# CSIR-UGC-NET/JRF | GATE

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# Mass Spectrometry

# Study Material

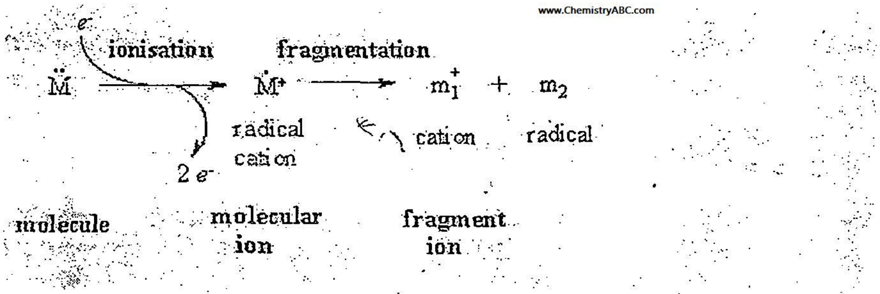
## CHEMICAL SCIENCES

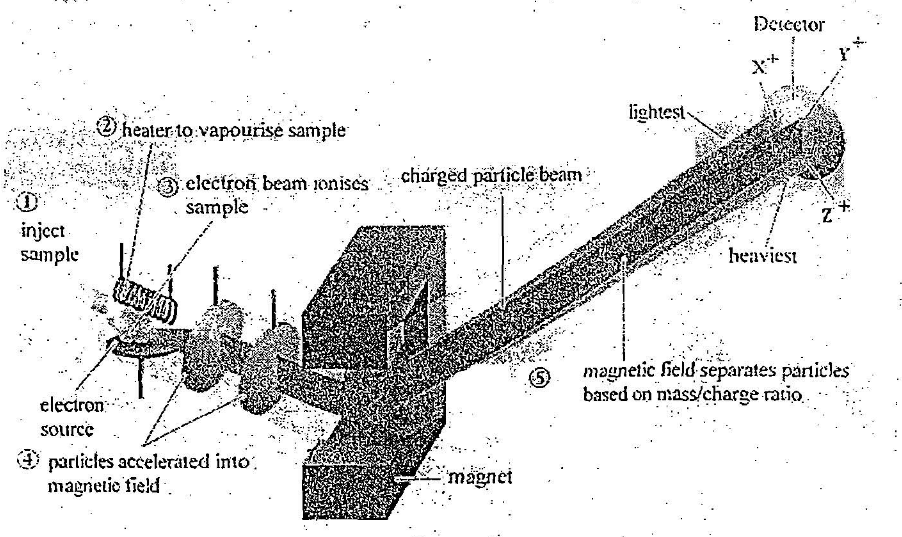
1. What is mass Spectrometry(MS)? What information does mass spectrometry provide?

**Soln.** Mass spectrometry is an analytical tool used for measuring the moecular mass of a sample. Mass spectrometry is based on slightly different principles to the other spectroscopic methods. The physics behind mass spectrometry is that a charged particle passing through a magnetic field is deflected along a circular path on a radius that is proportional to the **mass to charge** ratio, m/e.

In an **electron impact** mass spectrometer, a high energy beam of electrons is used to displace an electron from the organic molecule to form a **radical cation** known as the molecular ion. If the molecular ion is too unstable then it can **fragment** to give other smaller ions.

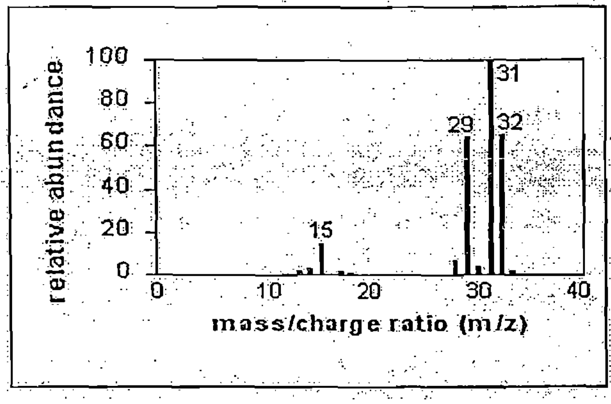
The collection of ions is then focused into a beam and accelerated into the magnetic field and deflected along circular paths according to the masses of the ions. By adjusting the magnetic field, the ions can be focused on the detector and recorded.




**Molecular ion:** The ion obtained by the loss of an electron from the molecule. This is always radical cation.
**Bass Peak:** The most intense peak in the MS, assigned 100% intensity.
M+: Symbol often given to the molecular ion.
**Radical cation:** +ve charged species with an odd number of electrons.
**Fragment ions or cation:** Lighter cations formed by the decomposition of the molecular ion. These often correspond to stable carbocations. +ve charged species with an even number of electrons.

A simple spectrometrum that of methanol is shown here. $CH_3OH^+$. (The molecular ion) and framgment ions appear in this spectrum.




| ions | m/z |
|---|---|
| $CH_3OH^{+\cdot}$ | 32 |
| $H_2C{=}OH^+$ | 31 |
| $HC{\equiv}O^+$ | 29 |
| $H_3C^+$ | 15 |

Major peaks are shown in the table next to the spectrum.

The x-axis of this bar graph is the increasing m/z ratio. The y-axis is the relative abundance of each ion, which is related to the number of times an ion of that m/z ratio strikes the detector. Assignemtn of relative abundance begins by assigning the most abundant ion a relative abundance of 100% ($CH_2OH^+$ in this spectrum). All other ions are shown as a percentage of that most abundant ion. For example, there is approximately 64% of the ion $CHO^+$ compared with the ion $CH_2OH^+$ *in this spectrum*. The y-axis may also be shown as abundance (not relative). Relative abundance is a way to directly compare spectra produced at different times or using different instruments.

EI ionization introduces a great deal of energy into molecules. It is known as a "hard" ionization method. This is very good for producing fragments which generate information about the structure of the compound, but quite often the molecular ion does not appear or is a smaller peak in the spectrum.

Of course, real analyses are performed on compounds far more complicated than methanol. Spectra interpretation can become complicated as initial fragments undergo further fragmentation, and as rearrangement occur. However, a wealth of information is contained in a mass spectrum and much can be determined using basic organic chemistry "common sense".

**Following is some general information which will aid EI mass spectra interpretation:**

**Molecular ion ($M^+$):** If the molecular ion appears, it will the highest mass in an EI spectrum (except for isotope peaks discussed below). This peak will represent the molecular weight of the compound. Its apperance depends on the stability of the compound. Double bonds, cyclic structures and aromatic rings stablizie the molecular ion and increase the probability of its appearance.

**Reference Spectra:** Mass spectral patters are reproducible. The mass spectra of many compounds have been published and may be used to identify unknowns. Instrument computers generally contain spectral libraries which can be searched for matches.

**Fragmentation:** General rules of fragmentation exist and are helpful to predict or interpret the fragmentation pattern produced by a compound. Functional groups and overall structure determine how some portions of molecules will resist fragmenting, while other portions will fragment easily. A detailed discussion of those rule is beyond the scope of this introduction, and further information may be found in your organic textbook or in mass spectrometry reference books. A few brief examples by functional group are described (see examples)

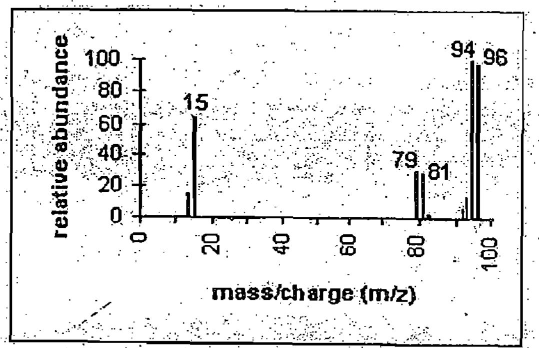
**Isotopes:** Isotopes occur in compounds analyzed by mass spectrometry in the same abundane that they occur in nature. A few of the isotope commonly encountered in the analyses of organic compounds are below along with an example of how they can aid in peak identification.

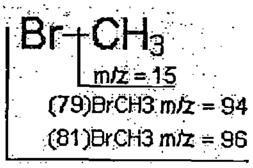
Relative Isotope Abundance of Common Elements:

| Element | Isotope | Relative Abundance | Isotope | Relative Abundance | Isotope | Relative Abundance |
|---|---|---|---|---|---|---|
| Carbon | $^{12}C$ | 100 | $^{13}C$ | 1.11 | | |
| Hydrogen | $^{1}H$ | 100 | $^{2}H$ | .016 | | |
| Nitrogen | $^{14}N$ | 100 | $^{15}N$ | .38 | | |
| Oxygen | $^{16}O$ | 100 | $^{17}O$ | .04 | $^{18}O$ | .20 |
| Sulfur | $^{32}S$ | 100 | $^{33}S$ | .78 | $^{34}S$ | 4.40 |
| Chlorine | $^{35}Cl$ | 100 | | | $^{37}Cl$ | 32.5 |
| Bromine | $^{79}Br$ | 100 | | | $^{81}Br$ | 98.0 |

**Methyl Bromide:** An example of how isotope can aid in peak identification.

**The ratio of peaks containing $^{79}$Br and its isotope $^{81}$Br(100/98) confirms the presence of bromine in the compound.**



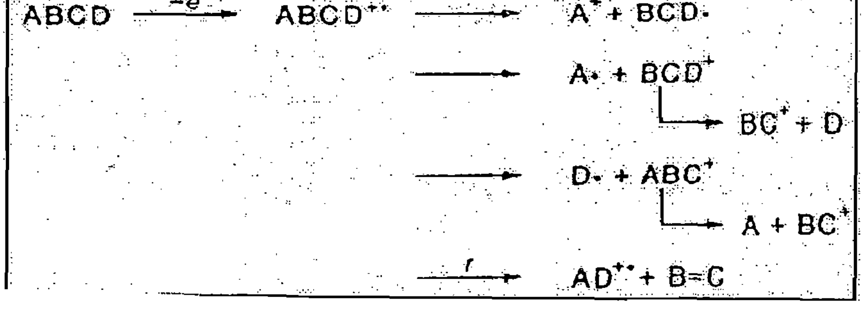

**Important Aspects of fragmentation:**

**Unimolecular Decomposition Reactions I:**

- EI MS reactions are unimolecular (as opposed to other techniques, such as laser ablation ionization)
- $M^{+\cdot}$ are made with a wide range of internal energies.
    - "Cool" $M^{+\cdot}$ will not decompose
    - ABCD + $e^-$ > $ABCD^{+\cdot}$.

**Unimolecular Decomposition Reactions II:**

- "Excited" or "Hot" $M^{+\cdot}$ will decompose in a chain of energy - dependent reactions.
    - Now things get interesting.
    - Each one with a neutral loss
    - Rearrangement: $NO^+$ from $(NH_4)_2SO_4$.



## Site of Initial Ionization I

- e⁻ most vulnerable to ionization are those of highest energy
  - HOMO: highest occupied molecular orbital
    - Also form the weakest bonds
  - IP is defined as the energy to remove the weakest bound electron (n > π > σ)
  - n: lone pairs from heteroatmoms

R:Ö:R  H₂C::CH₂  H:C:H (with H above and below)

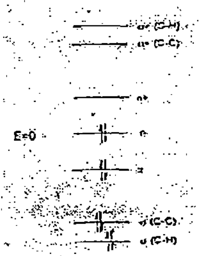


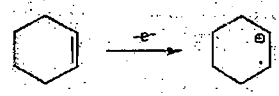
Figure 3.2. Relative energies of molecular orbitals in organic compounds

## Site of Initial Ionization II

- n > π > σ

n: $CH_3OH \xrightarrow{-e^-} CH_3\dot{O}H$

π:



σ: $CH_3-CH_2-CH_3 \xrightarrow{-e^-} CH_3-CH_2 \cdot CH_3$

Figure 3.4. Examples showing notation for localization of initial ionization site.

## Factors that Influence Ion Abundance I

- Most important: <u>Stability</u> of the product ion
  - Electron sharing stabilization
    - From non-bonding orbital of heteroatom (n)

      $CH_3-C^+=O \leftrightarrow CH_3-C\equiv O^+$ (*m/z* 43)
  - Resonance stabilization

    $CH_2=CH-^+CH_2 \leftrightarrow {}^+CH_2-CH=CH_2$ (*m/z* 41)

    Benzyl: $C_6H_5CH_2^+$ >> phenyl $C_6H_5^+$
  - "Distonic radical ions"
    - Separation of charge and radical sites

    $CH_3CH_2CH_2CH=O^{+\cdot} \rightarrow \cdot CH_2CH_2CH_2CH=O^+H$

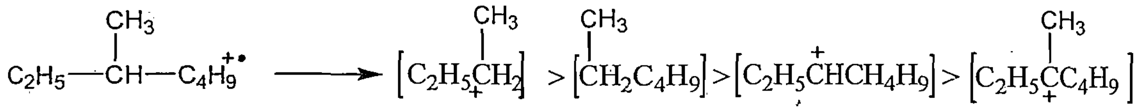
    $CH_3NH_2^{+\cdot} \rightarrow \cdot CH_2N^+H_3$

**Factors that influence ion abundance II:**

- **Stevensons' Rule:**
  - In a cleavage of a single bond in an OE.
    ABCD$^{+\bullet}$ can give A$^{+\bullet}$ BCD or A$^{+\bullet}$ BCD
  - The framgment with the higher tendency to retain the unpaired electron should have the higher ionization energy (converse true)
    - It will be the less abundant ion in the spectrum.

**Factors that influence ion abundance III:**

- **Loss of the largest alkyl ($C_nH_{2n+1}$)**
  - Exception to Stevenson's rule: abundance decreases with increasing ion stability.



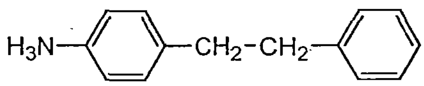
**Factors that influence ion abundance IV:**

- Stability of the neutral product
  - Stability of ion is much more important
  - A favorable product site for the unpaired electron can provide additional influence.
    - Electronegative sites such as oxygen (•OR)
  - The neutral product can be a molecule
    - Small stable molecules of high ionization energy are favoured.
      - $H_2, CH, H_2O, C_2H_4, CO, NO, CH_3OH, H_2S, HCl, CH_2=C=O,$ and $CO_2$
      - Looses of 2, 16, 18, 28, 30, 32, 34, 36, 42, 44.

**Factors that influence ion abundance V:**

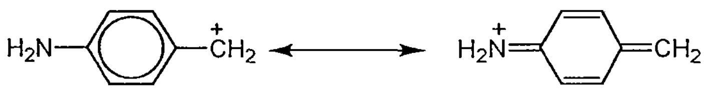
- **Entropy/Sterie Effects:**
  - Most favored reactions for enthalpy often have steric restrictions (e.g. rearrangement)
  - Dissociation favors products with less restrictive entropy requirements even if the enthalpy barrier is higher (i.e. a simple bond cleavage)

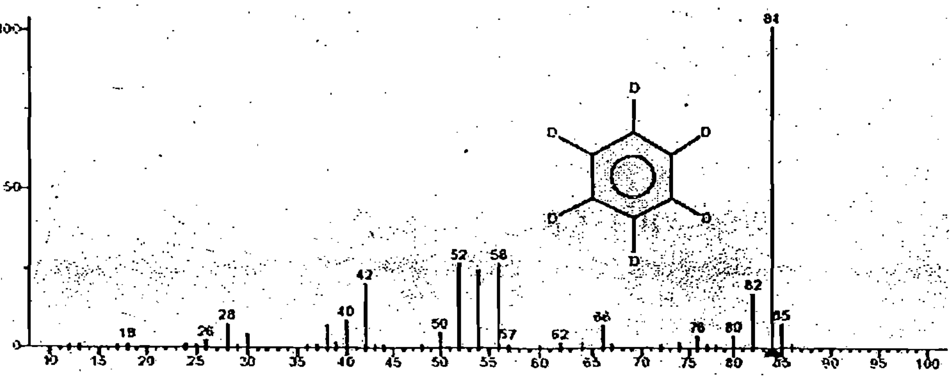
- **Unknown 4.1**
  - Predict the most abundant ion in the spectrum of:



**Factors that influence ion abundance VI:**

- Cleaving $CH_2$–$CH_2$ bond is sterically easiest
- P-aminobenzyl cation is very stable via resonance.

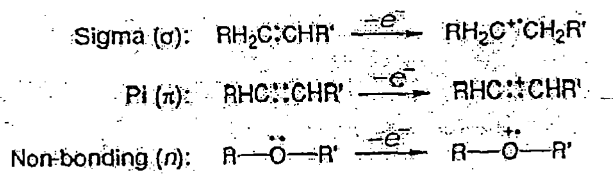




- Comments: N-rule, H losses.
- "Choose peak groups".

**Reaction initiation at radical or charge sites:**

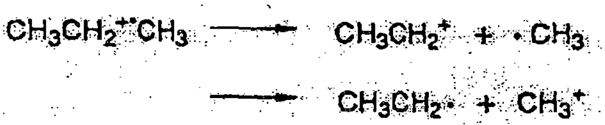
- Fragmentation reactions are often initiated at the favored site for the unpaired electron or the charge.
- The most favored radical and charge sites in the molecular ion are assumed to arise from loss of the molecules's electron of lowest ionization energy.
  - Favorability $\sigma < \pi < n$ – electrons : see example spectra.




Unlike M– charge localization is implied.

**Reaction Classifications I:**

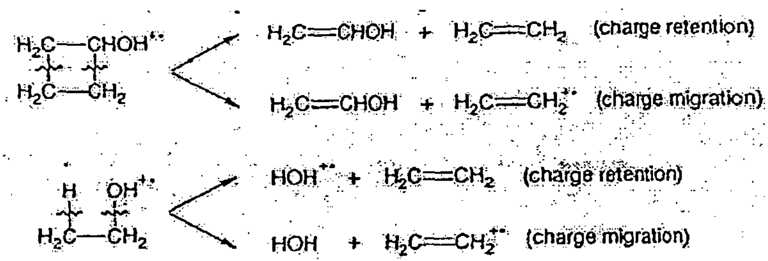
- Decomposition of odd electron ions involving single bond cleavage results in an even electron ion and a neutral radical.



- Stevenson's rule applies.
- Reminder: in $C_xH_yN_zO_n$
  - RPDB = x + 1/2y–1/2z+1
  - y+z is odd $\Rightarrow$ RPDB ends in 1/2 $\Rightarrow$ $EE^+$
  - y+z even $\Rightarrow$ RPDB whole $\Rightarrow$ $OE^+$.

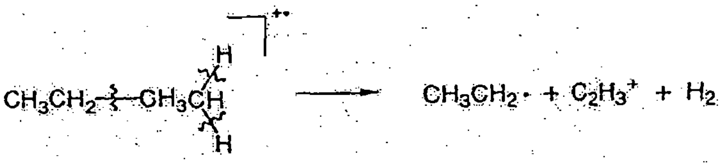
**Reaction Classification II:**

- Decompositions of odd electron ions involving two bond cleavages can results in an odd electron ion and a neutral.
  - Rearrangments
  - Decomposition of rings.



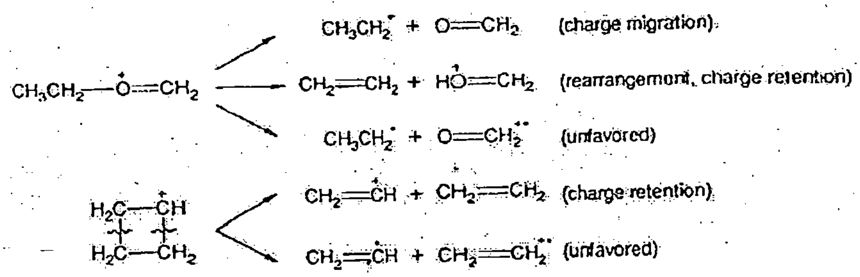

**Reaction Classification III:**

- Cleavage of three bonds in $M^+$ (or any $OE^+$) produces an $EE^+$.



**Reaction Classification IV:**

- "Even - electron rule"
  - Decompositions of even electron ions typically result in another even electron ion and a neutral.
  - Odd electron formation is not energetically favorable.



**Reaction Classifications V:**

Table 4.1. *Types of ion decompositions*

| Precursor ion | Number of bonds cleaved | Product ion[a] | |
|---|---|---|---|
| | | Charge retention | Charge migration |
| $OE^{+\cdot}$ $(M^{+\cdot})$ | 1 | $EE^+$ (σ) | $EE^+$ (i) |
| $OE^{+\cdot}$ $(M^{+\cdot})$ | 2 | $OE^{+\cdot}$ (αα) | $OE^{+\cdot}$ (αi) |
| $OE^{+\cdot}$ $(M^{+\cdot})$ | 3 | $EE^+$ (ααα) | [$EE^+$ (ααi)][b] |
| $EE^+$ | 1 | [$OE^{+\cdot}$][b] | $EE^+$ |
| $EE^+$ | 2 | $EE^+$ | [$OE^{+\cdot}$][b] |

[a] Designations "α" and "i" are alpha and inductive cleavages, respectively, as explained in the text. Two i reactions lead to the same charge behavior (retention or migration) as two α reactions. Brackets indicate products of reactions discussed in Chapter 8.
[b] Not favored.

- $OE^+$ formation from fragmentation is only favored for cleavage of two bonds of precursor $OE^+$.
  - This is why we mark important $OE^+$ ions in spectrum.

**Sigma-Bond dissociation (σ):**

- **E.g. alkanes.**
  - Every valence electron is shared in a bond
  - A bond finds itself with 1-electron, breaks.

$$\text{Alkanes:}\quad R^{+\cdot}CR_3 \xrightarrow{\sigma} R\cdot + \overset{+}{C}R_3$$

  - Ionization of $C_2H_6$ increases C–C bond length by 30%, halves its dissociation energy.
- Fragmentation is favoured at more substituted C

$$(CH_3)_3C{-}CH_2CH_3 \xrightarrow{-e^-} (CH_3)_3C^{+\cdot}CH_2CH_3 \xrightarrow{\sigma} \underset{100\%}{(CH_3)_3C^+} + \cdot CH_2CH_3$$

**Alkanes and Branched Alkanes:**

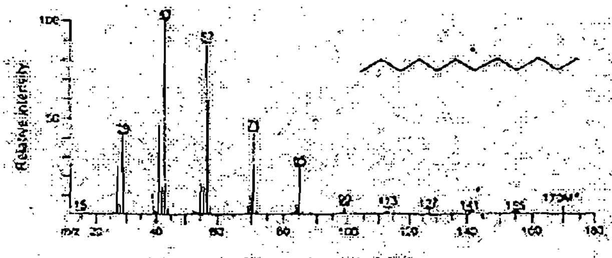


Figure 3.2. Mass spectrum of dodecane.

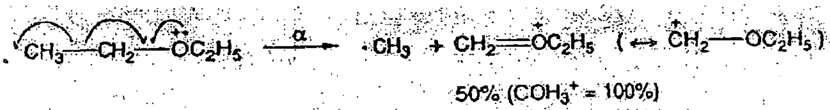
- Only important OE⁺ is $M^{+}$
- $C_3H_7$ & $C_4H_9$ are most stable
- Loss of $H_2$ and H
- 27 < 29 ; 41 < 43 ; 55 < 57 ; 69 < 71

Mass spectrum of 4-methylundecane.

- Fragmentation at substituted C
- Loss of the larger alkyl

**Radical-Site Initiation ($\alpha$-cleavages) I:**

- Unpaired electron at radical site has strong tendency to be paired.
  - Donate unpaired electron to form new bond.
  - Need a 2nd electron, take it from bond of adjacent C atom ("$\alpha$ carbon")

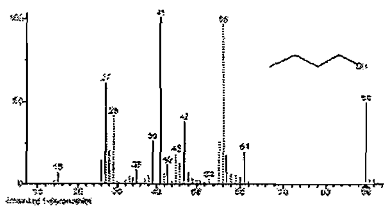


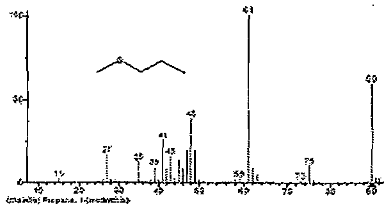
  - Fishook arrow is movement of single electron.
  - Same as "homolytie cleavage" of organic chem
  - Only radical site moves, + stays.

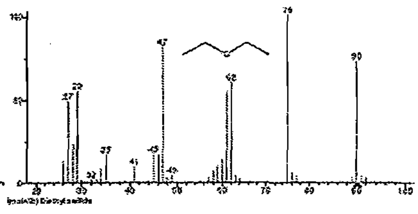
**Radical - Site Initiation ($\alpha$-cleavage) II:**

- Tendency of radical site to initiate reaction:
  - Parallels tendency of radical site to denote electron.
  - $N > S, O, \pi, R > Cl, Br > H$
  - But it is affected by its environment in molecule.
  - Unknonw 4.2: What will be the most abundant fragment of $HO-CH_2-CH_2-NH_2$?

