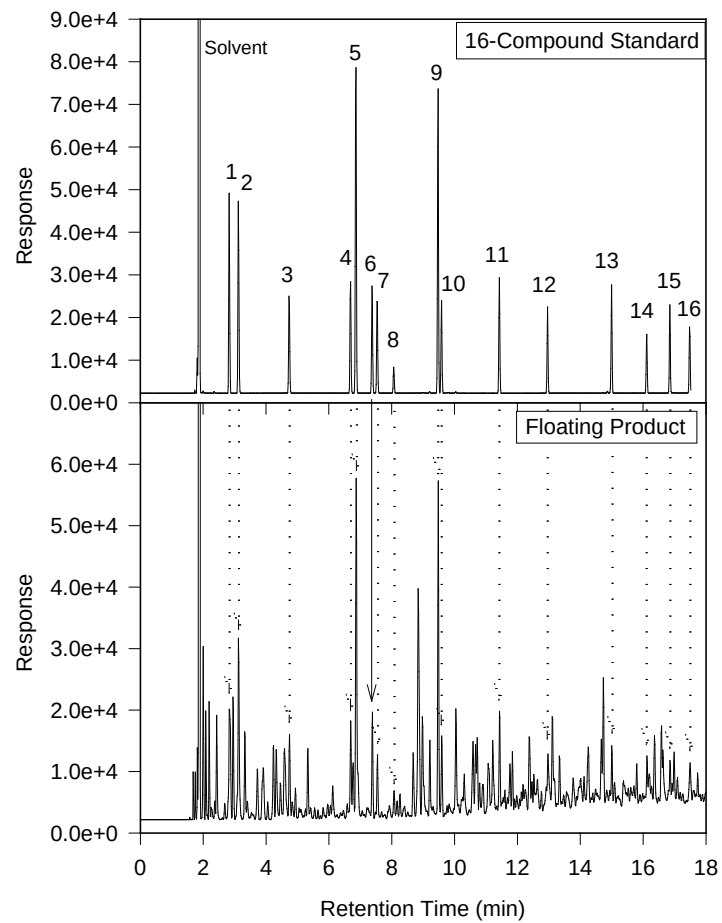
Calibration

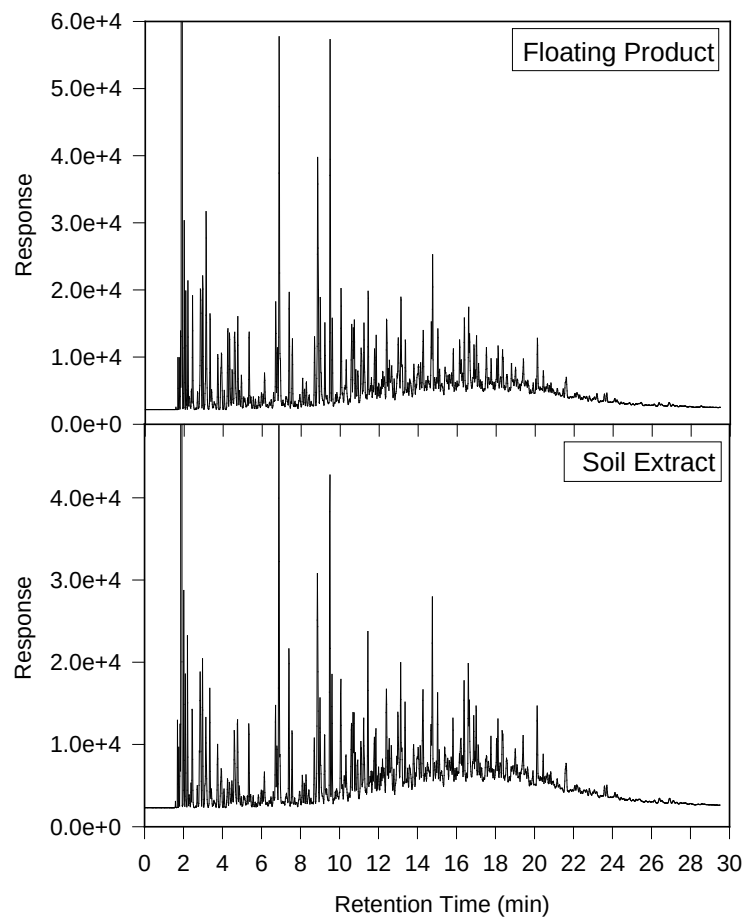


Example

Number	Name	Retention Time (min)
1	2-Methylhexane	2.83
2	2,2,4-Trimethylpentane	3.12
3	3-Methylheptane	4.74
4	Ethylbenzen	6.69
5	m-Xylene	6.86
6	o-Xylene	7.38
7	Nonane	7.54
8	Cumene	8.07
9	1,2,4-Trimethylbenzene	9.48
10	Decane	9.59
11	Undecane	11.42
12	Naphthalene	12.96
13	1-Methylnaphthalene	15.00
14	Tetradecane	16.12
15	2,3-Dimethylnaphthalene	16.85
16	Pentadecane	17.48





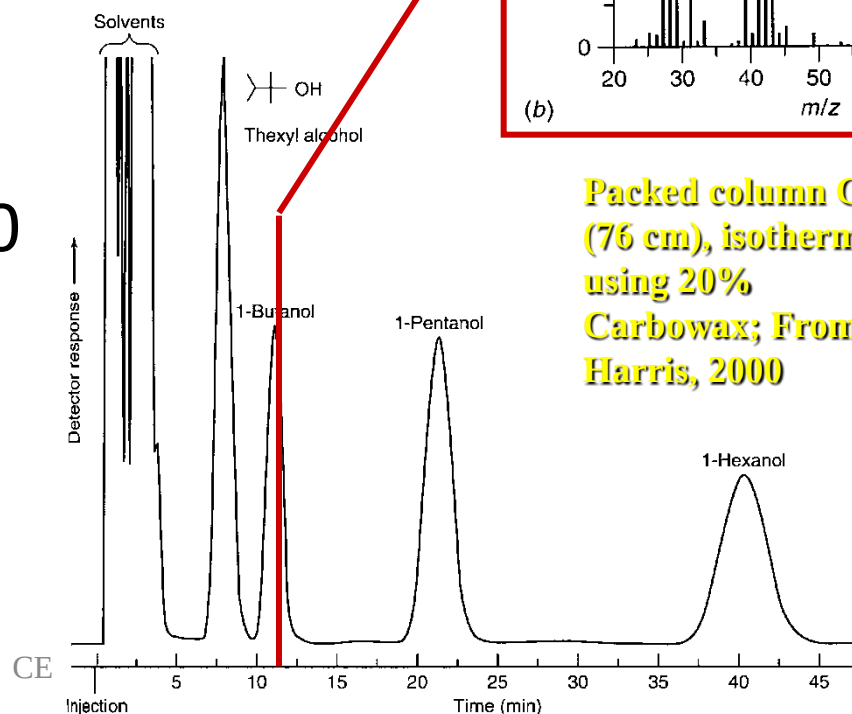


Mass Spectrometry

- General References on Instrument Design
 - Skoog, Principles of Instrumental Analysis
 - 1985 (3rd ed): parts of Chapter 18
 - 1991 (4th ed): parts of Chapter 18
 - 1998 (5th ed): parts of Chapter 20
 - Howe, Williams & Bowen, Mass Spectrometry, Principles & Applications
 - 1981 (2nd ed): Chapter 1 & 12
 - Loconto, Trace Environmental Quantitative Analysis
 - 2001: pp356-370
 - Budde, Analytical Mass Spectrometry
 - 2001: parts of Chapter 1 & 2

Use of MS with Chromatography

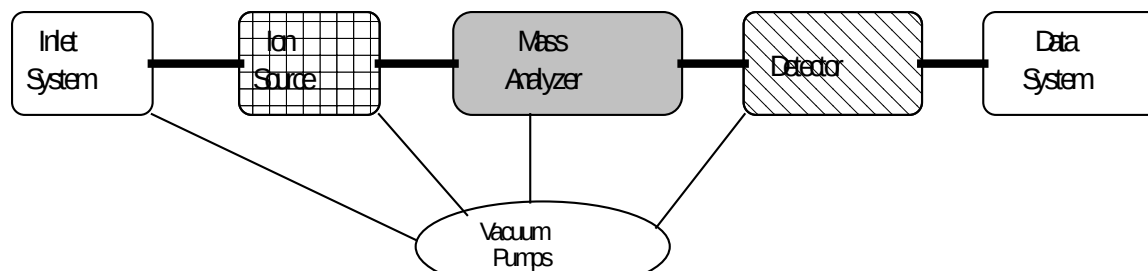
- Provides a 3rd dimension to chromatograms with molecular weight info
- GC/MS
 - Used in environmental field for 20 years
- LC/MS
 - Newer



