Updated: 11 November 2014

Print version

CEE 772: Instrumental Methods in Environmental Analysis

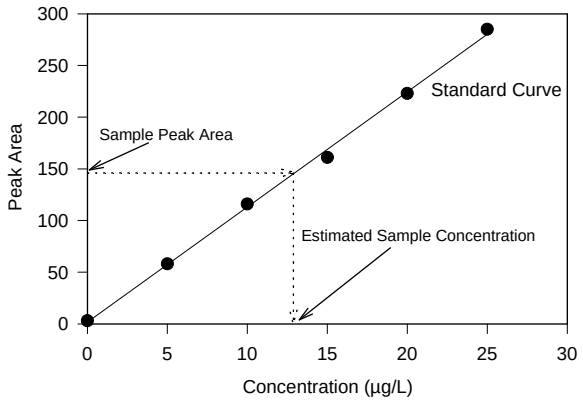
Lecture #19

Mass Spectrometry: Basics

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

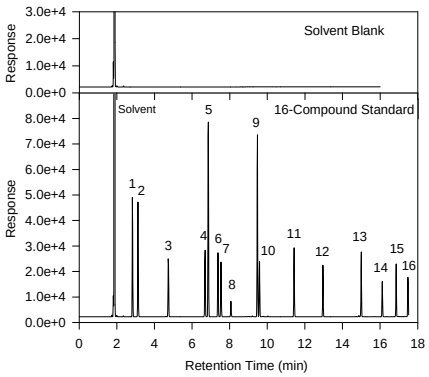
(Harris, Chapt. 23, 24 & 25)
(641-664, 699-706; 742-749)

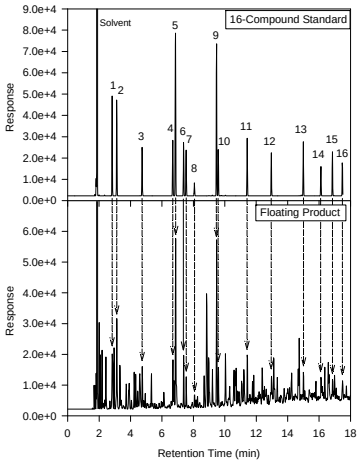
Calibration

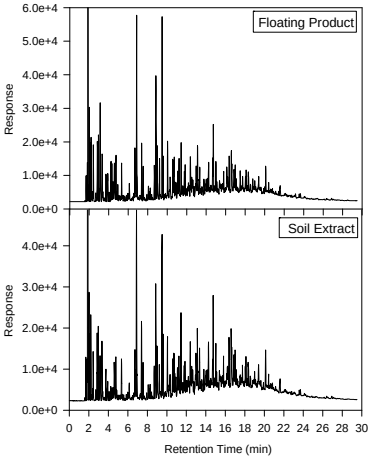


Example

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




16-Compound Standard
Solvent
Floating Product
Response
Retention Time (min)

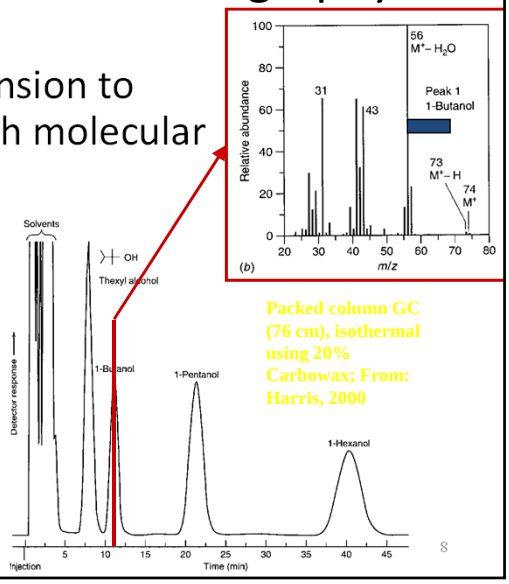

Floating Product
Soil Extract
Response
Retention Time (min)

