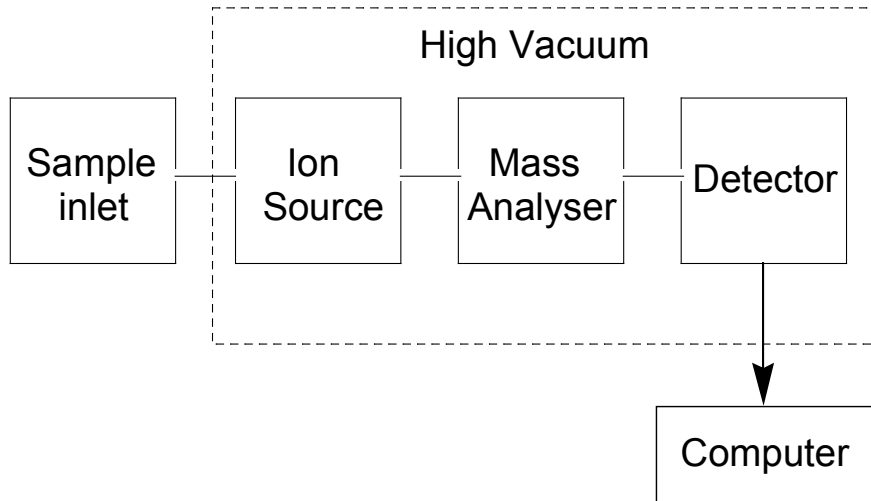
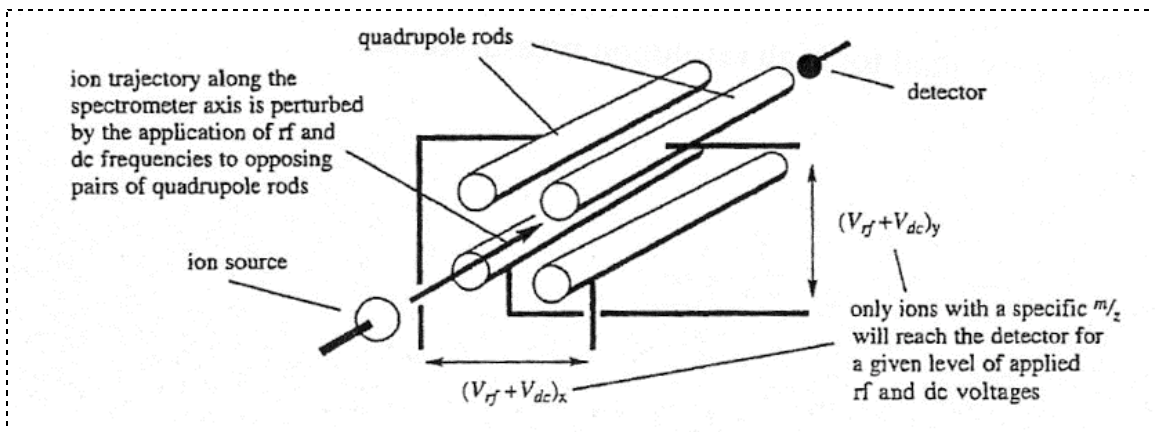
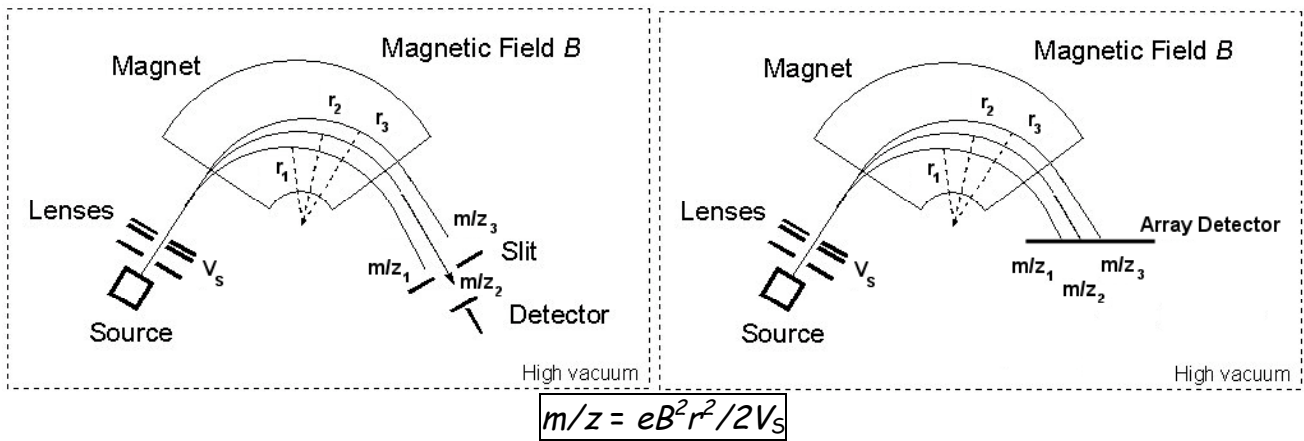
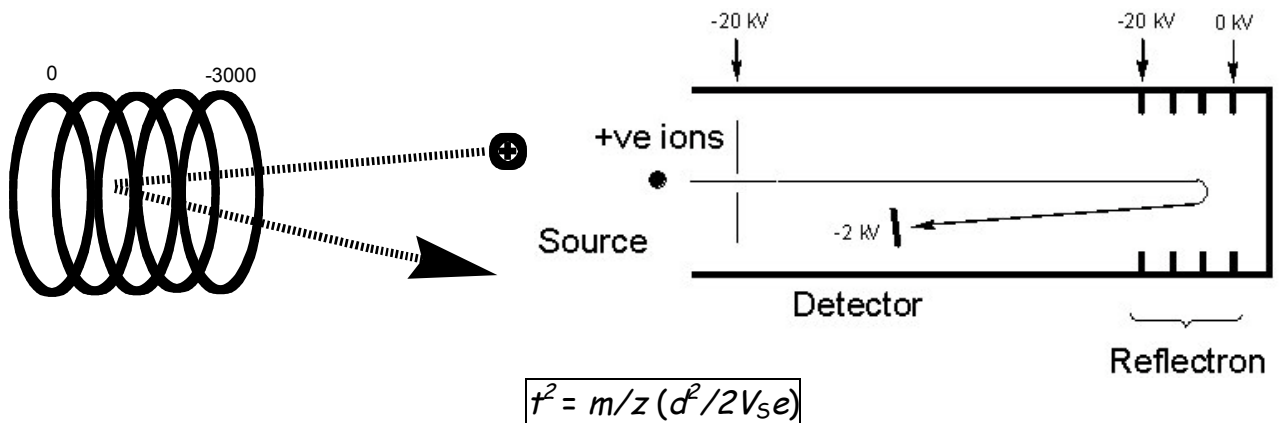
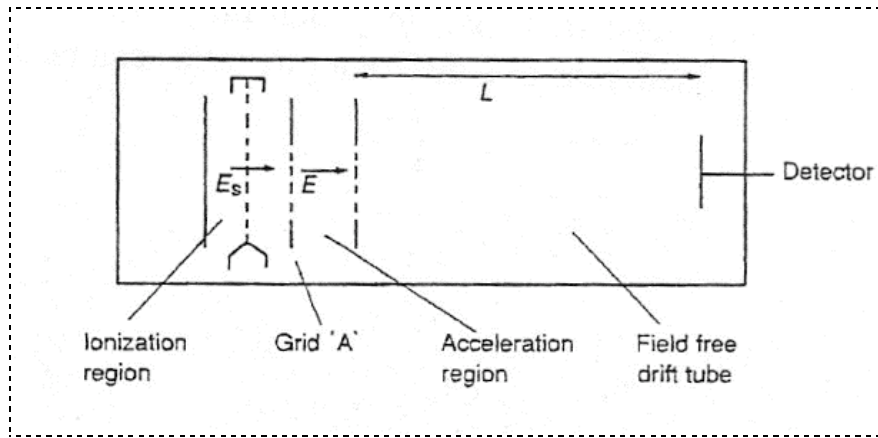