Packed column GC
(76 cm), isothermal
using 20%
Carbowax; From:
Harris, 2000

Basics of an MS instrument

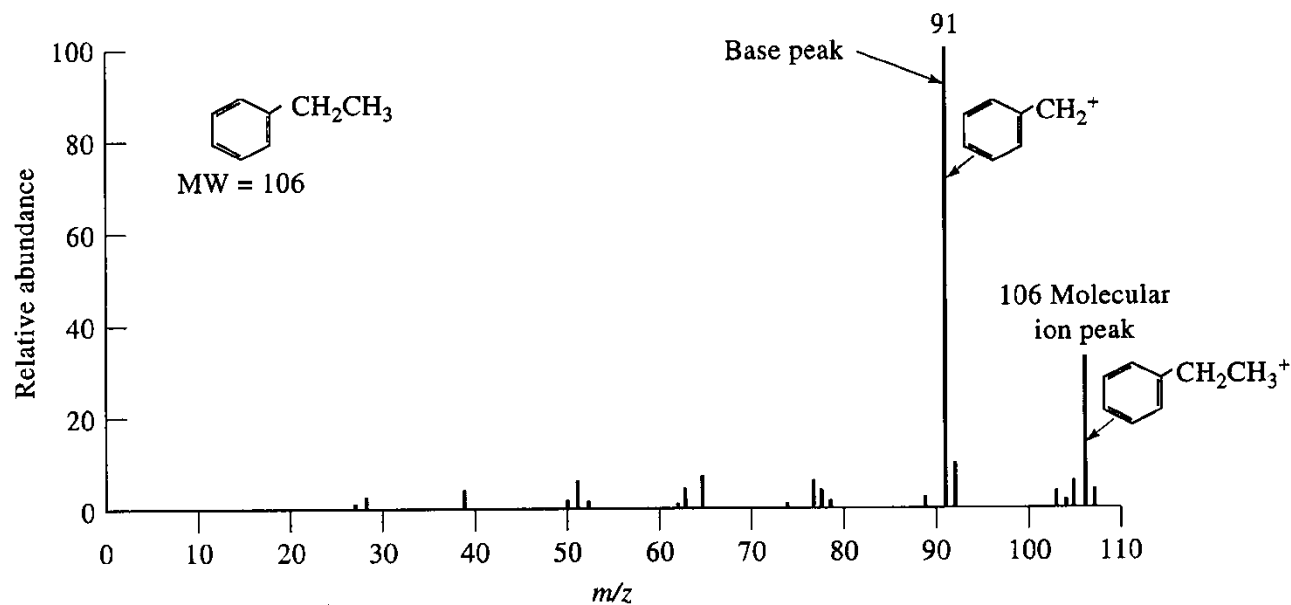
- Major components



- Vacuum: 10^{-4} to 10^{-6} torr

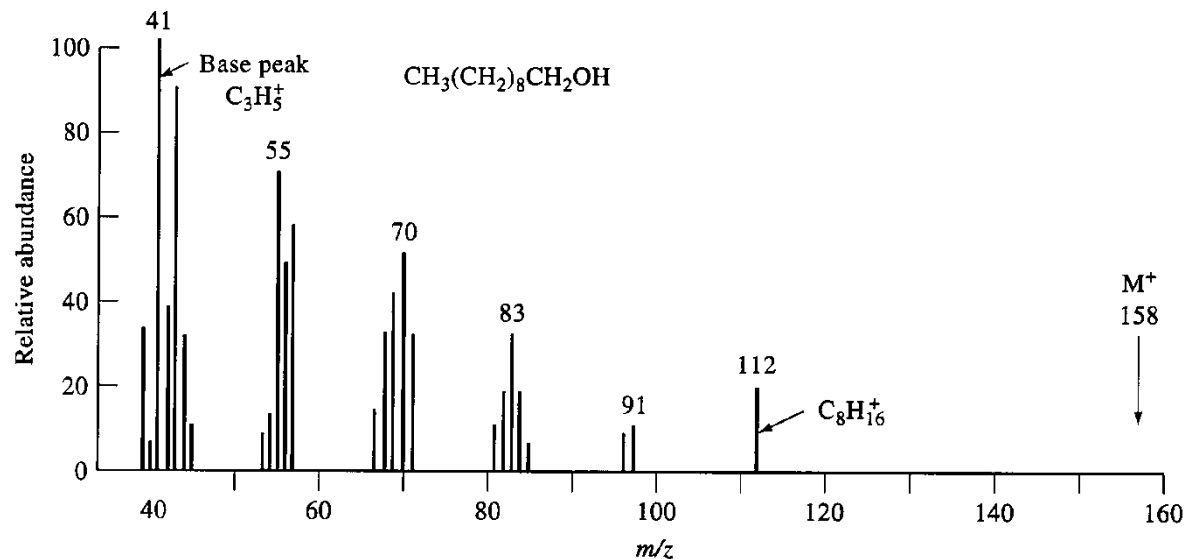
Mass Spectra

- Ethyl Benzene

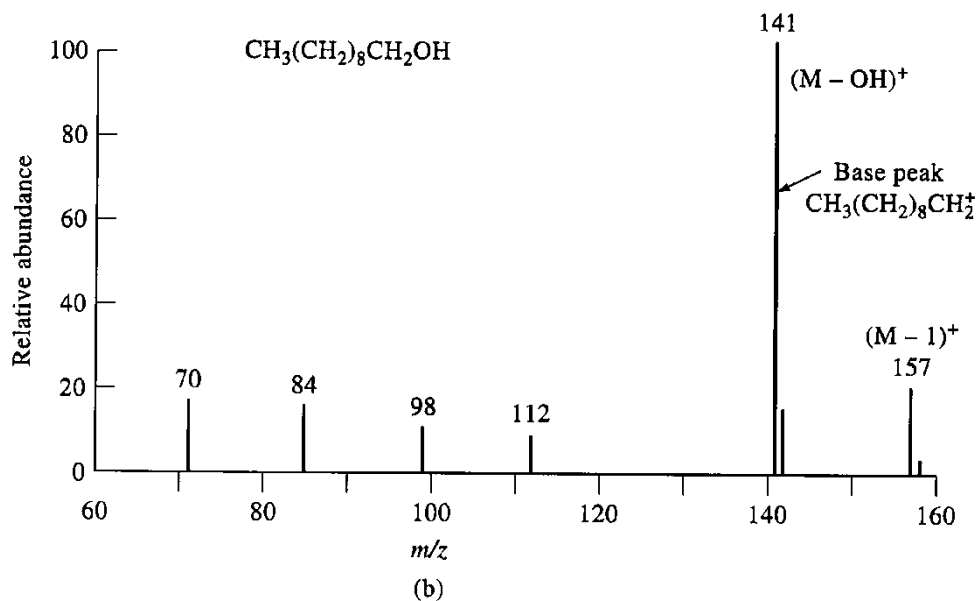


- 1-decanol
 - A. Hard Source

Fr:

