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CEE 772:
Instrumental Methods in Environmental Analysis

Lecture #22

Mass Spectrometry: Chemical Ionization

(Skoog,)

(Harris, Chapt.)

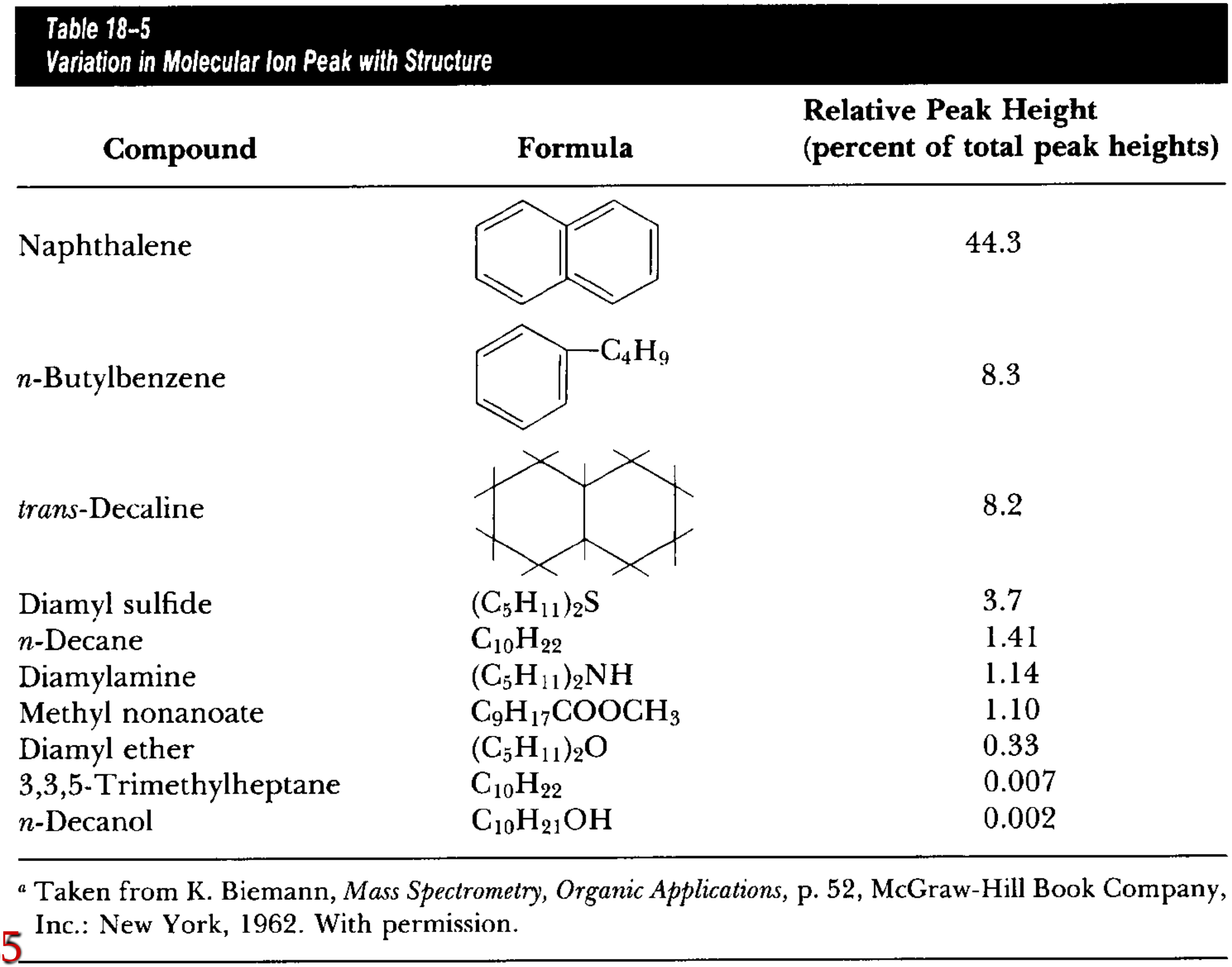

Table 18-5
Variation in Molecular Ion Peak with Structure

Compound	Formula	Relative Peak Height (percent of total peak heights)
Naphthalene		44.3
n-Butylbenzene	$-C_4H_9$	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