**HW8: Explain the reaction pathways leading to the formation of important ions:**

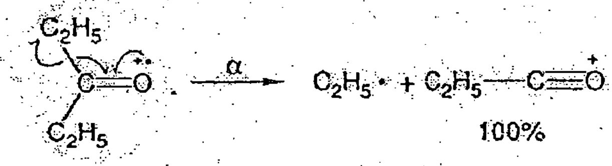




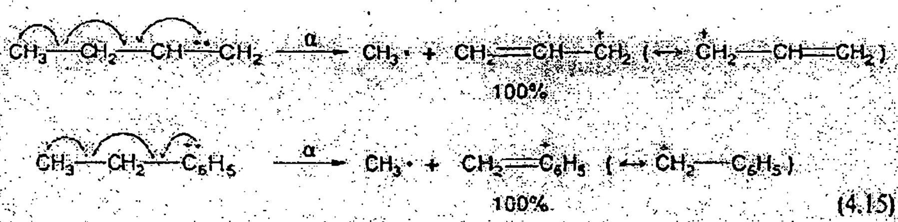


## Radical-Site Initiation (α-cleavage) III

- Carbonyls:




- Double-bonds:




## Loss of Largest Alkyl in α-cleavage

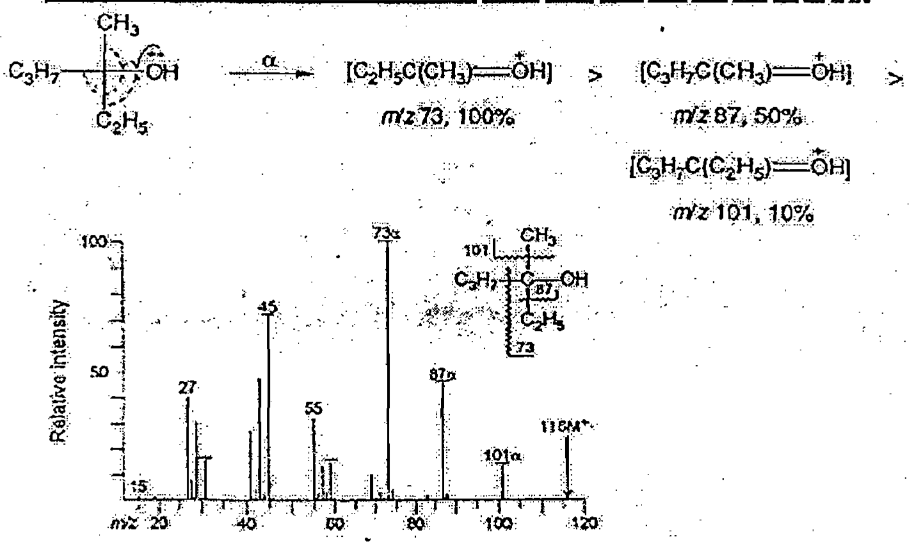
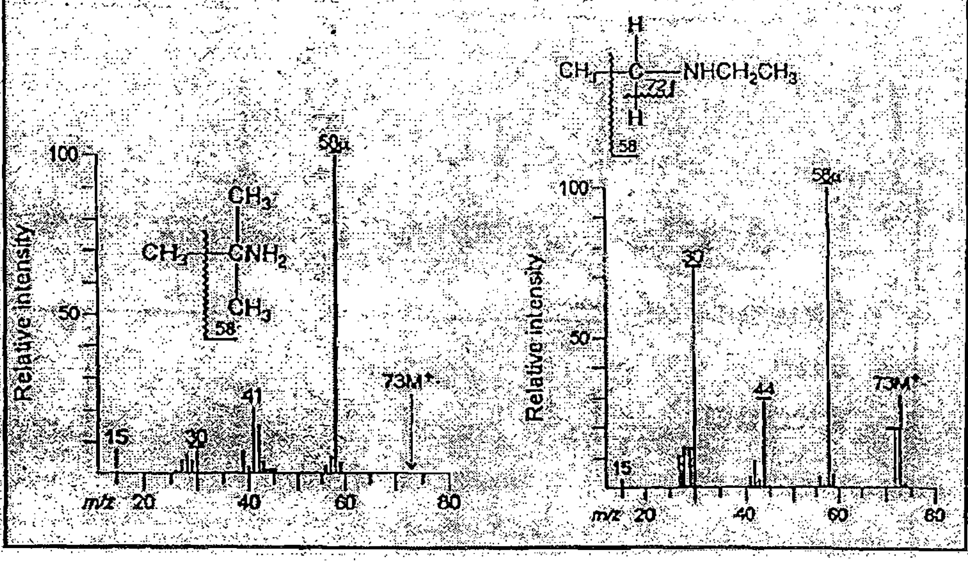


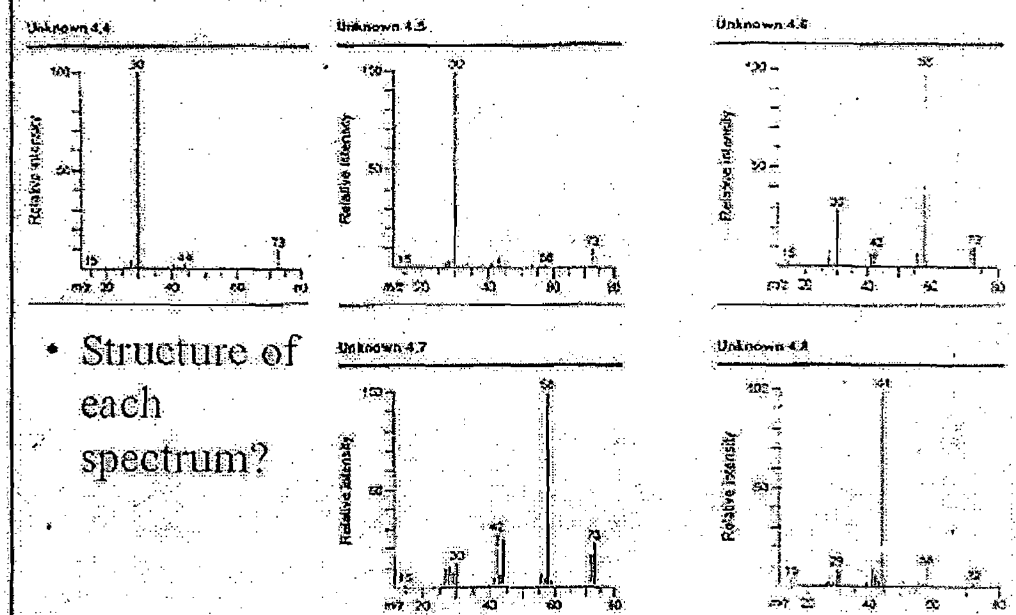

Figure 4.2. Mass spectrum of 3-methyl-3-hexanol.

# α-Cleavage of Aliphatic Amines

- Very dominant, due to e⁻ donating ability of N



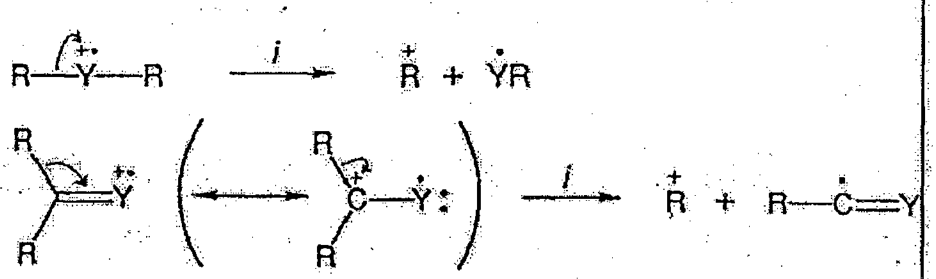

# Spectra of Isomeric $C_4H_{11}N$




- Structure of each spectrum?

# Charge-Site Initiation ($i$-cleavage)

- Inductive cleavage ("heterolytic dissociations" of O-Chem)
- For $OE^{+\bullet}$



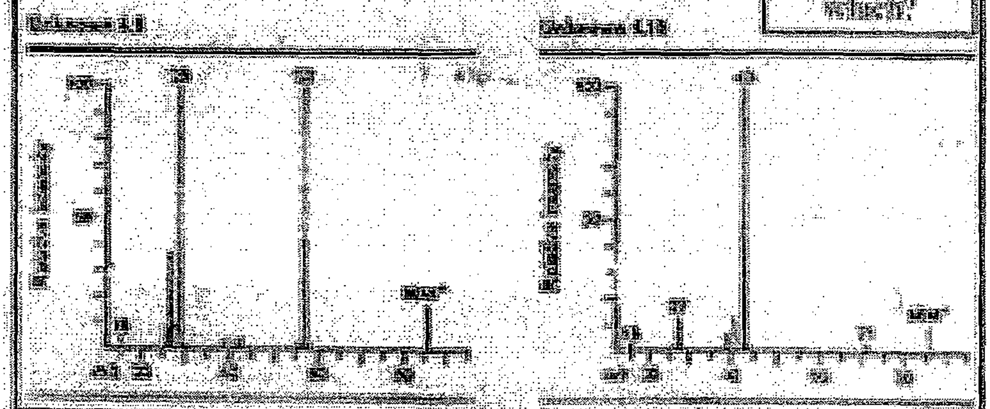
- Example:

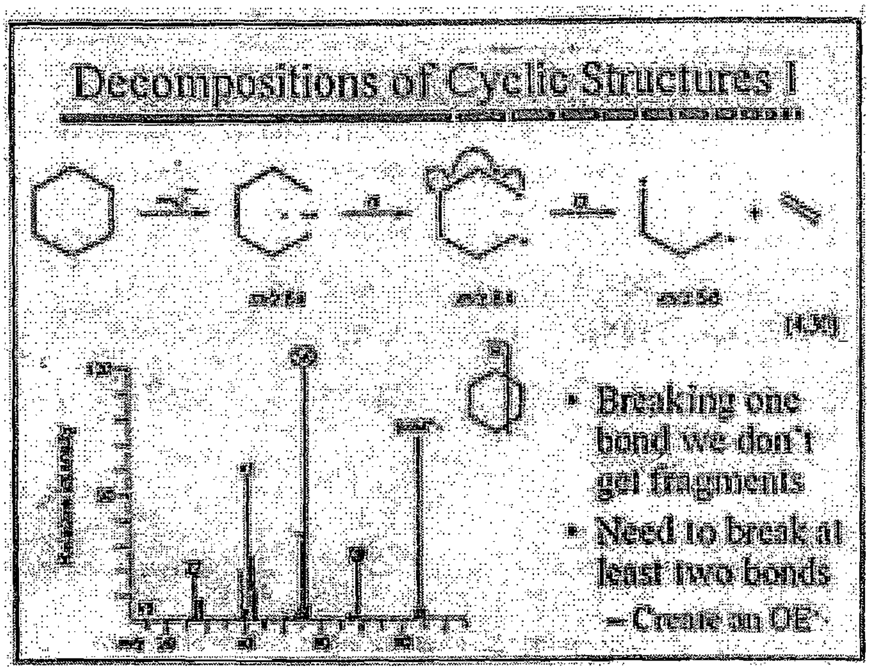
$$C_2H_5-\overset{+\bullet}{O}C_2H_5 \xrightarrow{i} C_2H_5^{+} + \cdot OC_2H_5$$

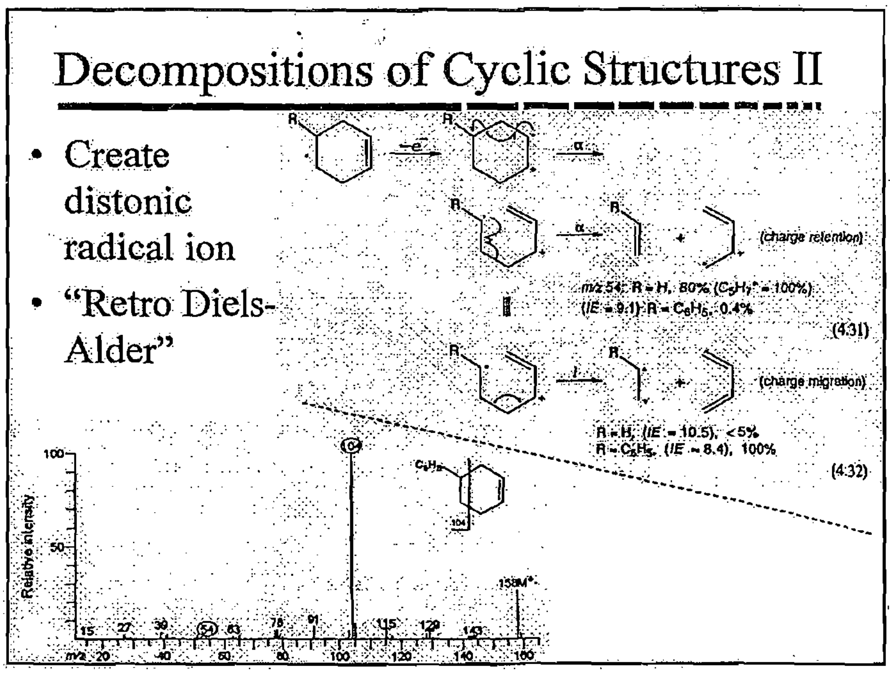
40%

# $i$-cleavage for Aliphatic Ketones

3-pentanone and 3-methyl 2-butanone. Which is which?

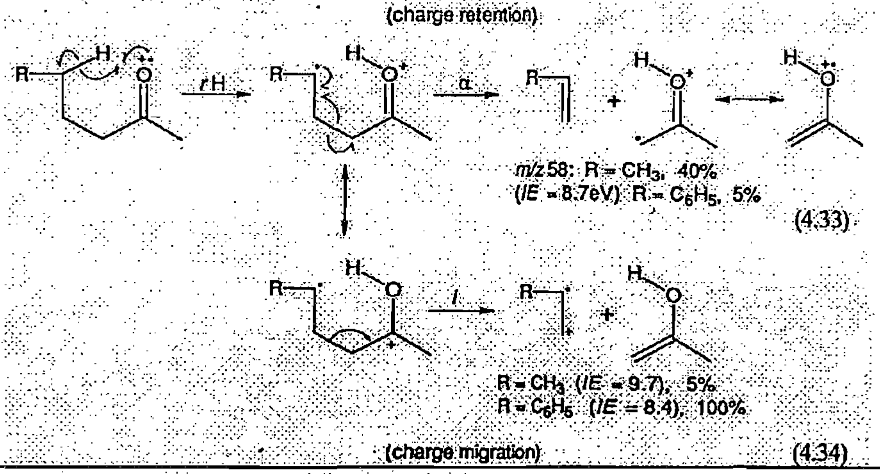



Decompositions of Cyclic Structures I
(4.30)
• Breaking one bond we don't get fragments
• Need to break at least two bonds
– Create an OE⁺·


Decompositions of Cyclic Structures II
• Create distonic radical ion
• "Retro Diels-Alder"
(charge retention)
(4.31)
(charge migration)
R = H, (IE = 10.5), <5%
R = C6H5, (IE = 8.4), 100%
(4.32)
Relative intensity
158M⁺·
m/z

# Radical Site Rearrangements

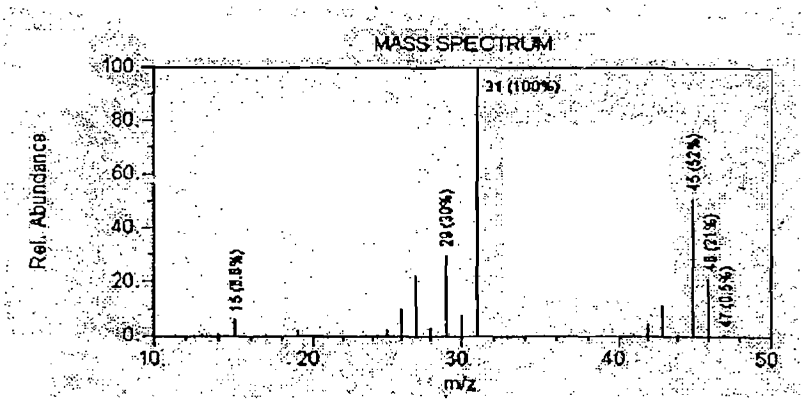
- "McLafferty Rearrangement"
  - Unpaired e⁻ donated to form new bond to adjacent atom, 2nd electron comes from adjacent bond, that breaks



# MASS SPECTROMETRY: FRAGMENTTION

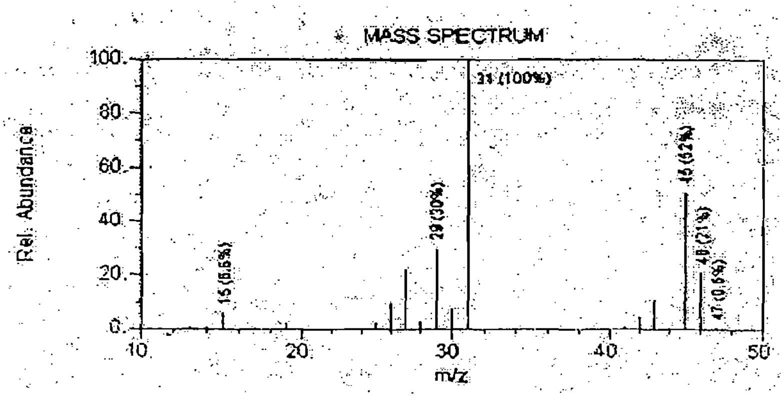
1. **Fragmentation of Alcohols:**

(1) Identify the molecular ion in this spectrum.



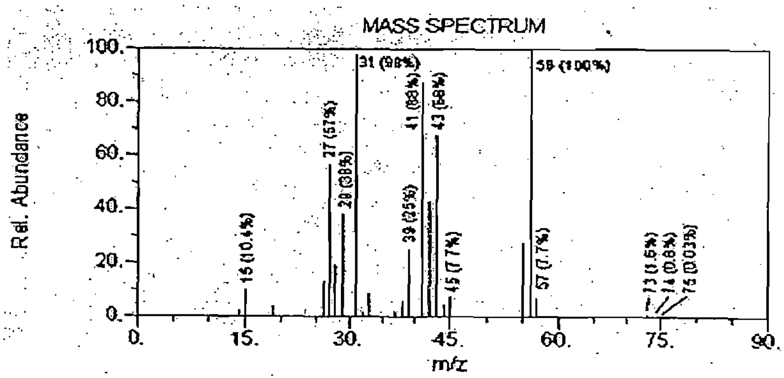

(a) 45 (b) 46 (c) 47 (d) 49

(2) For this same spectrum, choose the compound that the spectrum represents.



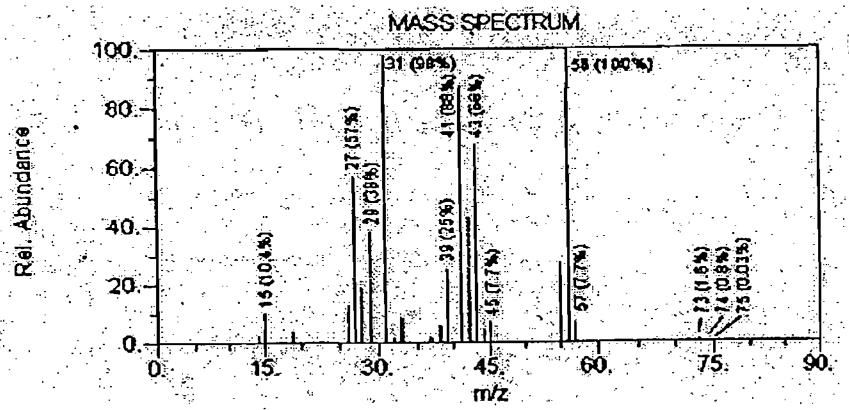

(a) Formic acid (b) 1-propanol (c) Ethanol (d) Methanol
(e) Isopropyl alcohol.

(3) Find the alkyl ion series in the spectrum below. (Check the hint)



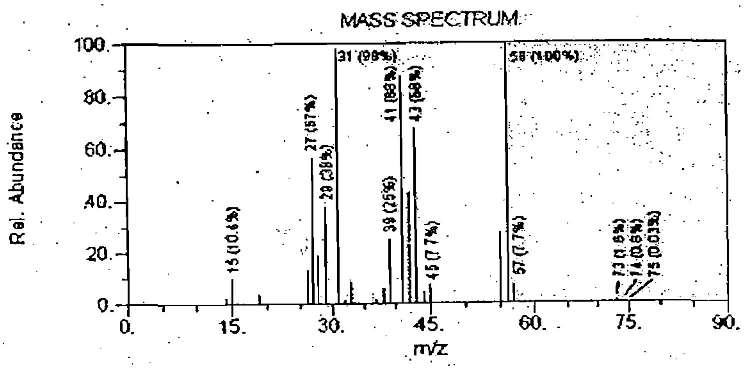

(a) 15, 29, 43, 57 (b) 31, 45 (c) None

(4) Find the alkyl LOSS ion series in the same spectra shown below. (Check the hint)



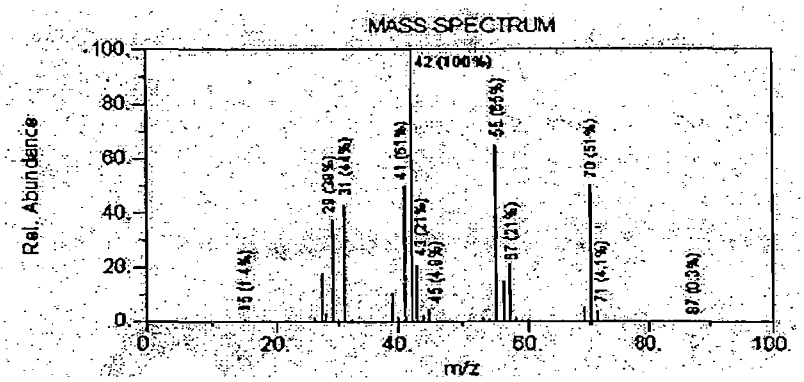

(a) 15, 29, 43, 57 (b) 31, 45 (c) None

(5) For the same spectrum shown in the previous two questions, choose the compound that the spectrum represents.

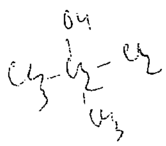



(a) 2-methyl-2-propanol (b) 1-butanol
(c) 2-butanol (d) 1-pentanol (e) 2-methyl-1-propanol

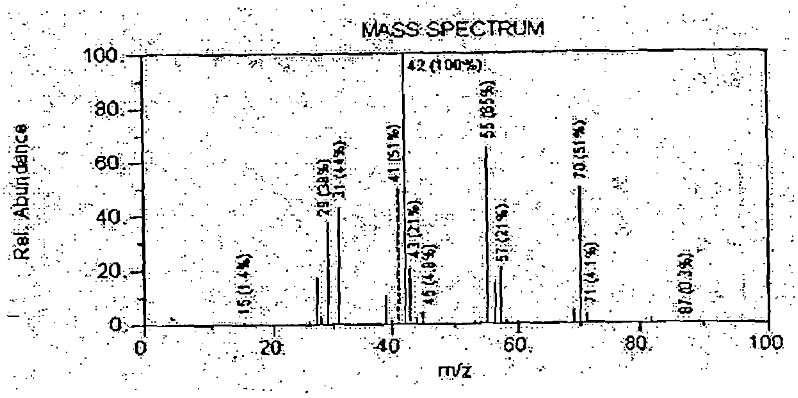
(6) Identify the molecular ion in this spectrum.




(a) 70 (b) 71 (c) 87 (d) 88



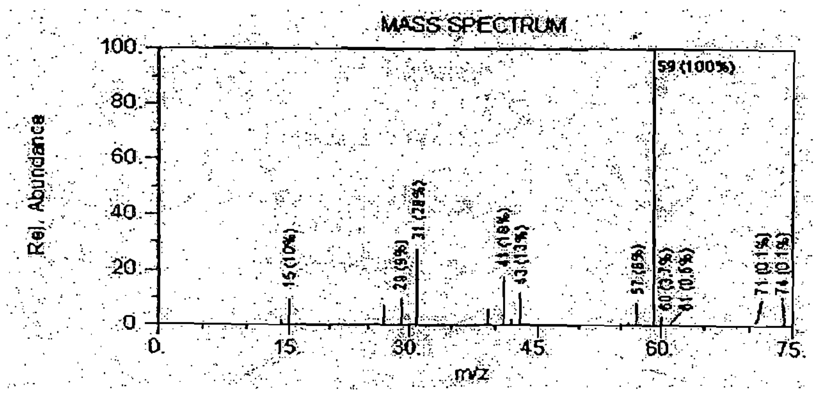
(7) For the same spectrum, choose the compound that the spectrum represents.




(a) 1-hexanol (b) 1-pentanol (c) 2-methyl-2-butanol

(d) 2-pentanol (e) 1-butanol

(8) Choose the compound that this spectrum represents.

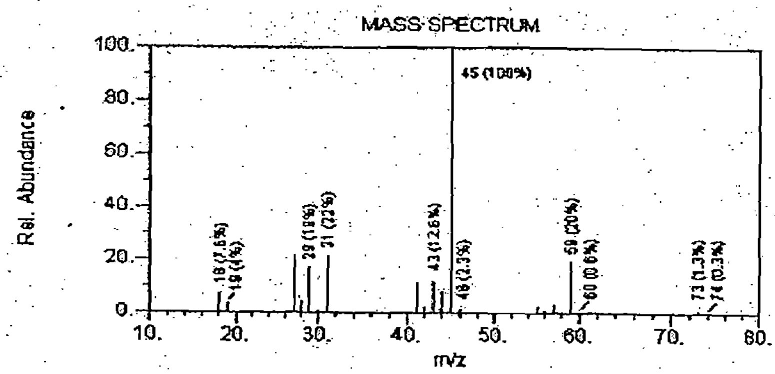



(a) 2-methyl-2-butanol (b) 2-methyl-2-propanol

(c) 2-butanol (d) 1-butanol

(e) 2-methyl-1-propanol

(9) Choose the compound that this spectrum represents.

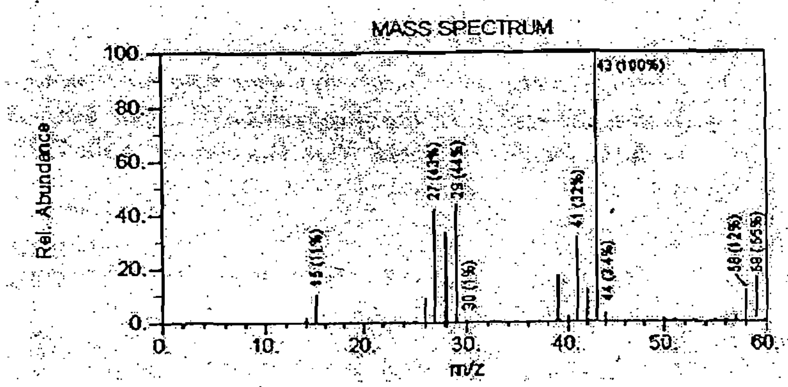



(a) 2-pentanol (b) 2-methyl-2-propanol

(c) 1-butanol (d) 2-methyl-1-propanol (e) 2-butanol.

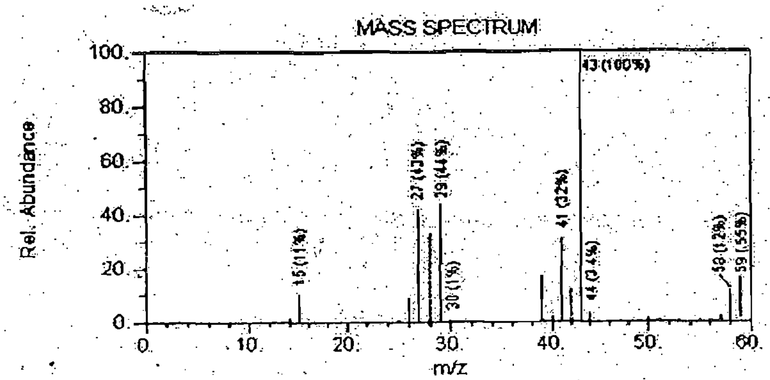
2. **Fragmentation of Alkenes:**

(1) The molecular ion in the spectrum below is 58. What alkyl group was lost to form the intense fragment at m/z 43?



