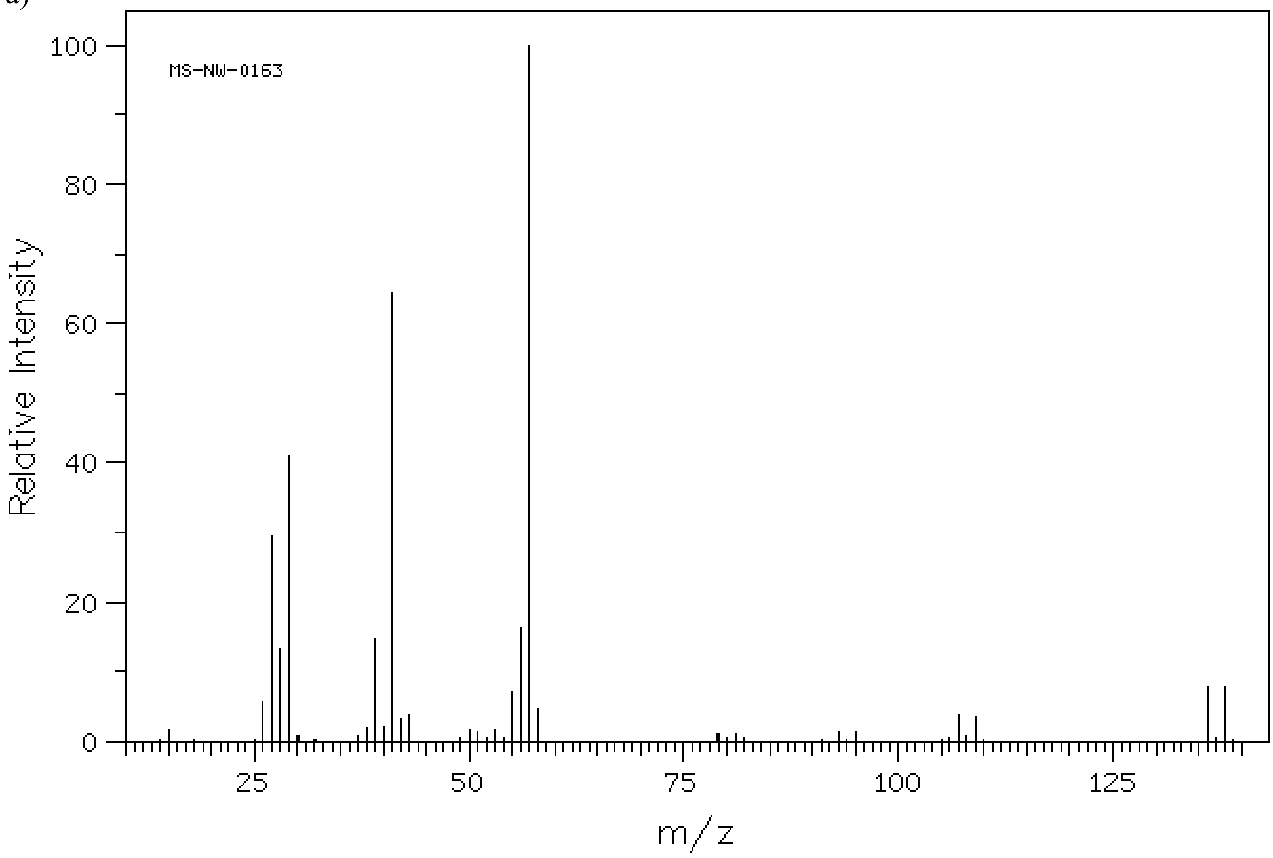
Chemguide – answers

MASS SPECTRA: THE M+2 LINE

1. a)



The two equally tall lines in the molecular ion region are typical of the presence of a bromine atom with its two isotopes with masses of 79 and 81. There is another pair of similar lines at 107/109.

If you take 81 away from 138 (or 79 away from 136), that leaves you with 57. That could well be C_4H_9. Removing bromine from the 107/109 fragments leaves a mass of 28, C_2H_4.