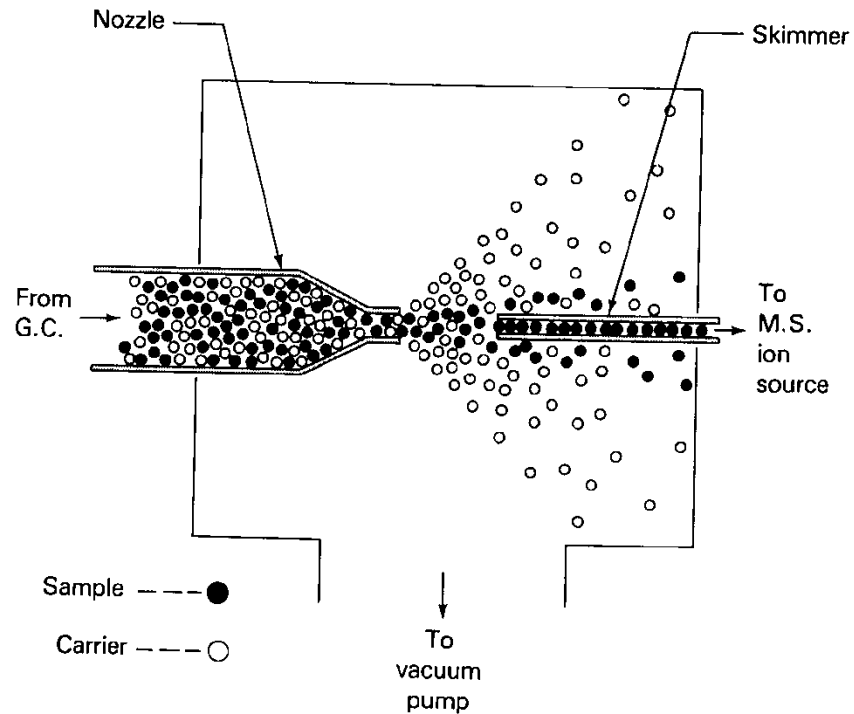


- B. Soft Source



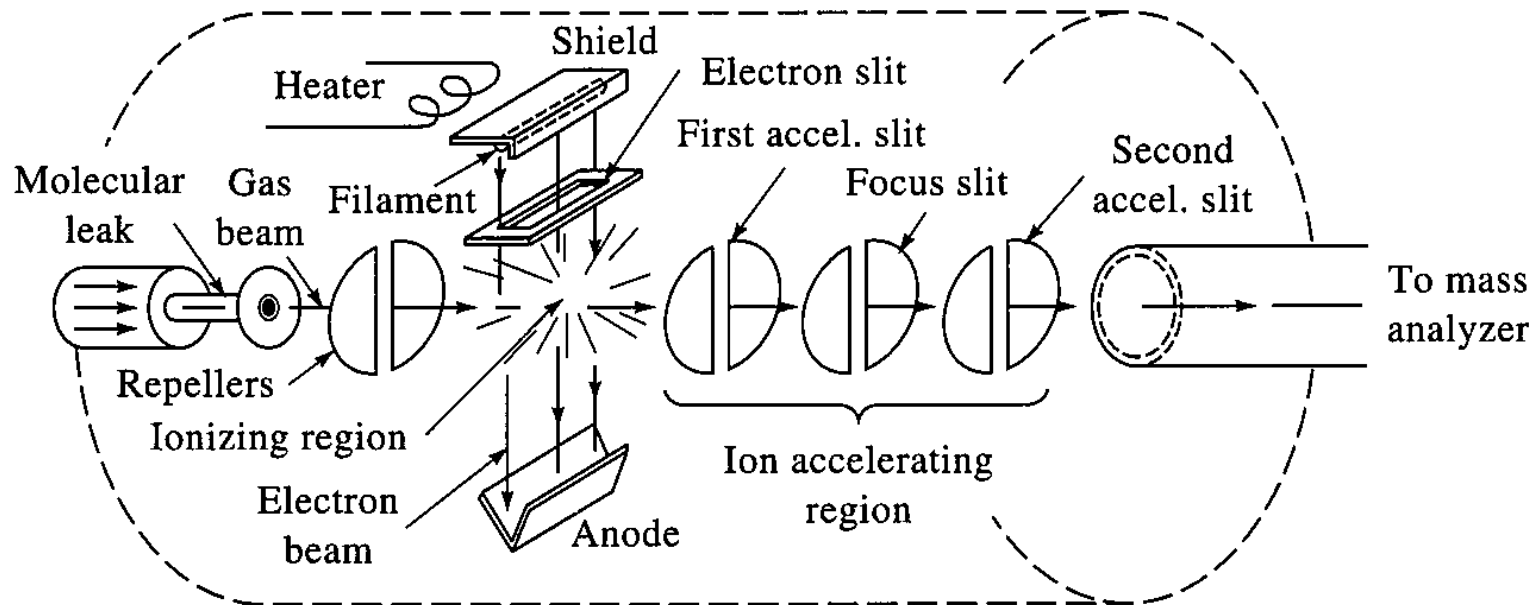
Interfaces

- Jet Separator



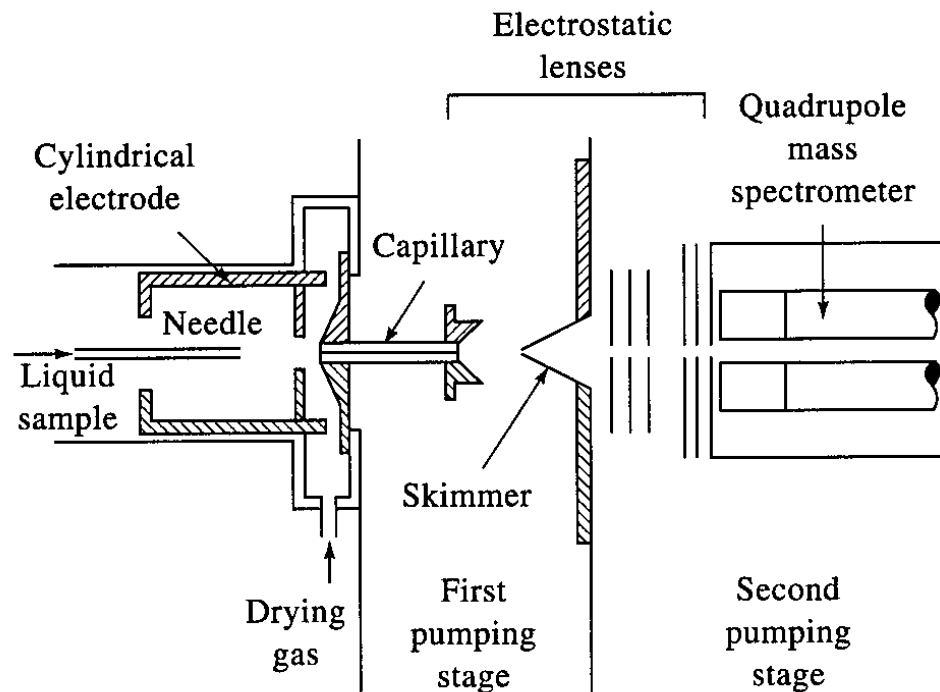
Ion Source

- Electron Impact



Interface & Ion Source

- Electrospray Ionization



Mass Spectral Interpretation

- References

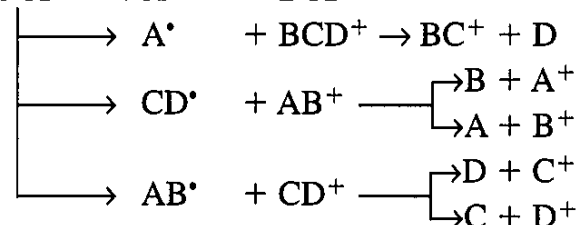
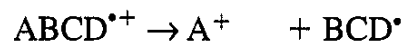
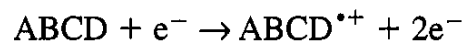
- McLafferty, 1980; Interpretation of Mass Spectra,
3rd Ed.,
 - University Science Books, Mill Valley, CA

Mass Spec

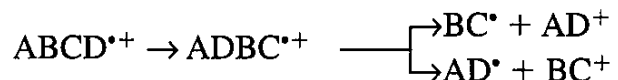
- Typical reactions in electron impact

Molecular ion formation

Fragmentation



Rearrangement followed by fragmentation



Collision followed by fragmentation

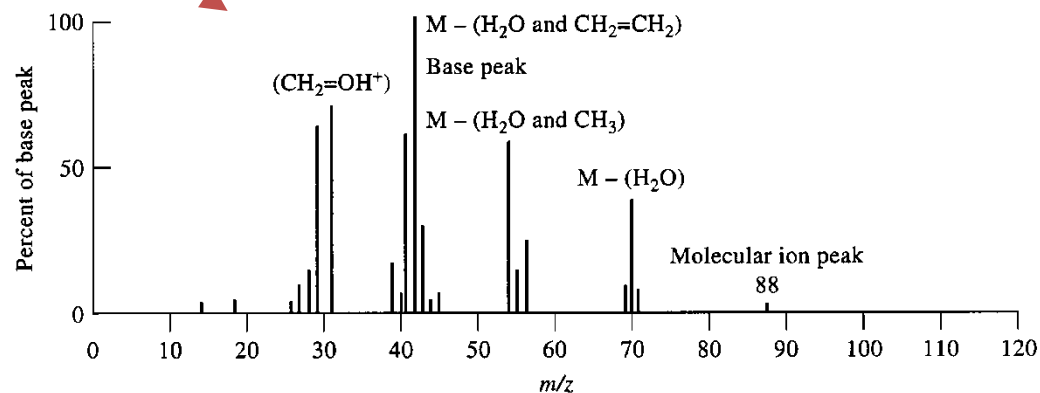
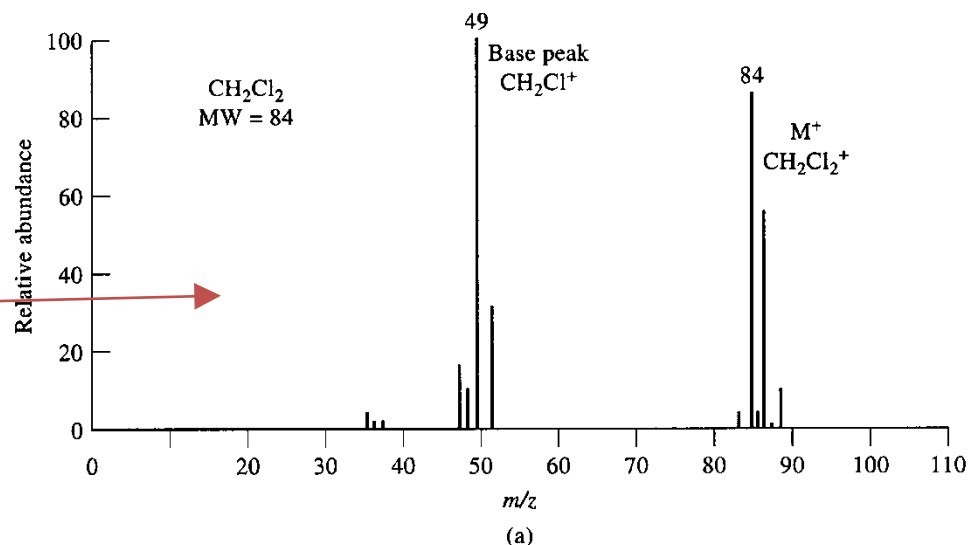