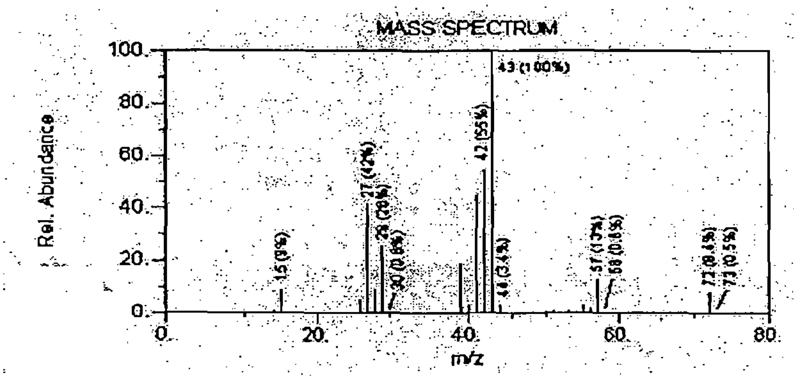

(a) methyl ($CH_3$) (b) ethyl ($CH_3CH_2$) (c) propyl ($CH_3CH_2CH_2$)

(2) For this same spectrum, choose the compound that the spectrum represents.



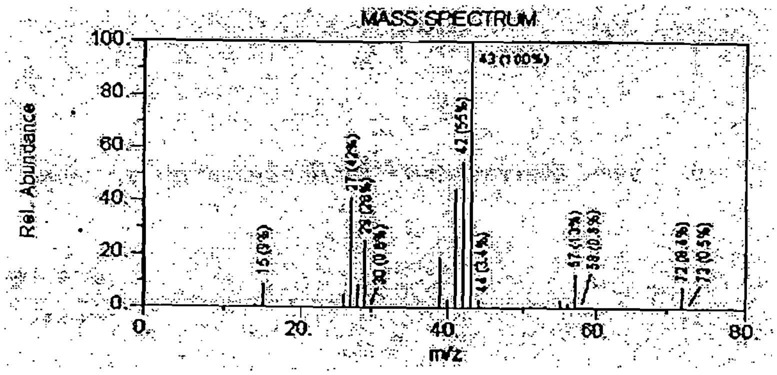

(a) 2-methyl butane (b) butane (c) pentane (d) cyclobutane
(e) 1-butene

(3) The highest cluster of peaks in a spectrum many contain the molecular ion and its isotope peak(s). In the spectrum below, how many carbons are represented by the molecular ion peak 72 and its isotope peak 73?



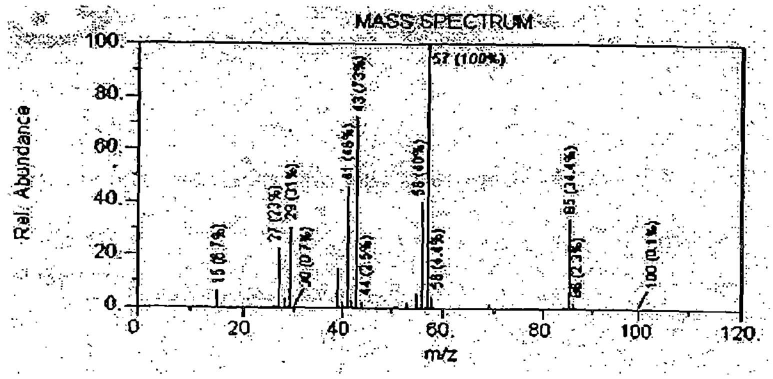

(a) 3 (b) 4 (c) 5 (d) 6

(4) For this same spectrum, choose the compound that the spectrum represents.



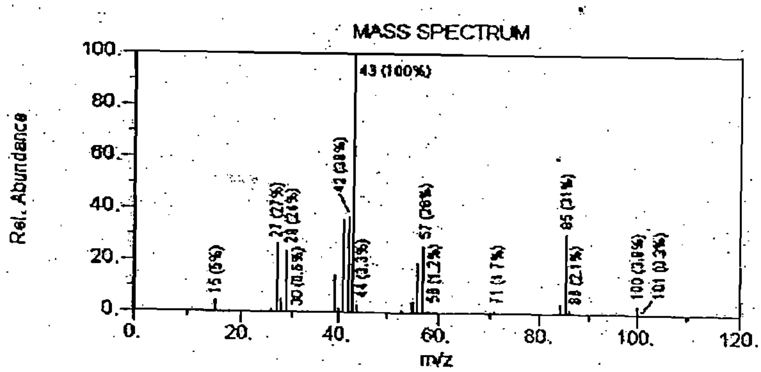

(a) Hexane
(b) 1-pentene
(c) 2-methyl pentane
(d) 2, 2-dimethyl propane
(e) Pentane

(5) Choose the compound that this represents.



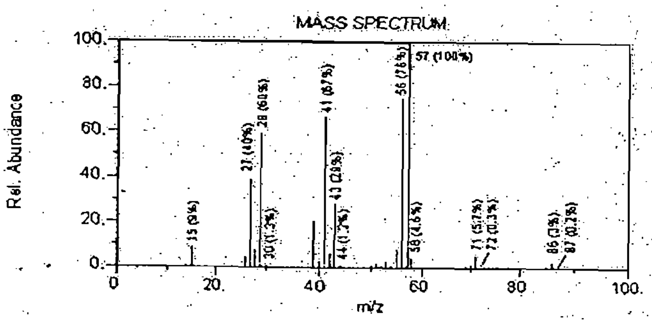

(a) 2, 2-dimethyl pentane
(b) 2-methyl hexane
(c) heptane
(d) 3, 3-dimethyl butane
(e) octane

(6) Choose the compound that this spectrum represents.




(a) octane
(b) 2, 2-dimethyl pentane
(c) 2-methyl hexane
(d) 3, 3-dimethyl butane
(e) heptane

(7) Choose the compound that this spectrum represents.

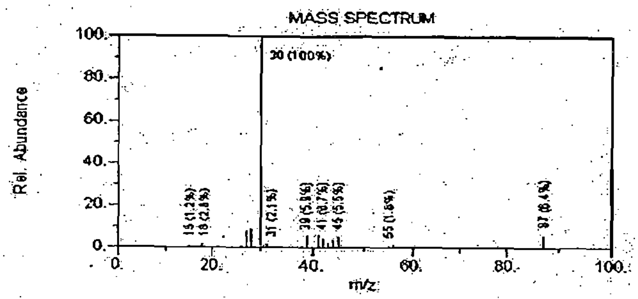



(a) 3-methyl pentane
(b) 2, 2-dimethyl butane
(c) heptane
(d) hexane
(e) 2-methyl pentane

**3. Fragmentation of Amines:**

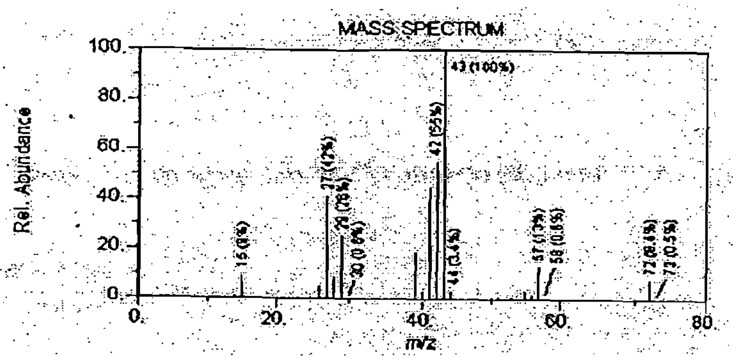
(1) Compound containing C, H, O atoms will have molecular weights that are even numbers. However, if one nitrogen is added the molecular weight will be an odd number. Test this by calculating the molecular weight of ethylamine ($CH_3CH_2NH_2$).
(a) 44 (b) 45 (c) 46

(2) Choose the compound that this spectrum represents.



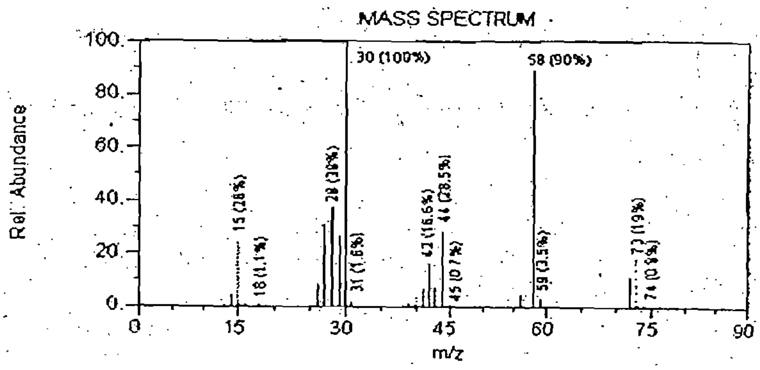

(a) 1-hexanamine
(b) 1-pentanamine
(c) N-methyl-1-butanamine
(d) 2-methyl-2-butanamine
(e) 1-butanamine

(3) Choose the compound that this spectrum represents.



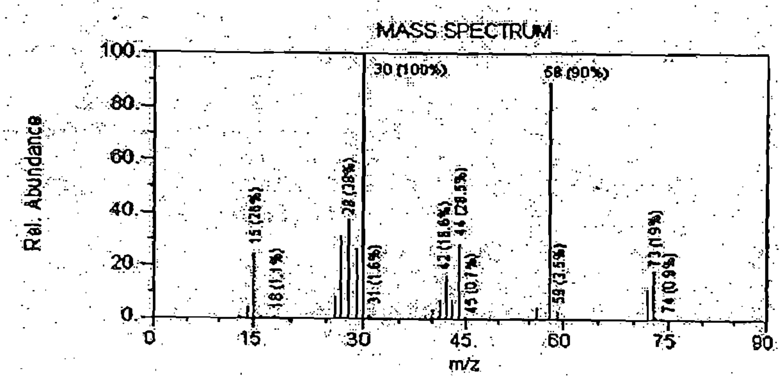

(a) 1-hexanamine
(b) N-methyl-1-butanamine
(c) 1-pentanamine
(d) 2-methyl-2-butanamine
(e) 1-butanamine

(4) Find the alkyl LOSS ion series in the spectra shown below. (Check the hint)



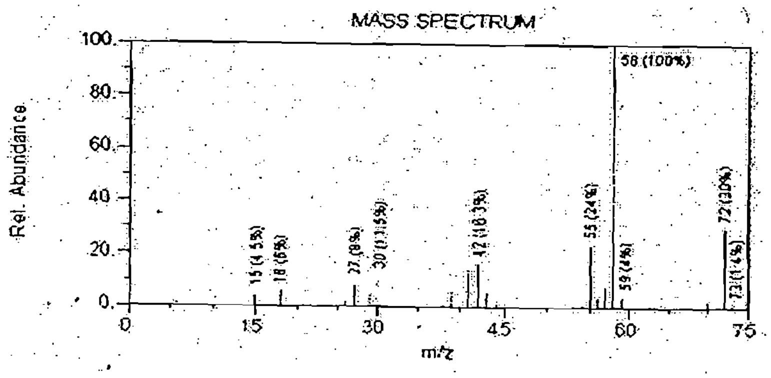

(a) 15, 29, 43 (b) 30, 44, 58 (c) None.

(5) From this same spectrum, choose the compound that the spectrum represents.



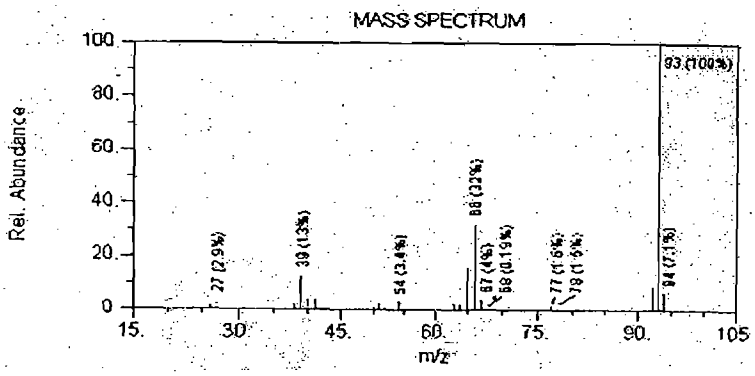

(a) methylhydrazone acetaldehyde
(b) 1-pentanamine
(c) diethylamine
(d) 2-methyl-2-propanamine
(e) 1-propanamine

(6) Choose the compound that this spectrum represents.




(a) N-methyl-1-butanamine
(b) 2-methyl-2-butanamine
(c) 1-pentanamine
(d) 1-hexanamine

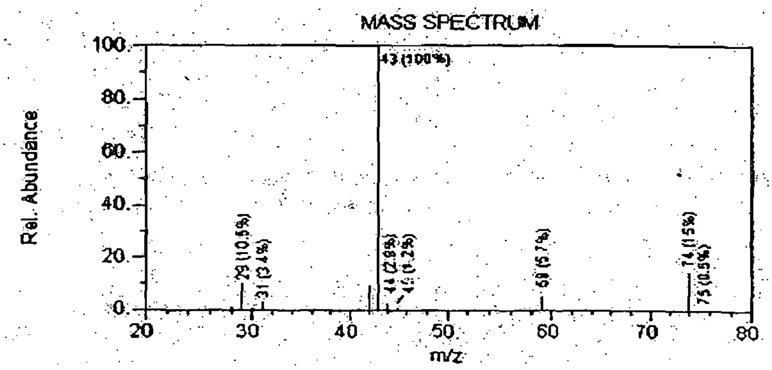
(7) Choose the compound that this spectrum represents.




(a) 1-methyl-1H-pyrrole
(b) aniline
(c) benzylamine
(d) 2, 4-hexadienenitrile
(e) 2-methyl-benzenamine

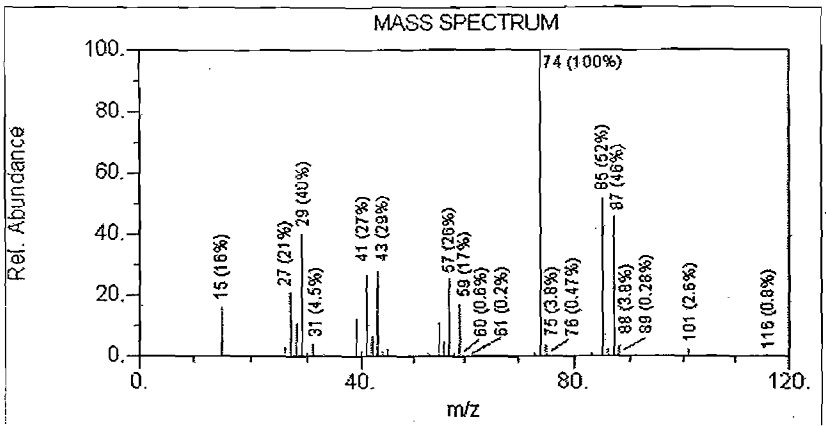
4. **Fragmentation of Esters:**

(1) Choose the compound that this spectrum represents.



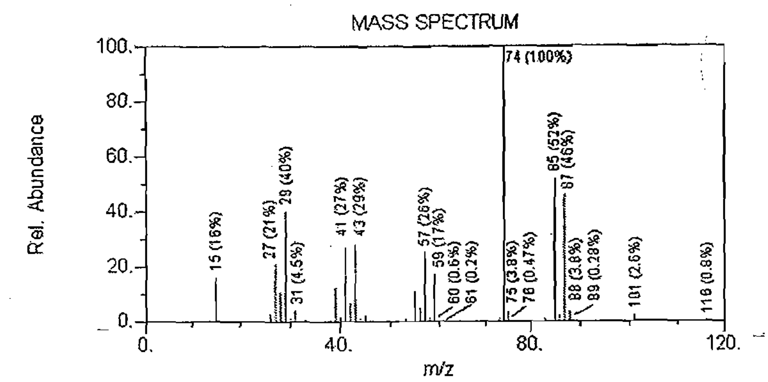

(a) ethyl methanoate
(b) methyl ethanoate
(c) propanoic acid
(d) ethyl ethanoate
(e) 2-propenoic acid.

(2) For this spectrum identify the ion series formed by loss of alkyl fragments.



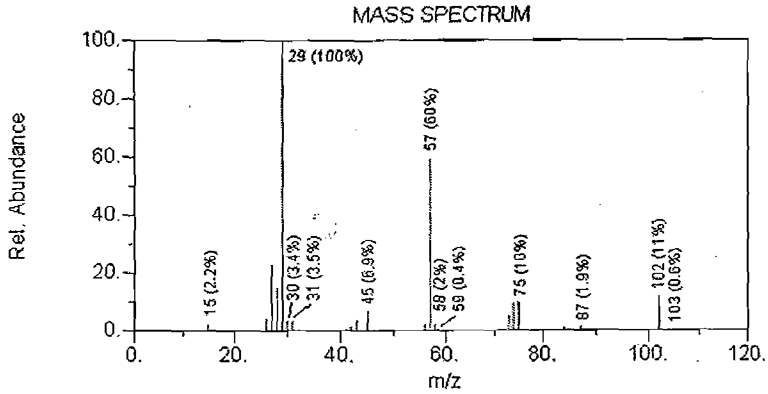

(a) 15, 29, 43, 57, 71
(b) 31, 45, 59, 87, 101
(c) None

(3) For this same spectrum, choose the compound that the spectrum represents.



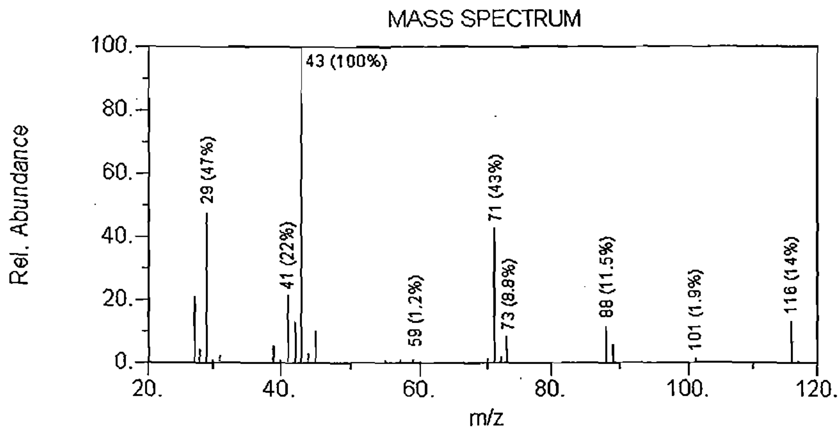

(a) methyl pentanoate
(b) methyl butanoate
(c) butyl ethanoate
(d) ethyl butanoate
(e) ethyl pentanoate

(4) Choose the compound that this spectrum represents.



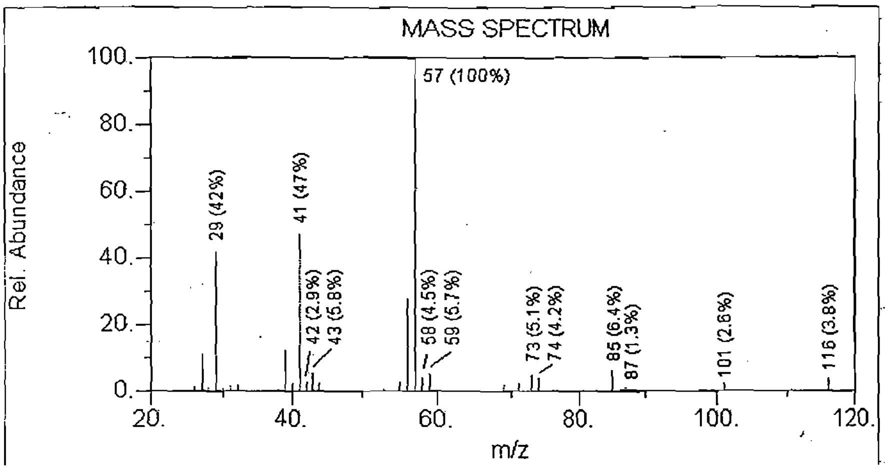

(a) isopropyl ethanoate
(b) butyl formate
(c) ethyl ethanoate
(d) ethyl propionate
(e) ethyl butanoate

(5) Choose the compound that this spectrum represents:




(a) ethyl butanoate
(b) ethyl pentanoate
(c) methyl 3-methylbutanoate
(d) ethyl 2-methylpropanoate
(e) methyl butanoate

(6) Choose the compound that this spectrum represents:



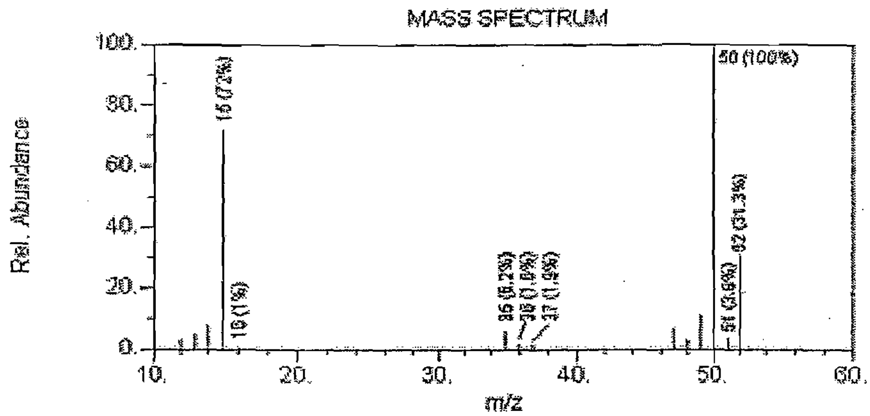

(a) ethyl pentanoate
(b) methyl butanoate
(c) ethyl butanoate
(d) 2, 2-dimethyl propanoic acid, methyl ester
(e) butyl ethanoate

5. **Fragmentation of Halides:**

(1) The mass of an atom is listed in the periodic table as an average of its isotopes. For example, chlorine has two isotopes, (35) Cl and (37)Cl, but is listed as having an atomic mass of 35.45. In a mass spectrometer the actual isotopes are observed in their natural abundances. What molecular ion peak(s) would you observe in the mass spectrum of ethyl chloride ($CH_3CH_2Cl$)?

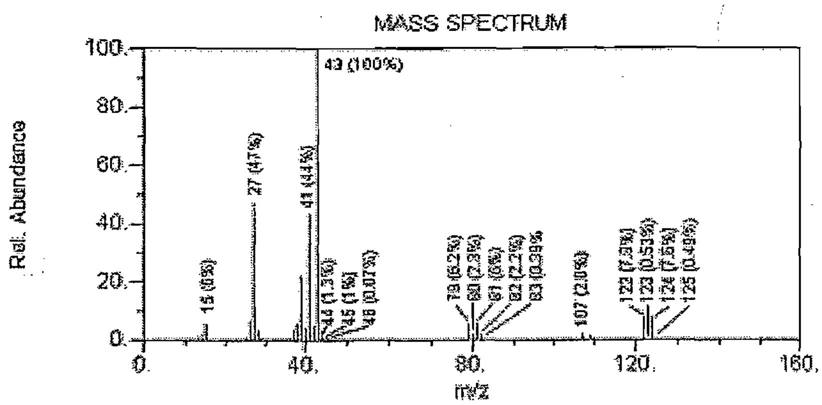
(a) 64
(b) 65
(c) 66
(d) 64 and 65
(e) 64 and 66

(2) Choose the compound that this spectrum represents.



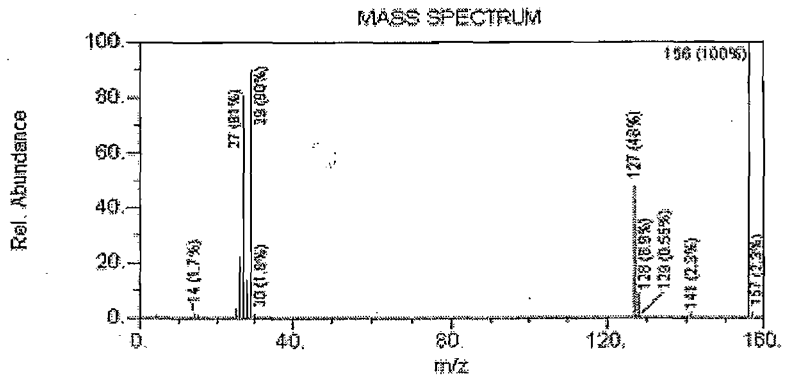

(a) chloromethane
(b) difluoromethane
(c) methylene chloride
(d) hydrogen chloride
(e) difluoroamine

(3) Choose the compound that this spectrum represents.



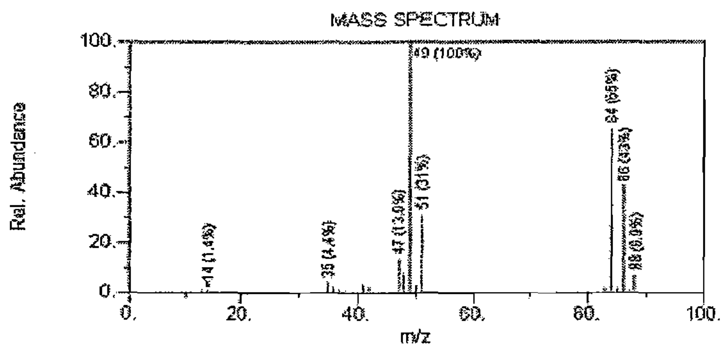

(a) bromoethane
(b) 1,4-dichloro-2-butene
(c) 1-bromopropane
(d) 2-bromopropane
(e) methyl iodide

(4) Choose the compound that this spectrum represents.



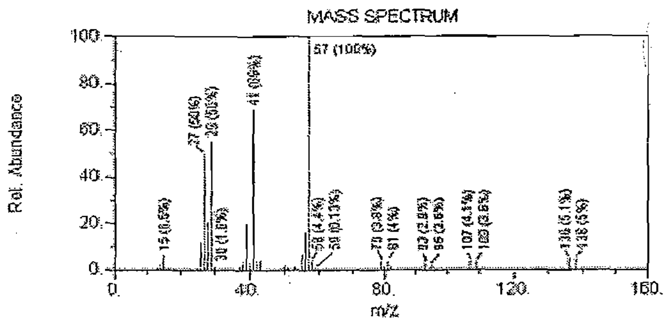

(a) methyl iodide
(b) 3-bromo-cyclohexene
(c) iodoethane
(d) 2-bromo-1-chloropropane
(e) bromo-benzene

(5) Choose the compound that this spectrum represents.