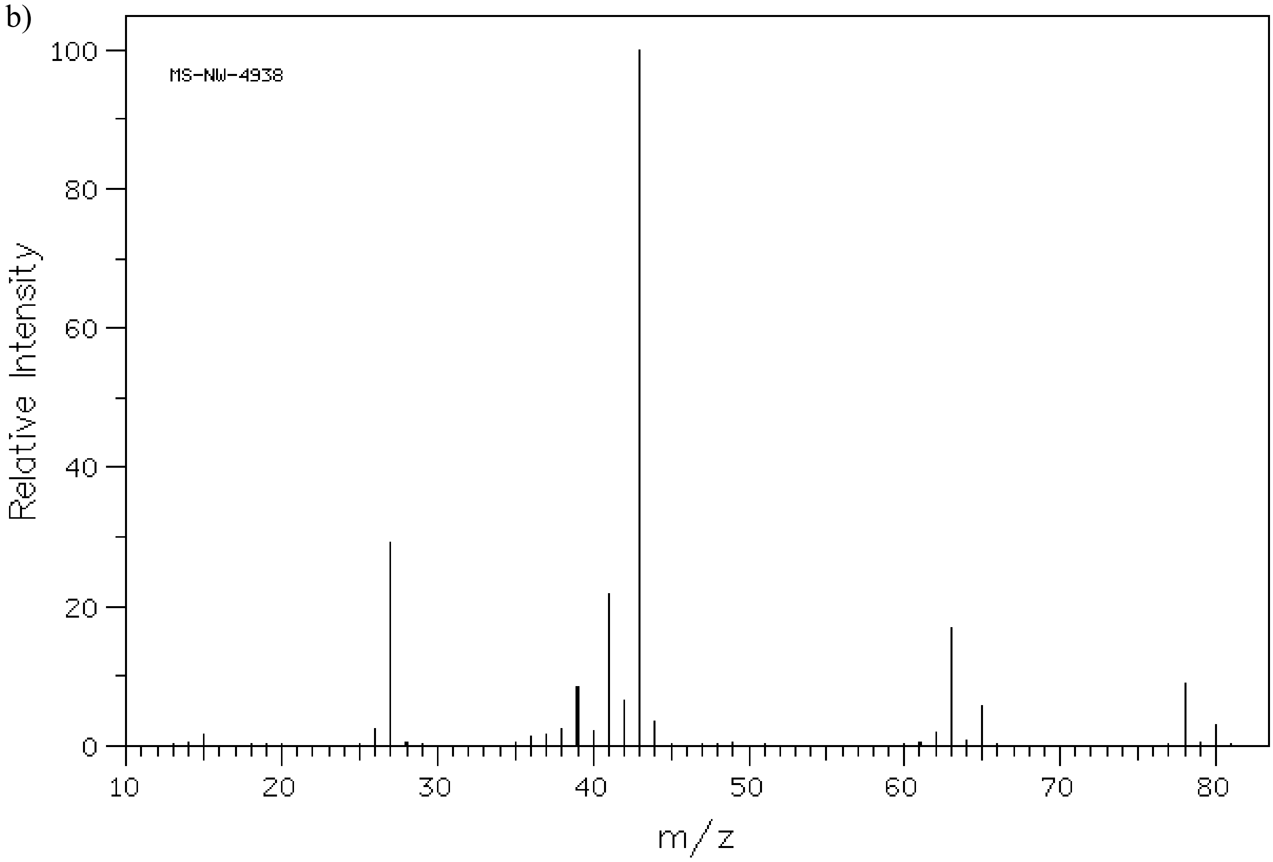
So those 107/109 fragments could be $[CH_2CH_2Br]^+$ or $[CH_3CHBr]^+$, depending on whether the bromine is at the end or in the middle of a chain.

The strong line at 57 is simply showing a $[C_4H_9]^+$ ion, so that doesn't add anything. The strong line at 41 would correspond to a $[C_3H_5]^+$ fragment, which doesn't fit anything we have found so far. You mustn't expect to be able to account for all the lines in a mass spectrum.

The line at 29 is useful, though, because it corresponds to a $[C_2H_5]^+$ fragment. So the molecule probably contains a CH_3CH_2 group.

Putting this together, the molecule could be $CH_3CH_2CH_2CH_2Br$ or $CH_3CHBrCH_2CH_3$, but it couldn't be the other isomer of these compounds, $(CH_3)_3CBr$, because that doesn't have any of the structures we have found so far. Curiously, though, the mass spectrum of $(CH_3)_3CBr$ does actually have a line at 29, presumably because of rearrangements which can happen in the mass spectrometer. It is, however, missing the lines at 107/109. This example shows that interpreting mass spectra isn't as easy as it sometimes seems at an introductory level!

b)



If you look at the molecular ion region there are two lines with their lengths in the ratio of what looks like 3:1. There are also two similar lines at m/z = 63 and 65. That looks like the presence of a single chlorine atom in the molecule, with its two isotopes with masses 35 and 37 in a 3:1 ratio.

If you take 37 from 80 (or 35 from 78), you are left with 43. That could be 3 carbons and 7 hydrogens - in other words, a C_3H_7 group.

Notice that there is also a strong line at 43, suggesting a $C_3H_7^+$ fragment.

