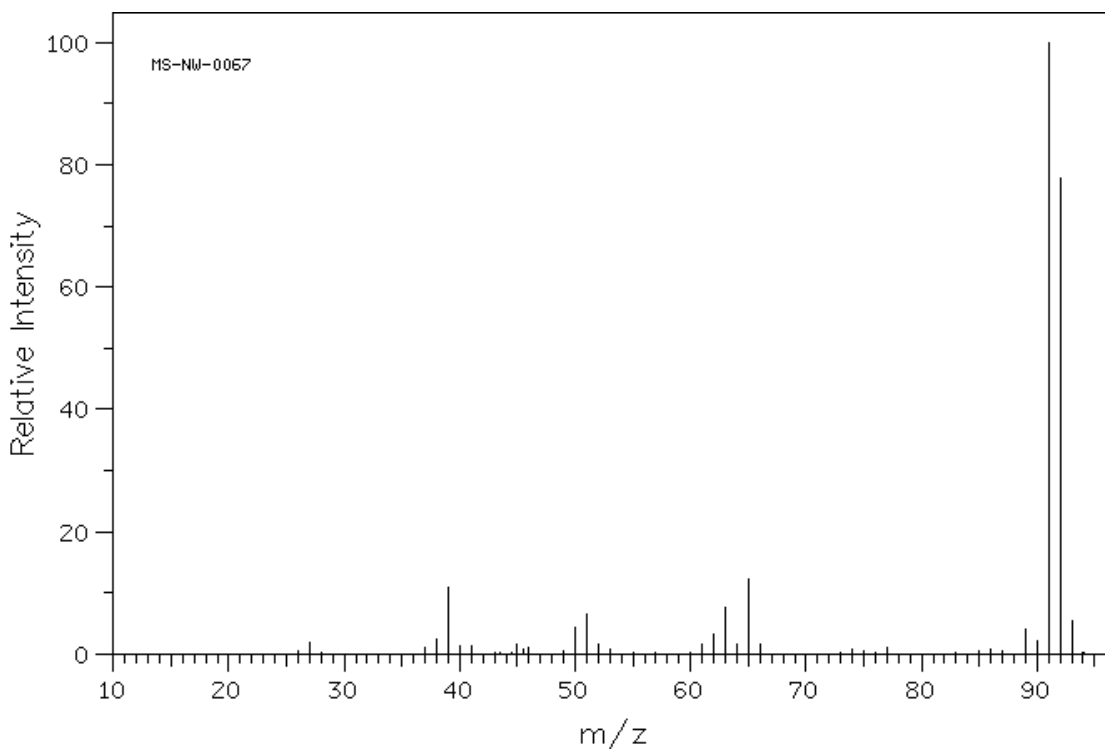


Mass Spectrometry Handout

Mass spectrometry is used for determining the molecular weight of a compound and possibly identifying components of a compound. Mass spectrums identify a **cation radical** or cation. If the particle of interest is not positively charged, it will not be seen. An example of a mass spectrum is given below. There are a couple of terms that you should with which you should become familiar.



Mass spectrum of toluene. Courtesy of the Integrated Spectral Data Base System for Organic Compounds by the Japanese National Institute of Advanced Industrial Science and Technology. <http://www.aist.go.jp/RIODB/SDBS/menu-e.html> Many spectra will be used from this resource.

Terms

M/Z: mass to charge ratio. For our purposes, the charge will be assumed to be one so that the value of m/z corresponds to the mass.

Mass ion peak: M^+ is the molecular ion for the molecule. For toluene which has a molecular weight of 92, it is the peak at 92. For most molecules the M^+ peak is seen on the mass spectrum but it is not seen if formation of a stable cation is possible. (i.e. tertiary alcohols)

$M+1$ peak: This peak is one mass unit greater than the mass ion peak. For toluene, this peak is seen at 93.

$M+2$ peak: This peak is two mass units greater than the mass ion peak. For toluene, this peak is barely seen at 94.

Base peak: This peak is the peak with the relative intensity of 100 %. The base peak is caused by the most stable cation. For toluene, the base peak is at 91.

Resolution: Resolution is measured from peak heights and spacing. The two resolutions are low resolution and high resolution. Low resolution is to whole numbers (i.e. 44) while high resolution is to more numbers (i.e. 44.04356)

Possible methods to make the cation for MS

EI: Electron ionization with a stream of high energy electrons (70 electron volts). All of the spectra shown in class will be EI.

CI: Chemical Ionization is caused by a carrier gas (usually methane) reacting with electrons to make primary ions (CH_4^+ and CH_3^+). These ions then react with sample. This may be used when the mass ion peak does not show up with EI.

FAB: Fast atom bombardment is accomplished by using Xenon atoms.

ESI: Electrospray ionization concerns using a voltage across a spray coming out of a liquid chromatograph machine. John Fenn won the Nobel price in 2002 for this technique which is used on proteins and peptides.

Soft Laser Desorption: This technique is where a laser is used to form a cation from large molecules. Koichi Tanaka won the Nobel prize in 2002 for this technique and an example of this technique is MALDI. (Matrix Assisted Laser Desorption/Ionization)

Types of MS

MS: The first type is to use just a MS to generate a mass spectrum. This is an older technique and has been overtaken by other methods.