Mass Spec

- Electron Impact

- Methylene Chloride

- 1- Pentanol



Mass Spectrometry

- Glutamic Acid

- Electron impact

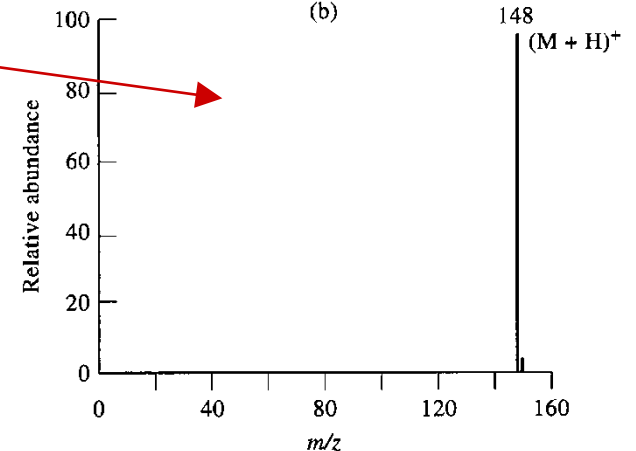
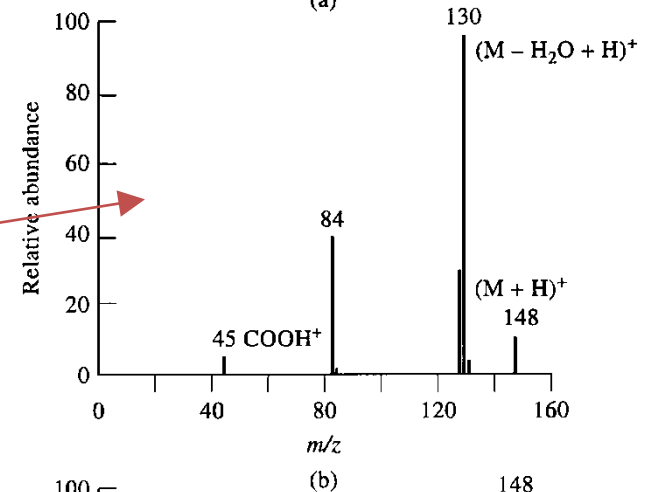
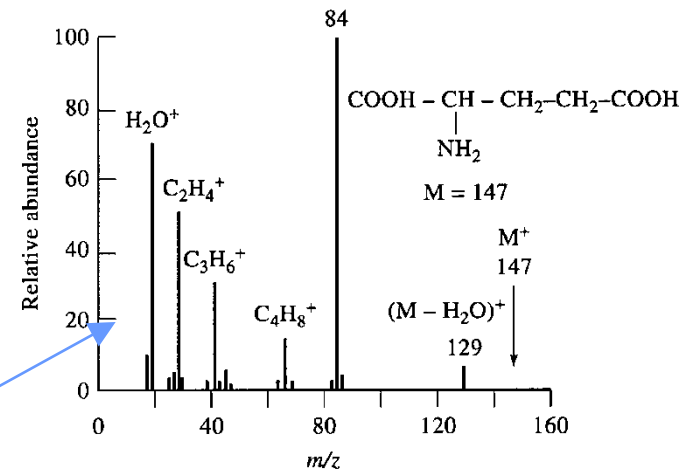
- Harsh, more fragments

- Field Ionization

- intermediate

- Field Desorption

- Very mild, mostly molecular ion



Isotopic Abundances

- Elemental Signatures

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.

From: McLafferty, 1980

Number of Carbon atoms

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*:

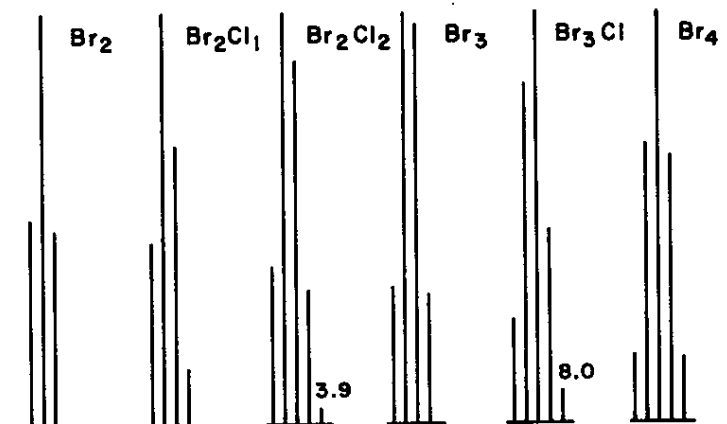
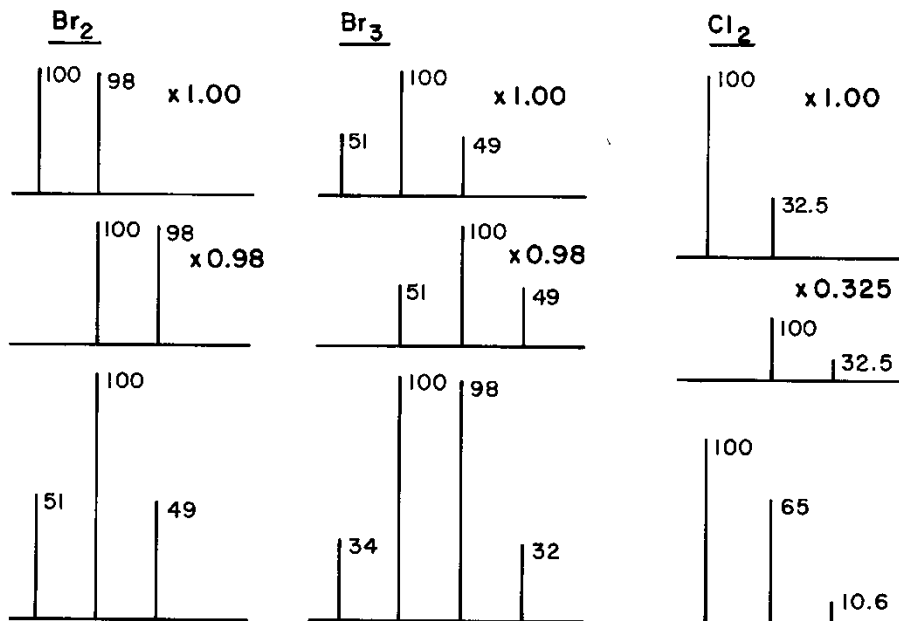
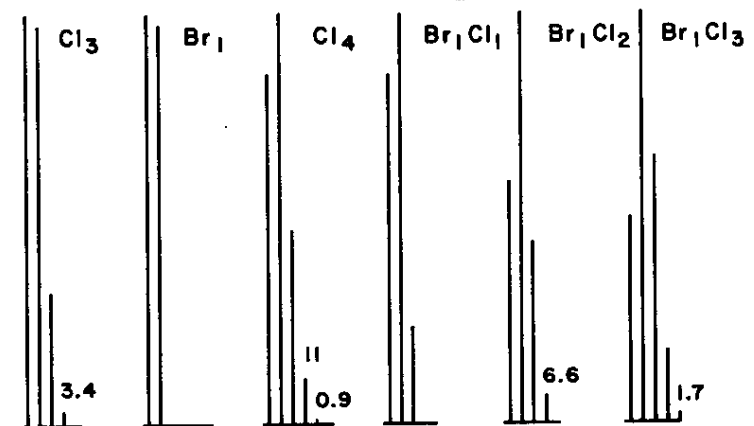
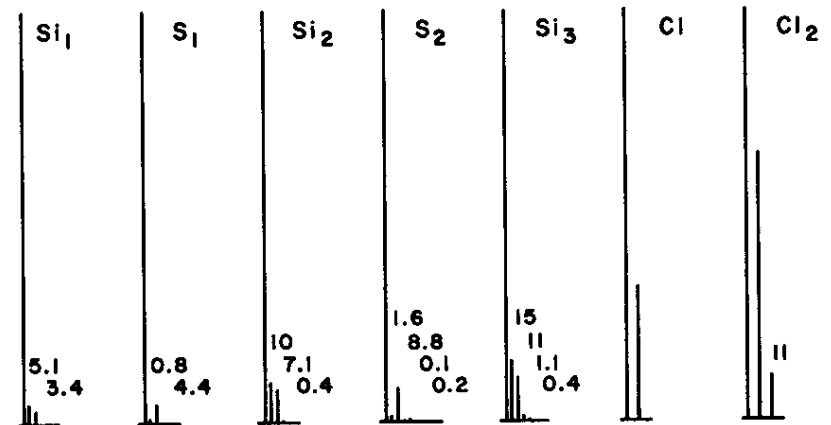
(A + 1): N, 0.37; O, 0.04; Si, 5.1; S, 0.80.

(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.