(a) chloromethane
(b) 2-chloro-1,3-butadiene
(c) dichlorine monoxide
(d) trifluoroethane
(e) methylene chloride

(6) Choose the compound that this spectrum represents.




(a) 2-bromo-1-chloro propane

(b) trichloromonofluoromethane

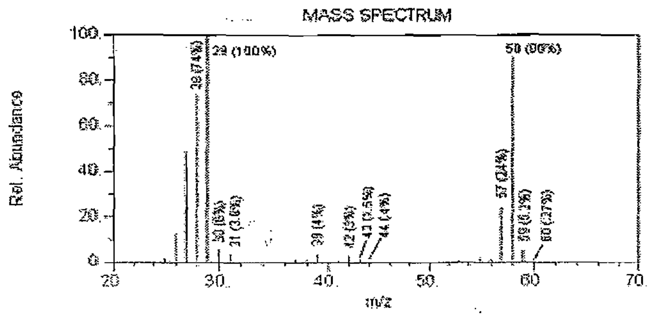
(c) 1-bromobutane

(d) 1-bromopropane

(e) 1-chloro-4-ethynyl-benzene

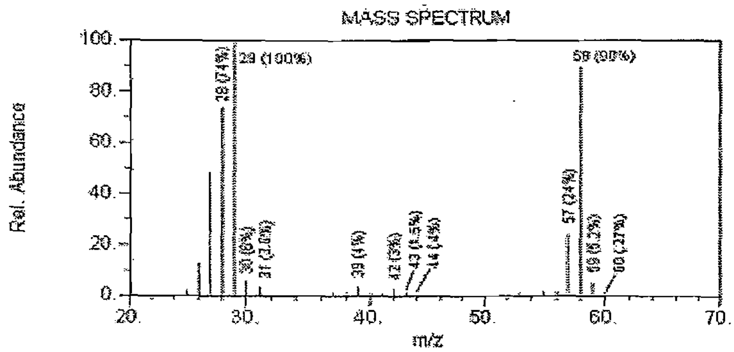
## 6. Fragmentation of Aldehydes:

(1) How many oxygens are in the molecular ion peak in this spectrum?




(a) 0 (b) 1 (c) 2

(2) For this same spectrum, choose the compound that the spectrum represents.




(a) butanal

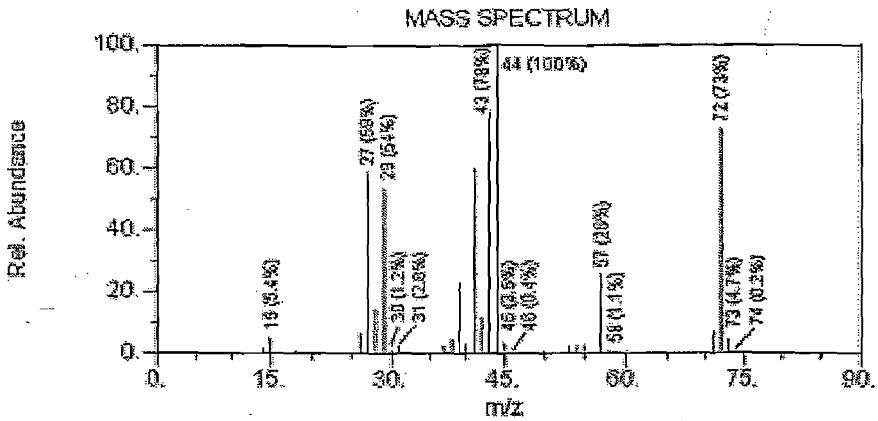
(b) propanal

(c) 2-propenal

(d) methoxy-ethene

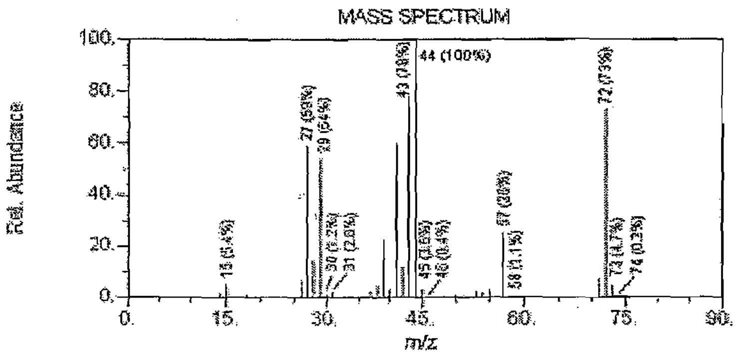
(e) ethanediol

(3) Find the alkyl ion series in the spectra below.



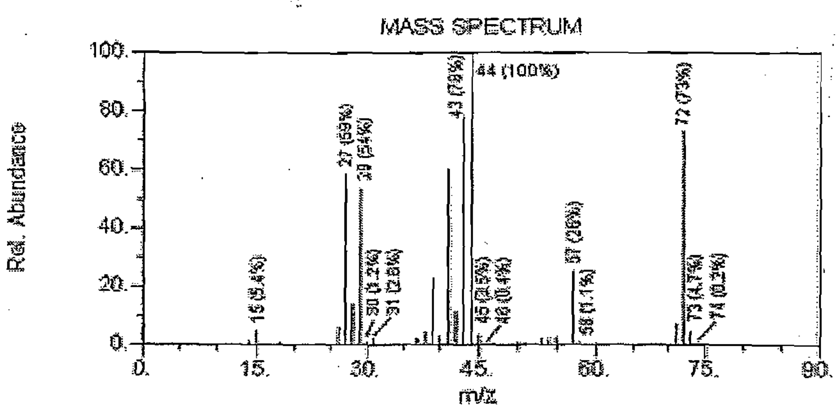

(a) 15, 29, 43 (b) 29, 43, 57 (c) none

(4) Find the alkyl LOSS ion series in the same spectra shown below.



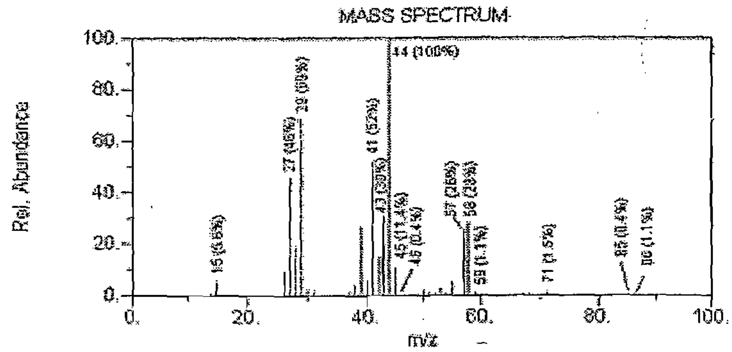

(a) 15, 29, 43 (b) 29, 43, 57 (c) none

(5) For this same spectrum, choose the compound that the spectrum represents.



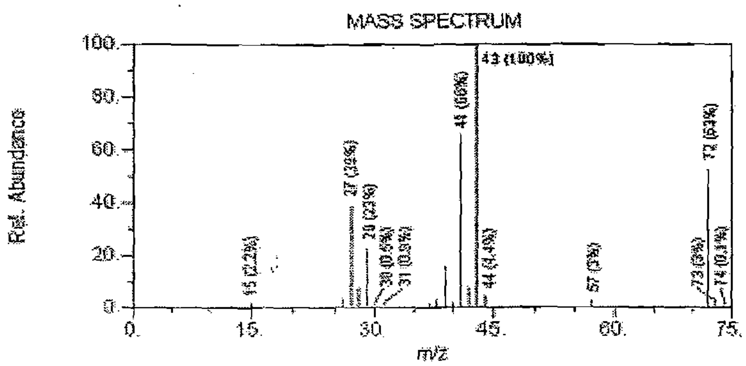

(a) 2-propenal
(b) 2-methyl propanal
(c) pentanal
(d) 2-oxo-propanal
(e) butanal

(6) Choose the compound that this spectrum represents.



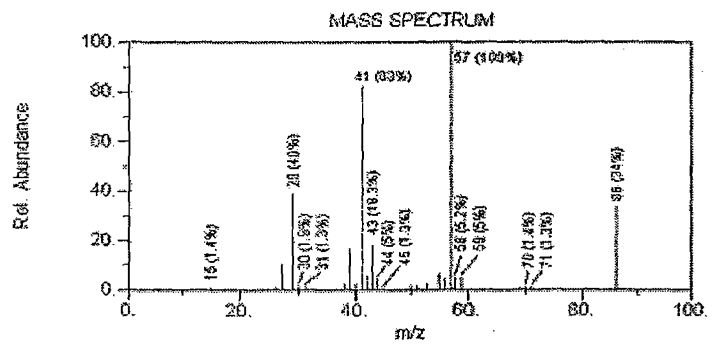

(a) hexanal (b) 3-methyl butanal (c) pentanal
(d) 2-methyl propanal (e) 2,2-dimethyl propanal

(7) Choose the compound that this spectrum represents.




(a) 2-methyl propanal (b) butanal
(c) 2-oxo-propanal (d) 2-propenal (e) pentanal

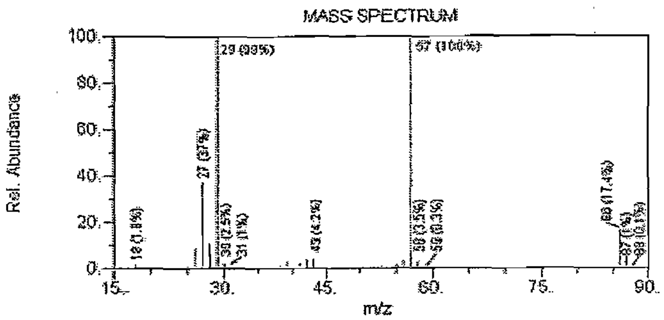
(8) Choose the compound that this spectrum represents.




(a) 2,2-dimethyl propanal (b) hexanal
(c) 2-oxo-propanal (d) 3-methyl-butanal (e) pentanal

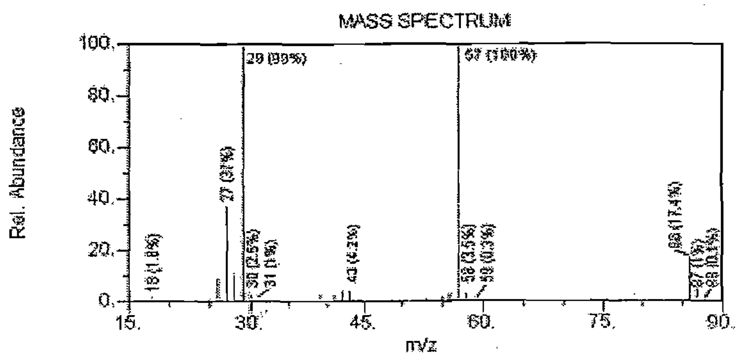
**7. Fragmentation of Ketones:**

(1) Find the alkyl ion series in the spectra below.



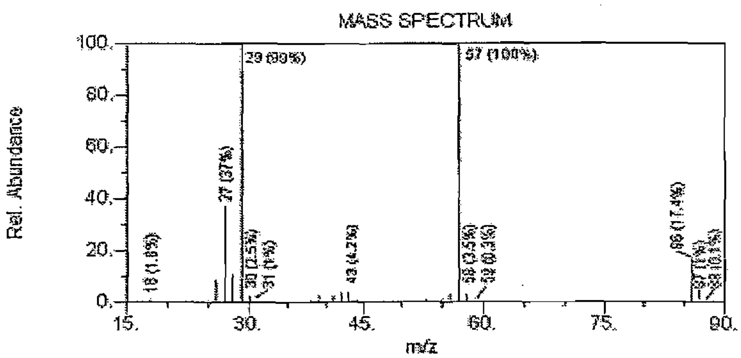

(a) 29, 43 (b) 43, 57 (c) none

(2) Find the alkyl LOSS ion series in the same spectra shown below.



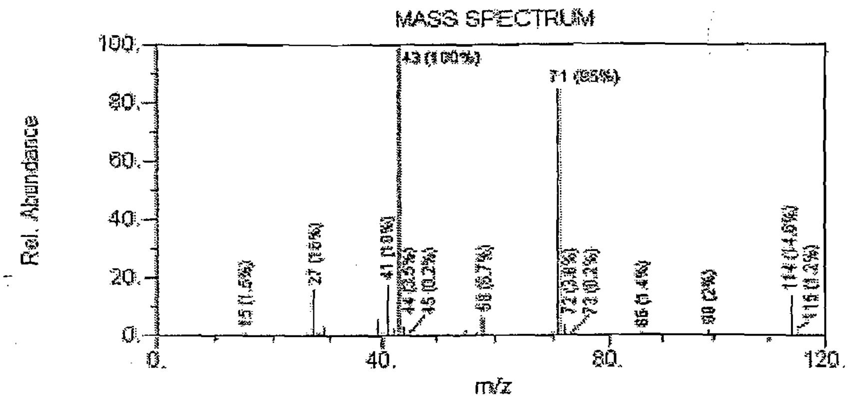

(a) 29, 43 (b) 43, 57 (c) none

(3) For this same spectrum, choose the compound that the spectrum represents.



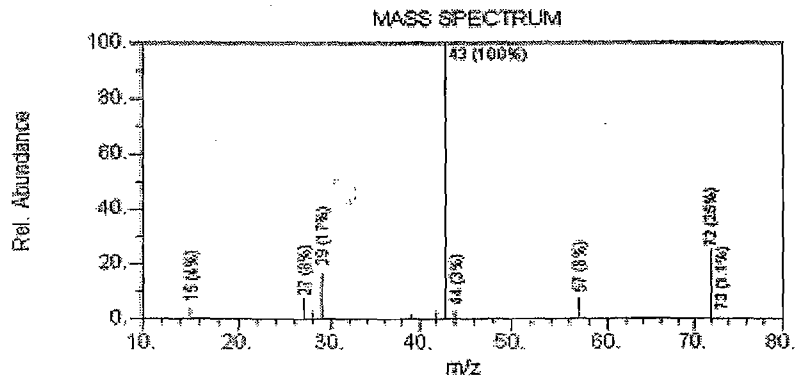

(a) 4-heptanone (b) 3-methyl-2-butanone
(c) 3-pentanone (d) 2-butanone (e) 2-pentanone

(4) Choose the compound that this spectrum represents.



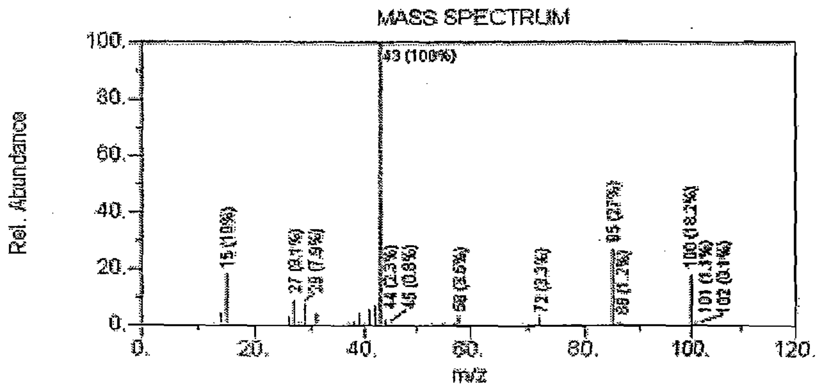

(a) 2-heptanone
(b) 4-heptanone
(c) 3-pentanone
(d) 4-methyl-2-heptanone
(e) 2,4-dimethyl-3-pentanone

(5) Choose the compound that this spectrum represents.



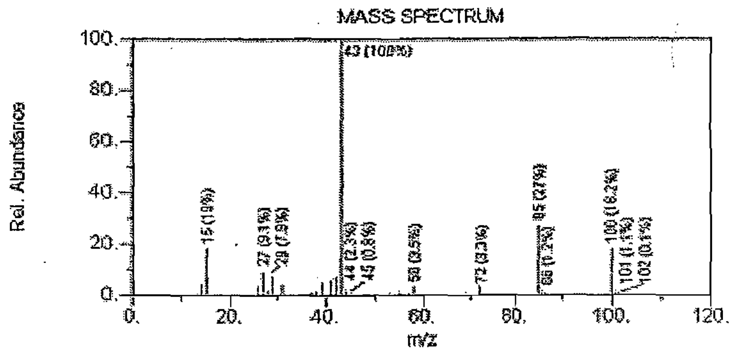

(a) cyclobutanone
(b) 2-butanone
(c) 2-propanone
(d) 3-pentanone
(e) 1-hydroxy-2-propanone

(6) How many oxygens are in the molecular ion peak in this spectrum?



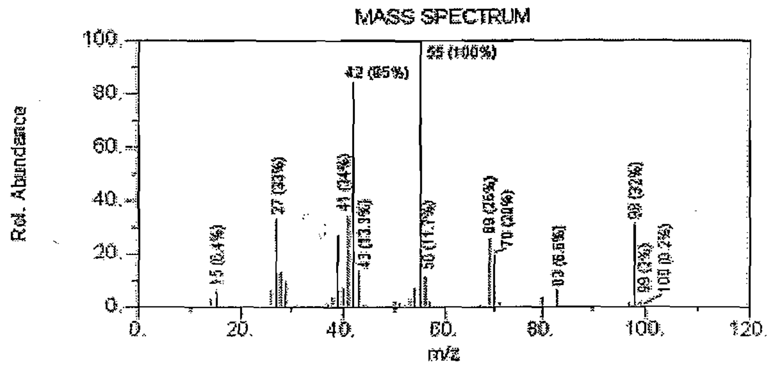

(a) 0
(b) 1
(c) 2
(d) 3

(7) For this same spectrum, choose the compound that the spectrum represents.



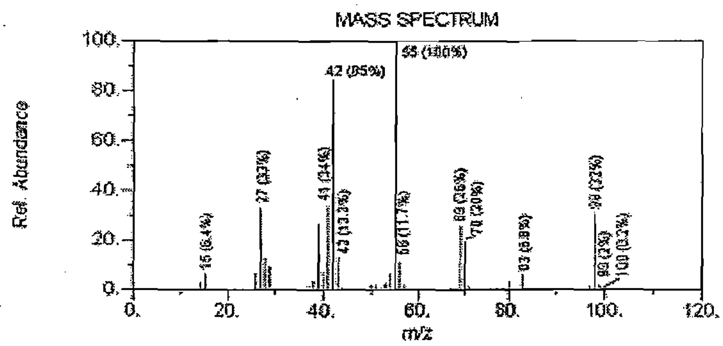

(a) 4-methyl-cyclohexanone
(b) 2,4-pentanedione
(c) 2-hexanone
(d) 3,3-dimethyl-2-butanone
(e) cyclohexanone

(8) In this spectrum, the molecular ion is 98 and there is one oxygen atom. Calculate the number of rings + double bonds in this compound. (Check the hint!)




(a) 0 (b) 1 (c) 2 (d) 3

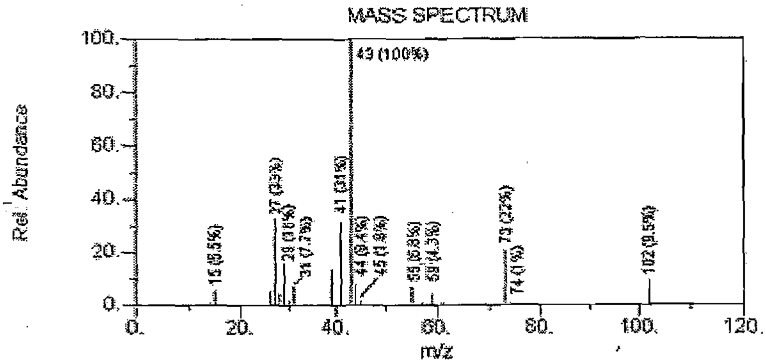
(9) For this same spectrum, choose the compound that the spectrum represents.




(a) 3-methyl-2-butanone
(b) 2-hexanone
(c) 4-methyl-3-penten-2-one
(d) 3-methyl-2-pentanone
(e) cyclohexanone

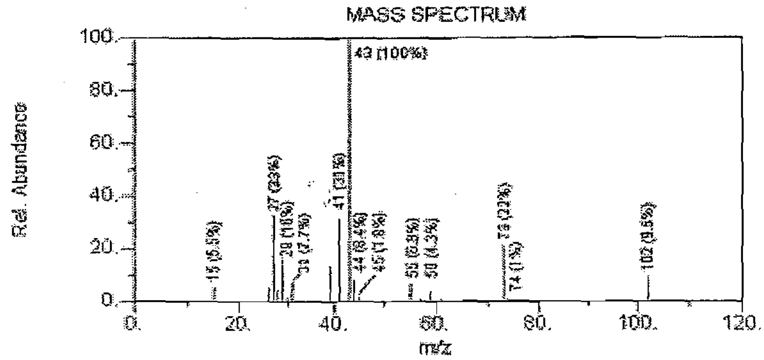
**Fragmentation of Ethers:**

1. Find the alkyl ion series in the spectra below. (Check the hint!)



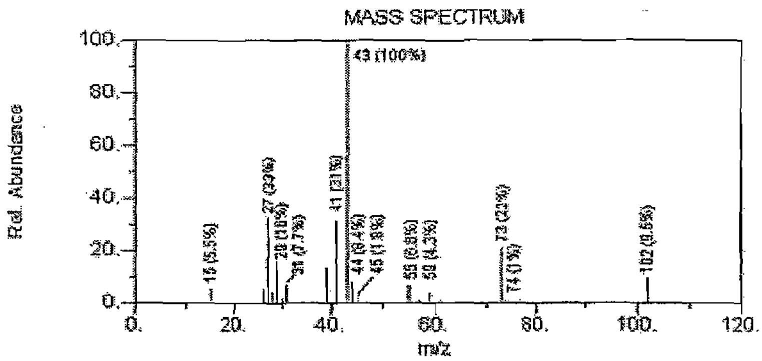

(a) 29, 43 (b) 59, 73 (c) none

(2) Find the alkyl LOSS ion series in the same spectra shown below. (Check the hint!)



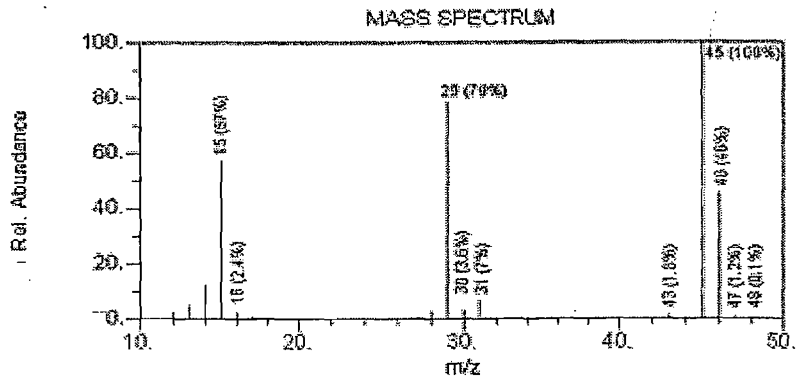

(a) 29, 43 (b) 59, 73 (c) none

(3) For this same spectrum, choose the compound that the spectrum represents.



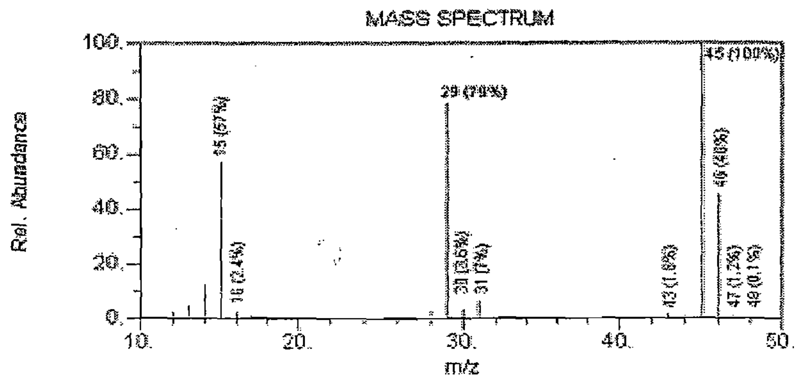

(a) ethylene oxalate
(b) isobutyl methyl ether
(c) 1-ethoxy-2-methyl propane
(d) dipropyl ether
(e) diisopropyl ether

(4) What ion is the most likely candidate to make the m/z 29 peak in the spectrum below?



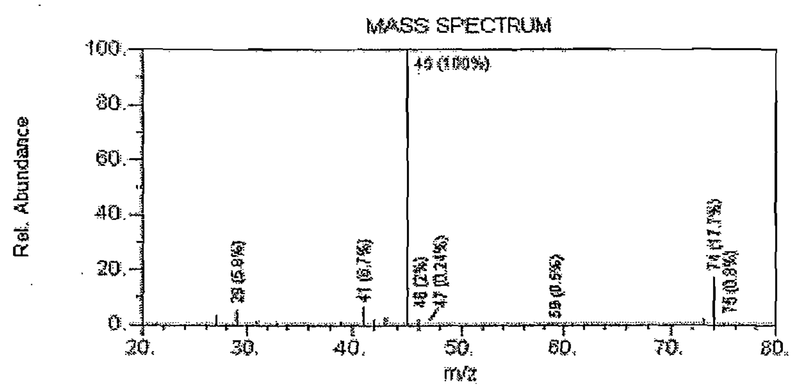

(a) HCO (b) $CH_2CH_3$

(5) For this same spectrum, choose the compound that the spectrum represents.



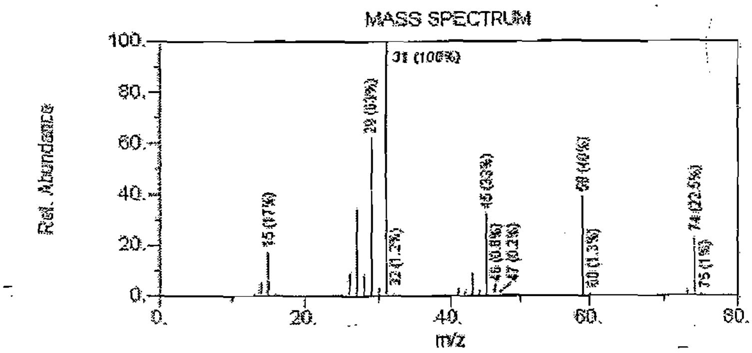

(a) methoxy-ethane (b) methoxy-ethene
(c) dimethyl ether (d) formamide (e) oxetane

(6) Choose the compound that this spectrum represents.



