



Answering Questions on Identifying Unknown Organic Compounds

Before reading through this Factsheet you should:

- Have some practical experience of organic chemistry tests and preparations (Factsheet 60);
- Have a good understanding of different spectroscopic techniques (Factsheets 54, 55 and 56);
- Have a good understanding of AS/A2 organic chemistry;
- Have a good understanding and knowledge of organic functional groups and their reactions.

After working through this Factsheet you will be able to:

- Identify unknown organic chemicals when supplied with the necessary information in a written exam or practical situation.

The aim of this Factsheet is to build on knowledge of organic chemical testing and spectroscopic techniques to enable candidates to attempt a specific type of question.

Candidates are often asked to identify an organic compound having been given some information about that compound. Sometimes all of the relevant information is supplied, and sometimes in practical situations candidates are given instructions so as the necessary information can be discovered by chemical testing.

Information supplied in the question

Exam Hint: Read the question carefully, assume any information about the unknown chemical supplied is important and must be considered. "Tick off" the information to make sure you have used all of it.

Such problems on identifying unknown organic problems generally begin by supplying the first 'clues'. Often this will be information about the composition:

E.g. Compound X contains carbon, hydrogen and oxygen only.

Sometimes the molecular mass or even the molecular formula is supplied.

Results of Chemical Tests

In a practical exam or assessment, candidates may be given instructions to carry out simple organic tests, or in a written exam results of such tests may be described. Inferences must be drawn from these about the unknown compound.

Exam Hint: Do not treat each piece of information or test result in isolation. Use **all** of the knowledge gained about the compound to **build a picture** of the unknown structure.

The following table is not a definitive list of chemical tests (see Factsheet 60 for more information) but is included to help candidates make links between test observations and inferences about unknown organic compounds.

Reagents	Positive Test Result	Possible Inferences about Unknown Organic Compound
Dry PCl_5 solid	Steamy white fumes of HCl	-OH group present. Could be alcohol or carboxylic acid.
Sodium carbonate or sodium hydrogen carbonate	Effervescence, CO_2 produced	Carboxylic acid.
2,4-dinitrophenylhydrazine	Red-orange crystalline precipitate	$\text{C}=\text{O}$ present. Aldehyde or ketone.
Ammoniacal silver nitrate	Silver mirror or grey precipitate	Aldehyde.
Fehling's solution	Blue solution fades, red precipitate forms	Aldehyde.
Iodine and sodium hydroxide (or potassium iodide and sodium chlorate (I))	Yellow precipitate, antiseptic smell. Triiodomethane – iodoform	$-\text{COCH}_3$ group or $-\text{CHOHCH}_3$ group present.
Acidified potassium dichromate (VI)	Colour change orange to green.	Oxidation occurs. Could be primary alcohol, secondary alcohol or aldehyde.
Bromine water	Colour change orange/brown to colourless.	$\text{C}=\text{C}$ present.
Sodium hydroxide, acidification with nitric acid, then addition of silver nitrate solution.	White precipitate, soluble in dilute ammonia solution	$\text{C}-\text{Cl}$ present.
	Cream precipitate, soluble in concentrated ammonia solution.	$\text{C}-\text{Br}$ present.
	Yellow precipitate, insoluble in concentrated ammonia solution.	$\text{C}-\text{I}$ present.

Obviously if test results are negative, negative inferences can be made. E.g. If PCl_5 is added to an unknown organic chemical and there is no observable reaction, the unknown does **not** contain the -OH group. Similarly, if there is no colour change on addition of acidified potassium dichromate, the substance will not oxidise - e.g. tertiary alcohol or ketone.

Spectroscopic Data

See Factsheets 54, 55 and 56 for more detail on interpreting mass, IR and simple NMR spectra. In questions involving unknown organic compounds it is essential that candidates can obtain the following information from supplied spectra:

- **Mass spectra** can supply the molecular mass of the unknown compound – the highest trace reading on the spectrum gives the mass of the 'parent ion' which is equal to the molecular mass.
- **IR spectra** supply information about types of bonds present such as O-H and C=O. Use this information to when deducing the structure of an unknown organic compound.

