

HL Answers to Spectroscopic identification of organic compounds: Question 16

(a) From the elemental analysis

Element	Amount / mol	Simplest ratio
Carbon	$43.96/12.01 = 3.66$	5
Hydrogen	$6.66 / 1.01 = 6.60$	9
Oxygen	$23.43 / 16.00 = 1.46$	2
Chlorine	$25.95 / 35.45 = 0.73$	1

The empirical formula of **Compound P** is $C_5H_9O_2Cl$

(b) The M^+ peak at $m/z = 136$ leads to the conclusion that the molar mass of **Compound P** containing just ^{35}Cl is 136 g mol^{-1} and with the less abundant isotope of chlorine, ^{37}Cl it is 138 g mol^{-1} so the molecular mass is the same as the empirical mass and the molecular formula is therefore $C_5H_9O_2Cl$. The fragment at $m/z = 107$ suggests loss of an ethyl group to leave $C_3H_4O_2^{35}Cl^+$ and the fragment at $m/z = 73$ could be due to loss of $CH_3CH^{35}Cl$ to leave $C_3H_5O_2^+$. The lost $CH_3CH^{35}Cl^+$ ion could then be responsible for the peak at $m/z = 63$.

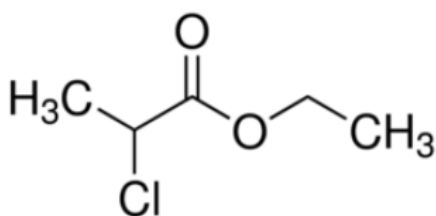
(c) The absorptions centred just below 3000 cm^{-1} are due to the C–H bonds and the sharp absorption at about 1750 cm^{-1} shows the presence of a carbonyl group, C=O. There are no broad absorptions due to an O–H bond but there is an absorption at about 1190 cm^{-1} which could be due to a C–O bond making **Compound P** an ester. C–Cl bonds vibrate lower than 1000 cm^{-1} so cannot be seen on this spectrum.

(d) The ^1H NMR spectrum data can be summarised as follows.

Position of signal/ δ ppm	Splitting pattern	Integration trace
1.31	triplet	3
1.67	doublet	3
4.23	quartet	2
4.39	quartet	1

Normally it is possible to distinguish between isomers of esters from their ^1H NMR spectra. However the presence of the chlorine atom makes it difficult in this case as chlorine, like oxygen, also affects the chemical shift. The splitting patterns and integration traces for $\text{CH}_3\text{CHClCOOCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{COOCHClCH}_3$ will be the same so the compound could be an ester derived either from 2-chloropropanoic acid or from propanoic acid. The methyl group with the signal split into a triplet is bonded to a $-\text{CH}_2-$ group and the methyl group split into a doublet is bonded to a $-\text{CH}-$ group however the shifts for the signals for the two methyl groups are very close (1.31 ppm and 1.67 ppm) so difficult to assign. Similarly the two quartets with integration traces of one and two are equally close and both lie within the 3.7 – 4.7 ppm range of the shift for $-\text{CO}-\text{OCH}_2-$ or $-\text{CO}-\text{OCHCl}-$. Therefore on the information given **Compound P** could be either **ethyl 2-chloropropanoate** or **1-chloroethyl propanoate**. If you had the compound in the lab you could easily identify which isomer it is by hydrolysing it and seeing whether chloropropanoic acid or propanoic acid is obtained.

ethyl 2-chloropropanoate



1-chloroethyl propanoate