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

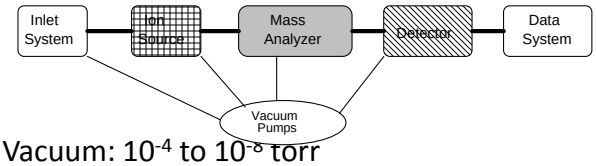
- Provides a 3rd dimension to chromatograms with molecular weight info
- GC/MS
  - Used in environ-mental field for 20 years
- LC/MS
  - Newer



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

Basics of an MS instrument

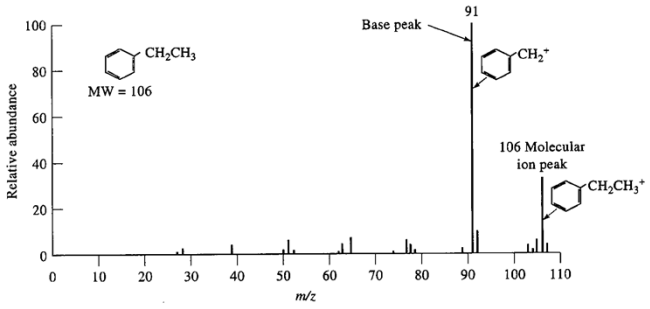
- Major components



- Vacuum: 10^{-4} to 10^{-8} torr

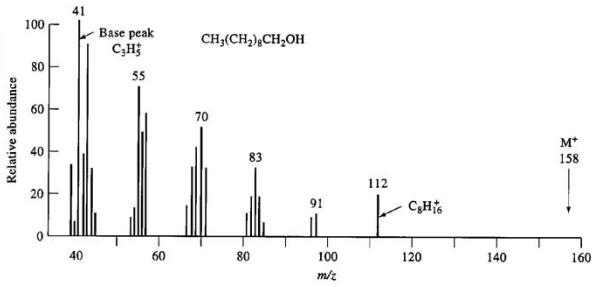
Mass Spectra

- Ethyl Benzene

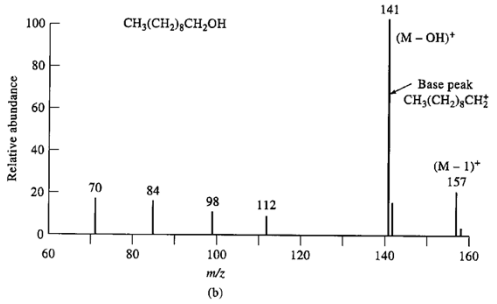


Fra

- 1-decanol
  - A. Hard Source



  - B. Soft Source



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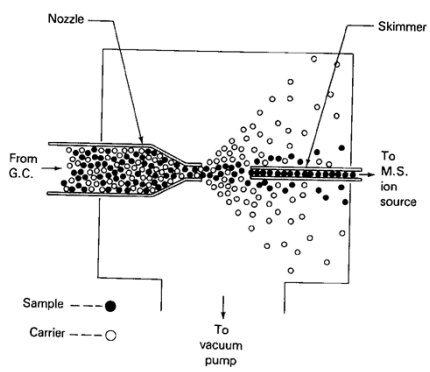
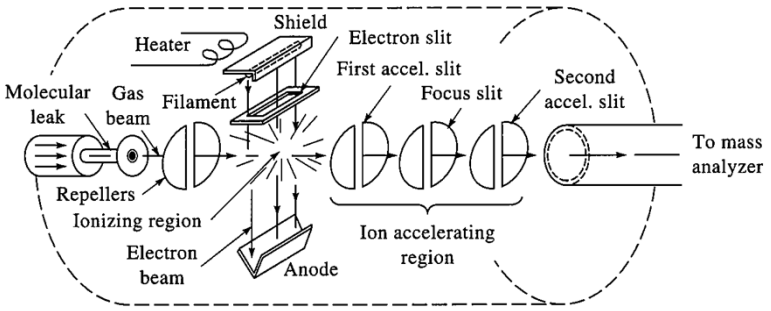
Interfaces