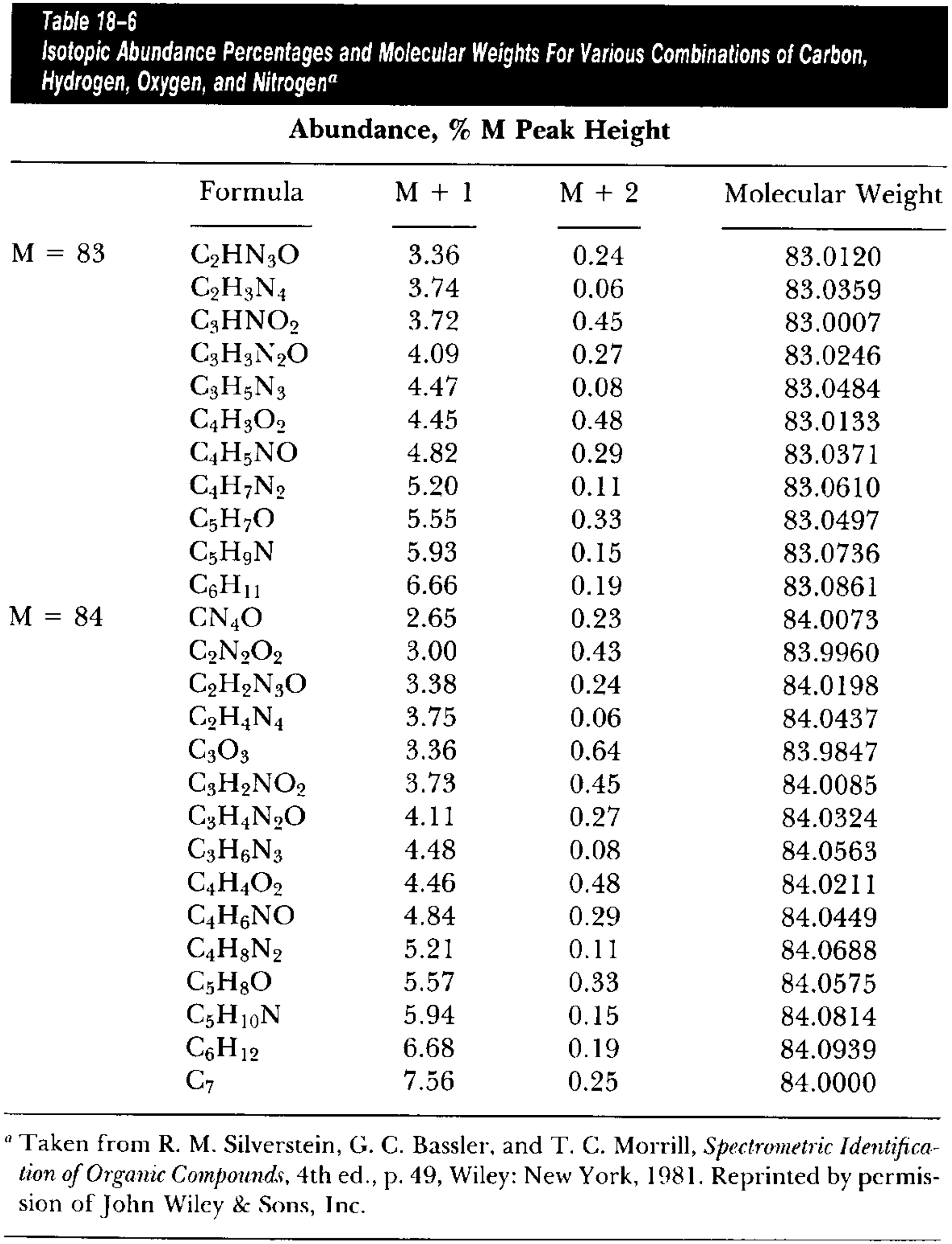

Table 18-6

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

	Formula	Abundance, % M Peak Height		Molecular Weight
		M + 1	M + 2	
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