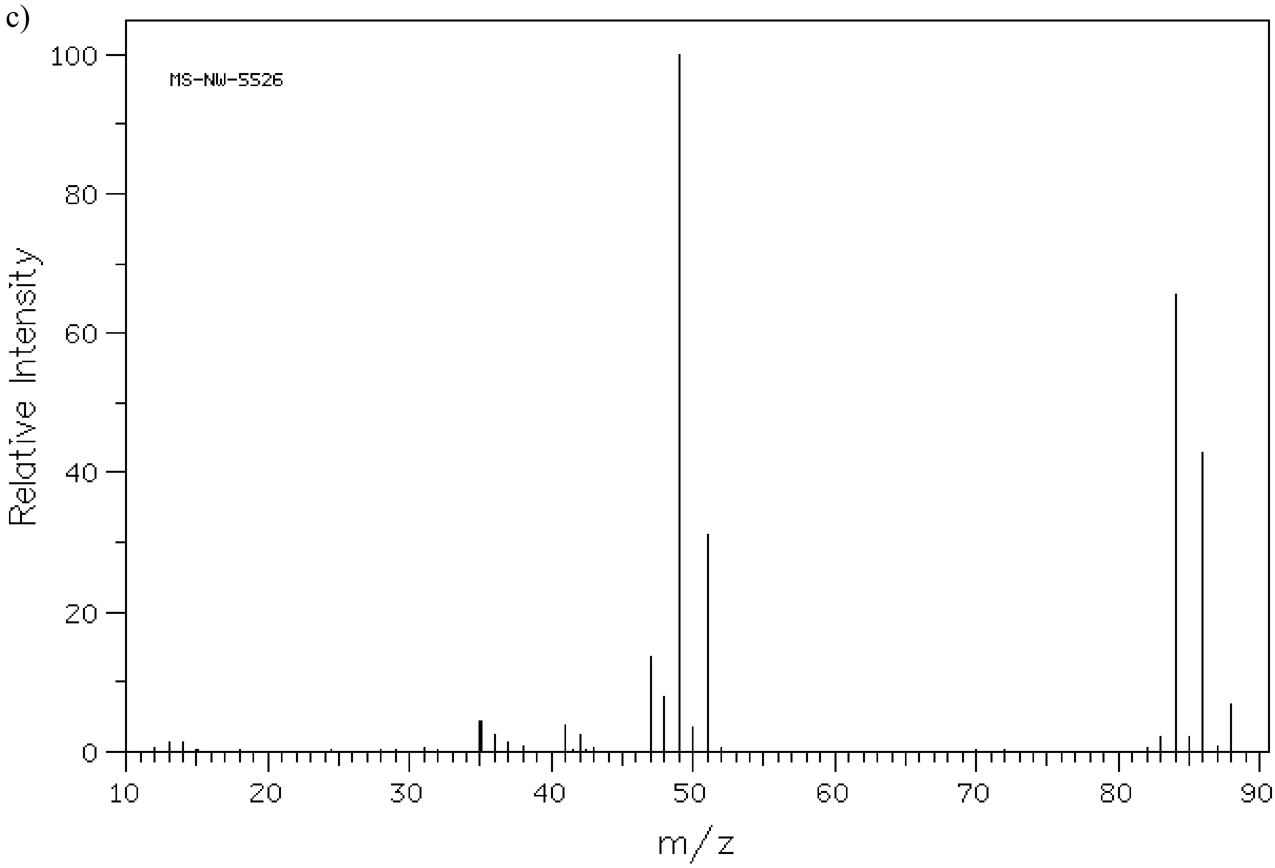
Don't jump to conclusions yet, because that could be $[CH_3CH_2CH_2]^+$ or $[CH_3CHCH_3]^+$ with the positive charge in the centre of the chain. Can you find any evidence about where the original chlorine atom was attached?

Look at the lines at 63 and 65. If you take away the masses of the chlorine isotopes from these, you are left with a mass of 28 - consistent with the fragment being either $[CH_3CHCl]^+$ or $[CH_2CH_2Cl]^+$.

But there is virtually no line with a mass of 29, and so almost certainly no CH_3CH_2 group which you would expect to see if the chlorine was attached at the end of the chain.

The compound is therefore probably 2-chloropropane - $CH_3CHClCH_3$.

c)



The pattern of three lines in the molecular ion region at m/z = 84, 86 and 88 and with peak heights in the ratio of 9:6:1 (you could confirm this by measuring them, but it is a fairly recognisable pattern) is typical of a molecule with 2 chlorine atoms.

If you take 2 x 35 away from 84 (or 2 x 37 away from 88, or 35 + 37 away from 86 - but why make life difficult?), you are left with 14 - a CH_2 group.

The compound must be CH_2Cl_2.

Just out of interest, look at the strong lines at 49 and 51 which appear to be in the ratio of 3:1. These are produced by loss of a chlorine radical leaving the ion CH_2Cl^+, giving lines at 14 + 35, and 14 + 37. Because these now contain only a single chlorine atom, they are in the ratio of 3:1.

An easier one to finish up with!

Don't worry if you missed some things when you were looking at these questions. Working out a molecular formula is usually easy. Beware, though, of jumping to conclusions without having given some thought to all the possible isomers that a molecular formula might have.

Questions in exams are usually fairly straightforward, and if a spectrum is open to two or more valid interpretations, your examiners should allow for this. And don't expect to be able to account logically for every single line - however strong it might be.