Ions in a Field: m/z to Determine Gross Structure

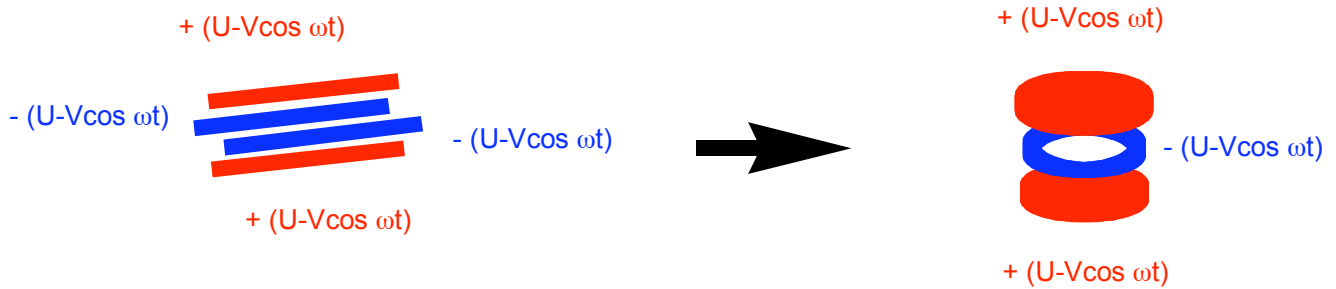


- Measuring m/z of ion beams: Magnetic Sector, Quadrupole, ToF





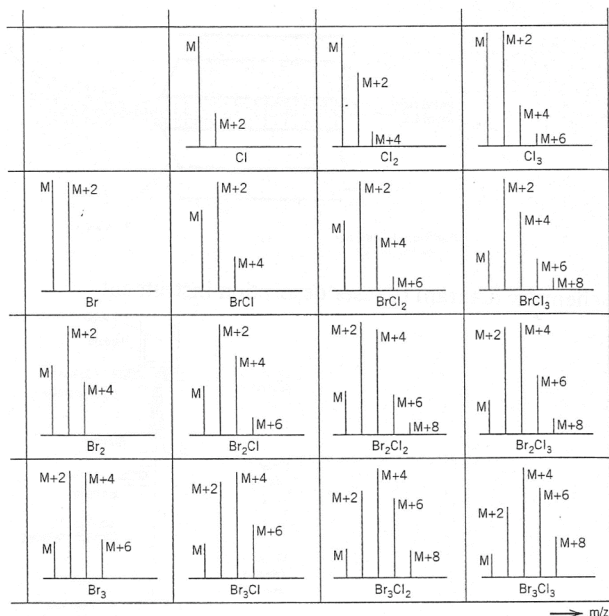
• Measuring m/z by trapping: Ion Cyclotron Resonance, Ion Trap