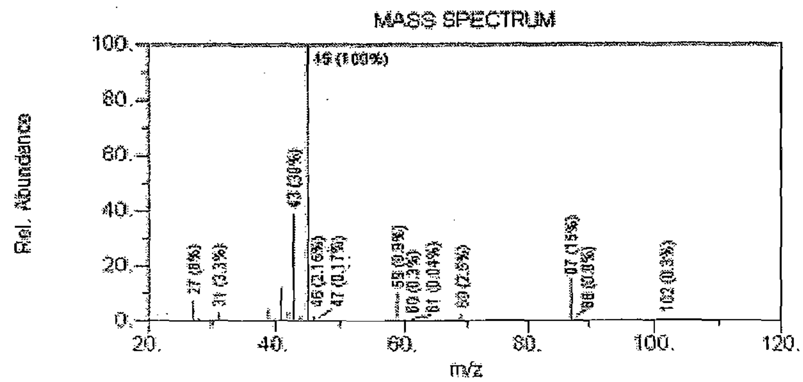

(a) tetrahydrofuran (b) 2-methoxy propane
(c) methyl propyl ether (d) ethyl ether (e) 1-methoxy butane

(7) Choose the compound that this spectrum represents.




(a) methyl propyl ether
(b) 1-methoxy butane
(c) 2-methoxy propane
(d) tetrahydrofuran
(e) ethyl ether

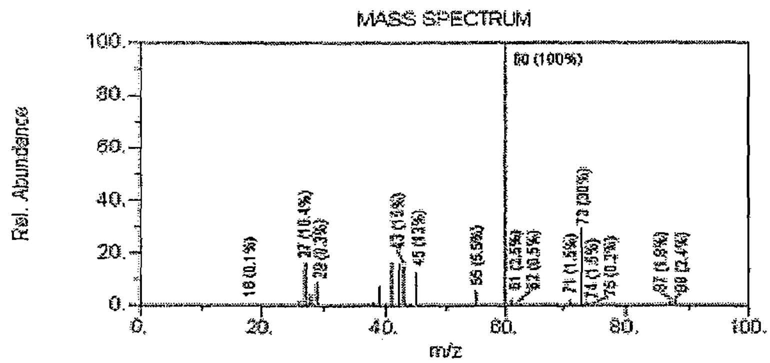
(8) Choose the compound that this spectrum represents.




(a) 1-ethoxy-2-methyl propane
(b) ethylene oxalate
(c) isobutyl methyl ether
(d) dipropyl ether
(e) diisopropyl ether

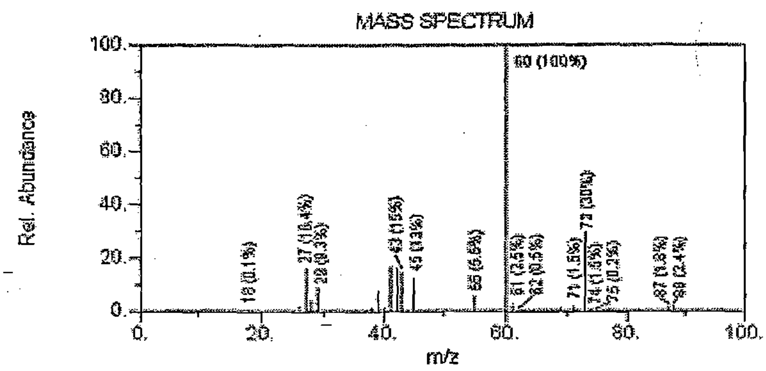
**Fragmentation of Acids:**

(1) Find the alkyl ion series in the spectra below. (Check the hint!)



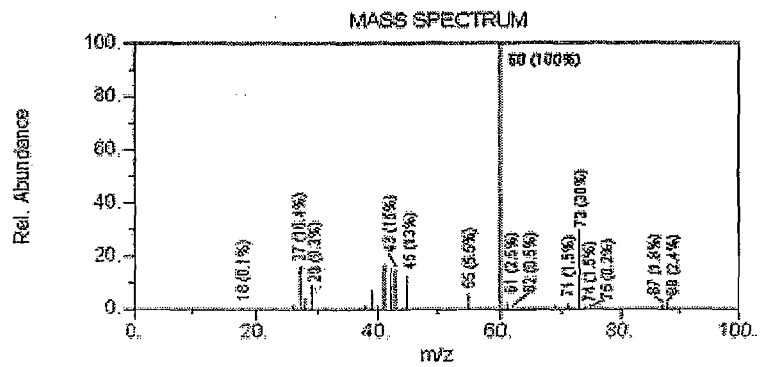

(a) 29, 43
(b) 45, 73
(c) none

(2) Find the alkyl LOSS ion series in the spectra shown below. (Check the hint!)



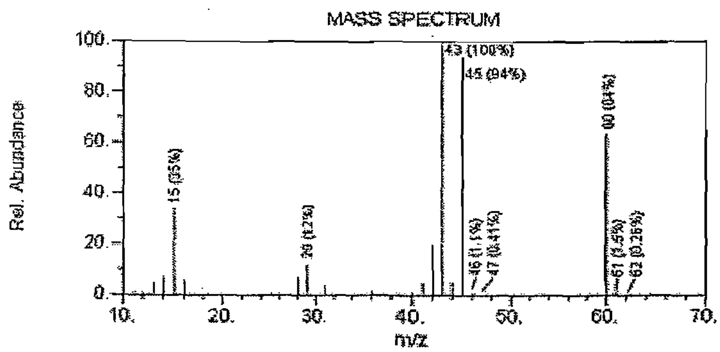

(a) 29, 43 (b) 45, 73 (c) none

(3) From this same spectrum, choose the compound that the spectrum represents.



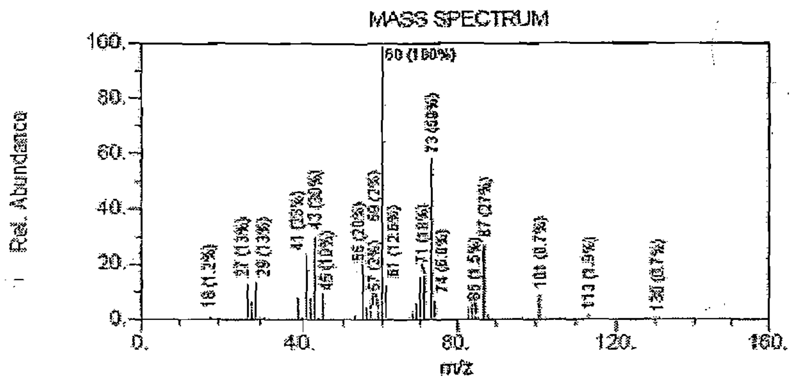

(a) 2-propanoic acid
(b) hydrazine carboxylic acid, methyl ester
(c) butanoic acid
(d) 2-methyl propanoic acid
(e) 1-methoxy butane

(4) Choose the compound that this spectrum represents.



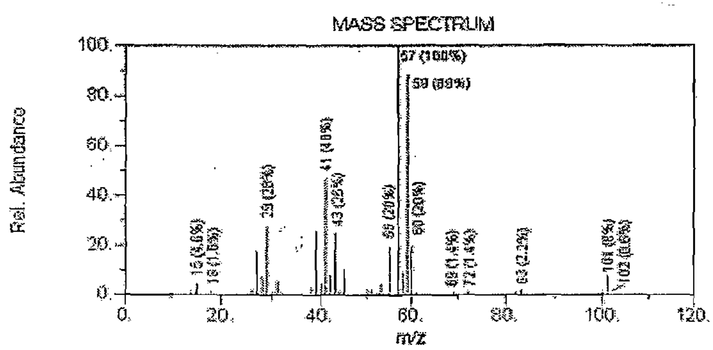

(a) methyl formate
(b) acetic acid
(c) hydroxy acetonitrile
(d) 2-propenoic acid
(e) butanoic acid

(5) Choose the compound that this spectrum represents.



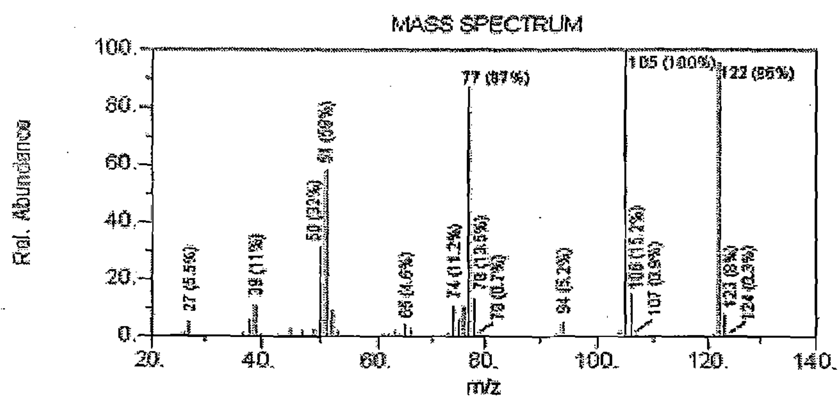

(a) butanoic acid, propyl ester
(b) heptanoic acid
(c) benzoic acid
(d) octanoic acid
(e) 2-methyl propanoic acid

(6) Choose the compound that this spectrum represents.




(a) cyclopentane carboxylic acid
(b) 3,3-dimethyl-butanoic acid
(c) 2-ethyl-butanoic acid
(d) benzoic acid
(e) 2,2-dimethyl-butanoic acid

(7) Choose the compound that this spectrum represents.



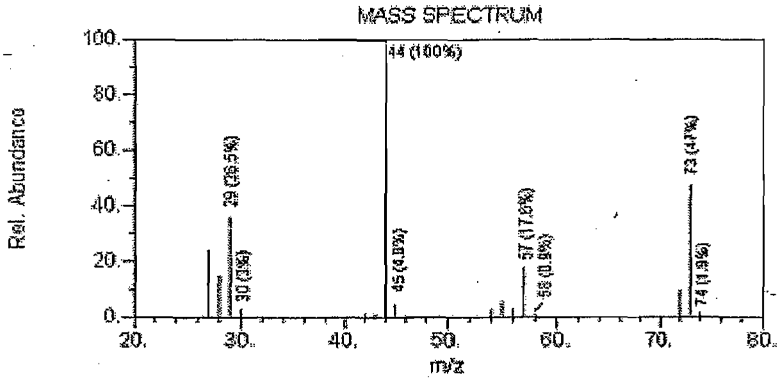

(a) 2-methyl benzaldehyde
(b) benzoic acid
(c) heptanoic acid
(d) 2-hydroxy benzaldehyde
(e) ethyl chloroacetate

**Fragmentation of Amides:**

(1) Compounds containing C, H, O atoms will have molecular weights that are even numbers. However, if one nitrogen is added the molecular weight will be an odd number. Test this by calculating the molecular weight of butanamide ($CH_3CH_2CH_2CONH_2$).

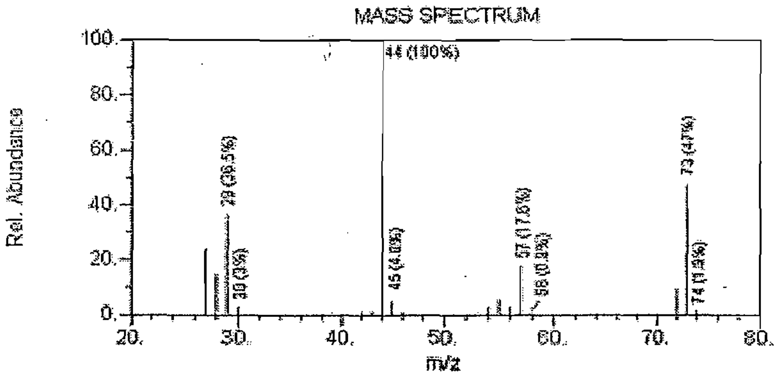
(a) 85 (b) 86 (c) 87 (d) 88

(2) Find the alkyl LOSS ion series in the spectra shown below. (Check the hint!)



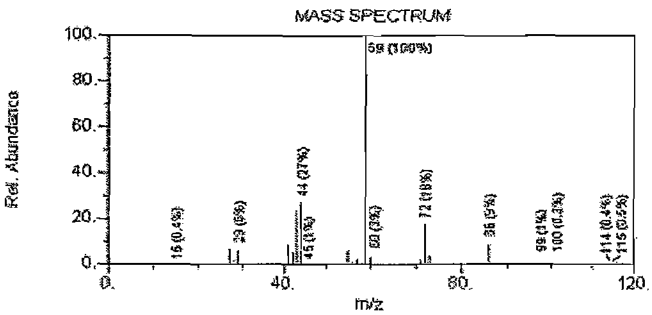

(a) 29, 43, 57 (b) 44, 58, 72 (c) none

(3) For this same spectrum, choose the compound that the spectrum represents.



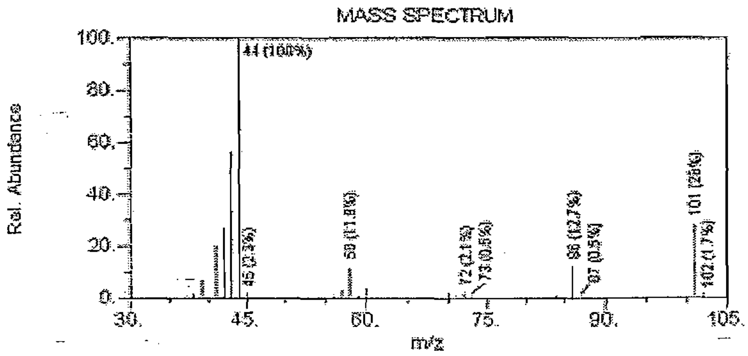

(a) propanamide (b) acrylamide (c) glycine
(d) thiocyanic acid, methyl ester (e) N,N-dimethylformamide

(4) Choose the compound that this spectrum represents.



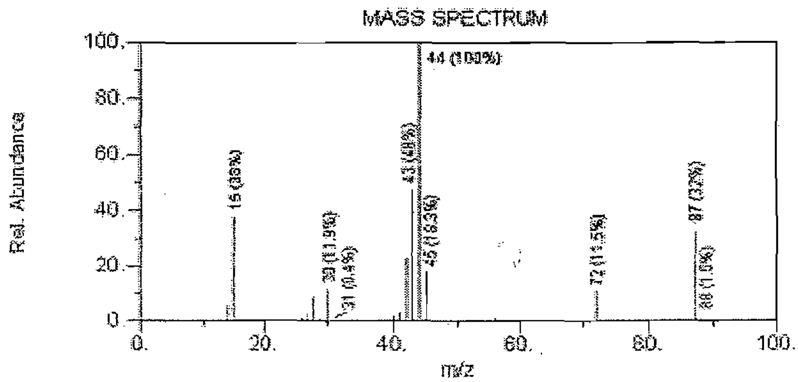

(a) N,N-diethylacetamide (b) N,N-diisopropylformamide
(c) pentanamide (d) N-butylacetamide (e) hexanamide

(5) Choose the compound that this spectrum represents.



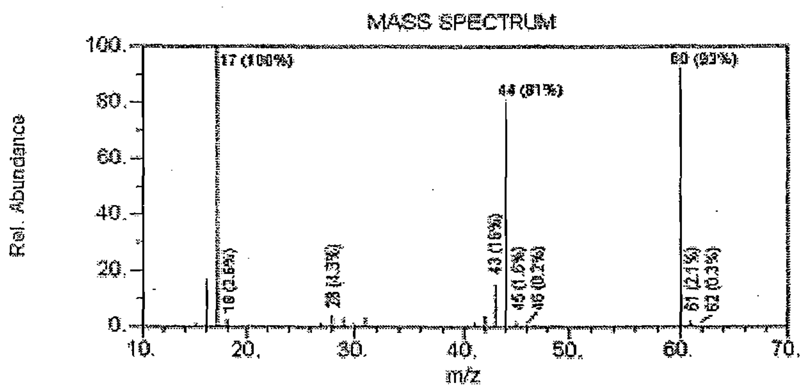

(a) 2,2-dimethylpropanamide (b) pentanamide
(c) N-(n-Propyl)ethanamide (d) hexanamide (e) N,N-dimethylacetamide

(6) Choose the compound that this spectrum represents.




(a) butanamide (b) 2,2-dimethylpropanamide (c) N,N-dimethylacetamide
(d) morpholine (e) propanamide

(7) Choose the compound that this spectrum represents.

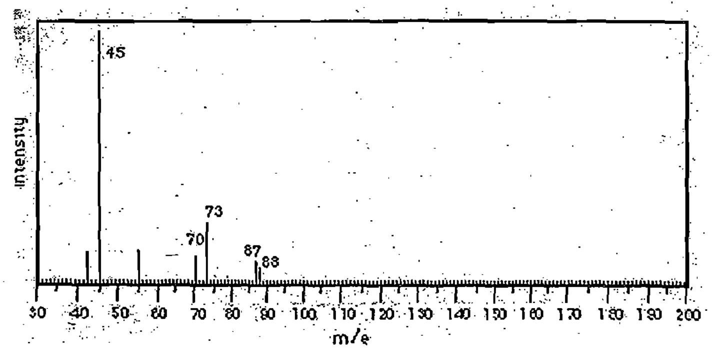



(a) hydroxyacetonitrile (b) urea (c) isocyanatomethane
(d) methyl nitrite (e) nitro methane

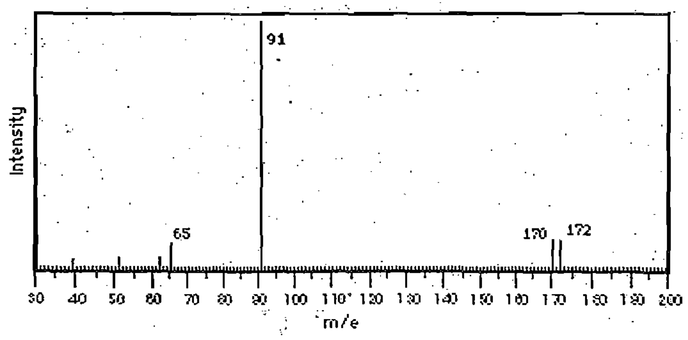
## Mass Spectra - Assignement

Find out the molecular structure number of the basis of following mass spectra data.

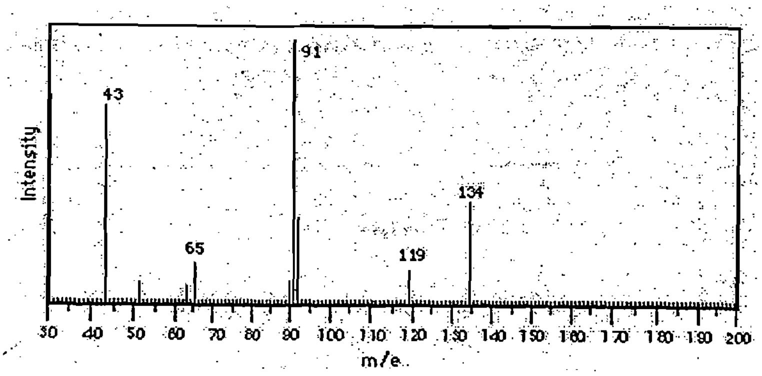
1. $C_5H_{12}O$, MW = 88.15



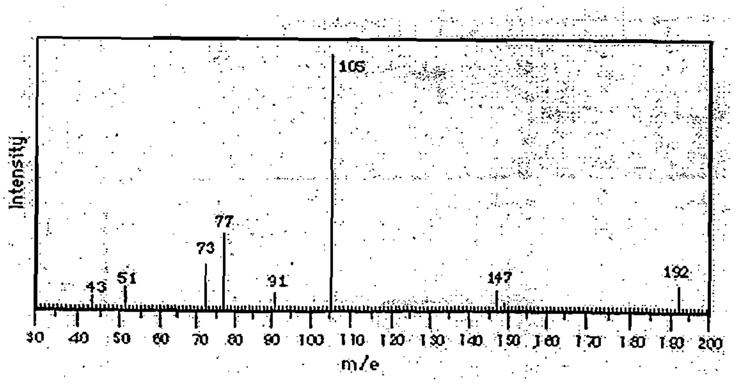

2. $C_7H_{12}Br$, MW = 171.04



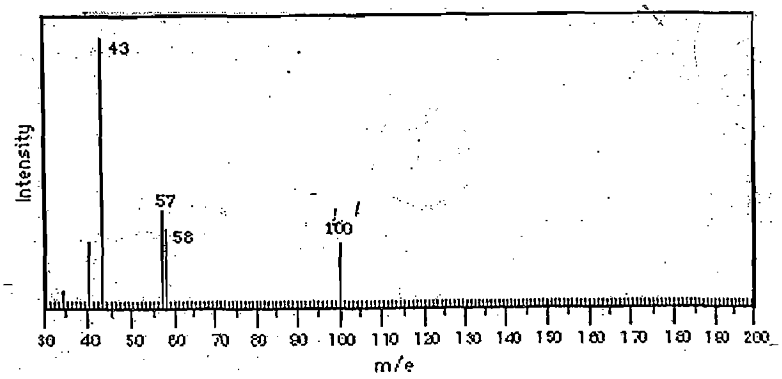

3. $C_9H_{10}O$, MW = 134.18




4. $C_{11}H_{12}O_3$, MW = 192.21



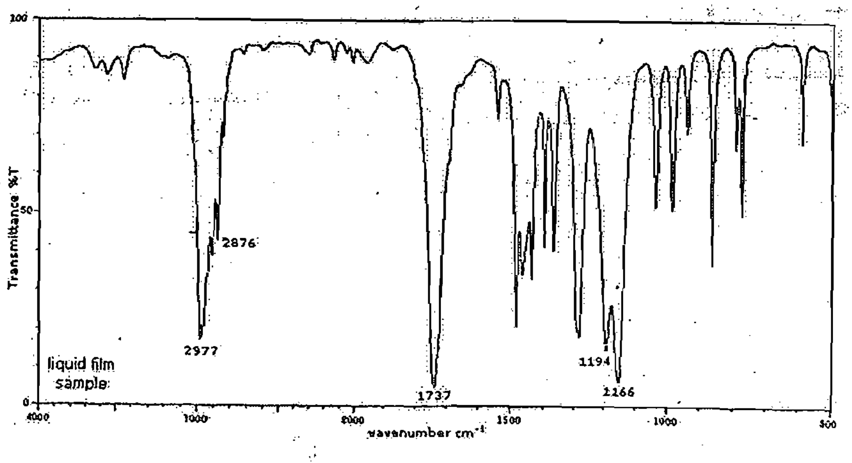
5. Analysis: $C_5H_8O_2$, MW = 100.12

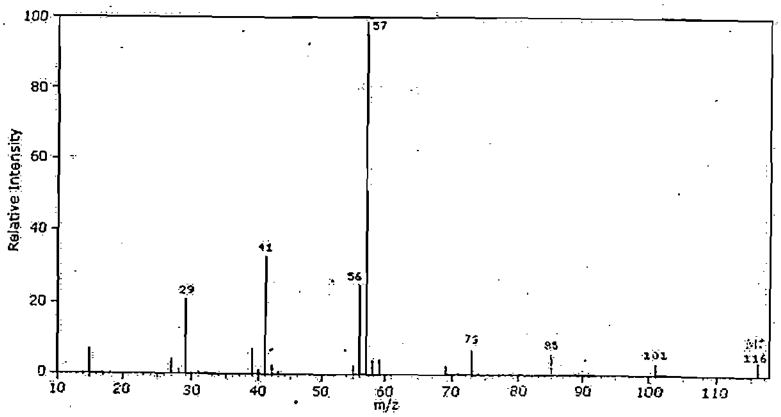


# COMBINED IR AND MASS SPECTROCOPY PROBLEMS

1. A pleasant smelling liquid having a boiling point of 101°C.

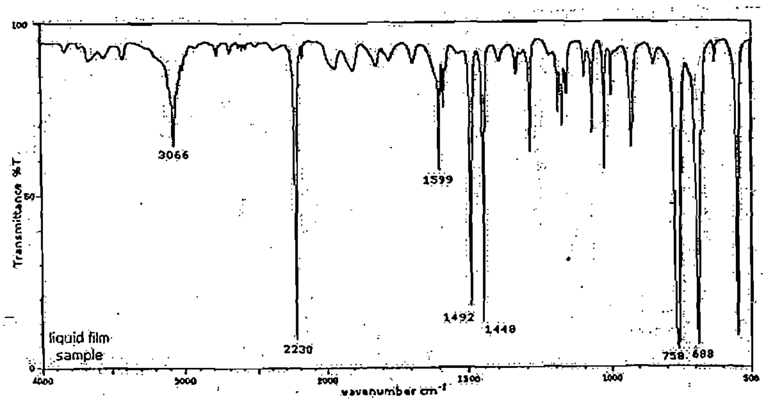
| Major infrared absorptions | Major ions in the mass spectrum |
|---|---|
| 2880 to 2980 $cm^{-1}$ | 29 |
| 1737 (str) | 41 |
| 1194 (str) | 56 |
| 1166 (str) | 57 (base) |
| | 73 |
| | 85 |
| | 101 (small) |
| | 116 molecular ion. |

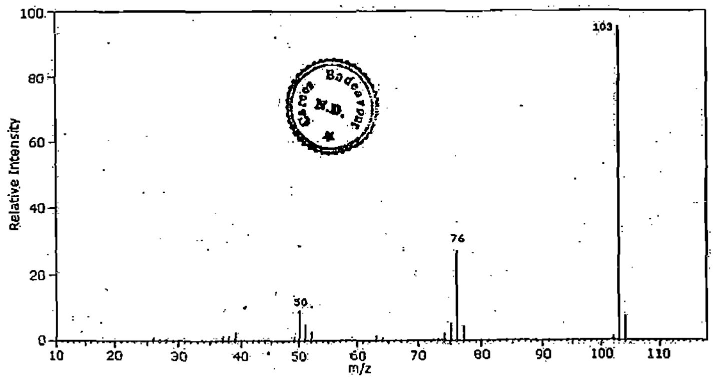



2. An oily liquid having a boiling point of 191° C and a melting point of –13°C.

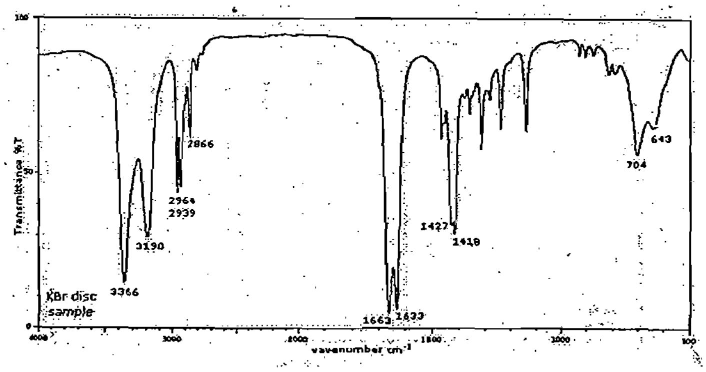
| Major infrared absorptions | Major ions in the mass spectrum |
|---|---|
| 3066 $cm^{-1}$ | 50 (small) |
| 2230 (str) | 76 |
| 1599 | 103 base on ion and molecular ion |
| 1492 | 104 is ca. 8% of base |
| 758 | |
| 688 | |