GC/MS: This type stands for gas chromatograph/mass spectroscopy. The GC separates compounds while the MS determines the mass spectrum for each component. **CBU HAS a functioning GC/MS instrument. GC/MS instruments are easy to break and VERY EXPENSIVE to repair. Therefore, most students will not get to use the GC/MS but might in advanced chemistry courses.**

LC/MS: This type stands for liquid chromatography/mass spectroscopy. It is a newer method and uses an HPLC to separate compounds before they are analyzed.

MS/MS: This type stands for having two mass spectral machines in tandem. The first MS separates the molecule into parent ions. The parent ions are then collapsed to form daughter ions in the second machine.

FT-MS: This type stands for Fourier Transform-Ion Cyclotron Resonance Mass Spectrum.

TOF: Time of flight separates the particles.

Quadrupole Mass Filter: This type uses four (hence quadrupole) voltage carrying rods to separate the particles.

How to Read a Mass Spectrum

1) Look to see if the M^+ peak is even or odd. If it is even like in toluene above (92), the molecule contains an even number of nitrogens (0 being even). If the M^+ peak is odd, the molecule contains an odd number of nitrogens.

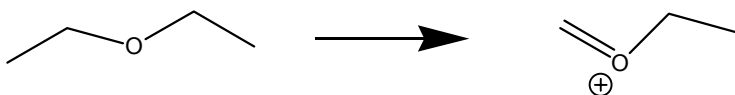
2) Look at the M+2 peak in comparison to the M+ peak. This will help you identify which elements may be present.

<u>M+ (relative intensity)</u>	<u>M+2 (relative intensity)</u>	<u>Element Present</u>
100	100	Br
100	35	Cl
100	4.4	S

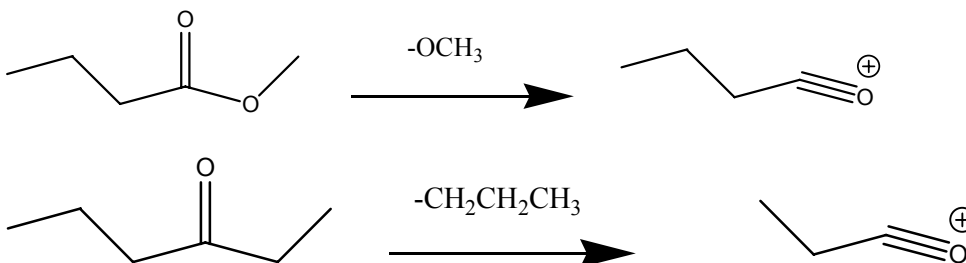
3) Look at the fragmentation patterns. Functional groups fragment in predictable ways. Some examples of functional groups are below.

a) Look for CH₂ next to benzene
m/z 91 (look back at toluene for an example.)

b) Ethers fragment at the alpha carbon to furnish the stable carbocation. Look for loss of the group attached to the alpha carbon. In the example of diethylether below, -15 or methyl.



c) Carbonyl compounds are carbon double bonded to an oxygen. Loss of one of the side groups forms the very stable acylium ion. Examples below are for an ester and a ketone.



d) Some other fragmentation patterns are rearrangements like a Diels Alder or the McLafferty rearrangement.

Calculations

1) Divide the M +1 peak by 1.1 to determine the number of carbons present in the molecule. Some examples follow.

a) Assume the M+ peak is 100 % relative intensity and the M +1 peak is at 10 %. Dividing the M + 1 peak by 1.1 tells you that there are 9 carbons in the compound. This method rarely gives you exact whole numbers.

b) Assume the M^+ peak is at 40 % relative intensity and the $M+1$ peak is at 4.8. The M^+ must be converted to 100 %. Dividing 100 by 40 gives a factor of 2.5. Multiplying 4.8 by 2.5 gives a value of 12. Dividing 12 by 1.1 gives 10.9 carbons. The M^+ peak was NOT 100 so it had to be converted to 100 and multiplying it by 2.5 made it 100. The $M+1$ peak had to be multiplied also.

2) Rule of 13

The rule of 13 will give you a molecular formula for the alkane (C and H) for a corresponding molecular weight. Some examples follow.

a) Assume you have a molecular weight of 400. Divide 400 by 13 which gives you 30.7692. Thirty is the number of carbon atoms. Multiply the remainder (.7692) times 13 to get 10. Add this number, 10, to the whole number, 30, to get the number of hydrogens, 40. So the molecular formula is $C_{30}H_{40}$ which equals 400.

b) Assume you have a compound that you think is caffeine. You do a mass spectrum and it gives you a molecular weight of 194. Dividing 194 by 13 gives you 14.9231. Multiplying 0.9231 by 13 gives you 12. Therefore, the molecular formula of the alkane is $C_{14}H_{26}$. Caffeine has four nitrogen atoms and two oxygen atoms which equals 88. Subtract 6 carbons and 16 hydrogens to get 88. Therefore, the molecular formula for caffeine is $C_8H_{10}N_4O$.

3) Exact calculation from a high resolution mass spectrum.

N_2O and CO_2 both give a low resolution M^+ peak at 44. However, they give different values at high resolution.

$N = 14.00307$

$O = 15.99491$

$C = 12.00000$

CO_2 is 43.9898 while N_2O is 44.0011. These compounds will show up at those exact numbers at high resolution allowing you to decide the molecular formula.

Want more work with MS?

Try <http://svmsl.chem.cmu.edu/vmsl/default.htm> for the virtual mass spectrum lab.