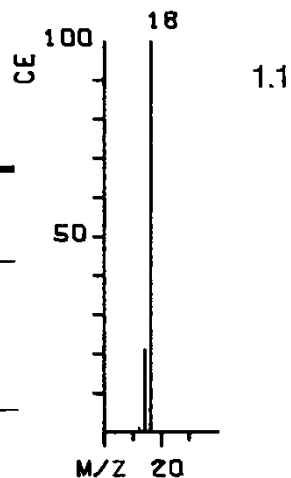
Abundance Char

- Isotopic Abundances for combinations of "A+2" elements



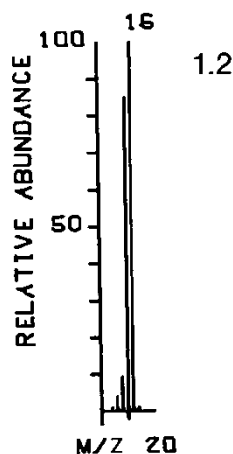
Unknown 1.1

m/z	Rel. abund.
1	<0.1
16	1.0
17	21.
18	100.



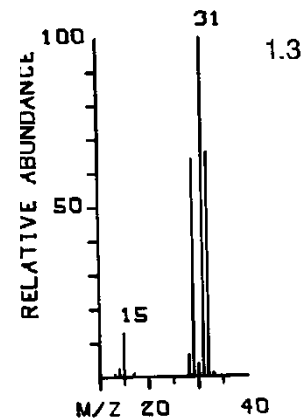
Unknown 1.2

m/z	Rel. abund.
1	3.1
12	1.0
13	3.9
14	9.2
15	85.
16	100.
17	1.1



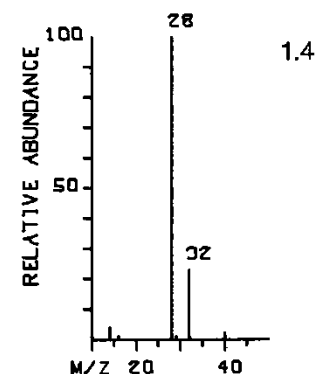
Unknown 1.3

m/z	Rel. abund.	m/z	Rel. abund.
12	0.3	28	6.3
13	0.7	29	64.
14	2.4	30	3.8
15	13.	31	100.
15.5	0.2	32	66.
16	0.2	33	1.0
17	1.0		



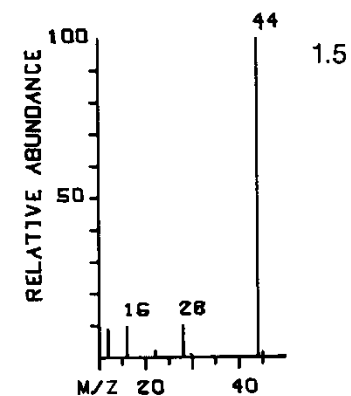
Unknown 1.4

m/z	Rel. abund.
14	4.0
16	0.8
17	1.0
18	5.0
20	0.3
28	100.
29	0.8
32	23.
34	0.1
40	2.0
44	0.10



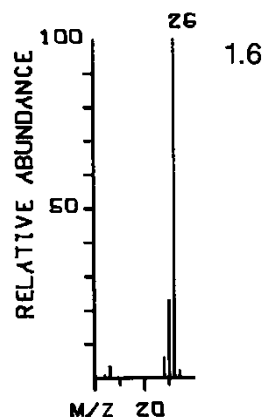
Unknown 1.5

m/z	Rel. abund.
12	8.7
16	9.6
22	1.9
28	9.8
29	0.1
44	100.
45	1.2
46	0.4



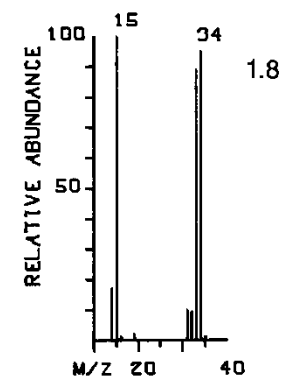
Unknown 1.6

<i>m/z</i>	Rel. abund.
12	0.9
13	3.6
24	6.1
25	23.
26	100.
27	2.2



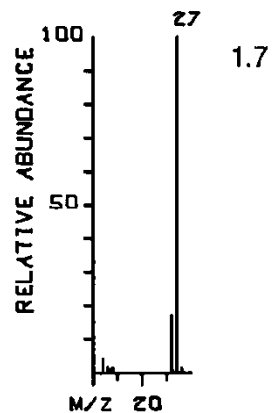
Unknown 1.8

<i>m/z</i>	Rel. abund.
14	17.
15	100.
16	1.0
19	2.0
20	0.3
31	10.
32	9.3
33	89.
34	95.
35	1.1



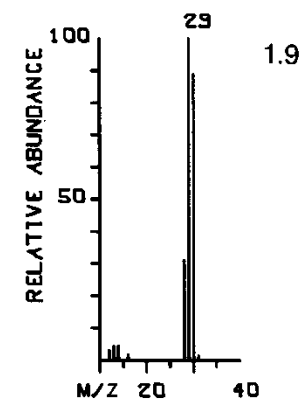
Unknown 1.7

<i>m/z</i>	Rel. abund.
12	4.2
13	1.7
13.5	0.9
14	1.6
26	17.
27	100.
28	1.6



Unknown 1.9

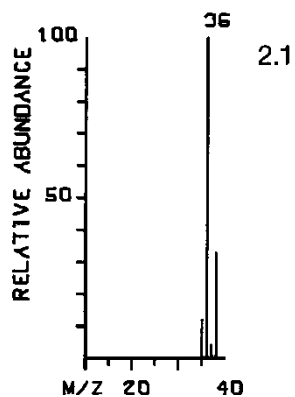
<i>m/z</i>	Rel. abund.
12	3.3
13	4.3
14	4.4
16	1.7
28	31.
29	100.
30	89.
31	1.3



From: McLafferty, 1980

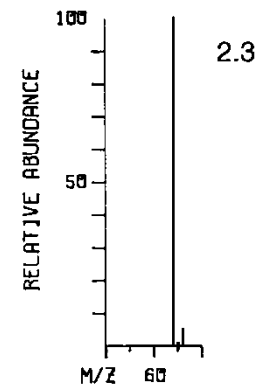
Unknown 2.1

<i>m/z</i>	Rel. abund.
35	12.
36	100.
37	4.1
38	33.



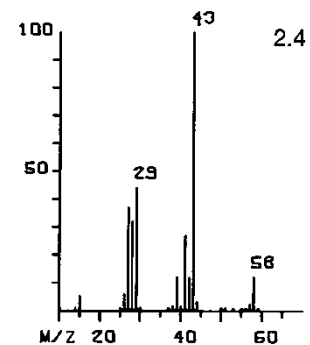
Unknown 2.3

<i>m/z</i>	Rel. abund.
64	100.
65	0.9
66	5.0



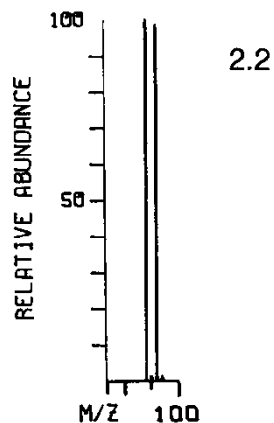
Unknown 2.4

<i>m/z</i>	Rel. abund.	<i>m/z</i>	Rel. abund.
12	0.1	40	1.6
13	0.3	41	27.
14	1.0	42	12.
15	5.3	43	100.
25	0.5	44	3.3
25.5	0.4	48	0.1
26	6.1	49	0.4
26.5	0.1	50	1.2
27	37.	51	1.0
27.5	0.1	52	0.3
28	32.	53	0.7
29	44.	54	0.2
30	1.0	55	0.9
36	0.1	56	0.7
37	1.0	57	2.4
38	1.8	58	12.
39	12.	59	0.5



Unknown 2.2

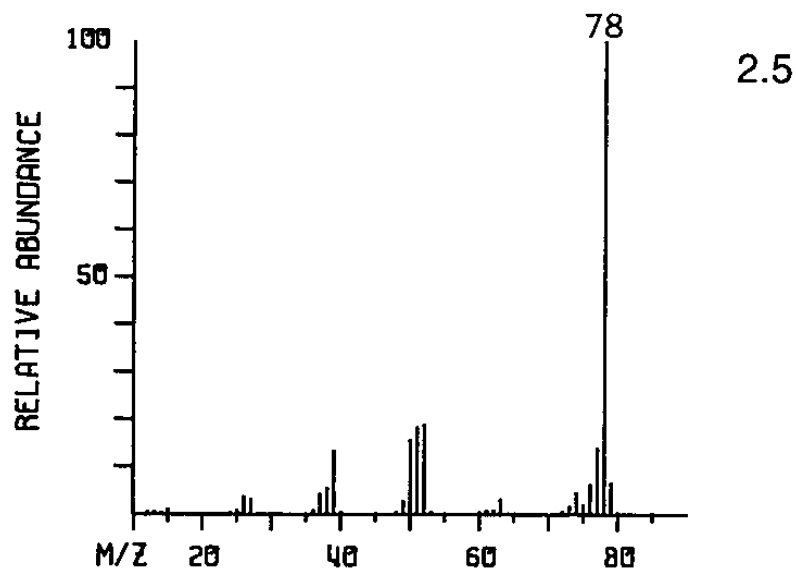
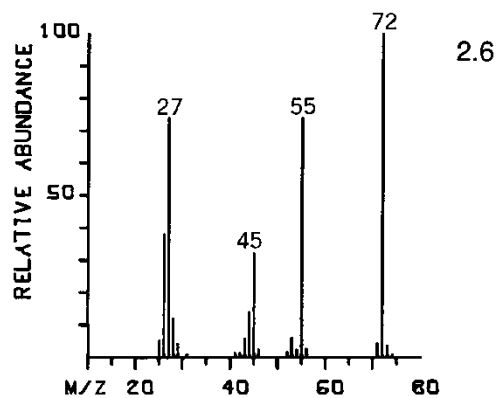
<i>m/z</i>	Rel. abund.
94	100.
95	1.1
96	96.
97	1.1