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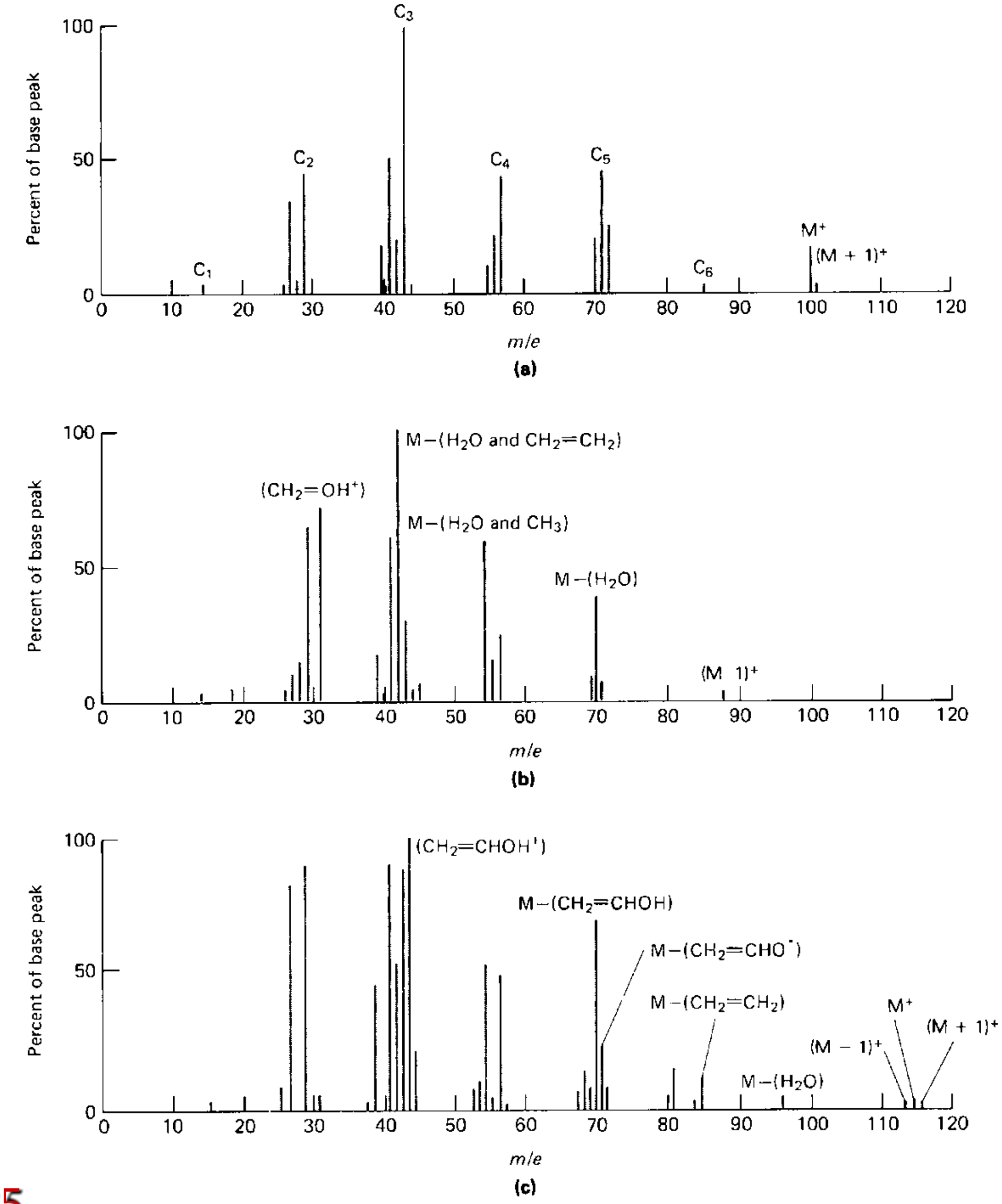
[a] Taken from R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th ed., p. 49, Wiley: New York, 1981. Reprinted by permission of John Wiley & Sons, Inc.

From: Skoog, 1985



From: Skoog, 1985

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

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

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

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

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

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

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

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

CI: proton transfer

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

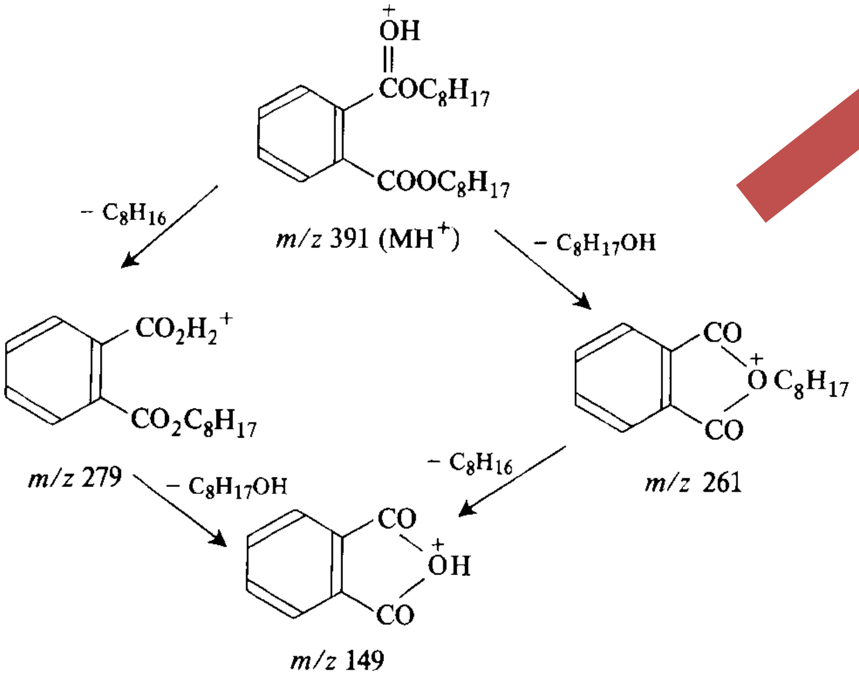
Table 5.1 Proton affinity ranges for representative analytes and proton affinities of the conjugate bases of several important reagents ions