- Jet Separator



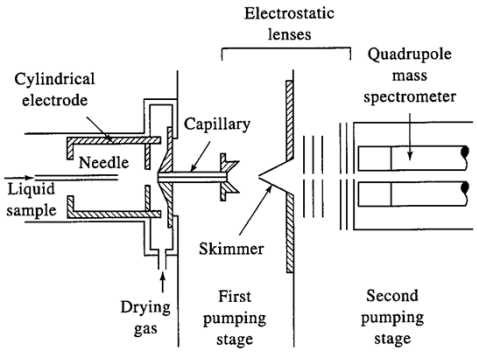
Ion Source

- 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

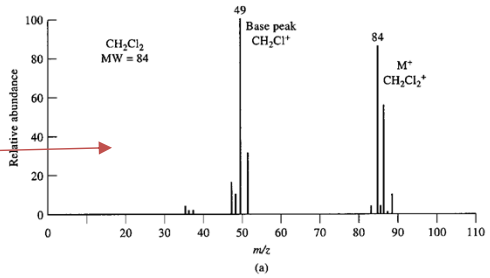
Mass Spec

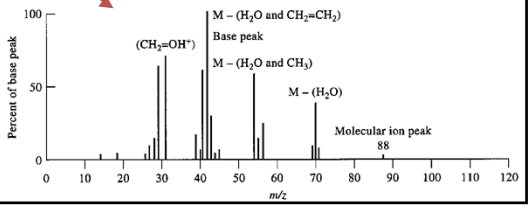
- Typical reactions in electron impact

Molecular ion formation	
Fragmentation	$ABCD + e^- \rightarrow ABCD^{\bullet +} + 2e^-$ $ABCD^{\bullet +} \rightarrow A^+ + BCD^\bullet$ $\rightarrow A^\bullet + BCD^+ \rightarrow BC^+ + D$ $\rightarrow CD^\bullet + AB^+ \rightarrow B + A^+$ / $A + B^+$ $\rightarrow AB^\bullet + CD^+ \rightarrow D + C^+$ / $C + D^+$
Rearrangement followed by fragmentation	$ABCD^{\bullet +} \rightarrow ADBC^{\bullet +} \rightarrow BC^\bullet + AD^+$ / $AD^\bullet + BC^+$
Collision followed by fragmentation	$ABCD^{\bullet +} + ABCD \rightarrow (ABCD)^{\bullet 2+} \rightarrow BCD^\bullet + ABCDA^+$

Mass Spec

- Electron Impact
  - Methylene Chloride
  - 1- Pentanol





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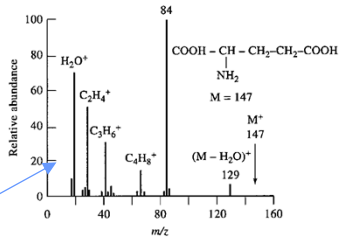
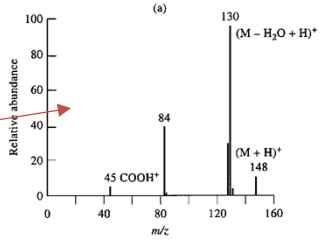
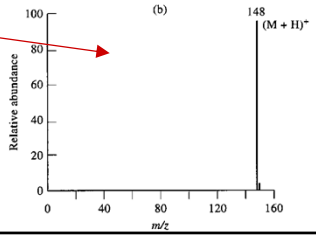
Mass Spec

- 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 Mass	A Per cent	A + 1 Mass	A + 1 Per cent	A + 2 Mass	A + 2 Per cent	Element type
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"

[a]Wapstra and Gove (1971).
[b]1.1 ±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:

