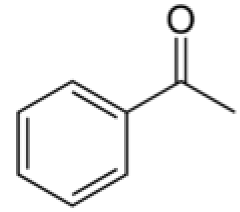
CHEM4604-GC-MS lab- Example of Mass Spectrum Interpretation

Example: Acetophenone (C_8H_8O): FM = 120.15 g/mol



Generalized Interpretation of Mass Spectrum:

(STEP 1) Label the M^+ peak first and then the M + 1 an M + 2 peaks if present. Also label major fragment peaks.

M^+ peak = 120.00 m/*z* (This is the atomic mass of the compound, intensity = 3552)
M + 1 peak = 121.00 m/*z* (Contributed by Carbon 13, intensity = 311)
M + 2 peak = 122.00 m/*z* (Contributed to by isotopes of oxygen, carbon, halogens and others, intensity = 21)

Base Peak: 105.00 m/*z* ($C_7H_5O^{+\bullet}$)
Other Common Ions: 77.00 m/*z* ($C_6H_5^{+\bullet}$); 51.00 m/*z* ($C_4H_3^{+\bullet}$)

(STEP 2) Apply the Nitrogen rule (An even number for the M^+ peak means there either are no nitrogens or there is an even number of nitrogens. An odd M^+ peak means there is at least one nitrogen present or an odd number).

No nitrogens for this molecule (even and there is no loss of a fragment containing two nitrogens).

(STEP 3) Calculate the elemental composition if possible.

(A) C13 has 1.1% abundance relative to C12 and contributes to the M^{+1} peak.
Therefore the **intensity of M^{+1} = 0.011 x (intensity of M^+ peak) x (# carbons)**

Rearranging: (# carbons) = $\dfrac{\text{Intens.}\,M^{+1}\ \text{peak}}{(\text{Intens.}\ M^{+}\ \text{peak})\text{x}0.011} = \dfrac{311}{3552\text{x}0.011}$ = **<u>7.96</u>**

This neglects the trivial 0.04% contribution by O17. Always round up but if the M+1 peak is small there is a large relative error, and you might need to test for 7 and 9 carbon atoms.

(B) O18 has 0.2% abundance relative to O16 and contributes to the M^{+2} peak
Therefore **the intensity of M^{+2} from oxygen = 0.002 x (intensity of M^+ peak) x (# oxygens)**

C13 also contributes to M^{+2} since two C13 can occur, therefore **the intensity of M^{+2} from C13 at two different carbons is = (0.011 x 8 carbons) x (0.011 x 8 carbons) x (intensity of M^+ peak)/2** since the probability of having two C13 is the product of the probability for each, but this counts each pair twice and the value is divided by two. **For oxygen and**

carbon together the intensity of M^{+2} = 0.002 x (intensity M^+ peak) x (# oxygens) + (0.011 x 8 carbons)^2 x (intensity M^+ peak)/2

Rearranging:

$$\frac{\text{Intens.of } M^{+2} \text{ peak}}{\text{Intens.of } M^{+} \text{ peak}} = 0.002\text{x(\#oxygens)} - \frac{(0.011\text{x } 8 \text{ carbons})^2}{2}$$

solving for # oxygen

$$(\text{\#oxygens}) = \frac{\left(\frac{\text{Intens.of } M^{+2} \text{ peak}}{\text{Intens.of } M^{+} \text{ peak}} - \frac{(0.011\text{x } 8 \text{ carbons})^2}{2}\right)}{0.002} = \frac{\left(\frac{21}{3552} - 0.00297\right)}{0.002} = 1.0$$

Alternatively the contribution of C13 at two different carbons is = $(0.011)^2$ x 8!/2!(8-2)! x (intensity of M^+ peak) since you are sampling 8 carbons 2 at a time. See http://www.chemicalforums.com/index.php?topic=36152.0 for calculating probabilities

(STEP 4) Calculate Index of Hydrogen Deficiency (IHD)

Calculate Hydrogens

120 (M^+ peak) – 96 (from carbons) – 16 (from oxygen) = 8 (only can come from hydrogens)

Expected hydrogens for saturated compound = 2x(# carbons) +2 = 2*(8 carbons) +2 = 18

Two hydrogens are missing for every ring or double bond formed

# of rings or double bonds = IHD = (# hydrogens in saturated compound - # hydrogens)/2 = (18 – 8) / 2 = 5

double bond = 1 IHD
triple bond = 2 IHD
1 ring = 1 IHD
benzene = 3 double bonds and 1 ring = 4 IHD