• Isotopic abundance

Isotope Abundances Based on the Common Isotope Set at 100%

Element	Abundance (%)			
		M + 1	M + 2	
Hydrogen	¹ H 100	² H 0.0115		
Carbon	¹² C 100	¹³ C 1.08		
Nitrogen	¹⁴ N 100	¹⁵ N 0.369		
Oxygen	¹⁶ O 100	¹⁷ O 0.0381	¹⁸ O	0.205
Fluorine	¹⁹ F 100			
Silicon	²⁸ Si 100	²⁹ Si 5.08	³⁰ Si	3.35
Phosphorus	³¹ P 100			
Sulfur	³² S 100	³³ S 0.800	³⁴ S	4.52
Chlorine	³⁵ Cl 100		³⁷ Cl	32.0
Bromine	⁷⁹ Br 100		⁸¹ Br	97.3
Iodine	¹²⁷ I 100			



Distinguishing Elements

Element	Distinguishing Characteristic
N	Odd M^+
S	Large $M + 2$ (about 4%)
Cl	$M + 2$ one-third as large as M^+
Br	$M + 2$ as large as M^+
I	Small $M + 1$ and $M + 2$

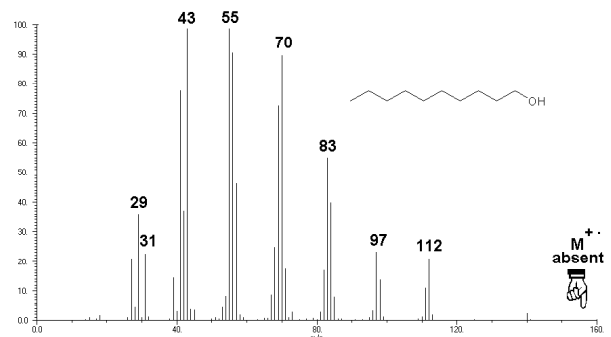
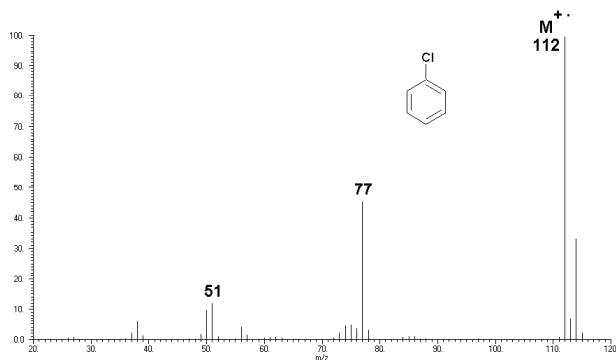
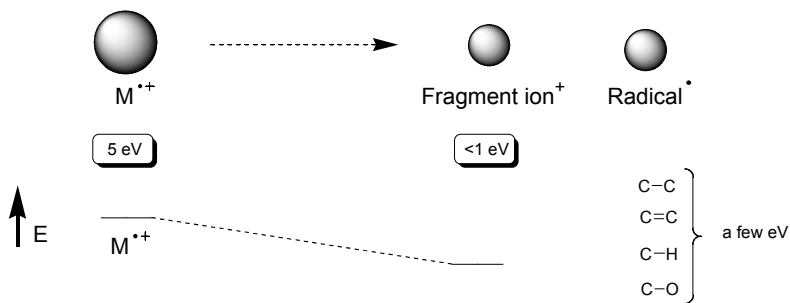
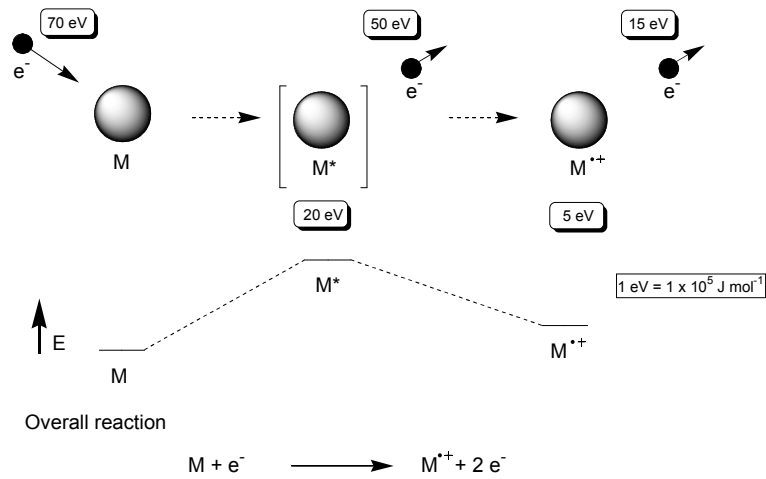
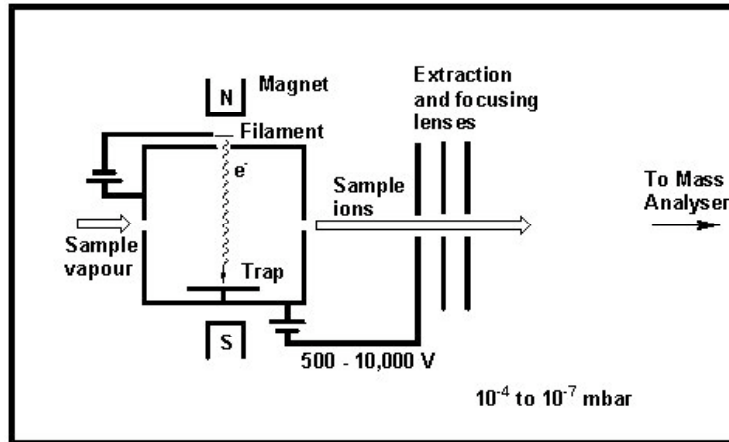
Masses and Isotope Abundance Ratios for Combinations of C, H, N, and O Corresponding to Mass 28