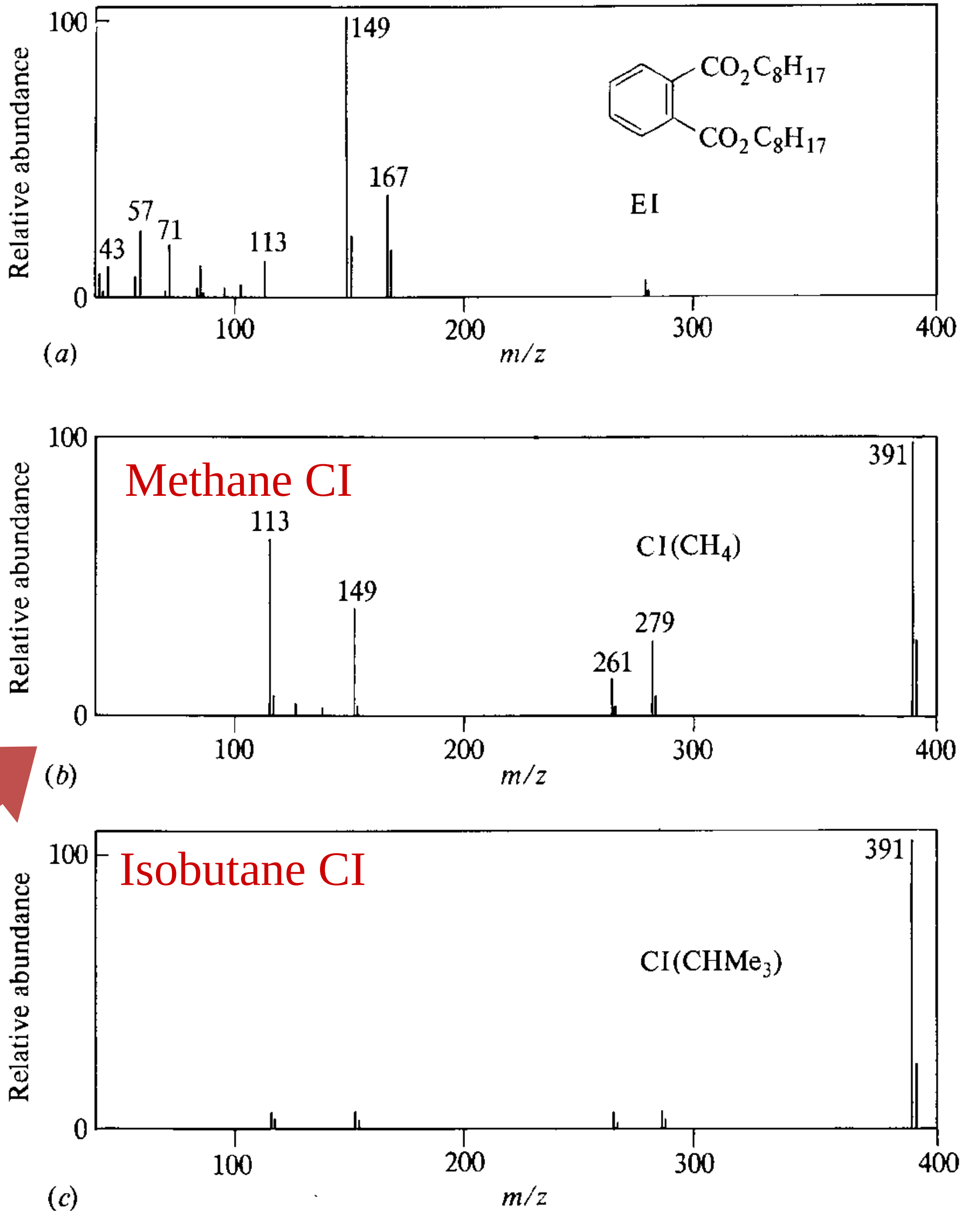
From: Budde, 2001

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 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 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