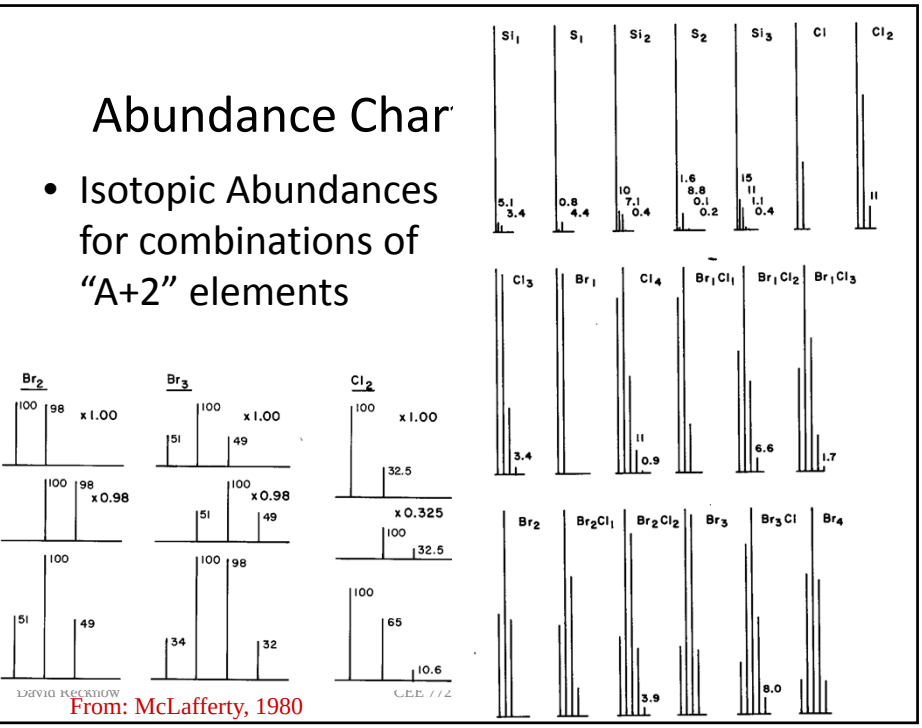
	(A + 1)	(A + 2)		(A + 1)	(A + 2)	(A + 3)
C_1	1.1	0.00	C_{16}	18	1.5	0.1
C_2	2.2	0.01	C_{17}	19	1.7	0.1
C_3	3.3	0.04	C_{18}	20	1.9	0.1
C_4	4.4	0.07	C_{19}	21	2.1	0.1
C_5	5.5	0.12	C_{20}	22	2.3	0.2
C_6	6.6	0.18	C_{22}	24	2.8	0.2
C_7	7.7	0.25	C_{24}	26	3.3	0.3
C_8	8.8	0.34	C_{26}	29	3.9	0.3
C_9	9.9	0.44	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): C_{25}, 0.02; C_{40}, 0.13; C_{100}, 5.7.

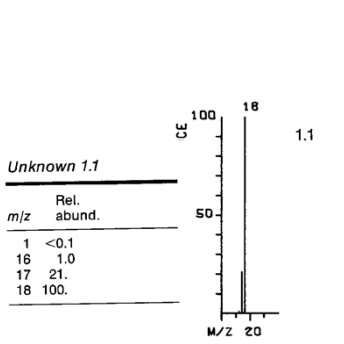
From: McLafferty, 1980

Abundance Char

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

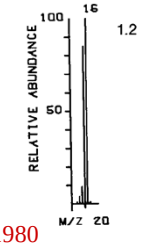


From: McLafferty, 1980



Unknown 1.1

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

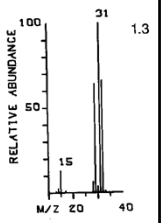


Unknown 1.2

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

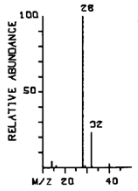
Unknown 1.3

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		



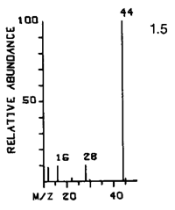
Unknown 1.4

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

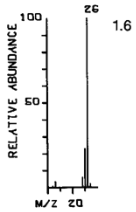
m/z	Rel. abund.
12	8.7
16	9.6
22	1.9
28	9.8
29	0.1
44	100.
45	1.2
46	0.4