From: McLafferty, 1980
David Reckhow

Unknown 2.6

<i>m/z</i>	Rel. abund.
25	5.2
26	38.
27	74.
27.5	0.3
28	12.
29	4.3
31	0.5
41	1.2
42	1.3
43	5.8
44	14.
45	32.
46	2.5
52	1.4
53	6.0
54	2.3
55	74.
56	2.6
57	0.2
71	4.3
72	100.
73	3.5
74	0.5

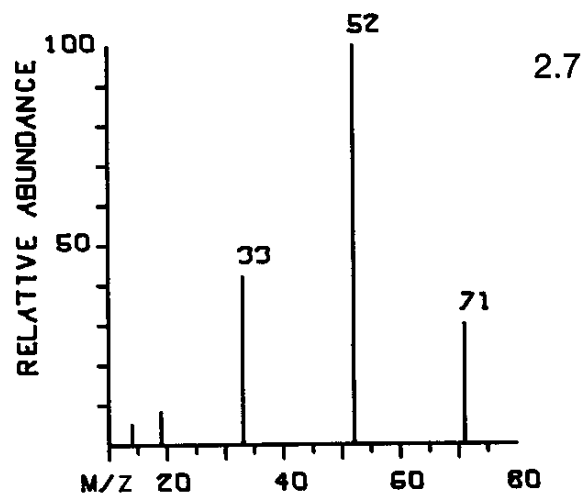


Unknown 2.5

<i>m/z</i>	Rel. abund.	<i>m/z</i>	Rel. abund.
12	0.2	53	0.8
13	0.4	60	0.2
14	0.4	61	0.4
15	1.0	62	0.8
24	0.4	63	2.9
25	0.8	64	0.2
26	3.2	72	0.4
27	2.6	73	1.0
36	0.9	74	3.9
37	3.8	75	2.2
39	13.	76	7.0
40	0.4	77	15.
50	16.	78	100.
51	19.	79	6.8
52	20.	80	0.2

Unknown 2.7

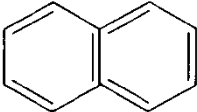
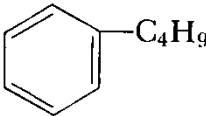
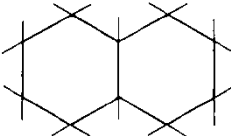
<i>m/z</i>	Rel. abund.
14	5.2
19	8.4
33	36.
52	100.
53	0.4
71	30.



Mass Spectral Interpretation

- References
 - Fred McLafferty, Interpretation of Mass Spectra
 - University Science Books, Mill Valley, CA
 - 3rd Ed., 1980
 - 4th Ed., 1993 (with František Tureček)
 - McLafferty & Venkataraghavan, 1982; Mass Spectral Correlations, 2nd Ed.,
 - American Chemical Society, Advances in Chemistry Series #40

Table 18-5
Variation in Molecular Ion Peak with Structure

Compound	Formula	Relative Peak Height (percent of total peak heights)
Naphthalene		44.3
<i>n</i> -Butylbenzene		8.3
<i>trans</i> -Decaline		8.2
Diamyl sulfide	(C ₅ H ₁₁) ₂ S	3.7
<i>n</i> -Decane	C ₁₀ H ₂₂	1.41
Diamylamine	(C ₅ H ₁₁) ₂ NH	1.14
Methyl nonanoate	C ₉ H ₁₇ COOCH ₃	1.10
Diamyl ether	(C ₅ H ₁₁) ₂ O	0.33
3,3,5-Trimethylheptane	C ₁₀ H ₂₂	0.007
<i>n</i> -Decanol	C ₁₀ H ₂₁ OH	0.002

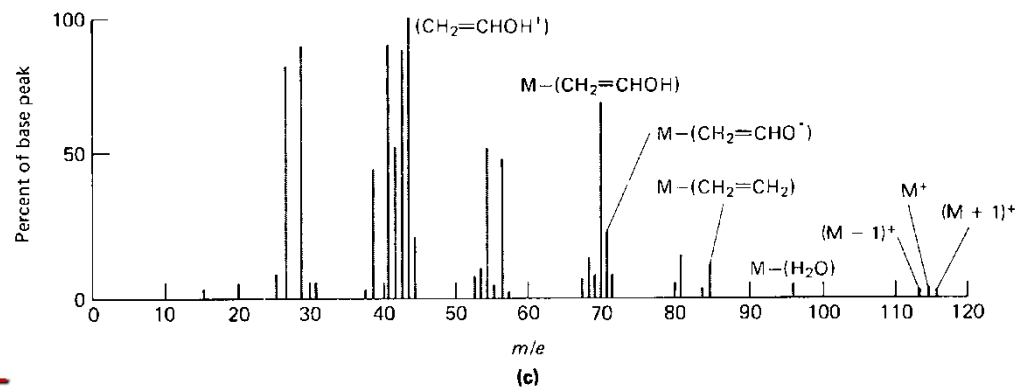
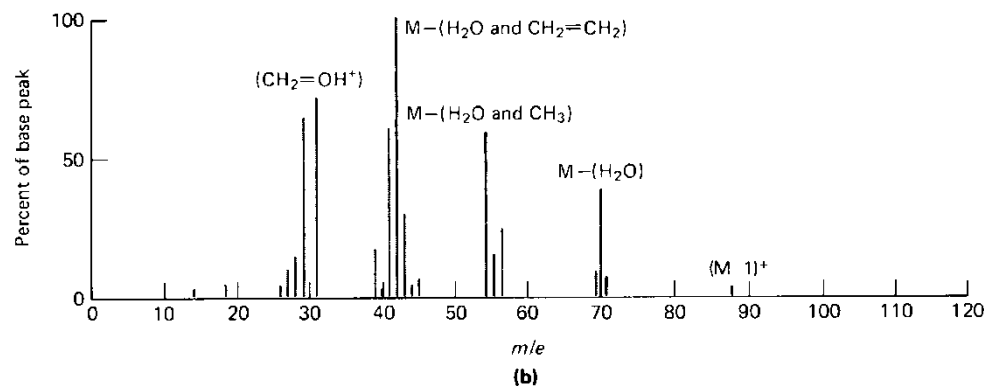
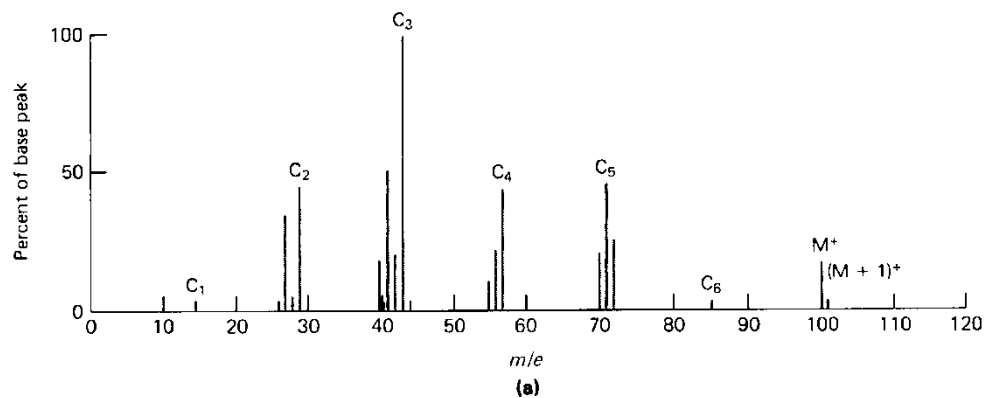
^a Taken from K. Biemann, *Mass Spectrometry, Organic Applications*, p. 52, McGraw-Hill Book Company, Inc.: New York, 1962. With permission.