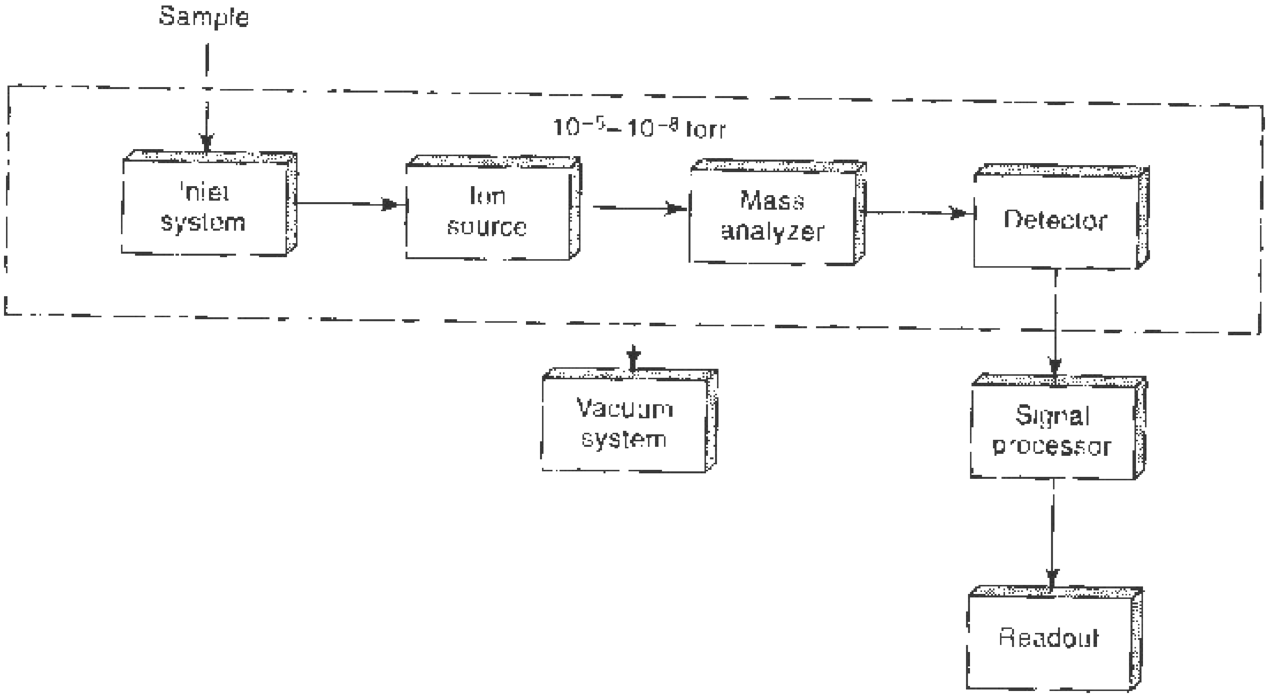


Figure 18-1, Skoog

MS Inlet System

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

MS - Batch Inlet

- Most common inlet system
- Gas or liquid sample is volatized externally, then leaks into ionization area
- A vacuum pressure of 10^{-4} to 10^{-5} torr is applied to the inlet system

MS – Direct Probe Inlet

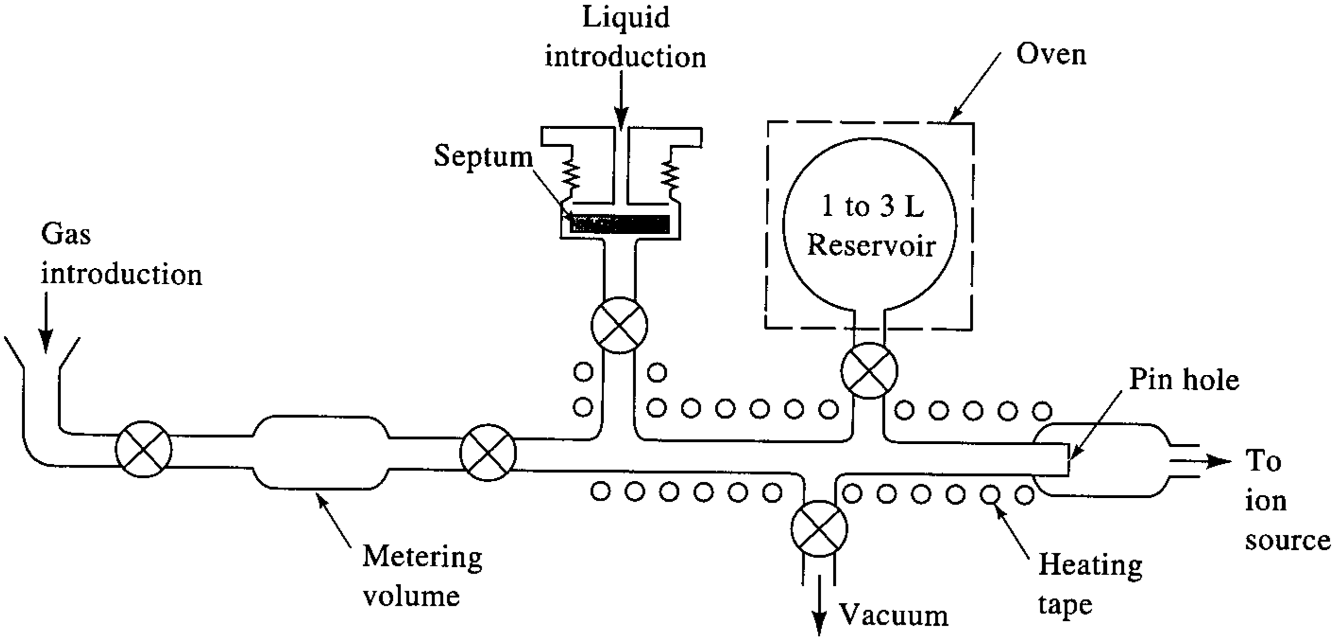
- Used for solids and nonvolatile liquids
- A sample holder (probe) is used to insert the sample into the ionization region
- A vacuum lock system is used to minimize the volume of air that must pumped from the system after the probe is inserted in the ionization area
- The probe’s tip is surrounded a heating coil to heat or cool the sample