From: McLafferty, 1980

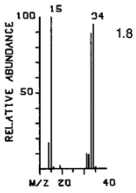
Unknown 1.6

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



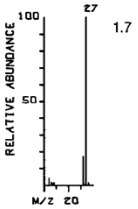
Unknown 1.8

m/z	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



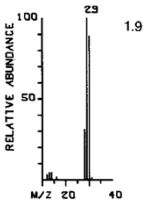
Unknown 1.7

m/z	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

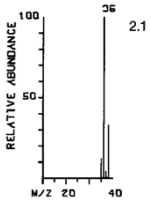
m/z	Rel. abund.
12	3.3
13	4.3
14	4.4
16	1.7
28	31.
29	100.
30	89.
31	1.3



From: McLafferty, 1980

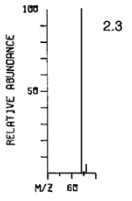
Unknown 2.1

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



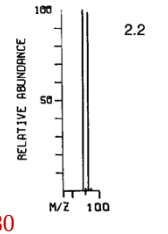
Unknown 2.3

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



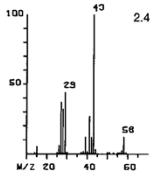
Unknown 2.2

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

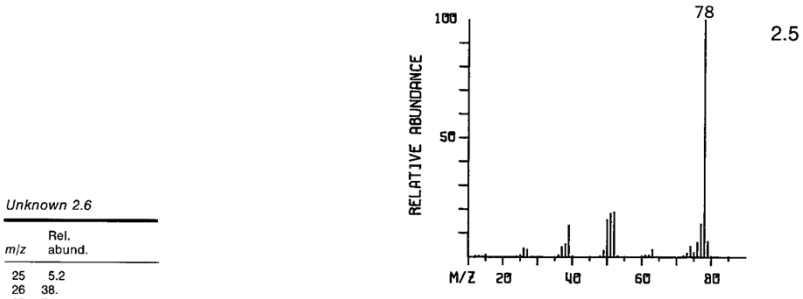


Unknown 2.4

m/z	Rel. abund.	m/z	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

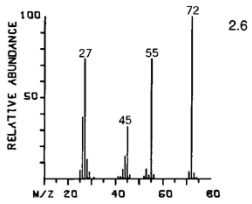


From: McLafferty, 1980



Unknown 2.6

m/z	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



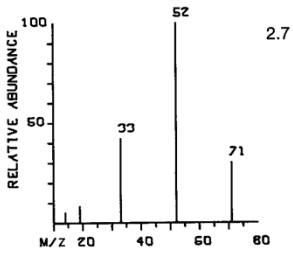
Unknown 2.5

m/z	Rel. abund.	m/z	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

From: McLafferty, 1980

Unknown 2.7

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

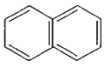
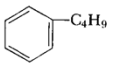
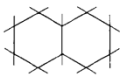


From: McLafferty, 1980

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
n-Butylbenzene		8.3
trans-Decaline		8.2
Diamyl sulfide	$(C_5H_{11})_2S$	3.7
n-Decane	$C_{10}H_{22}$	1.41
Diamylamine	$(C_5H_{11})_2NH$	1.14
Methyl nonanoate	$C_9H_{17}COOCH_3$	1.10
Diamyl ether	$(C_5H_{11})_2O$	0.33
3,3,5-Trimethylheptane	$C_{10}H_{22}$	0.007
n-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.