Table 18-6

Isotopic Abundance Percentages and Molecular Weights For Various Combinations of Carbon, Hydrogen, Oxygen, and Nitrogen^a

Abundance, % M Peak Height				
	Formula	M + 1	M + 2	Molecular Weight
M = 83	C ₂ HN ₃ O	3.36	0.24	83.0120
	C ₂ H ₃ N ₄	3.74	0.06	83.0359
	C ₃ HNO ₂	3.72	0.45	83.0007
	C ₃ H ₃ N ₂ O	4.09	0.27	83.0246
	C ₃ H ₅ N ₃	4.47	0.08	83.0484
	C ₄ H ₃ O ₂	4.45	0.48	83.0133
	C ₄ H ₅ NO	4.82	0.29	83.0371
	C ₄ H ₇ N ₂	5.20	0.11	83.0610
	C ₅ H ₇ O	5.55	0.33	83.0497
	C ₅ H ₉ N	5.93	0.15	83.0736
	C ₆ H ₁₁	6.66	0.19	83.0861
M = 84	CN ₄ O	2.65	0.23	84.0073
	C ₂ N ₂ O ₂	3.00	0.43	83.9960
	C ₂ H ₂ N ₃ O	3.38	0.24	84.0198
	C ₂ H ₄ N ₄	3.75	0.06	84.0437
	C ₃ O ₃	3.36	0.64	83.9847
	C ₃ H ₂ NO ₂	3.73	0.45	84.0085
	C ₃ H ₄ N ₂ O	4.11	0.27	84.0324
	C ₃ H ₆ N ₃	4.48	0.08	84.0563
	C ₄ H ₄ O ₂	4.46	0.48	84.0211
	C ₄ H ₆ NO	4.84	0.29	84.0449
	C ₄ H ₈ N ₂	5.21	0.11	84.0688
	C ₅ H ₈ O	5.57	0.33	84.0575
	C ₅ H ₁₀ N	5.94	0.15	84.0814
	C ₆ H ₁₂	6.68	0.19	84.0939
	C ₇	7.56	0.25	84.0000

^a Taken from R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th ed., p. 49, Wiley: New York, 1981. Reprinted by permission of John Wiley & Sons, Inc.



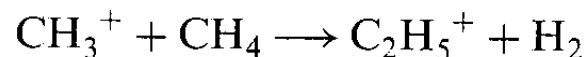
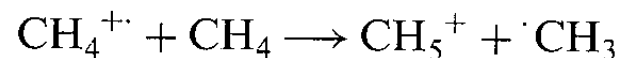
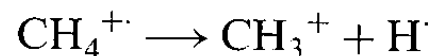
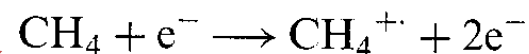
From: Skoog, 1985
David Reckhow

FIGURE 18-20 Electron impact mass spectra of some simple compounds: (a) *n*-heptane; (b) 1-pentanol; (c) *n*-heptanal.

Chemical Ionization

- Use of reagent gas at high pressures (0.2-2 torr)

- Methane
- Ammonia



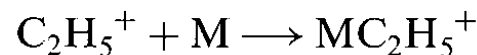
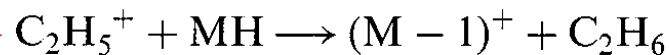
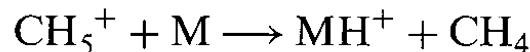
- Ionize reagent gas
- These ions react with and ionize analyte

- Pseudo-M ions

- M-1, M, M+1

- Adduct ions

- M+17, 29, 57



Cl: proton transfer

- Proton transfer will occur from conjugate bases of substances of lower affinity to those higher

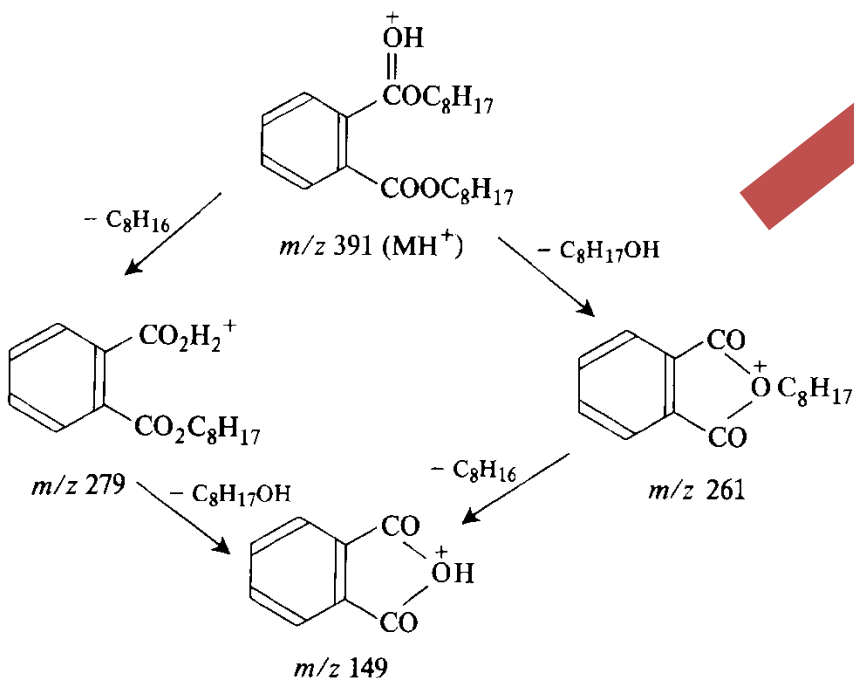
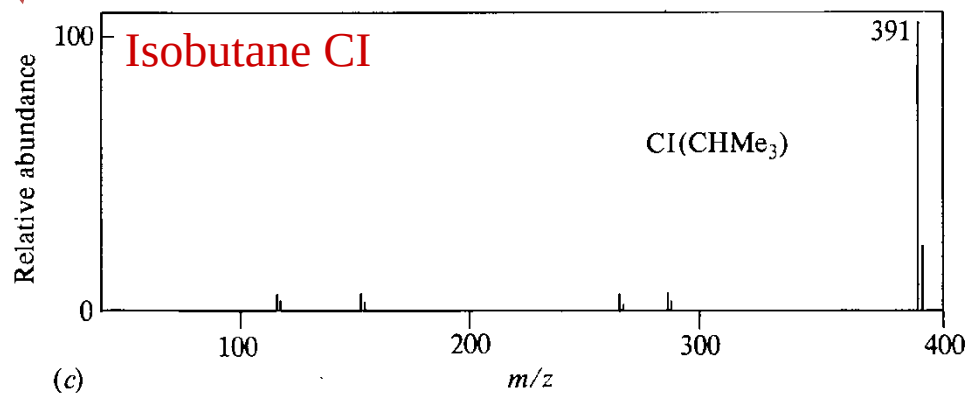
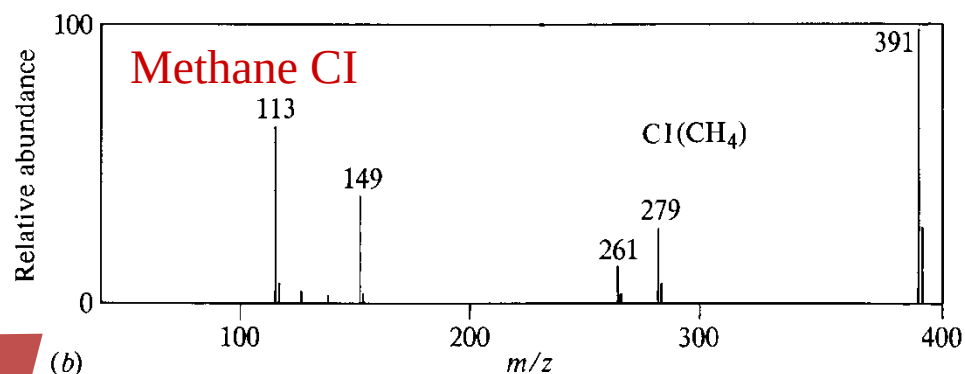
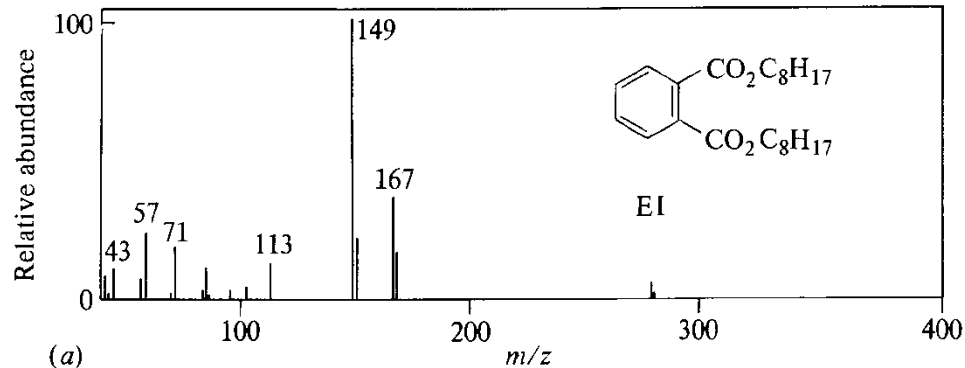
Table 5.1 Proton affinity ranges for representative analytes and proton affinities of the conjugate bases of several important reagents ions From: Budde, 2001



