

Mass Spectroscopy part 2

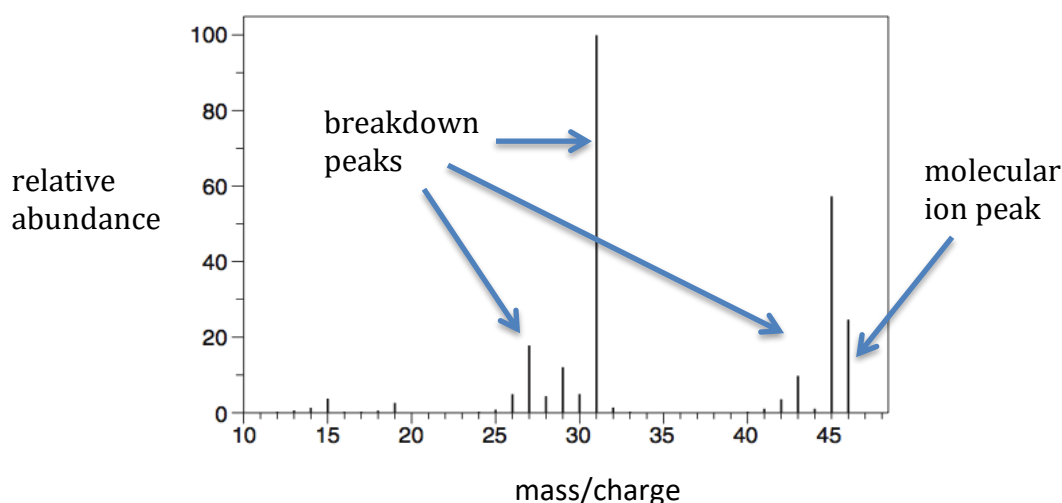
The Spectrum

[Click here for mass spectroscopy part 1](#)

A spectrum is the end result of what we discussed in part 1 is a **spectrum**.

A spectrum is a just a fancy word for a chart. On the vertical axis is **relative abundance**, which just means 'how much' you have of that ion i.e. the concentration of the ion from the detection part.

The horizontal axis is the '**mass to charge ratio**' which usually has the symbol m/z . A typical spectrum via the electron impact method is shown below. The word 'charge' is used as we are producing an **ion** in the machine. The charge is usually **1+**:



Molecular ion peak

The peak furthest to the right in the spectrum is known as the molecular ion peak. This is the most important peak as it tells you the molecular weight of the compound.

Breakdown peaks

These peaks to the left of the molecular ion peak are all due to fragments of the molecule. In the spectrometer the sample breaks up and the end result is peaks due to parts or fragments of the molecule.

- ✓ You can ignore these breakdown peaks until you do the organic analysis topic. It was just to show you what a spectrum looks like.

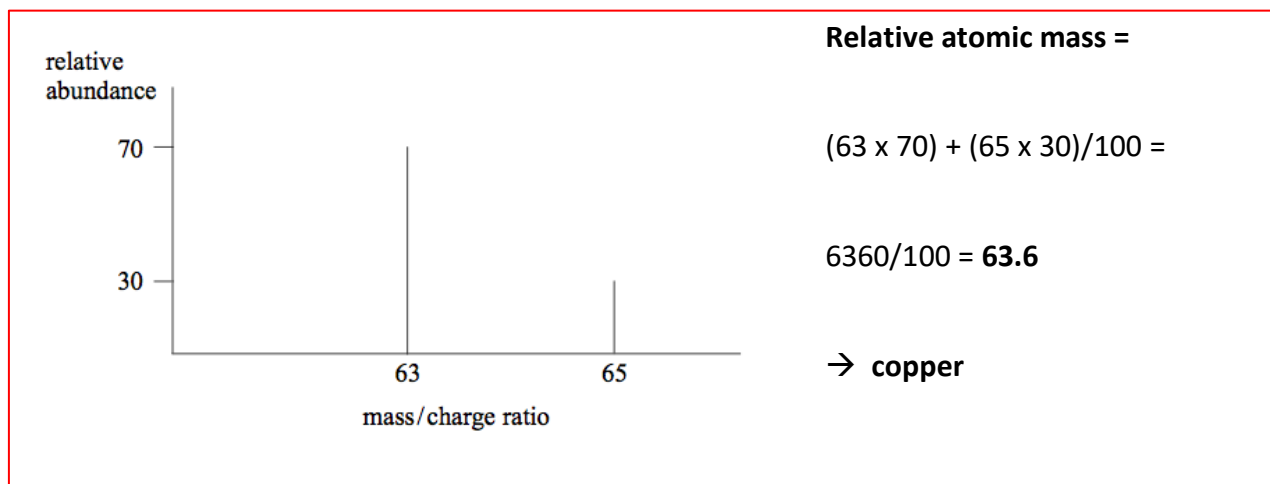
Relative Atomic Mass

An exam favourite is to give the mass spectrum of an element showing its various isotopes. From the spectrum you can calculate the relative atomic mass.