MS - Chromatographic Inlet System

- Capillary column output can be fed directly into the ionization region because its flow rate is very small
- Packed column output must flow through a jet separator to remove most of the carrier gas

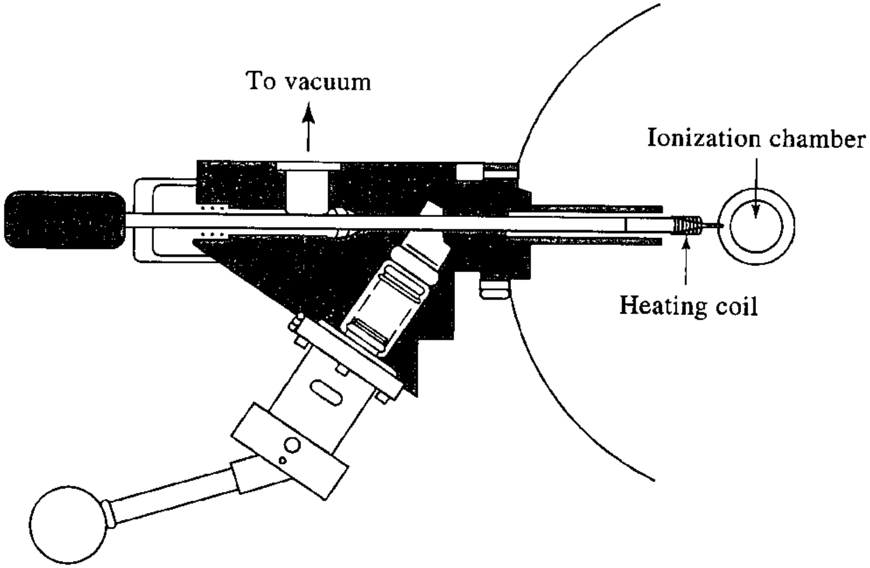
Sample Introduction

- General types of devices



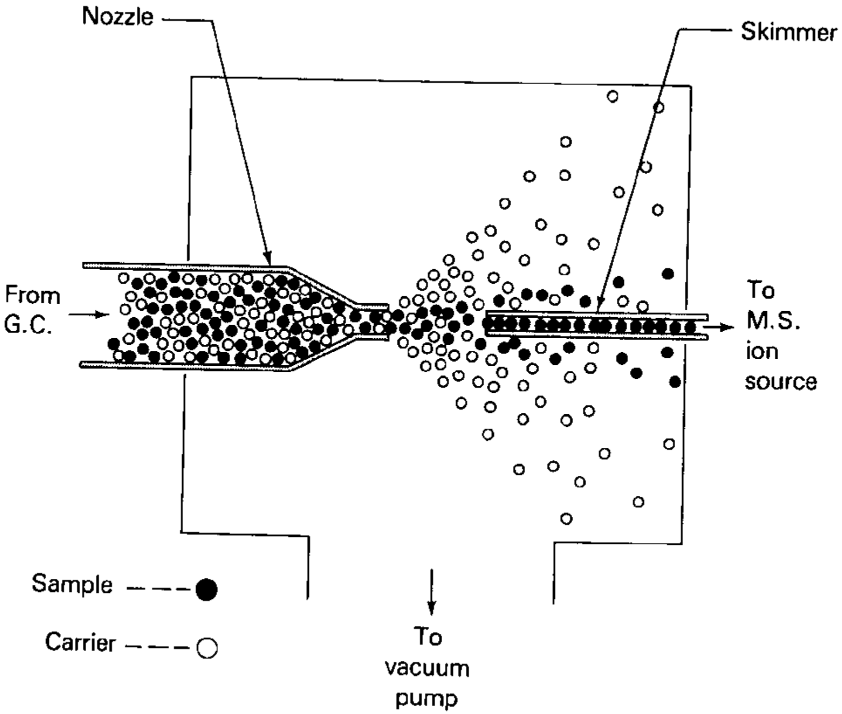
Sample Introduction

- Sample probe