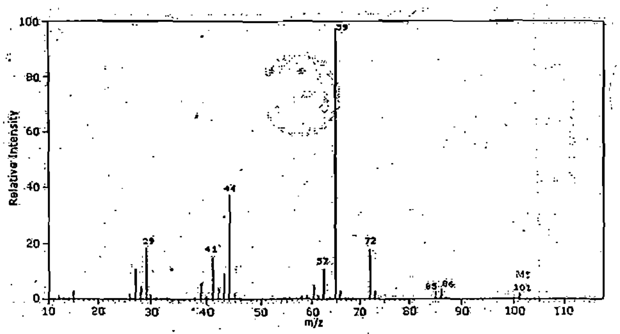



**3.** A colourless solid melting at 103 to 105°C

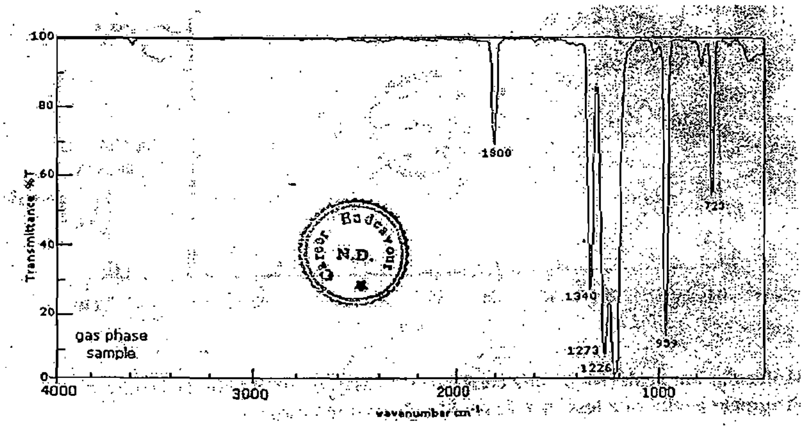
| **Major Infrared absorptions** | **Major ions in the mass spectrum** |
|---|---|
| 3366 and 3190 cm–1 (str and brd) | 29 |
| 2850 to 2970 | 41 |
| 1663 to 1633 (str) | 44 |
| 1418 and 1427 | 57 |
| 643 and 704 (brd) | 59 (base) |
| | 72 |
| | 85 and 86 (small) |
| | 101 (v. small) molecular ion |

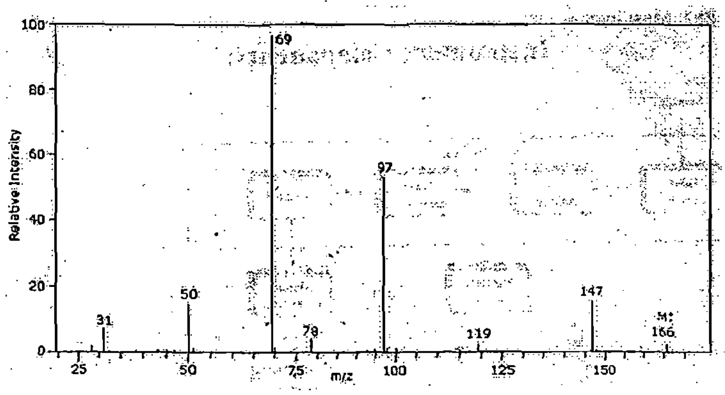





4. A colourless gas condensing at – 26°C.

| Major infrared absorptions | Major ions in the mass spectrum |
|---|---|
| 1800 $cm^{-1}$ | 31 |
| 1340 | 50 |
| 1273 (str) | 69 (base) |
| 1226 (str) | 78 (small) |
| 959 | 97 |
| 723 | 119 (small) |
| | 147 |
| | 166 (small) molecular ion |



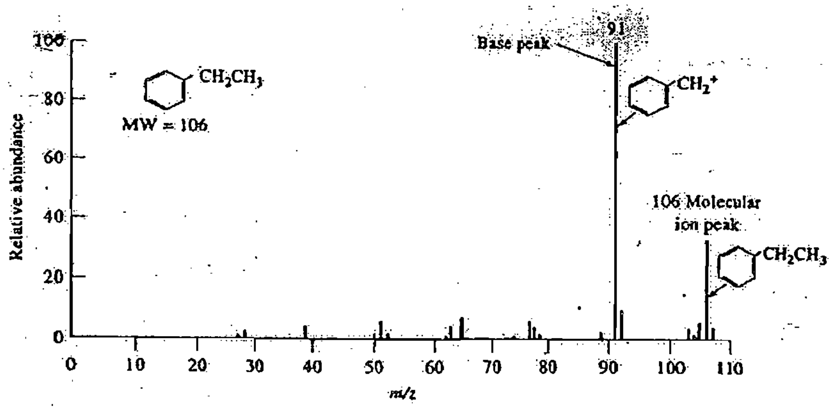



## Mass spectrometry: Instrumentation:

Based on **ionization of gas phase molecule followed by analysis of the masses of the ions produced.**

The Mass **Spectrum:**

Graph of ion intensity versus mass-to-charge ratio (m/z) (units daltons, Da)

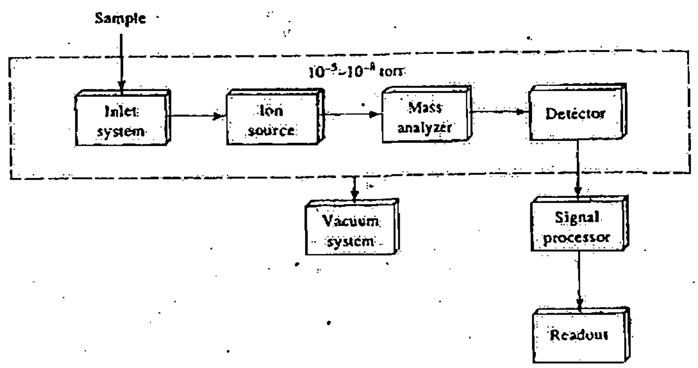



Molecular **ion peak ($M^+$):** m/z corresponds to MW of singly charged molecule

Fragment **peak:** m/z less than MW of singly charged molecule.

Base peak: Most intense m/z

### Instrument Components

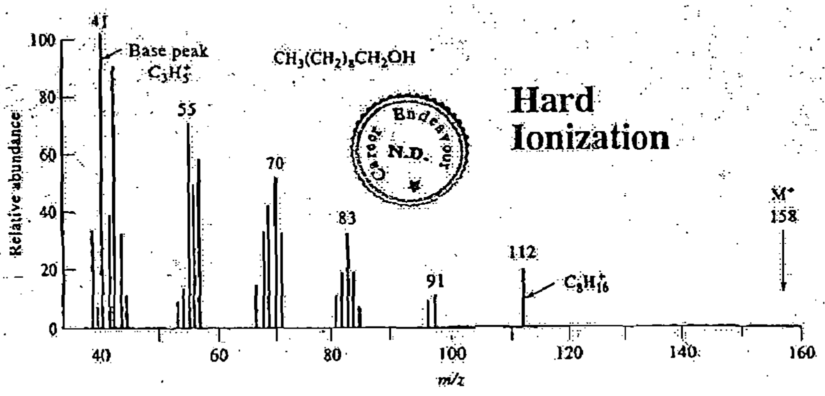



- Sample introduction system – vaporize sample
- Ion source – ionizes analyte gas molecules.
- Mass analyzer – separates ions according to m/z
- Detector – counts ions
- Vacuum system – reduces collisions between ions and gas molecules.

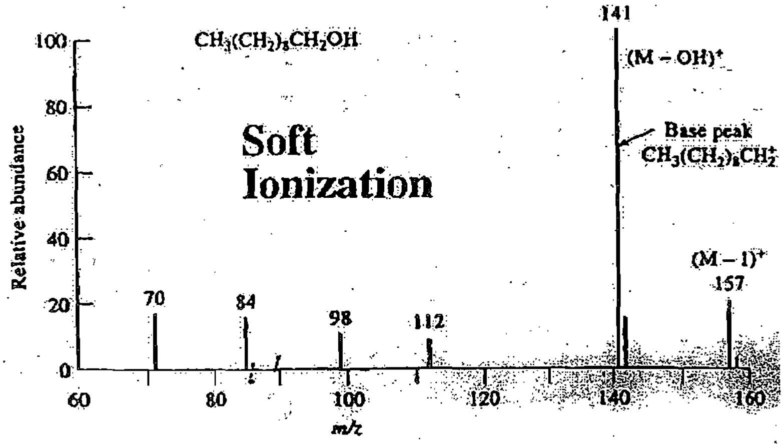
Ion sources:

| Basic Type | Name and Acronym | Ionizing Agent |
|---|---|---|
| Gas phase | Electron impact (EI) | Energetic electrons |
| | Chemical ionization (CI) | Reagent gaseous ions |
| | Field ionization (FI) | High-potential electrode |
| Desorption | Field desorption (FD) | High-potential electrode |
| | Electrospray ionization (ESI) | High electrical field |
| | Matrix-assisted desorption/ionization (MALDI) | Laser beam |
| | Plasma desorption (PD) | Fission fragments from $^{252}Cf$ |
| | Fast atom bombardment (FAB) | Energetic atomic beam |
| | Secondary ion mass spectrometry (SIMS) | Energetic beam of ions |
| | Thermospray ionization (TS) | High temperature |

**Hard ion:** Leaves excess energy in molecule–extensive fragmentation.
**Softion sources:** Little excess energy in molecule – reduced fragmentation.



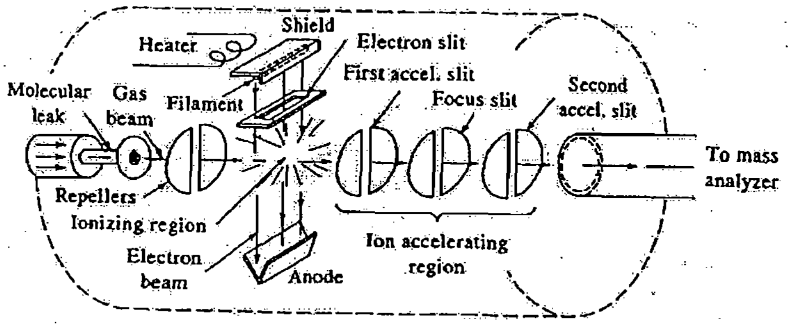
(a)



(b)

**Gas Phase Ion Sources:**
**(A) Electron Impact (EI) Ion Source:**
Electron bombardment of gas/vapor molecules.

$$M^+e^- (\sim 70\text{ eV}) \longrightarrow M^+ + 2e^- \text{ (about 10–4\% ionized)}$$




Electron energy ~ 70 eV
1 eV = $1.6\times10^{-19}$ C' 1V (1V = 1J × $C^{-1}$)
= $1.6\times10^{-19}$ J
= 96.486 kJ × $mol^{-1}$.

**EI Spectra:**
- Hard source (incident energy 70 eV >> than chemical bond)
- Molecules electronically, vibrationally and rotationally excited.
- Extensive fragmentation ⟹ fragment ions.

Molecular ion formation

Fragmentation

$ABCD + e^- \rightarrow ABCD^{+\cdot} + 2e^-$

$ABCD^{+\cdot} \rightarrow A^+ + BCD^\cdot$

→ $A^\cdot + BCD^+ \rightarrow BC^+ + D$

→ $CD^\cdot + AB^+$ → $B + A^+$ / → $A + B^+$

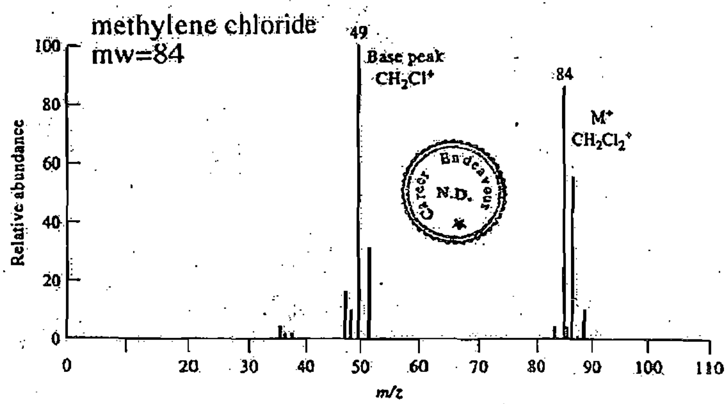
→ $AB^\cdot + CD^+$ → $D + C^+$ / → $C + D^+$

Rearrangement followed by fragmentation $ABCD^{+\cdot} \rightarrow ADBC^{+\cdot}$ → $BC^\cdot + AD^+$ / → $AD^\cdot + BC^+$

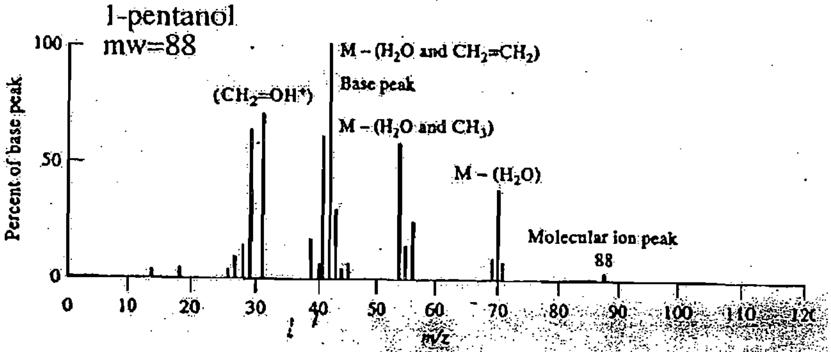
Collision followed by fragmentation $ABCD^{+\cdot} + ABCD \rightarrow (ABCD)_2^{+\cdot} \rightarrow BCD^\cdot + ABCDA^+$

- Base peak m/z << $M^+$.
- Complex spectra
  - Helps identification
  - Poor for measuring MW of compound.

Fragmentation patterns (Figure):



(a)



(b)

What about peaks at greater m/z than $M^+$?

Two sources:

- **Isotope Peaks:** Same chemical formula but different masses.

$^{12}C\ ^1H_2\ ^{35}Cl_2$ $m = 84$

$^{13}C\ ^1H_2\ ^{35}Cl_2$ $m = 85$

$^{12}C\ ^1H_2\ ^{35}Cl\ ^{37}Cl =$ $m = 86$ heights vary with abundance

$^{13}C\ ^1H_2\ ^{35}Cl\ ^{37}Cl$ $m = 87$

$^{12}C\ ^1H_2\ ^{35}Cl_2$ $m = 88$

$^{13}C$ is 1.1% $^{12}C$, $^{37}Cl$ is 32.5% $^{35}Cl$

• **Collision Product Peaks:** Only ommon peak is proton transfer to give $(M+1)^+$ peak (increases with increasing pressure).

**Advantages of EI:**
• High ion currents: Sensitive
• Fragmentation aids identification

**Disadvantages of EI:**
• Weak or absent $M^+$ peak inhibits determination of MW
• Molecules must be vapourized (MW < 103 Da)
• Molecules must be thermally stable during vaporization.

**(B) Chemical Ionization:**
• Many modern MS instruments can perform chemical ionizationin addition to EI.
EI ionization in excess (analyte 10–100 ppm) of reactant gas.
EI ionization of methane produces

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3$$

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

These ions react with analyte:

$$CH_5^+ + A \longrightarrow CH_4 + AH^+ \quad \text{proton transfer}$$

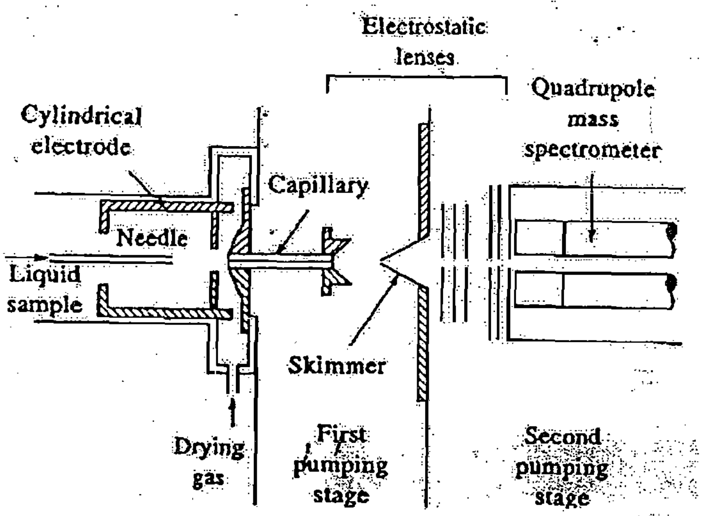
$$C_2H_5^+ + A \longrightarrow C_2H_4 + AH^+ \quad \text{proton transfer}$$

$$C_2H_5^+ + A \longrightarrow C_2H_6 + (A-H)^+ \quad \text{hydride elimination analyte}$$

• Most common ions $(M+1)^+$ and $(M-1)^+$
• Sometimes $(M+17)^+$ (addition of $CH_5^+$) or $(M+29)^+$ (addition of $C_2H_5^+$)

**Desorption/Ionization Sources:**
Applicable to non-volatile (> 105 Da) or non-stable analytes, energy applied to analyte causing desorption and ionization, exact mechanism still under investigation.

**(A) Electrospray Ionization (ESI):**
• Explosion of charged droplets containing analytes.
  • Solution analyte pumped through charged (1–5 kV) capillary
  • Small droplets become charged.
  • Solvent evaporates, drop shirnks, surface charge density increases.
  • Charge density reduced by expulsion of charged analyte molecules ("Coulomb explosion")
Soft ionization: little fragmentation
Easily adapted to FIA, capillary EP and HPLC.

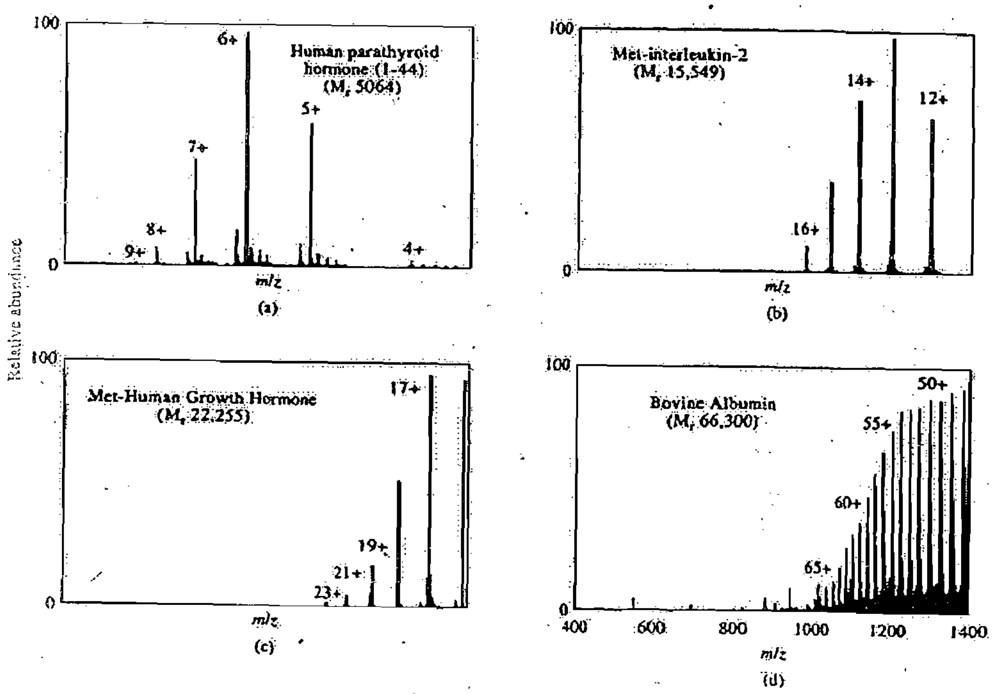



Very important technique for large (>105 Da) thermally fragile molecules.

- Peptides
- Proteins
- Polymers
- Oligonucleotides.

Analytes may accumulate multiple charges in ESI

$M^+, M^{2+}, M^{3+}$, ..............




(B) Fast Atom **Bombardment (FAB):**

Hard ionization: fragmentation

Sample in glycerol solution

Bombarded by high energy Ar or Xe atoms (few keV)

Atoms and ions sputtered from surface (ballistic collision)

Both $M^+$ and $M^-$ produced.

Applicable to small or large (> 105 Da) usstable molecules.

**(C) Matrix - Assisted Laser Desorption/Ionization (MALDI):**

• Soft ionization
• Analyte dissolved in solution of UV-absorber and solvent.
• Solid crystals of analyte + absorber grow (matrix)
• Pulsed laser fired at crystals in time-of-flight mass spectrometer (TOF-MS)
• Molecular ion desorbed from crystal surface.
• MALDI spectrum contains dimmer, trimers, .......... multiply charged molecules.
• No fragmentation.

| Matrix | Wavelength (nm) |
|---|---|
| Nicotinic acid | 266, 220–290 |
| Benzoic acid derivatives: | |
| 2,5-Dihydroxybenzoic acid | 266, 337, 355 |
| Vanillic acid | 266 |
| 2-Amino-benzoic acid | 266, 337, 355 |
| Pyrazine-carboxylic acid | 266 |
| 3-Aminopyrazine-2-carboxylic acid | 337 |
| Cinnamic acid derivatives: | |
| Ferulic acid | 266, 377, 355 |
| Sinapinic acid | 266, 337, 355 |
| Caffeic acid | 266, 337, 355 |
| 3-Nitrobenzylalcohol | 266 |

**Matrix properties:**

- **Small MW**
- **Absorb UV**
- **Able to crystallize**

## Mass Analyzers

Mass analyzers: Separate ions to measure m/z and intensity.

**Resolution:**

- Ability to differentiate peaks of similar mass.

$$R = \frac{\text{mean mass two peaks}}{\text{separation between peaks}} = \frac{\bar{m}}{\Delta m}$$

- Resolution depends on mass!
- If R = 1000

 Separate peaks at m/z = 100 and 100.1

or m/z = 1000 and 1001

or m/z = 10000 and 10, 000

- High resolution necessary for exact MW determination.

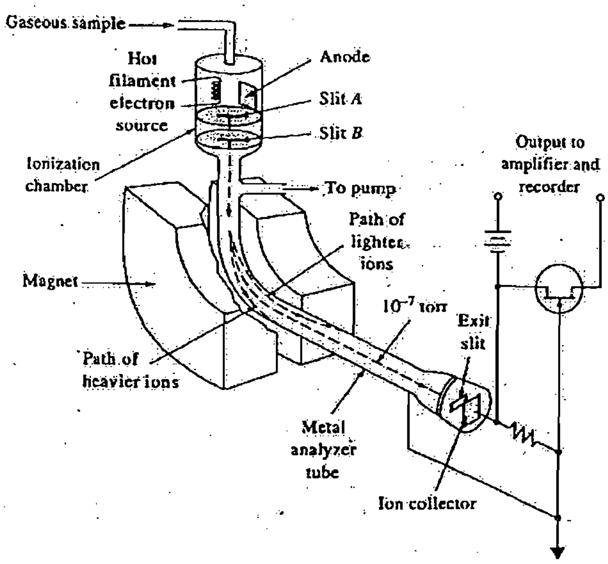
 nominal MW = 28

 actual MW $C_2H_4^+ = 28.0313$, $R > 2570$

 $CH_2N^+ = 28.017$

 $N_2^+ = 28.0061$

**(A) Magnetic Sector Analyzers:**




**Kinetic energy of ion:**

$$K.E. = z.e.V = \frac{1}{2}m.v^2$$

Charge (+1, +2 .............)

Electronic charge ($1.6\times10^{-19}$)

Potential difference (B-A)

Velocity (m/s)

mass (kg)

**Magnetic force:** $F_B = B.z.e.v$

**Centripetal force:** $F_C = \frac{m.v^2}{r}$

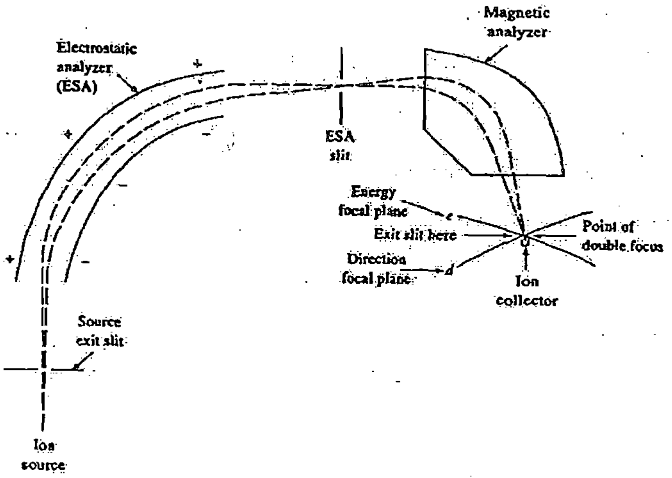
radius of sector (m)
For successful exit, two forces balance

$$B.z.e.v = \frac{m.v^2}{r} \qquad v = \frac{B.z.e.r}{m}$$

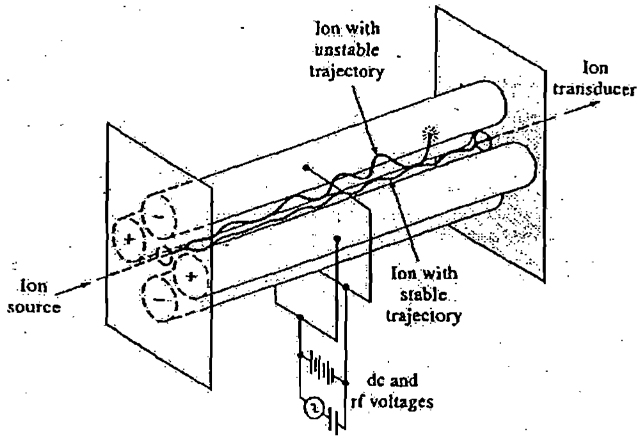
$$\frac{m}{z} = \frac{B^2r^2e}{2V}$$

For fixed radius and charge can
(a) Use permanent magnet, vary A and B potential (V)
Or, (b) Variable electromagnetic, fixed A and B potential (V)

**(B) Double-Focusing Analyzers:**
Single-focusing magnetic sector analyzers have $R_{max} < 2000$
(a) Translational energy aberrations.
(b) Angular aberrations.
Addition of electrostatic analyzer simultaneously minimizes both (a) and (b)
Electrostatic analyzer focuses ions of unique m/z at entrance slit to magnetic sector.