As you know relative atomic mass is an average of the mass of all the isotopes. All you have to do is multiply the mass of each peak by its relative abundance, add them together and then divide by 100 or:

$$(\text{Isotope 1 mass} \times \text{abundance}) + (\text{Isotope 2 mass} \times \text{abundance}) / \text{sum of abundance} = \text{RAM}$$

In the example below we have two isotopes of an element:



Calculating Abundance

If they give you the RAM and isotopic masses, then you could also calculate the **relative abundances** of each isotope.

Example

Again for Cl. We know the isotope masses are ^{35}Cl and ^{37}Cl and the RAM is 35.5.

We need to find the percentage of **one** of the isotopes and therefore the other must be 100 **minus** this value.

Let's call the abundance of the 35 isotope 'x'. Call it what you like! You could do it for the 37 isotope too, it doesn't matter which way round it is.

The other isotope therefore has to be 100-x. The general formula we are using is the same as for the RAM calculation above:

$$(\text{Isotope 1 mass} \times \text{abundance}) + (\text{Isotope 2 mass} \times \text{abundance}) / 100 = \text{RAM}$$

This gives us:

$$35x + 37(100-x) / 100 = 35.5$$

$$\rightarrow 35x + 37(100-x) = 3550$$

$$\rightarrow 35x + 3700 - 37x = 3550$$

$$\rightarrow -2x = -150$$

$$\rightarrow x = 75$$

This gives us the percentages i.e. $^{35}\text{Cl} = 75\%$ and $^{37}\text{Cl} = 25\%$. Therefore $75/25 \rightarrow \mathbf{3:1 \text{ ratio}}$.

Harder Example

You could get a question involving **3 isotopes**, where the abundances of two isotopes are unknown.

Example: for Mg there are three isotopes:

^{24}Mg isotopic mass 23.985, abundance 78.99%. ^{25}Mg isotopic mass 24.985 and ^{26}Mg isotopic mass 25.982.....and the RAM is 24.305. Calculate the abundances of the other two isotopes.

We know that the three abundances must add up to 100%. Therefore, we can do $100 - 78.99 = 21.01\%$, which must be the total of the abundances of isotopes 25 and 26.

Similarly to the Cl example above, we have to assign x to an isotope. Let's choose ^{26}Mg to be x. Therefore, ^{25}Mg must be $21.01-x$.

From here it is just simple maths again set up as follows:

$$(23.985 \times 78.99) + 24.985(21.01-x) + 25.982x/100 = 24.305$$

$$1894.575 + 524.935 - 24.985x + 25.982x = 2430.5$$

$$2419.51 + 0.997x = 2430.5$$

$$0.997x = 10.99$$

$$x = 11$$

Therefore, the ^{26}Mg isotope is 11% and the ^{25}Mg isotope must be $\mathbf{21.01-11 = 10\%}$.

Isotope peaks

Another question they often ask is how many peaks you'd expect, for example, in the mass spectrum of Br_2 .

You need to know that bromine has two isotopes at $m/z = 79$ and 81 (this is given in the question) in a 1:1 ratio i.e. same abundance of each isotope.

So, you'd expect two peaks at **79 and 81** (one for each bromine isotope).

But remember it is **Br₂**, which means we can add the two bromine atoms together. This gives various combinations of 79 + 81. We could have:

79 + 79 → peak at 158

81 + 81 → peak at 162

79 + 81 → peak at 160

As we could have 79 + 81 **or** 81 + 79, the peak at 160 has two possible ways to make it therefore will be double the abundance of the others i.e. double in height.

In total **5 peaks**: 79, 81, 158, 160 (double in height) and 162

Cl isotopes

The isotope ratios for Cl₂ are a bit more difficult than for Br as the starting isotope ratios are ³⁵Cl : ³⁷Cl = 3:1.

So how do we calculate the ratios of the Cl₂ peaks at **m/z = 70, 72 and 74**? You could just remember the ratio pattern is **9:6:1** or work it out as follows:

The 3:1 ratio means $\frac{3}{4}$ of the sample is ³⁵Cl isotope and the remaining $\frac{1}{4}$ is ³⁷Cl. Therefore, when combining these isotopes we need to multiply these fractions:

$$^{70}\text{Cl}_2 = \frac{3}{4} \times \frac{3}{4} = \frac{9}{16}$$

$$^{72}\text{Cl}_2 = \frac{3}{4} \times \frac{1}{4} = \frac{3}{16} \text{ but we need to } \times 2 \text{ as we did for the Br example above } \rightarrow \frac{6}{16}$$

$$^{74}\text{Cl}_2 = \frac{1}{4} \times \frac{1}{4} = \frac{1}{16}$$

So if we then just cancel the /16 parts, we are left with **9:6:1**. And that's how you could do it for any isotopes they might use.

Mass spectroscopy is also covered in the organic chemistry [analysis](#) topic but it isn't much more than what we have looked at here.

[Click here for mass spectroscopy part 1](#)