Formula	m/z Ratio	$M + 1$	$M + 2$
C_2H_4	28.0313	2.28	0.01
CO	27.9949	1.15	0.20
N_2	28.0062	0.74	0.00

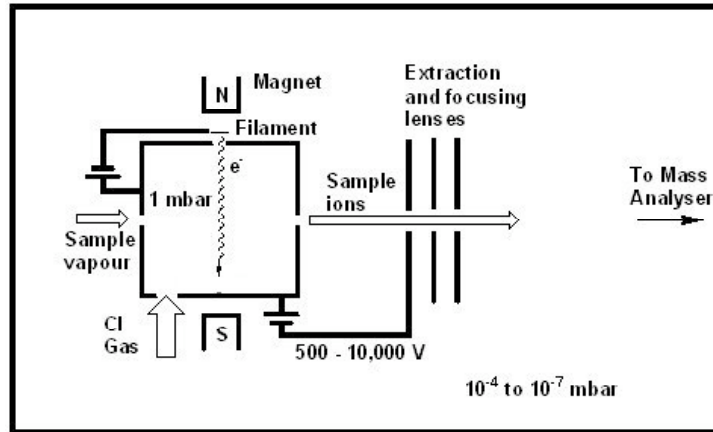
- Ion generation
 - a) Heated probe: EI, CI, FI
 - b) Desorption: FAB, SIMS, MALDI
 - c) Atmospheric pressure methods: APCI, APPI, ESI, DESI

Traditional Methods of Ionization: EI and CI

EI

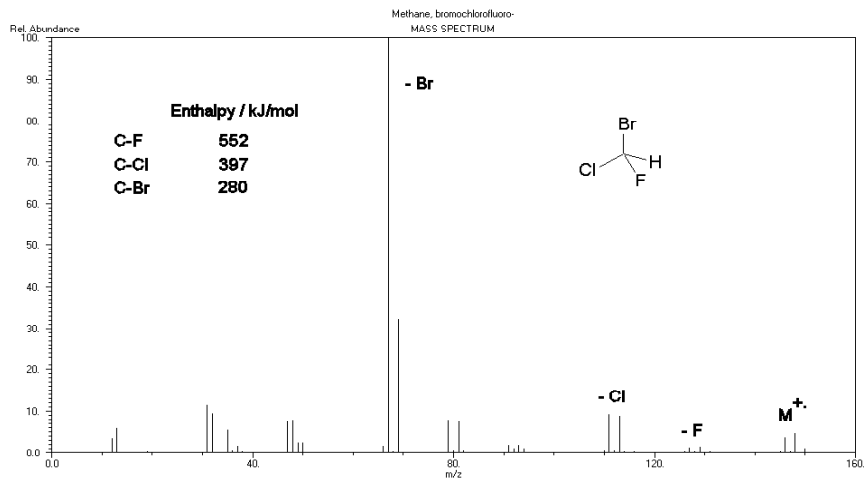


CI

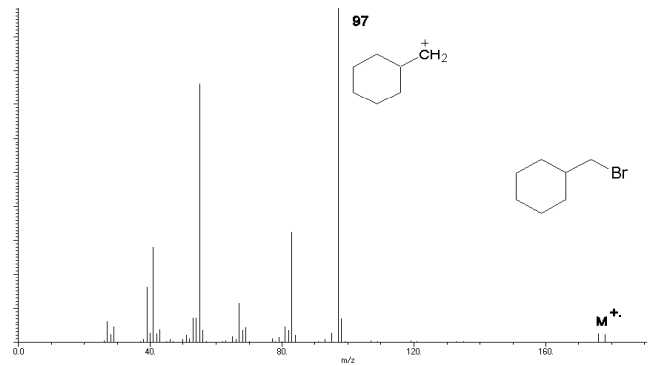
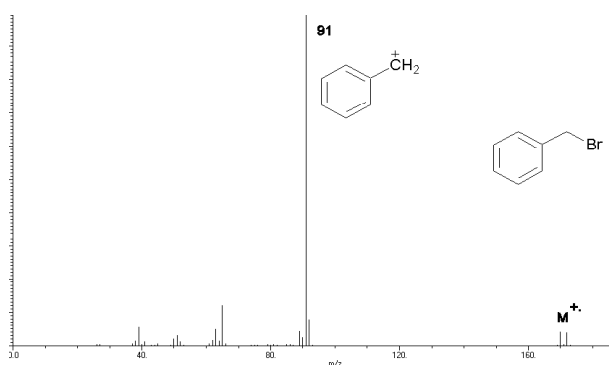