Worked Example 1

Organic compound X contains carbon, hydrogen and oxygen only.

Already certain organic chemicals can be ruled out – alkanes, alkenes, halogenoalkanes or nitrogen containing compounds.

Chemical tests on X:

Addition of PCl_5 – steamy white acidic fumes.

X contains the –OH group, so is likely to be an alcohol or carboxylic acid.

X is added to acidified potassium dichromate (VI) solution and warmed – a colour change of orange to green is observed.

X is oxidised, so cannot be a carboxylic acid, instead must be an alcohol.

X is added to iodine and sodium hydroxide and warmed – a yellow precipitate with an antiseptic smell is formed.

X contains the –CHOHCH₃ group (note that the previous tests discount the presence of the –COCH₃ group!).

X is a secondary alcohol.

Spectroscopic data:

The mass spectrum of X has a highest peak of $m/e=74$.

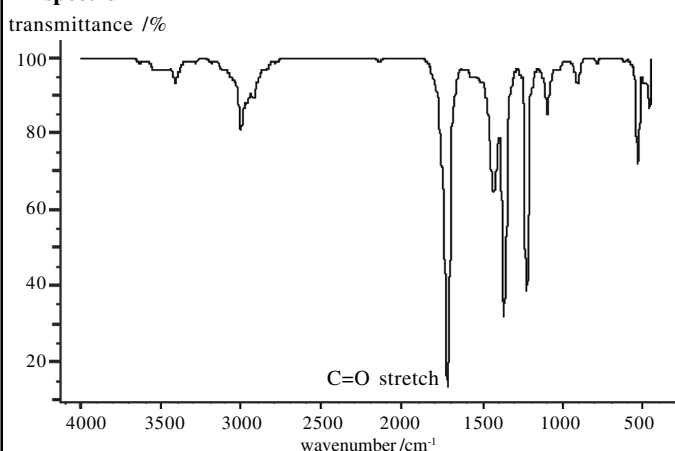
The molecular mass of X is 74.

Bringing together all of this information – X is a secondary alcohol of molecular mass 74, a name and structure can now be assigned to X:

X is butan-2-ol, $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$

Worked Example 2

Organic compound Y has the molecular formula $\text{C}_5\text{H}_{10}\text{O}$. The IR spectrum is supplied:

IR spectrum

The presence of a C=O group is confirmed here, so Y is an aldehyde or ketone. Y cannot be an acid as only one O atom is present, and from the number of C and H atoms present it can be concluded that there are no further multiple bonds aside from the C=O.

Chemical tests on Y:

Y is warmed with ammoniacal silver nitrate solution – no observable reaction.

Y is not an aldehyde, Y is a ketone. Care must still be taken here as there are still a number of possibilities:

e.g. pentan-2-one, pentan-3-one, 2-methylbutanone and so on.

Y is warmed with sodium hydroxide and alkali – no observable reaction.

The –COCH₃ group is not present in Y.

Now this structural information is available, the name and structure of Y can be deduced.

Y is pentan-3-one, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

Worked Example 3

Z is an organic compound containing the elements C, H and O only.

Chemical tests on Z:

Addition of PCl_5 – steamy white acidic fumes.

Z contains an –OH group, so is likely to be a carboxylic acid or an alcohol.

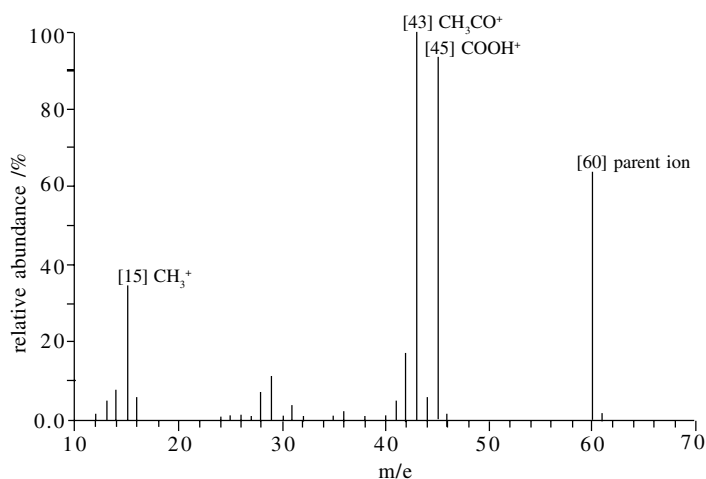
Addition of Z to sodium hydrogen carbonate solution – effervescence, gas produced turns lime water cloudy (carbon dioxide).