From: Skoog, 1985

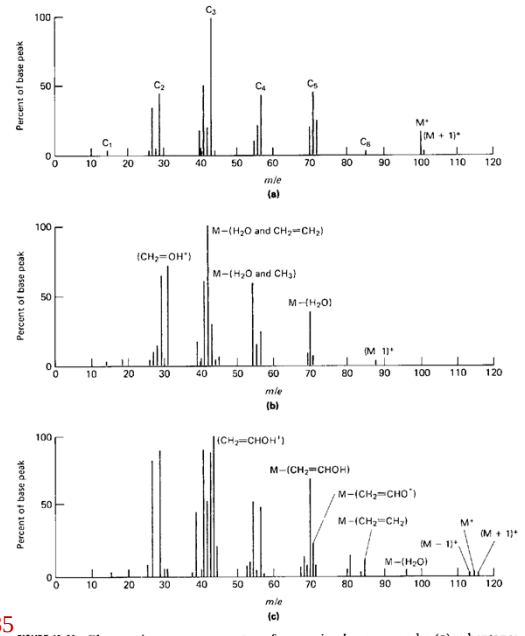
Table 18–6
Isotopic Abundance Percentages and Molecular Weights For Various Combinations of Carbon, Hydrogen, Oxygen, and Nitrogen[a]

		Abundance, % M Peak Height		
	Formula	M + 1	M + 2	Molecular Weight
M = 83	C_2HN_3O	3.36	0.24	83.0120
	$C_2H_3N_4$	3.74	0.06	83.0359
	C_3HNO_2	3.72	0.45	83.0007
	$C_3H_3N_2O$	4.09	0.27	83.0246
	$C_3H_5N_3$	4.47	0.08	83.0484
	$C_4H_3O_2$	4.45	0.48	83.0133
	C_4H_5NO	4.82	0.29	83.0371
	$C_4H_7N_2$	5.20	0.11	83.0610
	C_5H_7O	5.55	0.33	83.0497
	C_5H_9N	5.93	0.15	83.0736
	C_6H_{11}	6.66	0.19	83.0861
M = 84	CN_4O	2.65	0.23	84.0073
	$C_2N_2O_2$	3.00	0.43	83.9960
	$C_2H_2N_3O$	3.38	0.24	84.0198
	$C_2H_4N_4$	3.75	0.06	84.0437
	C_3O_3	3.36	0.64	83.9847
	$C_3H_2NO_2$	3.73	0.45	84.0085
	$C_3H_4N_2O$	4.11	0.27	84.0324
	$C_3H_6N_3$	4.48	0.08	84.0563
	$C_4H_4O_2$	4.46	0.48	84.0211
	C_4H_6NO	4.84	0.29	84.0449
	$C_4H_8N_2$	5.21	0.11	84.0688
	C_5H_8O	5.57	0.33	84.0575
	$C_5H_{10}N$	5.94	0.15	84.0814
	C_6H_{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



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.

30

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

$$CH_4 + e^- \longrightarrow CH_4^{+\cdot} + 2e^-$$

$$CH_4^{+\cdot} \longrightarrow CH_3^+ + H^\cdot$$

$$CH_4^{+\cdot} + CH_4 \longrightarrow CH_5^+ + {}^\cdot CH_3$$

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

$$CH_5^+ + M \longrightarrow MH^+ + CH_4$$

$$C_2H_5^+ + MH \longrightarrow (M-1)^+ + C_2H_6$$

$$C_2H_5^+ + M \longrightarrow MC_2H_5^+$$

CI: proton transfer

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

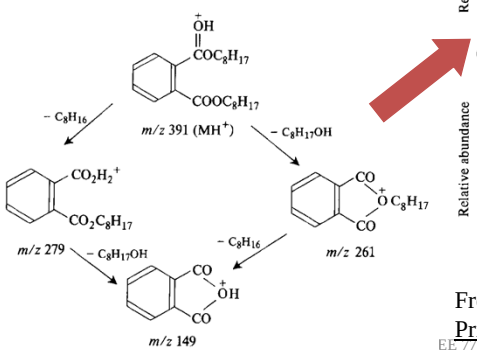
Table 5.1 Proton affinity ranges for representative analytes and proton affinities of the conjugate bases of several important reagents ions