Fragmentation

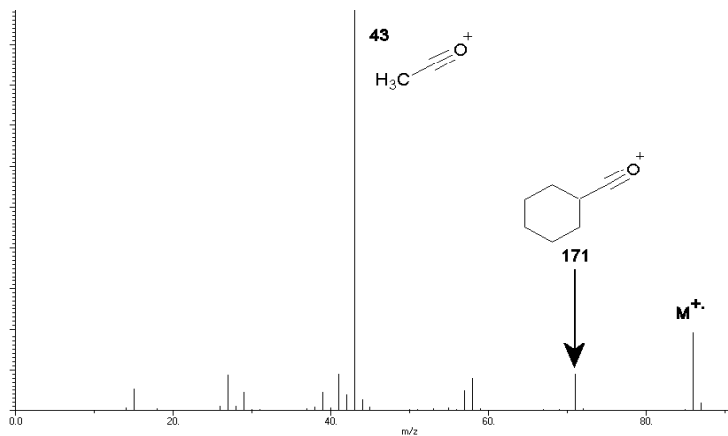
- Halogens



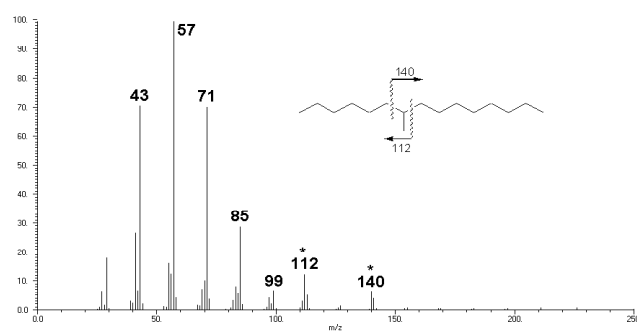
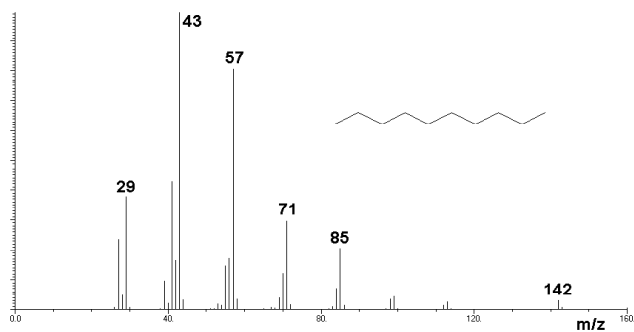
- Delocalization



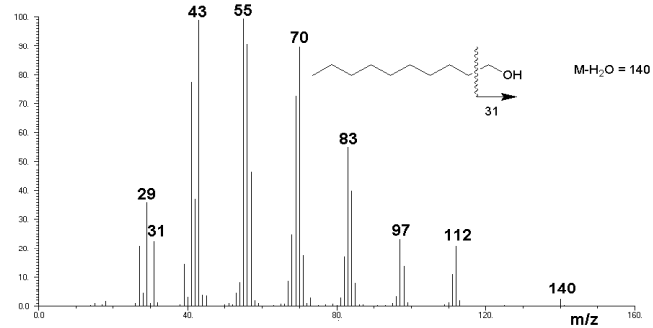
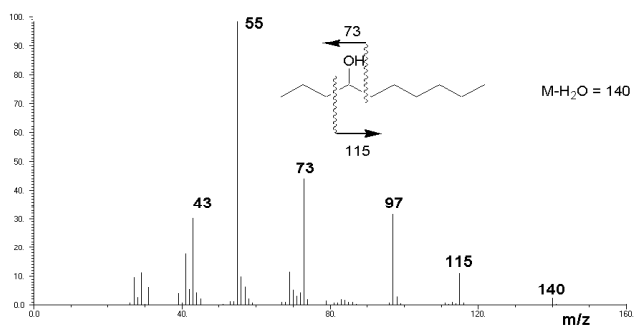
• Substituent Loss



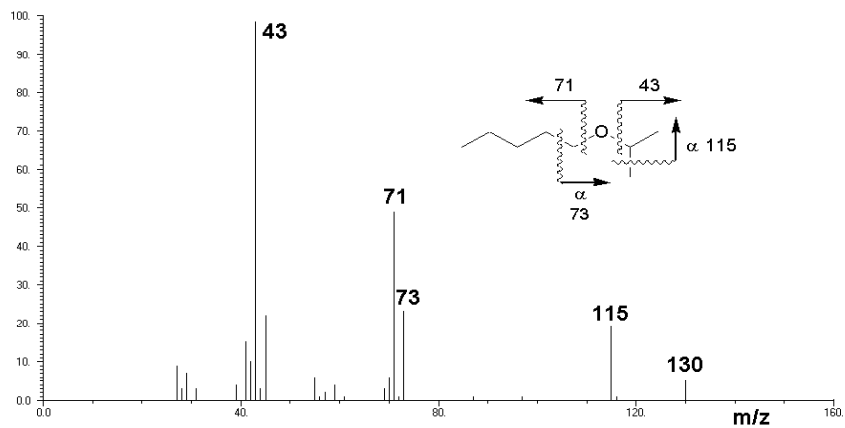
• Hydrocarbons



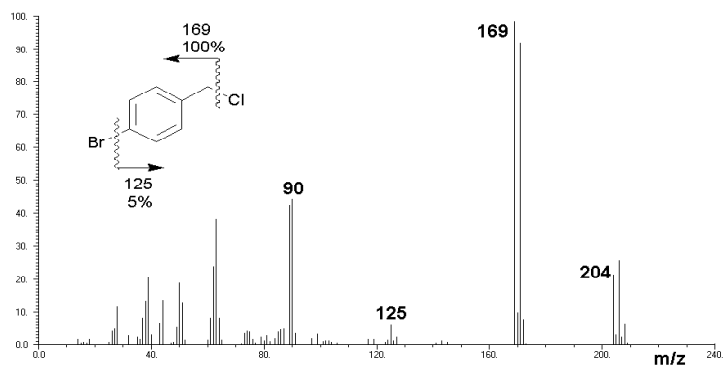
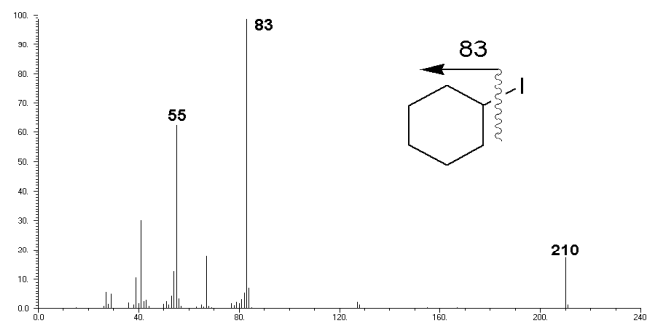
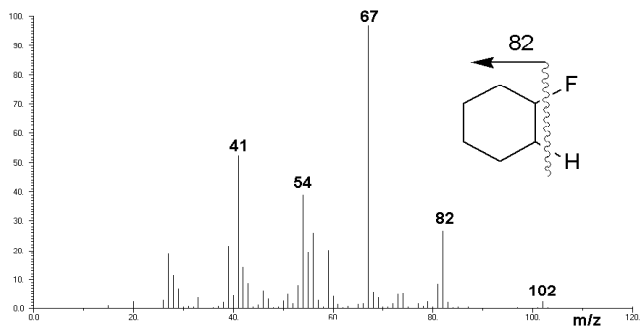
• Alcohols