Z is a carboxylic acid.

The molecular mass of Z is that of the parent ion, $\text{RMM} = 60$.

The name and structure of Z, a carboxylic acid of $\text{RMM} 60$, can now be deduced.

Z is ethanoic acid, CH_3COOH

Spectroscopic data:**Mass spectrum**

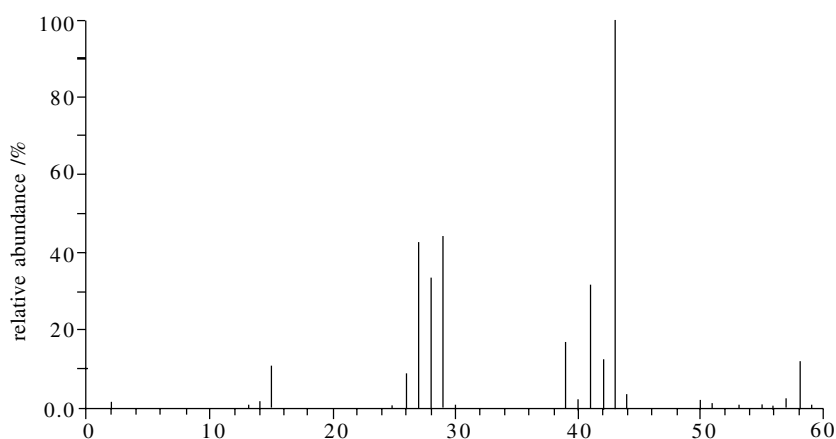
In summary, when attempting a question which requires the identification of an unknown organic compound:

- Use information supplied in the question introduction.
- Use information gained via chemical test results and spectra to **build a picture** of the chemical.
- Do not just use isolated pieces of information, but combine what you know from the various sources to gradually eliminate possibilities and then deduce the correct answer.

Practice Questions

1. Organic chemical A is a straight chain hydrocarbon.
On addition of bromine water to A there is no observable reaction.
The mass spectrum of A is supplied. Identify A.

mass spectrum



2. Organic chemical B contains the elements C, H and O only, with the carbons all positioned in a straight chain. The mass spectrum of B indicates that B has a molecular mass of 72.
The following chemical tests were carried out on B.

Chemical test	Observations
Addition of PCl_5	No observable reaction.
Addition of 2,4-DNP solution	Red/orange precipitate.
Addition of ammoniacal silver nitrate solution and warmed	Silver mirror formed on inside of test tube.

Identify B

3. C, D and E are all organic chemicals containing C, H and O only. C, D and E all contain 3 C atoms and just one functional group each.
Identify C, D and E from the following test results:

Test	C	D	E
PCl_5	No observable reaction	Steamy white acidic fumes	No observable reaction
2,4-DNP	Red/orange precipitate	No observable reaction	Red/orange precipitate
NaHCO_3 solution	No observable reaction	Effervescence, CO_2	No observable reaction
Heat with acidified $\text{K}_2\text{Cr}_2\text{O}_7$	Colour change orange to green	No observable reaction	No observable reaction
Warm with I_2/NaOH	No observable reaction	No observable reaction	Yellow precipitate with antiseptic smell

Answers
 1. Butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 2. Butanal, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
 3. C is propanal, $\text{CH}_3\text{CH}_2\text{CHO}$
 D is propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$
 E is propanone, CH_3COCH_3

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