Proton affinity (kcal/mol)	Representative analytes and conjugate bases
129.9	Methane (conjugate base of CH_5^+)
130–165	Fluoromethanes except CF_4 , ethane, propane, CO_2 , N_2O , NO_2 , SO_3 , HCl
162.6	Ethene (conjugate base of C_2H_5^+)
165.2	Water (conjugate base of H_3O^+)
165–175	Chloroethane, bromoethane, formaldehyde, HCN , trifluoroacetic acid
175–200	Alcohols, aldehydes, nitriles, benzene, toluene, propene, chlorobenzene
191.7	Isobutene (conjugate base of $\text{tert-C}_4\text{H}_9^+$)
204.1	Ammonia (conjugate base of NH_4^+)
200–225	Ketones, ethers, esters, alkylated benzenes, dienes
225–250	Amines, amine oxides, amides, <i>N</i> -heterocyclics, phosphines, other bases

CI S

- Spectra of di-
isooctylphthalate



From: Howe et al., 1981, Mass Spectrometry, Principles and Applications

Mass Spectral Interpretation

- References

- Fred McLafferty, Interpretation of Mass Spectra

- University Science Books, Mill Valley, CA

- 3rd Ed., 1980

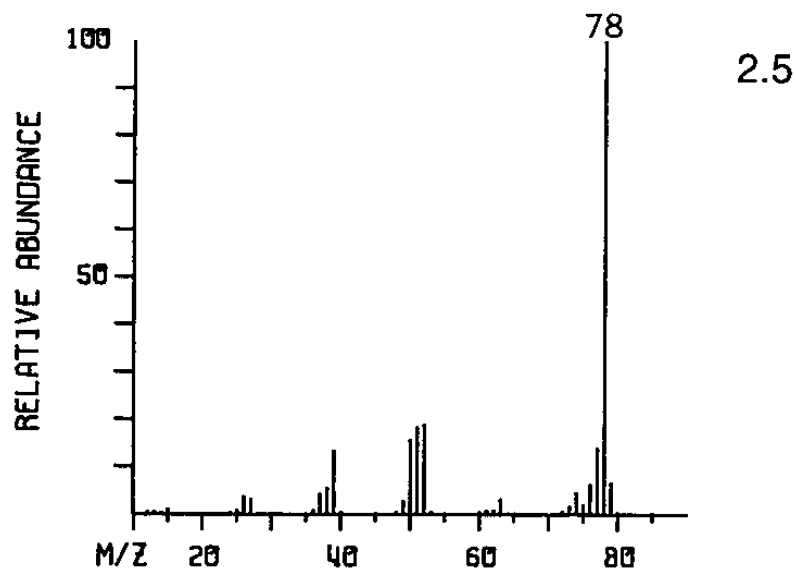
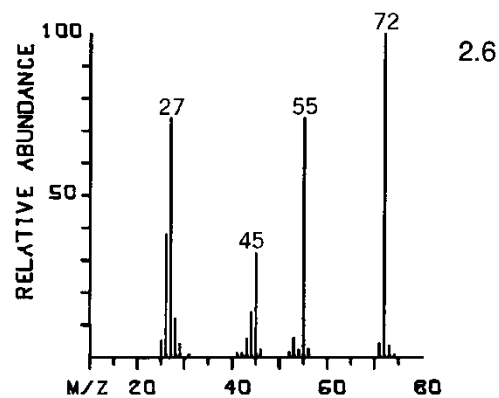
- 4th Ed., 1993 (with František Tureček)

- McLafferty & Venkataraghavan, 1982; Mass Spectral Correlations, 2nd Ed.,

- American Chemical Society, Advances in Chemistry Series #40

Unknown 2.6

<i>m/z</i>	Rel. abund.
25	5.2
26	38.
27	74.
27.5	0.3
28	12.
29	4.3
31	0.5
41	1.2
42	1.3
43	5.8
44	14.
45	32.
46	2.5
52	1.4
53	6.0
54	2.3
55	74.
56	2.6
57	0.2
71	4.3
72	100.
73	3.5
74	0.5

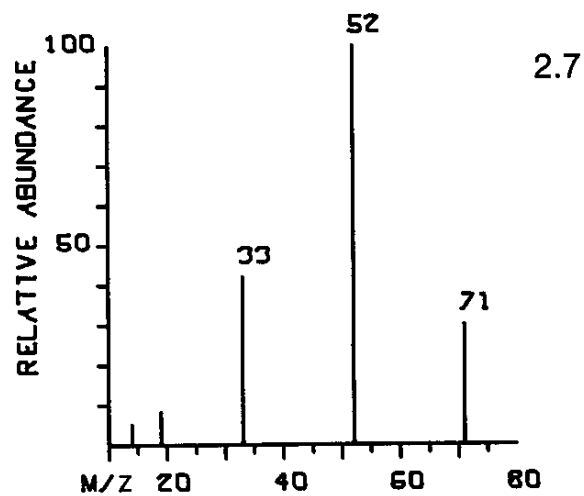


Unknown 2.5

<i>m/z</i>	Rel. abund.	<i>m/z</i>	Rel. abund.
12	0.2	53	0.8
13	0.4	60	0.2
14	0.4	61	0.4
15	1.0	62	0.8
24	0.4	63	2.9
25	0.8	64	0.2
26	3.2	72	0.4
27	2.6	73	1.0
36	0.9	74	3.9
37	3.8	75	2.2
39	13.	76	7.0
40	0.4	77	15.
50	16.	78	100.
51	19.	79	6.8
52	20.	80	0.2

Unknown 2.7

<i>m/z</i>	Rel. abund.
14	5.2
19	8.4
33	36.
52	100.
53	0.4
71	30.



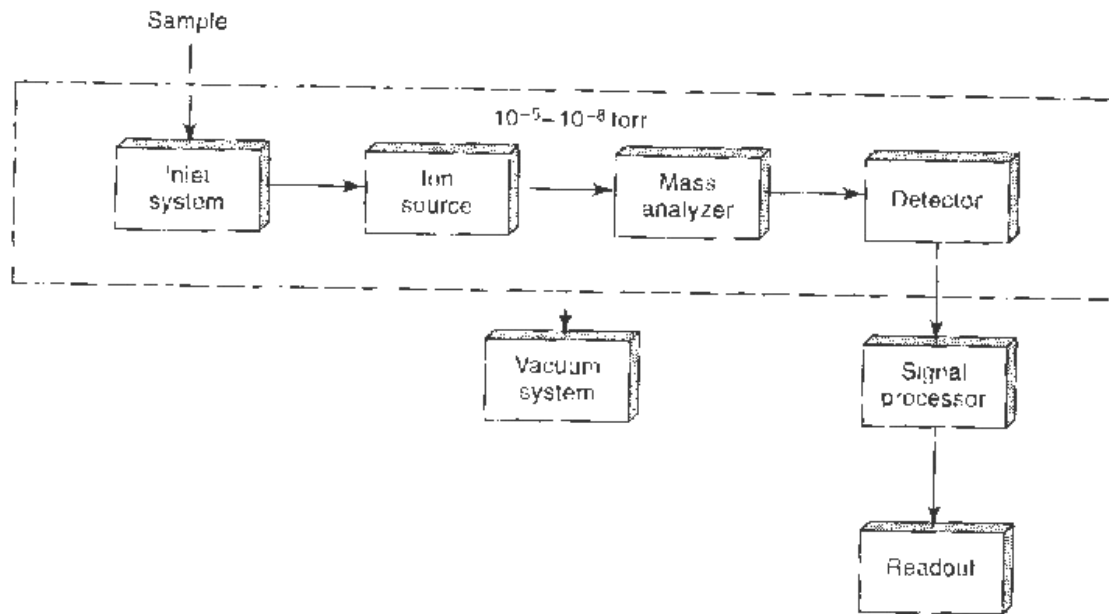
Mass Spectrometry

- General References on Instrument Design
 - Skoog, Principles of Instrumental Analysis
 - 1985 (3rd ed): parts of Chapter 18
 - 1991 (4th ed): parts of Chapter 18
 - 1998 (5th ed): parts of Chapter 20
 - Howe, Williams & Bowen, Mass Spectrometry, Principles & Applications
 - 1981 (2nd ed): Chapter 1 & 12
 - Loconto, Trace Environmental Quantitative Analysis
 - 2001: pp356-370
 - Budde, Analytical Mass Spectrometry
 - 2001, Oxford University Press,
 - parts of Chapter 1 & 2

Mass Spectrometry

- MS – molecules are ionized and separated based on their mass to charge ratio (m/z)
- The molecules are bombarded by electrons and the molecules release 1 or more electrons
- $M + e^- \rightarrow M^+ + 2e^-$

MS Schematic



MS Inlet System

- Introduce the sample to the MS
- 3 types
 - batch inlet
 - direct probe inlet
 - chromatographic inlet

References

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- Schoenberg, Ted, “The Hewlett Packard HP5890A GC/ HP5988A MS System,” 1997
- Skoog, Douglas; Leary, James; Principles of Instrumental Analysis, Saunders College Publishing, New York, 1992
- HP 5988A Mass Spectrometer System Hardware and Service Manual, 1985

- To next lecture