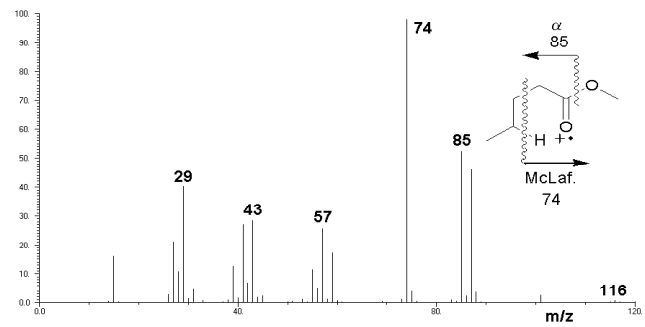
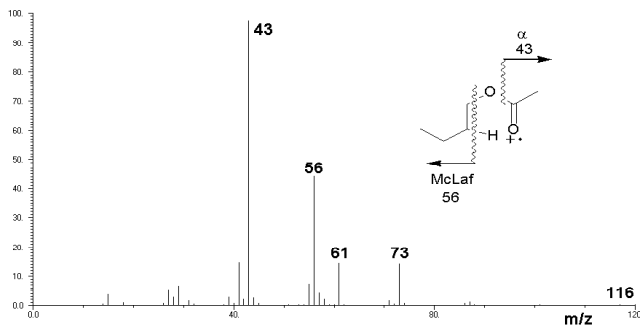
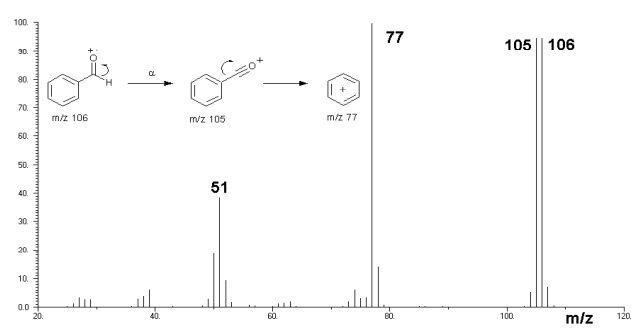
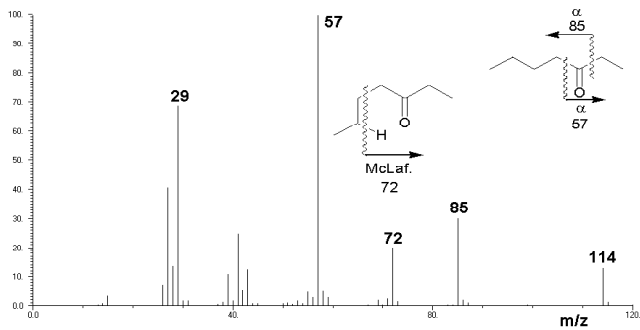
• Ethers



• Halogens

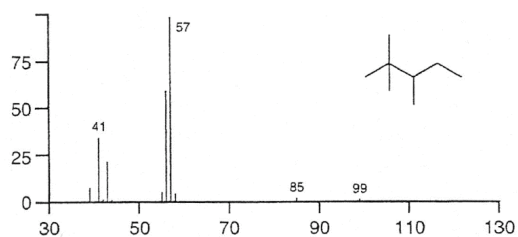


• Carbonyls



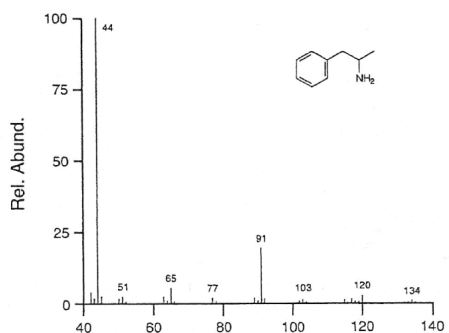
Fragmentation Examples

(a)

