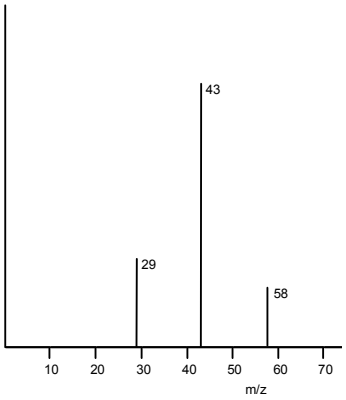
# HIGH RESOLUTION MASS SPECTROMETRY

## Using mass spectroscopy to find the $M_r$ of compounds

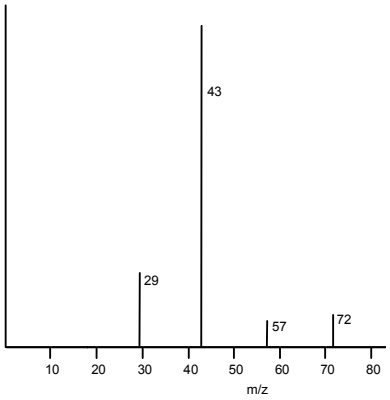
- The first species formed is called the molecular ion, $[M]^{+\bullet}$ (note that this is a radical and has a +ve charge).
- The signal for $[M]^{+\bullet}$ gives the $M_r$ of the compound – this is the peak with the greatest m/z value.
- Note common isotopes [Br: $^{79}Br$:$^{81}Br$ = 1:1; Cl: $^{35}Cl$:$^{37}C$; = 3:1]

***butane***



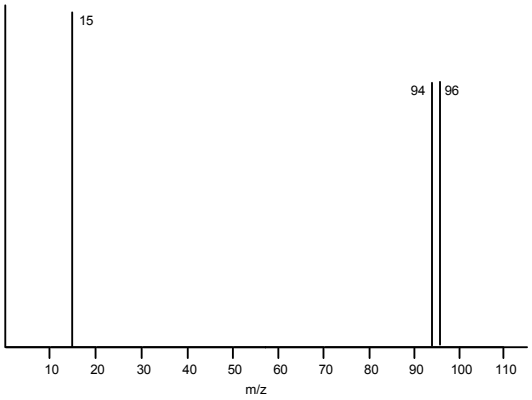

$M_r$ =

***butanone***




$M_r$ =

***bromomethane***




$M_r$ =

## Using mass spectroscopy to find the molecular formula of compounds

- High resolution mass spectrometers measure the m/z values to enough accuracy to find the molecular formula.
- If the $M_r$ of a compound is measured to several decimal places (based on the most common isotopes), it gives a unique molecular formula. For example, the only combination of atoms that has an $M_r$ of 60.0575 is $C_3H_8O$. By contrast, there are many possible molecular formulae for an $M_r$ of 60 (e.g. $C_2H_4O_2$, $CH_4N_2O$ and $C_3H_8O$). With low resolution mass spectrometry, a measured $M_r$ of 60 does not give the molecular formula, but a measured $M_r$ of 60.0575 with high resolution mass spectrometry tells us that the molecular formula is $C_3H_8O$.

| Low resolution $M_r$ | High resolution $M_r$ | Molecular formula | Possible molecules |
|---|---|---|---|
| 60 | 60.0211 | $C_2H_4O_2$ | $CH_3COOH$ $HCOOCH_3$ |
| 60 | 60.0575 | $C_3H_8O$ | $CH_3CH_2CH_2OH$ $CH_3CH(OH)CH_3$ $CH_3OCH_2CH_3$ |
| 60 | 60.0324 | $CH_4N_2O$ | $H_2NCONH_2$, |

- However, there is often more than one compound with the same molecular formula. This means that while high resolution mass spectrometry gives the molecular formula, it may not identify the compound. For example, if the $M_r$ is found to be 60.0575 and so the molecular formula is $C_3H_8O$, it does not tell us whether the compound is propan-1-ol, propan-2-ol or methyoxyethane.

*Accurate masses of atoms:*

**H = 1.0078 C = 12.0000 O = 15.9949 N = 14.0031 $^{35}$Cl = 34.9689 $^{37}$Cl = 36.9659**

1) A compound is found to have an accurate relative formula mass of 46.0417. It is thought to be either $CH_3CH_2OH$ or $H_2NCH_2NH_2$. Calculate the $M_r$ of each compound to 4 decimal places to work out which one it is.

$CH_3CH_2OH$ ……..

$H_2NCH_2NH_2$ ……..

Molecular formula = ……...

2) Analysis of an organic compound showed that its relative formula mass is 102. High resolution mass spectroscopy showed it to be 102.0678.

a) Which of the following three molecular formulas could the compound have? Calculate the $M_r$ of each compound to 4 decimal places to do this.

$C_5H_{14}N_2$ ……..

$C_5H_{10}O_2$ ……..

$C_3H_6N_2O_2$ ……..

Molecular formula = ……...

b) Draw and name two molecules that this could be.

…….

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…….

3) Calculate the accurate mass of the two molecular ion peaks in the high resolution mass spectrum of chloroethane.

*Peak 1* ……..…….

*Peak 2* ……..…….

4) How could high resolution mass spectroscopy be used to distinguish propane and ethenol?

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