**Quadrupole Analyzers:**

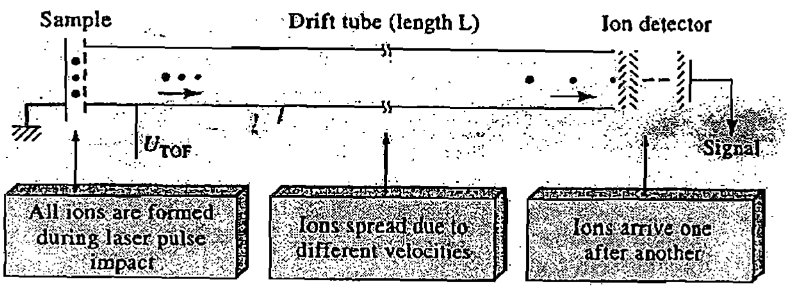


- Ions travel parallel to four rods
- Opposite pairs of rods have rapidly alternating potentials (AC).
- Ions try to follow alternating field in helical trajectories.
- Stable path only for one m/z value for each field frequency.
- Harder to push heavy molecule – m/z max < 2000
- $R_{max} \sim 500$.

**(D) Time of Flight (TOF) Analyzers:**

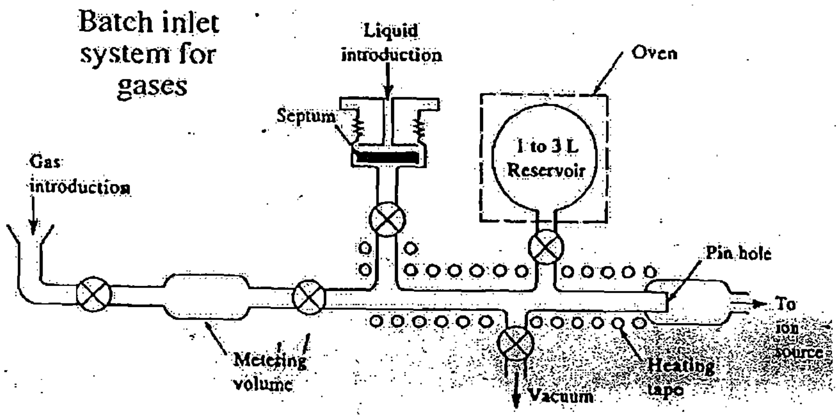
General pulse of ions (by laser, electrons) with same initial energy ions travel down field-free separate according to mass

- Light ions arrive first, heavy ions arrive later.
- Unlimited mass range $m/z_{max} > 100$ kDa.
- Poor resolution $R_{max} < 100$
- Poor sensitivity

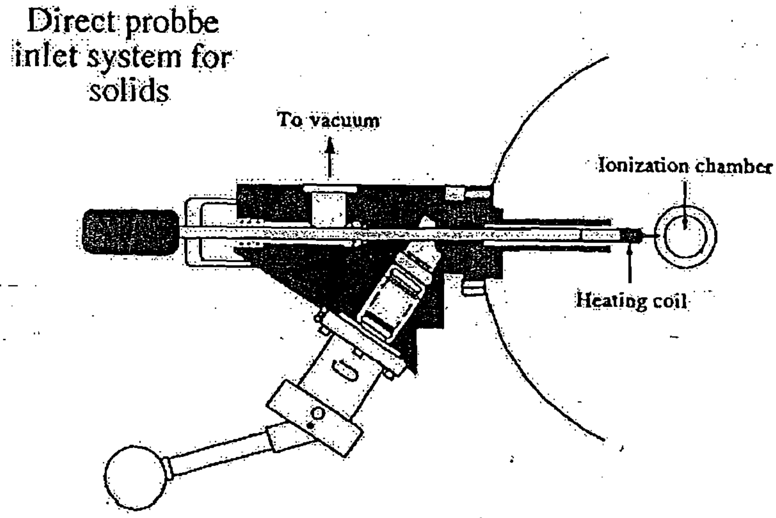



$$KE = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{L}{t}\right)^2$$

$$t = \sqrt{\frac{1}{2}mL^2} \qquad m \propto t^2$$




(a)



(b)

**(A) External (Batch) Inlet Systems:**

- Sample heated (< 400°C) in small external oven.
- Vapour admitted to ionizer through value.
- Gas stream added to entrain analyte.

**(B) Direct Probe**

- Sample vial inserted through air-lock into ionizer chamber
- Vial heated to vaporize sample
- Vial can be reduced to capillary or surface plate for small quantities.

**(C) Chromatograph/Electrophoresis/Injection Analysis:**
Can be modified to directly flow into ionizer region.

# Nitrogen Rule

**compound without nitrogen**

- **Even Mass fragments**
  Radical Cation
  OES
- **Odd Mass fragments**
  Cation
  EES

**compound with one nitrogen**

- **Fragment with 1N**
  1. Even Mass fragments
     Cation
     EES
  2. Odd Mass fragments
     Radical Cation
     OES
- **Fragment without N**
  1. Even Mass fragments
     Radical Cation
     OES
  2. Odd Mass fragments
     Cation
     EES

**compound with two nitrogen**

- **Fragment with 2N**
  1. Even Mass fragments
     Radical Cation
     OES
  2. Odd Mass fragments
     Cation
     EES
- **Fragment with 1N**
  1. Even Mass fragments
     Cation
     EES
  2. Odd Mass fragments
     Radical Cation
     OES
- **Fragment without N**
  1. Even Mass fragments
     Radical Cation
     OES
  2. Odd Mass fragments
     Cation
     EES

compound with three nitrogen

Fragment with 3N

1. Even Mass fragments — Cation EES

2. Odd Mass fragments — Radical Cation OES

Fragment with 2N

1. Even Mass fragments — Radical Cation OES

2. Odd Mass fragments — Cation EES

Fragment with 1N

1. Even Mass fragments — Cation EES

2. Odd Mass fragments — Radical Cation OES

Fragment without N

1. Even Mass fragments — Radical Cation OES

2. Odd Mass fragments — Cation EES

**Conclusion:**

| Nitrogen Rule | 1. Even Mass fragments | 2. Odd Mass fragments |
|---|---|---|
| 1. Fragment with 4N | Radical Cation or OES | Cation or EES |
| 2. Fragment with 3N | Cation or EES | Radical Cation or OES |
| 3. Fragment with 2N | Radical Cation or OES | Cation or EES |
| 4. Fragment with 1N | Cation or EES | Radical Cation or OES |
| 5. Fragment without N | Radical Cation or OES | Cation or EES |

**1. Molecule with 4N** — **Mol. wt. even**

Even mass fragmetns — Radical cation with event N or without N
Cation with odd N

Odd mass fragments — Radical cations with odd N atoms
Cation with even N or without N.

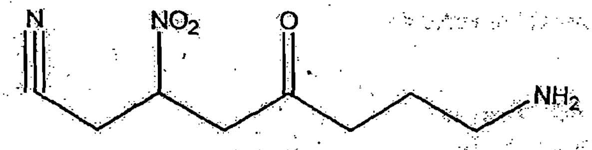
**2. Molecule with odd N** — **Mol. wt. odd**

Odd mass fragments — Radical cation with odd N
Cation either even N or without N

Even mass fragments — Radical cation with even N or without N
cations with odd N.

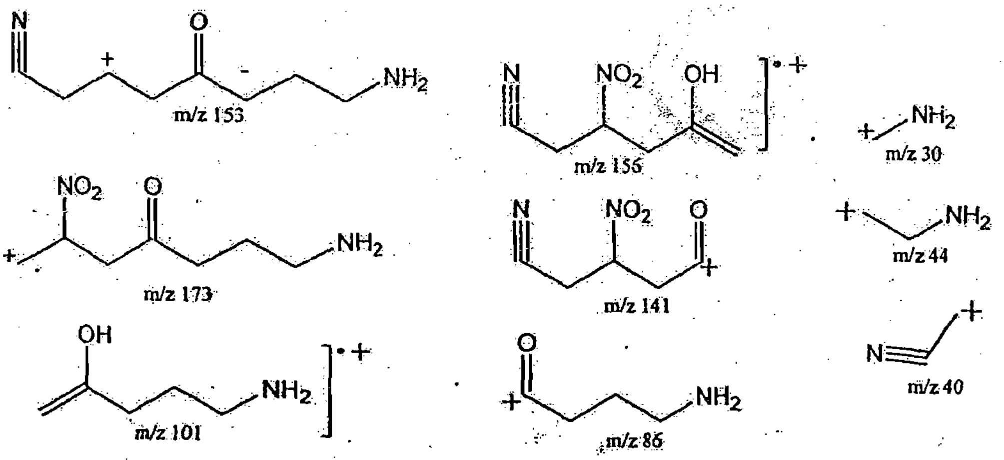
**3. Fragment without N**

| | |
|---|---|
| Even mass fragments Radical | All are OES. |
| Odd mass fragments Cations | All are EES |



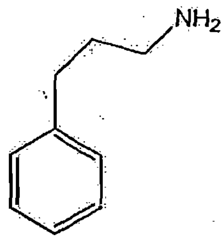

$C_8H_{13}N_3O_3$
Mass: 199

| Peak at m/z | identity | M-mass | OES/EES | type of fragment |
|---|---|---|---|---|
| 199 | mol ion | | | |
| 173 | C7H13N2O3 | M-CN | | |
| 156 | C6H8N2O3 | M-43 | | |
| 153 | C8H13N2O | M-NO2 | | |
| 141 | C5H5N2O3 | M-58 | | |
| 101 | C5H11NO | M-98 | | |
| 86 | C4H8NO | M-113 | | |
| 44 | C2H6N | M-155 | | |
| 40 | C2H2N | M-159 | | |
| 30 | CH4N | M-169 | | |

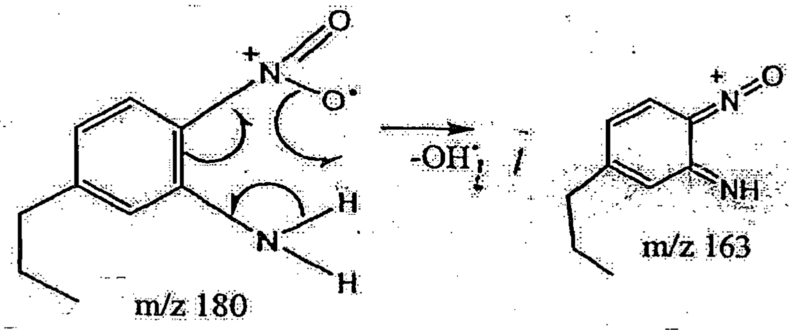


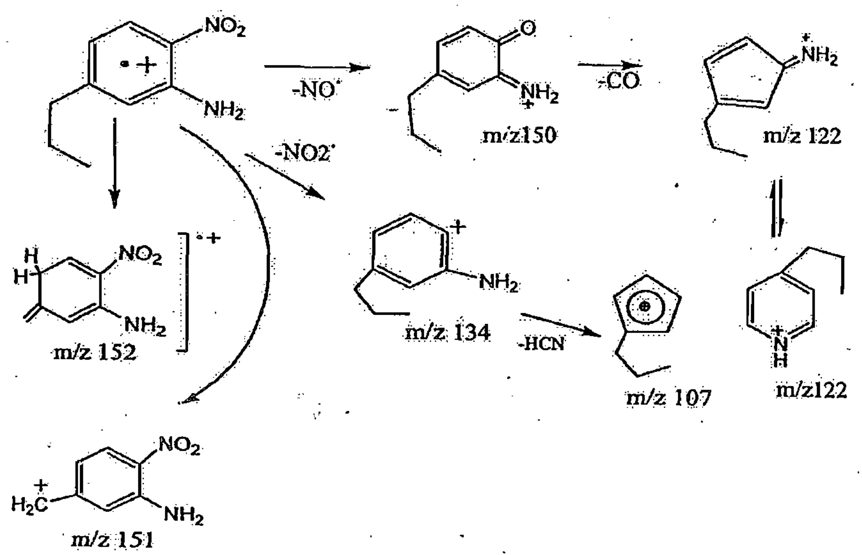

Example 1: One nitrogen containing molecule

| Peak at m/z | identity | M-mass | OES/EES | type of fragment |
|---|---|---|---|---|
| 135 | mol. Ion | | | |
| 134 | M-1 | 1 | | |
| 30 | CH2NH2 α-fission | 105 | | |
| 44 | C2H6N | 91 | | |
| 91 | C7H7 benzylic fission | 44 | | |
| 92 | C7H8 MR fragment | 43 | | |
| 65 | C5H5 | 70 | | |



**Example: Two nitrogen containing molecule.**




| m/z | type of fragment | OES/EES |
|---|---|---|
| 180 | | |
| 163 | | |
| 150 | | |
| 151 | | |
| 152 | | |
| 134 | | |
| 122 | | |

# MS problems

1. An organic compound (A) is composed of carbon, hydrogen and nitrogen, with carbon constituting over 60% of the mass. It shows a molecular ion at m/z=112 amu in the mass spectrum. Answer the following questions.

1. Write a plausible Molecular Formula for compound A:
2. How many Rings + Double Bonds must be present in compound A?

Answer 1.$C_6H_{12}N_2$ 2 rings and/or double bonds

2. An compound A, composed only of carbon, hydrogen and oxygen, also shows a molecular ion at m/z=112 amu.
Write a plausible Molecular Formula for compound B, assuming it has three double bonds and no rings.

Answer $C_6H_8O_2$

3. Compound A is composed only of carbon, hydrogen and oxygen, and shows a molecular ion at m/z=180 amu. Carbon accounts for 60% of the molecular mass.

(1) Write a plausible Molecular Formula for compound A.
(2) How many Rings + Double Bonds must be present in compound A?

Answer (1) $C_9H_8O_4$ (2) 6 rings and/or double bonds

4. While running a new reaction, a chemist notices the evolution of a gas. A sample of this gas gave a mass spectrum in which the molecular ion (m/z = 44) was the largest ion peak. The only other significant peaks were observed at m/z = 28 & m/z = 16. **What is this gas?**

Answer carbon dioxide $CO_2$

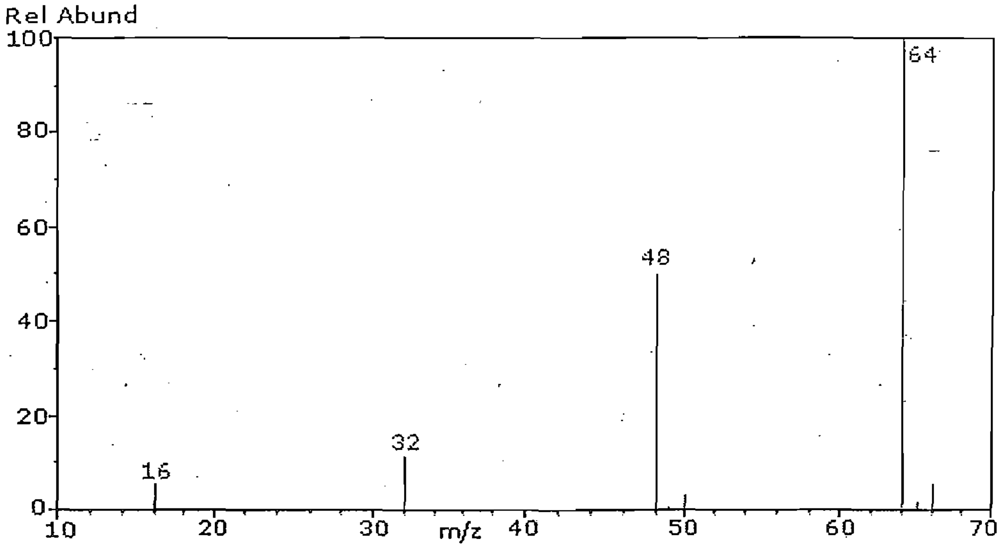
5. A liquid compound gave a mass spectrum showing a strong molecular ion at m/z = 156. The only fragment ions are seen at m/z = 127 & 29.
**Suggest a structure for this compound.**

Answer ethyl iodide

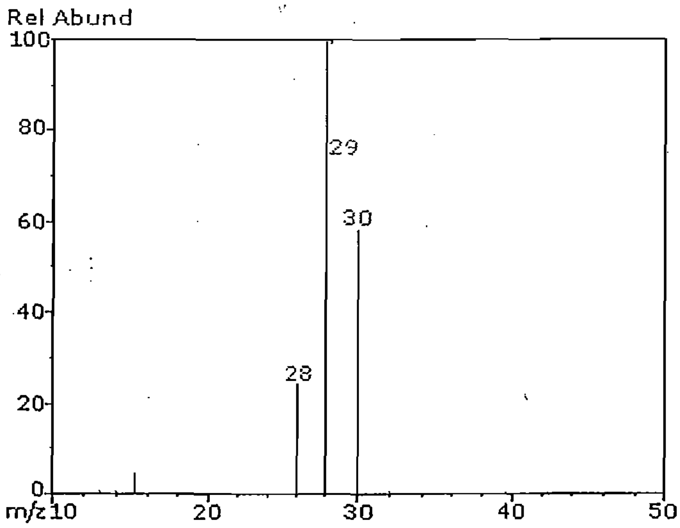
6. A liquid compound gave a mass spectrum in which the molecular ion appears as a pair of equal intensity peaks at m/e = 122 & m/z = 124. Small fragment ion peaks are seen at m/z = 107 & 109 (equal intensity), and at m/z = 79, 80, 81, & 82 (all roughly the same size). Large fragment ions are seen at m/z = 43 (base peak), 41 & 39.
**Suggest a name for this compound.**

Answer 2-bromopropane or 1-bromopropane

7.Two mass spectra of gaseous compounds are shown here:




Compound 1



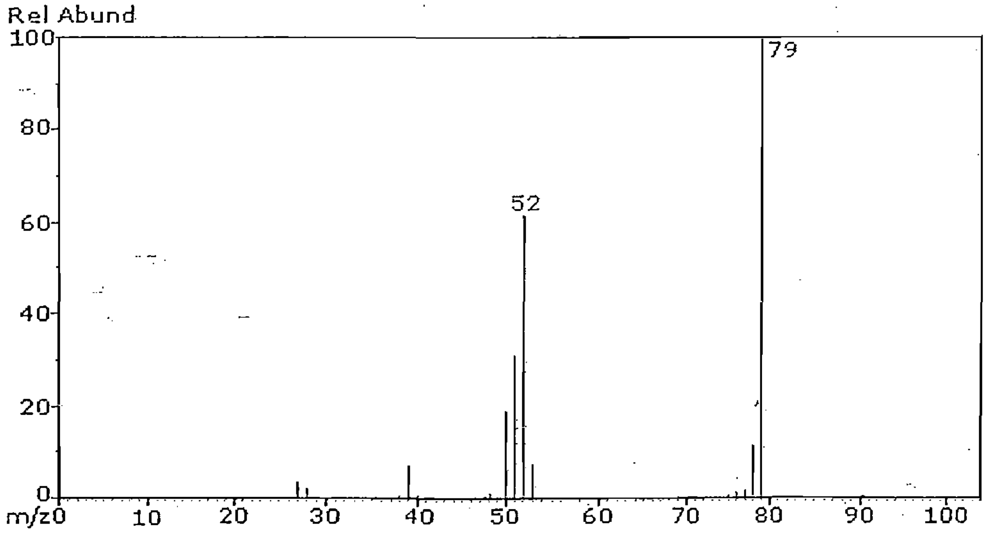

Compound 2

Enter the name .

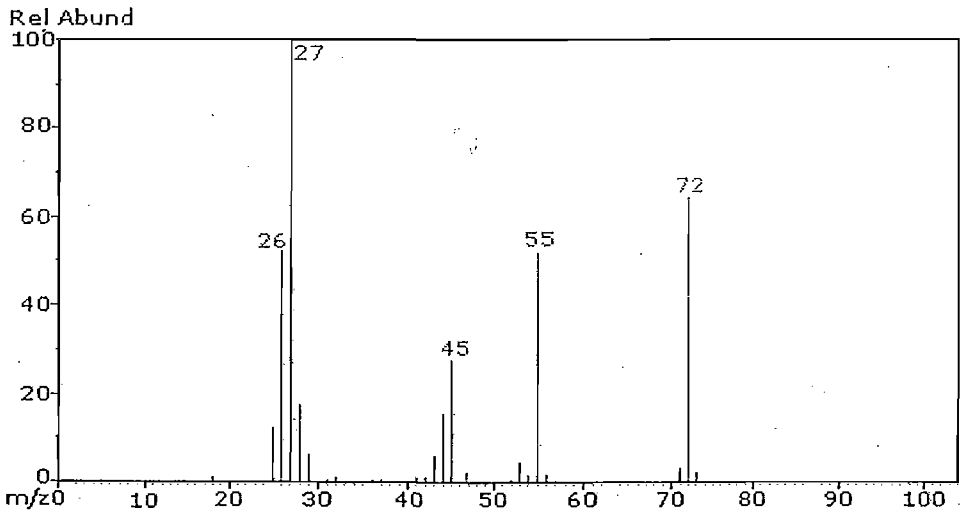
Answer

Compound 1: 2,3-butadione. (note cleavage in half to give a m/z=43 ion).
Compound 2: nitromethane. (note the odd mass molecular ion)

8.Two mass spectra of pure liquid compounds are shown here:




Compound 1

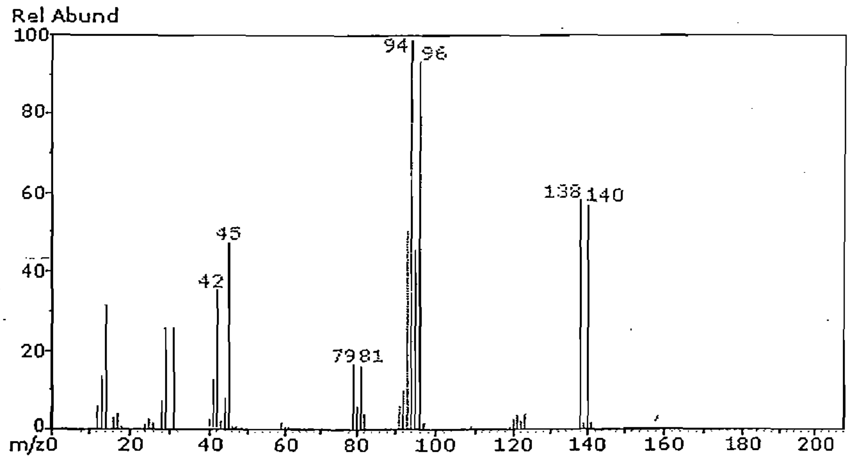



Compound 2

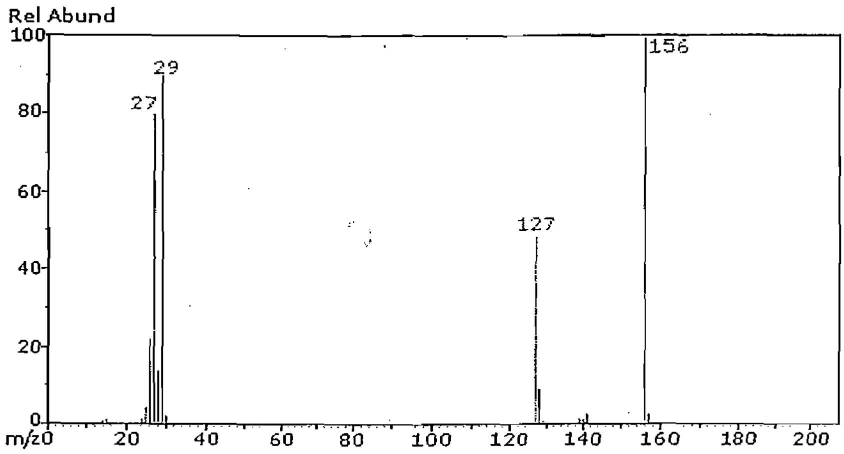
Enter the name .

Answer Compound 1: pyridine. (note the odd-mass molecular ion. Its high abundance indicates an aromatic ring). The m/z=52 ion may be loss of HCN.
Compound 2: propenoic acid (acrylic acid). The m/z=55 ion is loss of OH. The m/z=45 and 27 ions may be carboxyl and loss of carboxy

9.Two mass spectra of pure liquid compounds are shown here:




Compound 1

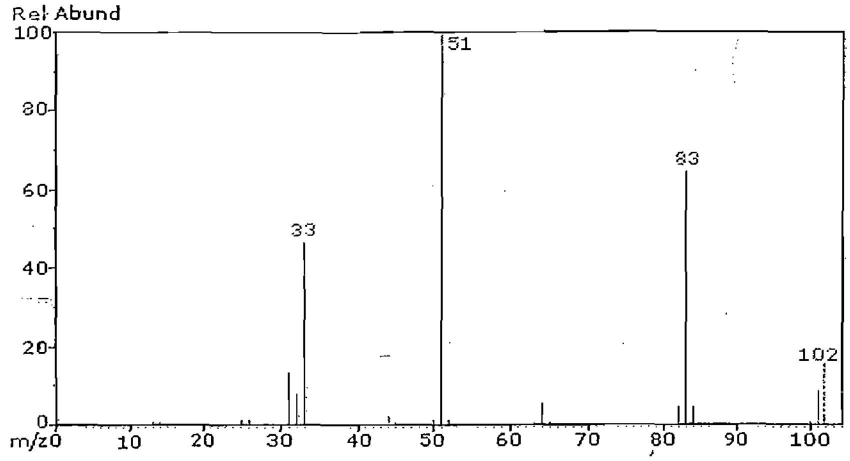



Compound 2

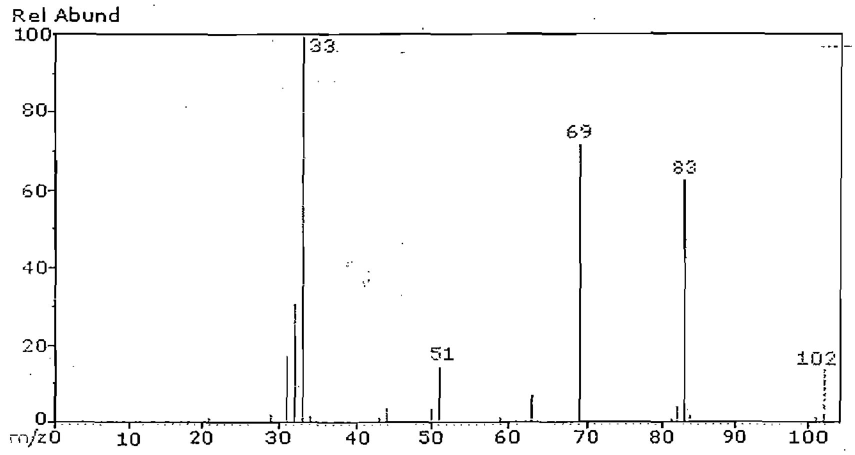
Enter the name.