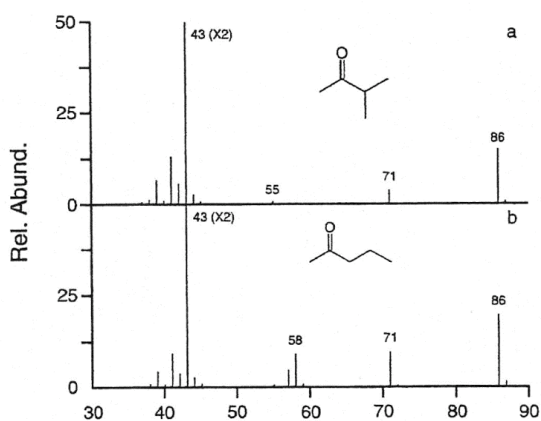


(b)

amphetamine

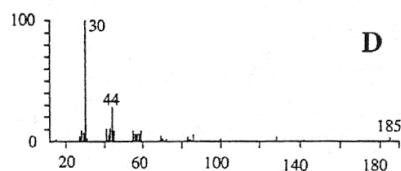
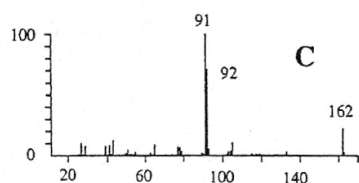
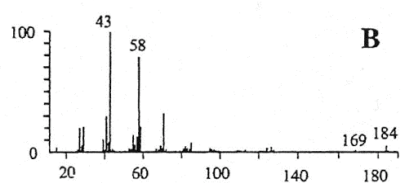
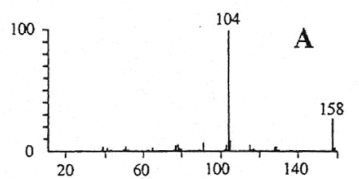


(c)



(d)

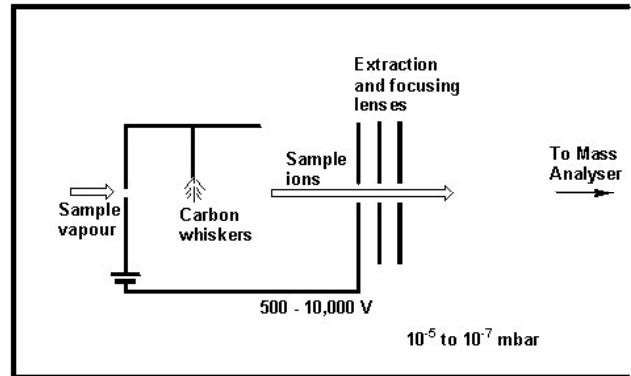
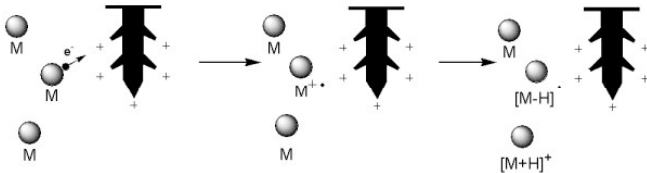
Match the following EI mass spectra to the following compounds: 1-dodecylamine; 2-dodecanone; 1-phenylhexane; 4-phenylcyclohexene. Assign the major fragmentations.



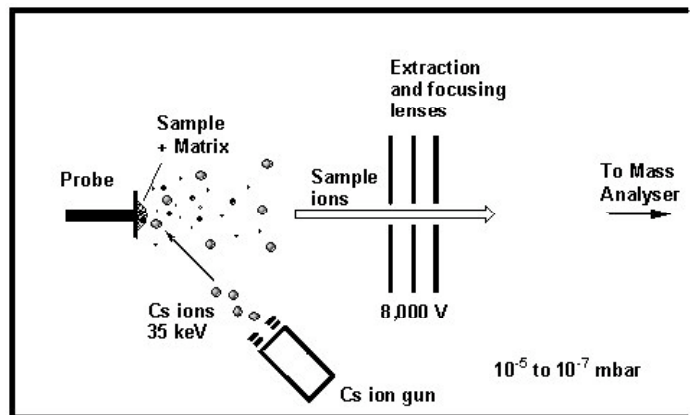
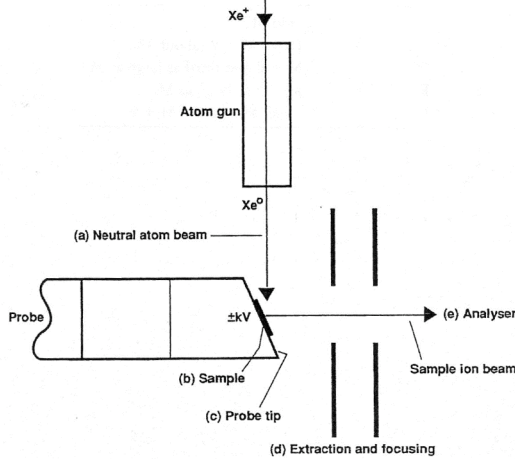
Other Ionization Methods

- Heated probe: EI, CI, FI
- Desorption: FAB, SIMS, MALDI
- Atmospheric pressure methods: APCI, APPI, ESI, DESI

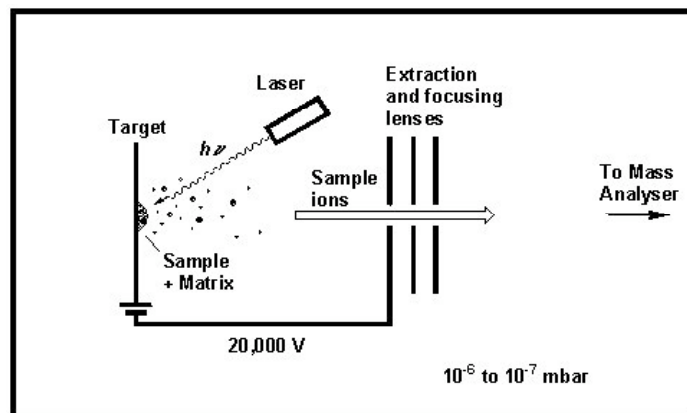
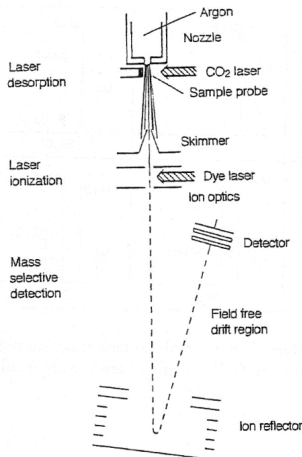
Field Ionization (FI)