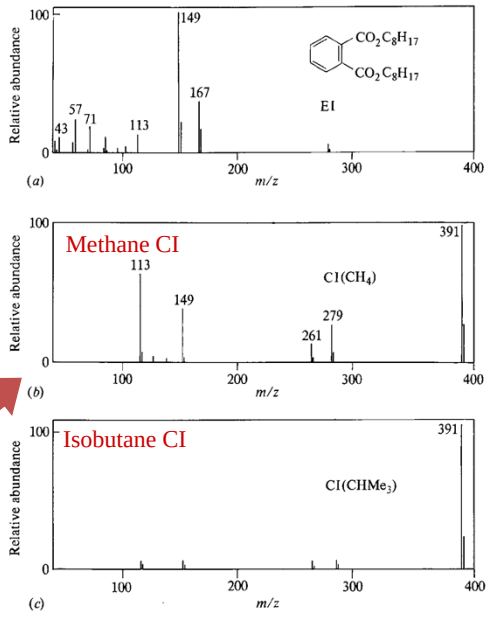
From: Budde, 2001

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 *tert*-$C_4H_9^+$)
204.1	Ammonia (conjugate base of NH_4^+)
200–225	Ketones, ethers, esters, alkylated benzenes, dienes
225–250	Amines, amine oxides, amides, *N*-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
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  - McLafferty & Venkataraghavan, 1982; Mass Spectral Correlations, 2nd Ed.,
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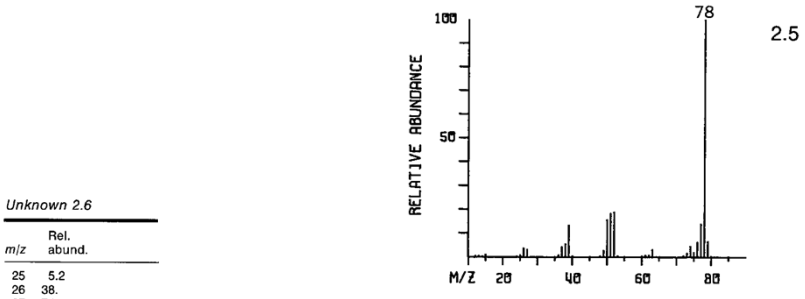
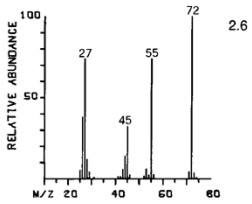


Unknown 2.6

m/z	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



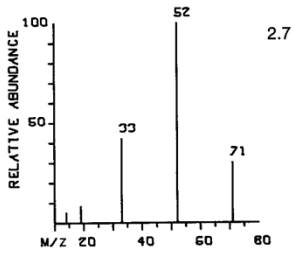
Unknown 2.5

m/z	Rel. abund.	m/z	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

From: McLafferty, 1980

Unknown 2.7

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



From: McLafferty, 1980

Mass Spectrometry

- General References on Instrument Design
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    - 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
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    - 2001: pp356-370
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    - 2001, Oxford University Press,
      - parts of Chapter 1 & 2

Mass Spectrometry

- MS – molecules are ionized and separated based on the 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

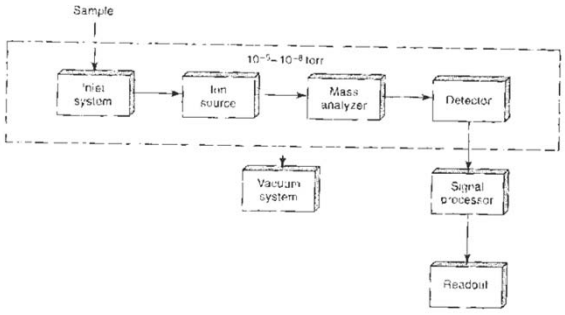

Figure 18-1, Skoog

MS Inlet System

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

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- To next lecture