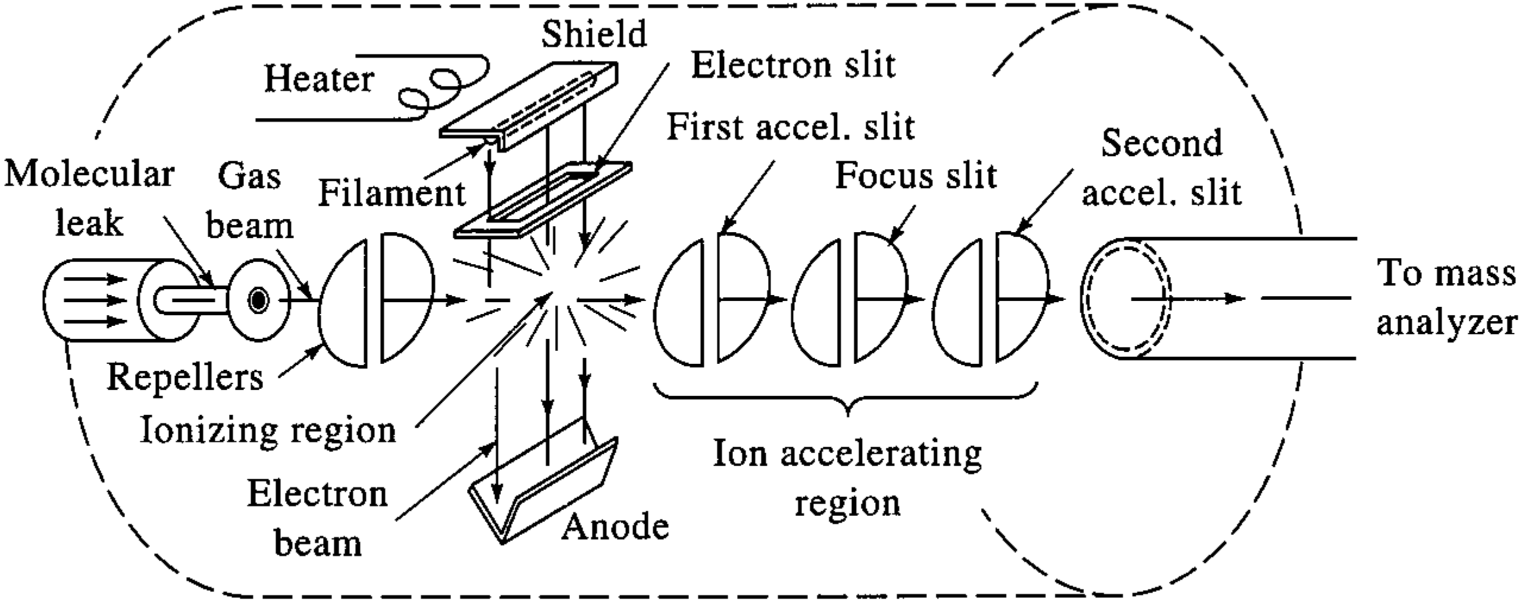
Interfaces

- Jet Separator



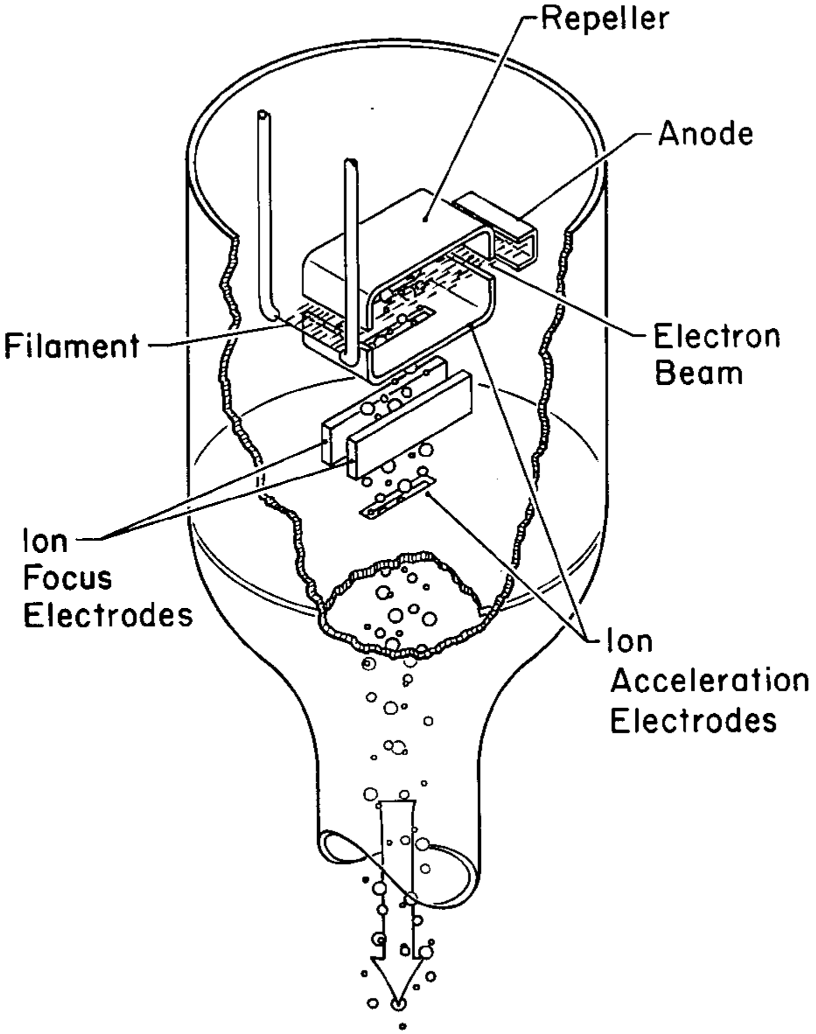
Ion Source

- Electron Impact



Ion Source

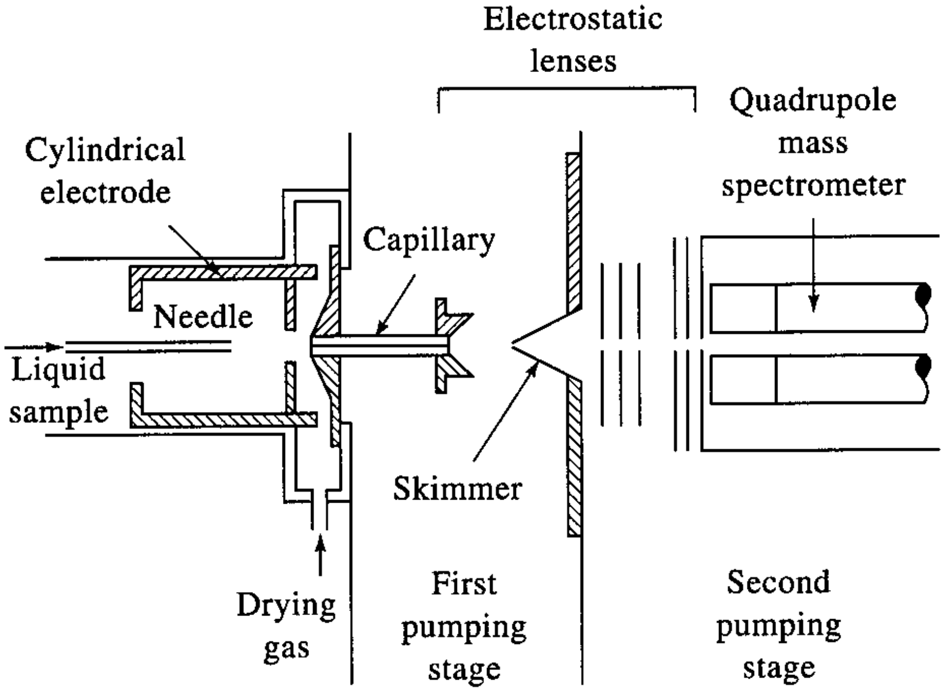
- Electron Impact



From: McLafferty, 1980

Interface & Ion Source

- Electrospray Ionization



Ion Source

- Electrical Impact Ionization (EI)
  - molecules are bombarded with electrons with KE of 70 eV that cause them to be ionized
  - EI causes great amount of fragmentation in large molecules causing the mass spectra to be difficult to interpret
- Chemical Ionization (CI)
  - the ion source is filled with a reagent gas, usually methane, at a pressure = 100 Pa. CH_4 react with electrons to form reactive products such as CH_5^+
  - CH_5^+ reacts with the molecule to form CH_4 and MH^+
  - Softer method – less fragmentation occurs

- To next lecture