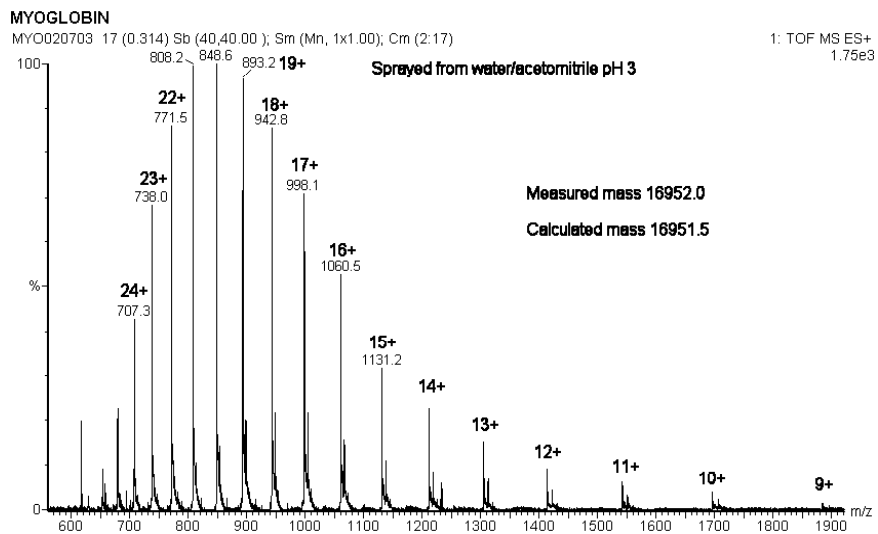
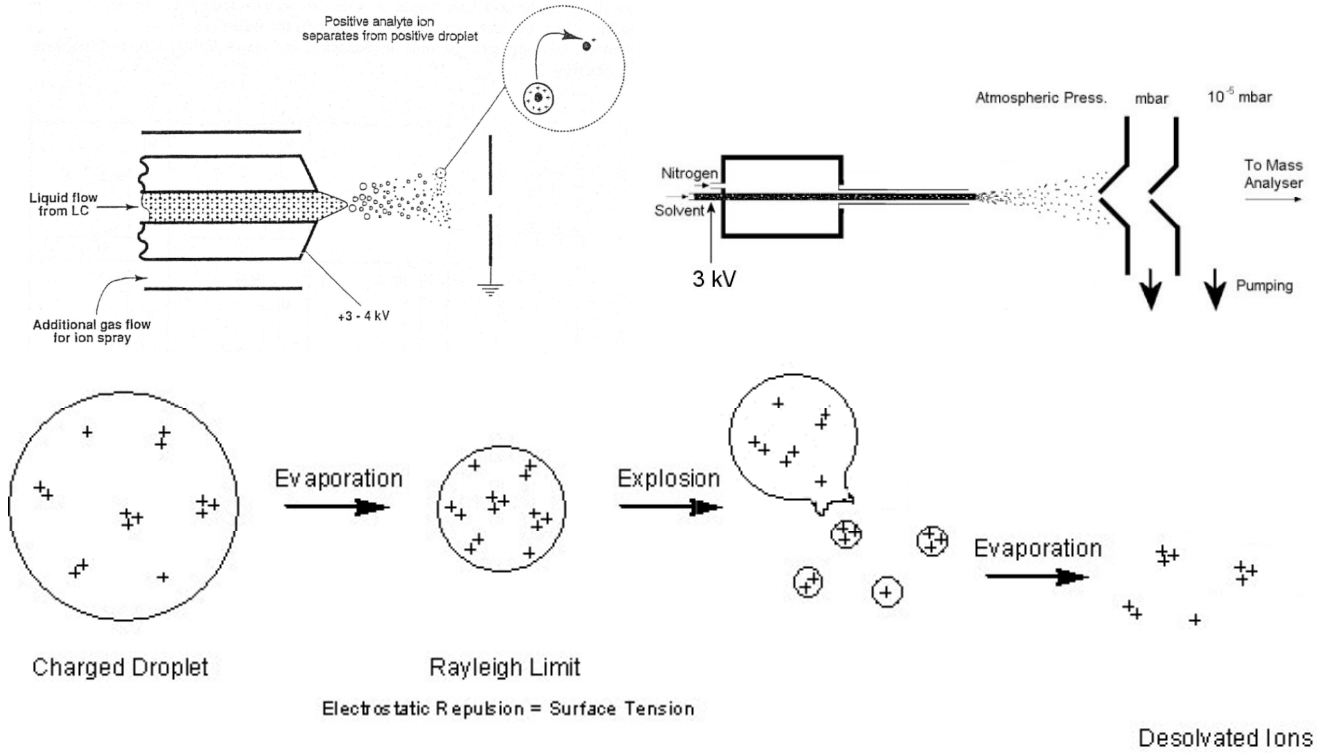
Fast Atom Bombardment (FAB) - cf SIMS



Laser Desorption (LDI) - normally Matrix Assisted (MALDI)



Electrospray (ESI)



Desorption Electrospray Ionization (DESI)