Answer Compound 1: bromoacetic acid (2-bromoethanoic acid). The isotopic ion pairs at m/z=138(140), 94(96), 93(95) & 79(81) indicate the presence of bromine. The base peak (m/z=94(96) is due to loss of carbon dioxide. The m/z=45 ion is carboxyl, and the m/z=42 ion may be ketene (loss of HOBr).
Compound 2: ethyl iodide (iodoethane). The large difference between the molecular ion and the m/z=127 fragment and the m/z=27 & 29 fragments suggests a high atomic weight atom. The m/z=127 peak tells us this is iodine.

10.The mass spectra of two constitutional isomers are shown here. Both are gases at room temperature. The molecular ion is the small peak at m/z = 102 amu.




Isomer 1




Isomer2

Enter the name .

Answer: Compound 1: 1,1,2,2-tetrafluoroethane. The nearest large fragment ion to the small molecular ion is at m/z=83, a loss of 19 amu. This suggests loss of fluorine. The m/z=51 ion represents half the molecule. A hydrogen shift is necessary to explain the m/z=33 ion.

Compound 1: 1,1,1,2-tetrafluoroethane. Important differences from isomer 1 are that the m/z=51 ion is much smaller, m/z=33 is much larger, and a new strong ion at m/z=69 has appeared. Since fluorine is present, this may be assigned as a trifluoromethyl cation.

# Additional Practice Problems for Molecular Formula Determination from Mass Spectrometry

ANSWER KEY

Use the M and M + 1 data to determine possible molecular formulas in each case. Unless otherwise stated, assume that carbon, hydrogen, oxygen and nitrogen are the only possible elements. Employ the process we used in the lab to do this using the table format shown below (you may require additional rows). Note: (M-ΣC) – O – N = H means that one takes the sum of the carbon atoms and subtracts this from the M peak (molecular ion). If other atoms such as bromine or iodine are present you may include these in the "sum" as well. Problem (e) will require you to normalize the data (see box below)

(a) M: m/z = 148 (100%); M + 1: m/z = 149 (11.25%).

m/z = 148 (M): *zero or even number of nitrogens*
m/z = 149 (M + 1): 11.25%/1.1% = 10.23 *Molecule has ten carbons.*
148 - 120 (C10) = 28 amu (atomic mass units) for oxygen, nitrogen and hydrogen.

| **Oxygens** | **Nitrogens** | **(M-ΣC) – O– N = H** | **Formula** | **Comments** |
|---|---|---|---|---|
| None | None | 28 - 0 - 0 = 28 | $C_{10}H_{28}$ | Violates hydrogen rule |
| One | None | 28 - 16 - 0 = 12 | $C_{10}H_{12}O$ | Reasonable |
| None | Two | 28 - 0 - 28 = 0 | $C_{10}N_2$ | Reasonable |

(b) M: m/z = 164 (100%); M + 1: m/z = 165 (4.62%); contains bromine.

m/z = 164 (M): *zero or even number of nitrogens*
m/z = 165 (M + 1) 4.62% / 1.1 = 4.20 *Molecule has four carbons.*
164 - 48 (C4) - 79 (Br) = 37 amu for oxygen, nitrogen and hydrogen.

| **Oxygens** | **Nitrogens** | **(M-ΣC) – O– N = H** | **Formula** | **Comments** |
|---|---|---|---|---|
| None | None | 37 - 0 - 0 = 37 | $C_4H_{37}Br$ | Violates hydrogen rule |
| One | None | 37 - 16 - 0 = 21 | $C_4H_{21}BrO$ | Violates hydrogen rule |
| Two | None | 37 - 32 - 0 = 5 | $C_4H_5BrO_2$ | Reasonable |
| None | Two | 37 - 0 - 28 = 9 | $C_4H_9BrN_2$ | Reasonable |

(c) M: m/z = 149 (100%); M + 1: m/z = 150 (11.3%).

m/z = 149 (M): *odd number of nitrogens*
m/z = 150 (M + 1): 11.3%/1.1% = 10.3 *Molecule has ten carbons.*
149 -120 (C10) -14 (at least one nitrogen) = 15 amu for oxygen, nitrogen and hydrogen. This is not enough amu for an oxygen atom, or for two more nitrogens. Only one formula is possible: $C_{10}H_{15}N$.

(d) M: m/z = 150 (100%); M + 1: m/z = 151 (11.52%). (See first box below)

m/z = 150 (M): *even number of nitrogen atoms*
m/z = 151 (M + 1): 11.52% / 1.1 % = 10.47 *Molecule has ten or eleven carbons.*

### How Do I Round Off the M+1/1.1% Number?

If the remainder is 0.4 or less, rounding down is usually adequate. A remainder of 0.7 or more should usually be rounded up. Remainders of 0.4 – 0.7 do not allow a precise determination of the number of carbons, so two carbon counts should be considered. Once the all the formula candidates are determined, then it may be possible to reject some of these based on other spectral data.

Continuing with the problem . . . Try both C10 and C11 possibilities.

C10: 150 - 120 (C10) = 30 amu for oxygen, nitrogen and hydrogen.

| Oxygens | Nitrogens | (M-ΣC) – O– N = H | Formula | Comments |
|---|---|---|---|---|
| None | None | 30 - 0 - 0 = 30 | $C_{10}H_{30}$ | Violates hydrogen rule |
| One | None | 30 - 16 - 0 = 14 | $C_{10}H_{14}O$ | Reasonable |
| None | Two | 30 - 0 - 28 = 2 | $C_{10}H_2N_2$ | Reasonable |

C11: 150 - 132 (C11) = 18 amu for oxygen, nitrogen and hydrogen.

| Oxygens | Nitrogens | (M-ΣC) – O– N = H | Formula | Comments |
|---|---|---|---|---|
| None | None | 18 - 0 - 0 = 18 | $C_{11}H_{18}$ | Reasonable |
| One | None | 18 - 16 - 0 = 2 | $C_{11}H_2O$ | Reasonable |

(e) M: m/z = 112 (53.60%); M + 1: m/z = 4.08%. Must normalize this data.

### Normalizing the Above Mass Spectral Data

| Molecular Ion: | m/z: | Relative Intensity: |
|---|---|---|
| M | 112 | 53.60% → 53.60 * 1.866 → 100% |
| M+1 | 113 | 4.08% → 4.08 * 1.866 → 7.61% |

To make the M peak equal to 100% it must be multiplied by a factor of (100/53.60) = 1.866. You then multiply M+1 by this factor as well. There is no M + 2 peak.

m/z = 112 (M): *even number of nitrogen atoms*
m/z = 113 (M + 1): 7.61% / 1.1 % = 6.92. *Molecule has seven carbons atoms.*
112 - 84 (C7) = 28 amu for oxygen, nitrogen and hydrogen.

| Oxygens | Nitrogens | (M-ΣC) – O– N = H | Formula | Comments |
|---|---|---|---|---|
| None | None | 28 - 0 - 0 = 28 | $C_7H_{28}$ | Violates hydrogen rule |
| One | None | 28 - 16 - 0 = 12 | $C_7H_{12}O$ | Reasonable |
| None | Two | 28 - 0 - 28 = 0 | $C_7N_2$ | Reasonable |

Not enough amu for two oxygen atoms. Of the two possible formulas, the first seems most reasonable.

ORG CHEM II LAB (Major's) NAME_______________
Due 4/21/99

## Mass Spectroscopy Problem Set 1

1. The mass spectrum of an unknown compound shows a molecular ion at m/e = 110, the molecular formula may be $C_8H_{14}$, $C_7H_{10}O$, $C_6H_{10}N_2$ or $C_6H_6O_2$. The relative size of the M, M+1, and M+2 Peaks are 100 :7.48: 0.03. Which of the above is the correct molecular formula?

2. Halogenated compounds are particularly easy to identify by their mass spectra because both chlorine and bromine are found as mixtures of two abundant isotopes. Chlorine occurs as $^{35}Cl$ (75.8%) and $^{37}Cl$(24.2%); bromine is found as $^{79}Br$(50.7%) and $^{81}Br$(49.3%). At what m/e do the molecular ion(s) occur for the following formulas? What are the relative percentages for each molecular ion?

   a) $CH_3CH_2Br$

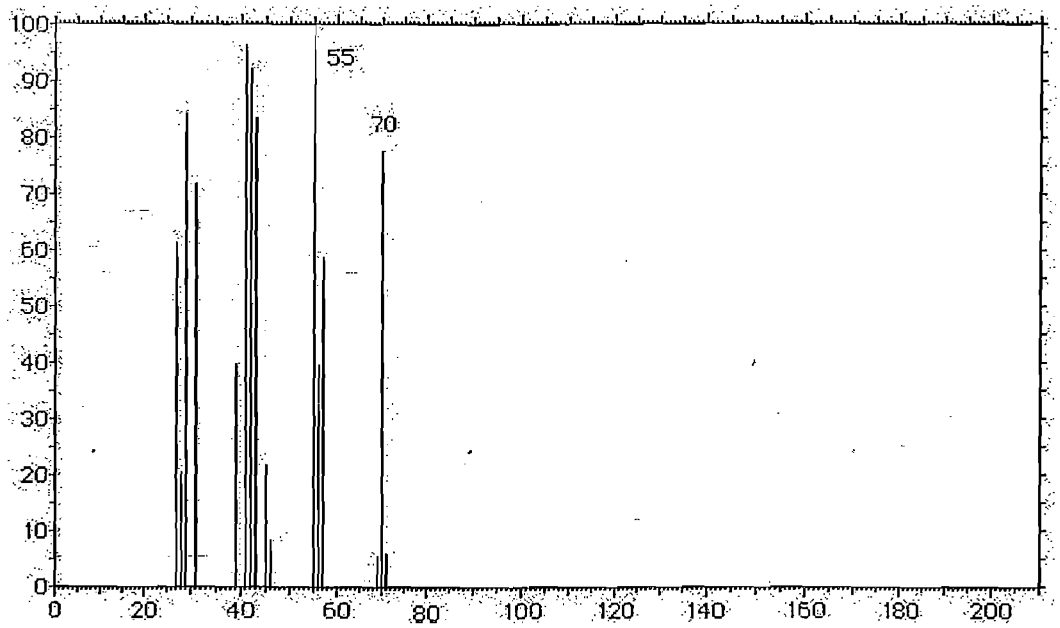
   b) $C_6H_4Br_2$

   c) $CH_3Cl$

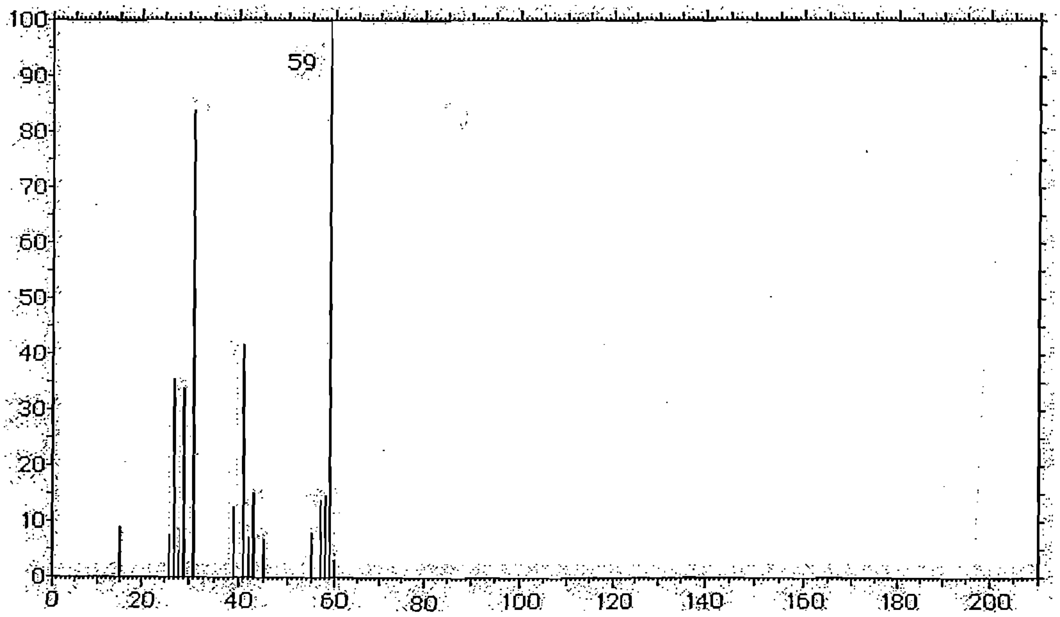
3. The peak with the highest mass in the mass spectrum of 2,2-dimethylpropane shows a m/e = 57. This peak is also the most abundant (i.e. the base peak). What molecular structure does this peak correspond to? Why is the molecular ion not observed?

4. Below are the mass spectra of 3-pentanol and 3-methyl-1-butanol. Which is which, explain?

A

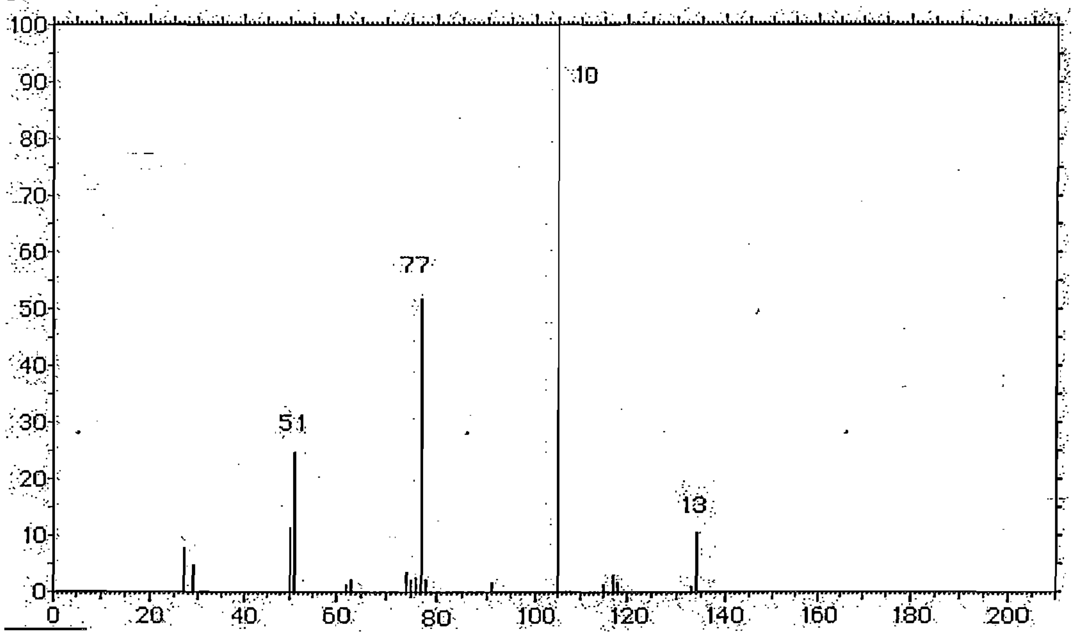



B

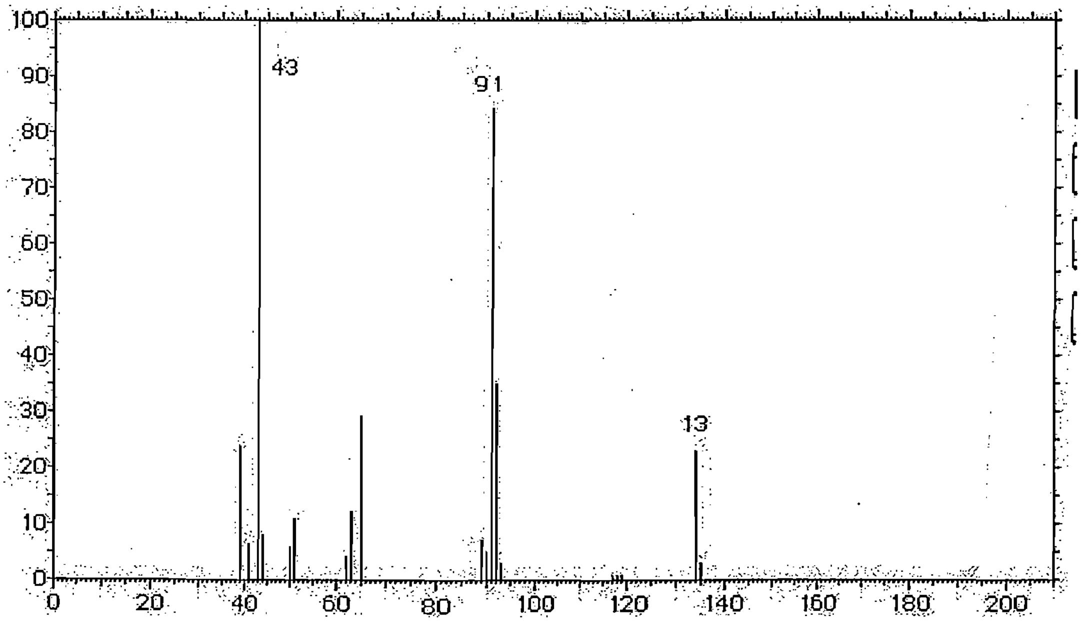


5. Below are the mass spectra of ethyl phenyl ketone and benzyl methyl ketone. Which is which, explain

A




B



Q1. A molecular formula can provide important information about the constitution of a compound. These questions test your ability to obtain this information.

**Which formulas are improbable for a stable compound?**

- ○ **Which formulas might represent a non-cyclic saturated compound?**
- ◉ **Which formulas might represent a compound having a double bond, but not a triple bond?**
- ○ **Which formulas might represent a compound having a benzene ring?**
- ○ **Which formulas might represent a compound having three rings and two double bonds?**
- ○ **Which formulas might represent a non-cyclic compound having a triple bond as the only unsaturation?**

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $C_{11}H_{20}O_4$ | $C_6H_9O_2Cl_3$ | $C_8H_{15}Cl_2$ | $C_8H_{17}Br_3$ | $C_4H_{10}O_2$ | $C_9H_{11}OCl$ | $C_6H_7O_3Br$ | $C_5H_9NO$ | $C_7H_5N_2Cl_2$ | None Fit |
| □ | □ | □ | □ | □ | □ | □ | □ | □ | □ |

**Empirical and Molecular Formulas**

Combustion analysis is commonly used to determine the percent composition of carbon and hydrogen in a sample of a pure compound. Oxygen can not be determined by combustion analysis, and is usually estimated by difference. Other elements such as nitrogen, chlorine and sulfur can be measured directly in other ways.

An empirical formula is derived from the elemental composition of a compound. It represents the simplest whole number ratio of the different kinds of atoms that make up a molecule of a given compound. The molecular formula of a compound gives the actual number of the different atoms in a molecule. To convert an empirical formula into a molecular formula a molecular weight measurement is needed.

The elemental order in such formulas is: CHOZ, where Z = other elements. Do not try to subscript numbers. For question VI enter two or more letters or **X** for none.

**I.** A gaseous compound is found to be 74.9% C and 24.9% H. What is the empirical formula of this compound? ... [ ]

**II.** A liquid compound is found to be 52.1% C and 13.1% H. What is the empirical formula of this compound? ... [ ]

**III.** A liquid compound is found to be 48.7% C, 13.6% H and 37.8% N. What is the empirical formula of this compound? ... [ ]

**IV.** A liquid compound is found to be 29.8% C, 6.3% H and 44.0% Cl. What is the empirical formula of this compound? ... [ ]

**V.** A dark blue solid is found to be 73.3% C, 7.8% H and 10.7% N. Its molecular weight is roughly 260.

What is the molecular formula of this compound? ... [ ]

**VI.** Which of the following molecular formulas, if any, have the same empirical formula?

**A.** $C_6H_4O_2$, **B.** $C_6H_{12}O_6$, **C.** $C_{12}H_8O_4$, **D.** $C_2H_4O_2$ ... [ ]

***I. CH4, II. C2H6O, III. C3H10N2***

***IV. C2H5OCl, V. C16H10O2N2***

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**The empirical formula for V. is C8H5ON**

**Question 1:**
Which of the following compounds will give a molecular ion having m/z = an odd number?

- [ ] $CH_3CH_2OH$
- [ ] $CH_2BrCl$
- [ ] $CH_3CO_2H$
- [ ] $CH_3CH_2NH_2$
- [ ] $(CH_3)_2NCH_2C{\equiv}N$

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**Question 2:**
What class of compounds is most likely to give a fragment ion at m/z = M-18?

- ○ alkenes
- ○ cycloalkanes
- ○ alcohols
- ○ alkyl iodides
- ○ benzene derivatives

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**Question 3:**
Which of the following compounds is most likely to have its base peak at m/z = 43?

- ○ $CH_3(CH_2)_4CH_3$
- ○ $(CH_3)_3CCH_2CH_3$

- cyclohexane
- $(CH_3)_2CHCH(CH_3)_2$

**Question 4:**

While running a new reaction, a chemist notices the evolution of a gas. A sample of this gas gave a mass spectrum in which the molecular ion (m/z = 44) was the largest ion peak. The only other significant peaks were observed at m/z = 28 & m/z = 16. **What is this gas?**

**Question 5:**

A liquid compound gave a mass spectrum showing a strong molecular ion at m/z = 156. The only fragment ions are seen at m/z = 127 & 29.
**Suggest a structure for this compound.**

**Question 6:**

A liquid compound gave a mass spectrum in which the molecular ion appears as a pair of equal intensity peaks at m/e = 122 & m/z = 124. Small fragment ion peaks are seen at m/z = 107 & 109 (equal intensity), and at m/z = 79, 80, 81, & 82 (all roughly the same size). Large fragment ions are seen at m/z = 43 (base peak), 41 & 39.
**Suggest a name for this compound.**

**1. The correct order for the basic features of a mass spectrometer is...**

- acceleration, deflection, detection, ionisation
- ionisation, acceleration, deflection, detection
- acceleration, ionisation, deflection, detection
- acceleration, deflection, ionisation, detection

**2. Which one of the following statements about ionisation in a mass spectrometer is incorrect?**

- gaseous atoms are ionised by bombarding them with high energy electrons
- atoms are ionised so they can be accelerated
- atoms are ionised so they can be deflected
- it doesn't matter how much energy you use to ionise the atoms

**3. The path of ions after deflection depends on...**

- only the mass of the ion

- only the charge on the ion
- both the charge and the mass of the ion
- neither the charge nor the mass of the ion

**4. Which of the following species will be deflected to the greatest extent?**

- $^{37}Na^+$
- $^{35}Na^+$
- $^{37}Na$
- $^{35}Na^{2+}$

**5. Which of the following is not a use for mass spectrometry?**

- calculating the isotopic abundance in elements
- investigating the elemental composition of planets
- confirming the presence of O-H and C=O in organic compounds
- calculating the molecular mass of organic compounds

**6. Which one of the following statements about the mass spectrum of $CH_3Br$ is correct?**

- the last two peaks are of equal size and occur at m/z values of 94 and 96
- the last two peaks have abundances in the ratio 3:1 and occur at m/z values of 94 and 96
- there is just one peak for the molecular ion with an m/z value of 95
- there is just one peak for the molecular ion with an m/z value of 44

**21. Which compound has a molecular ion at m/z = 58, an infra red absorption at 1650cm$^{-1}$**
**and just one singlet in its nmr spectrum?**

- butane
- $CH_3COCH_3$
- $CH_3CH_2CHO$
- 2-methylpropane

**25. Which one of the following methods would be best for finding the identity of an organic compound?**

- finding the m/z value of the molecular ion in its mass spectrum
- its proton nmr spectrum
- comparing its infra red spectrum with known examples
- measuring its melting point

Which Ion would undergo the greatest deflection in a massspectrometer?

A. $^{16}O^{+}$

B. $^{16}O^{2+}$

C. $^{18}O^{2+}$

D. $(^{16}O^{18}O)^{+}$

The answer is B. When the sample is passed through the massspectrometer, the ion's pathway passes through a magneticfield. The value that determines the amount an ion will bedeflected is the mass to charge ratio. This is simply the mass ofthe ion divided by the charge of the ion. Ions with thesmallest mass to charge ratio experience the greatestdeflection. The following are the mass to charge ratios ofeach choice:

A.) 16/1=16
B.) 16/2=8
C.) 18/2=9
D.) (16+18)/1=34

B has the smallest mass to charge ratio, so it has the greatestdeflection.

Q. Fluorine is monotopic ($^{19}F$), and chlorine consists of two isotopes ($^{35}Cl$ and $^{37}Cl$). In the mass spectrum of ClF, how many peaks does the parent ion contain?

- 1
- 2
- 3
- 4

The mass spectrum of diethyl sulfide, $(CH_3CH_2)_2S$, shows several groups of peaks with intense lines at *m/z* = 90, 75, 61, 46 and 29. Which statement is *inconsistent* with these data?

- The mass spectrum suggests that diethyl sulfide fragments by cleavage of both C–C and C–S bonds.
- The mass spectrum suggests that one fragmentation pathway for diethyl sulfide is by loss of an ethyl group.
- The parent ion is visible in the mass spectrum of diethyl sulfide.
- The mass spectrum suggests that diethyl sulfide fragments by sequential loss of the ethyl groups to leave an S atom.

Which of the following statements is *incorrect*?

- Mass spectrometry provides direct structural data.

- Mass spectrometry gives information about fragmentation patterns.
- Parent ions are not always observed in the mass spectra of compounds.
- Isotopic distribution patterns are observed in mass spectra.

Bromine has two isotopes $^{79}Br$ and $^{80}Br$, each ≈50% abundant. In the mass spectrum of tribromomethane ($CHBr_3$), the highest mass peaks are at $m/z$ = 250, 251, 252 and 253. The ratio of the intensities of these peaks is:

- 1 : 3 : 3 : 1
- 1 : 1 : 1 : 1
- 2 : 3 : 3 : 2
- 1 : 2 : 2 : 1