Chem Factsheet

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Functional Group Testing

Functional groups are specific groups of atoms and bonding patterns within molecules that are responsible for the characteristic chemical reactions of those molecules.

A particular functional group will undergo the same, or very similar, chemical reaction(s) regardless of the molecule it is a part of.

The following table shows the common functional groups studied at A-level. Most A-level specifications require you to be able to describe how to apply and interpret test-tube reactions to show the presence or absence of one or more of these functional groups in any particular molecule.

Functional Group	Functional Group	Functional Group	Functional Group
Alkene	Tertiary alcohol	Acyl chloride	Amide
Alkyne	Aldehyde	Acid anhydride	Phenol
Haloalkane	Ketone	Primary Amine	Nitrile
Primary Alcohol	Carboxylic acid	Secondary Amine	Nitro compound
Secondary Alcohol	Ester	Tertiary Amine	Phenyl

When analyzing an organic compound to determine its structure, one of the first steps is to identify which of these functional groups is present in the molecule by applying some simple test-tube reactions. This information can then be used to inform or confirm deductions made from more sophisticated analytical techniques such as infra-red spectroscopy, mass spectrometry and n.m.r. spectroscopy.

Note 1: The reactions and reactivity of a particular functional group can be modified by interaction with a nearby different functional group.

Note 2: Some tests are very specific and conclusive whereas others might only give an indication of the functional group present. In fact, some groups are not identifiable by simple test tube reactions.

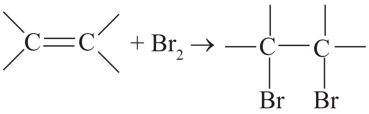
Note 3: A-level exam questions usually require a test to be applied to distinguish one compound from another, rather than identify particular functional groups.

Note 4: An “acceptable” test-tube reaction must involve a clearly visible change. In general, these will be (a) change, production or loss of colour (b) formation of a precipitate, including its colour (c) dissolution of a solid, including the colour of the resulting solution (d) effervescence, including the colour of the gas where appropriate.

Test 1 : Combustion of hydrocarbons

Method	Burn a small sample of the hydrocarbon in air in a fume cupboard.
Observations	Alkanes burn with non-smoky flame, alkenes with a slightly smoky flame and arenes with a very smoky flame.
Explanation	Comparing similar sized molecules (e.g. cyclohexane, cyclohexene and benzene) the % of carbon increases as the degree of unsaturation increases. When burned in the limited supply of oxygen provided by air, an increasing amount of this carbon will remain unburned and be released as soot. Note: Combustion is a useful test to confirm that a sample is carbon-based (organic) before proceeding with other tests.

Test 2 : Bromine water test for alkenes

Method	Add a few drops of aqueous bromine solution to 2cm^3 of the test sample and shake the mixture.
Observations	The orange-red bromine solution is decolourised. Note: “Decolourised”, not “goes clear”. Clear means transparent and *all* solutions are therefore clear.
Explanation	An electrophilic addition of the bromine to the C=C bond occurs resulting in a bromine atom being bonded to each of those C atoms. Bromine is coloured but bromides are colourless. Hence the decolourisation.
Equation	
Note	See test 11 – using bromine water to test for phenols.
Q1	Write an equation for this reaction being applied to but-1-ene. Name the organic product.

Test 3 : Testing for chloro-, bromo- and iodoalkanes

Method
(a) Add a few drops of the test sample to $5cm^3$ of dilute sodium hydroxide solution. Boil gently for 2-3 minutes.
(b) Cool the mixture from (a) and add dilute nitric acid drop wise until the solution is acidic, as shown by Universal Indicator paper.
(c) Add silver nitrate solution to the reaction mixture from (b)
(d) If a precipitate is observed in (c), divide the reaction mixture from (c) into two part and, with mixing, add dilute ammonia solution to the first and concentrated ammonia solution to the second.

Observations
(a) The haloalkane will become miscible with the aqueous solution after heating.
(c) A chloroalkane will cause a white precipitate to form, a bromoalkane a cream precipitate and an iodoalkane a yellow precipitate.
(d) The white precipitate will dissolve in both ammonia solutions, the cream precipitate will dissolve in only the concentrated ammonia solution and the yellow precipitate will dissolve in neither of the ammonia solutions.

Explanation
(a) The haloalkane is hydrolysed by reaction with a hydroxide ion nucleophile provided by the aqueous sodium hydroxide. The covalently bonded halogen atom is released into the solution in the form of a halide ion. The haloalkane is converted to an alcohol and, unlike the original haloalkane, this can hydrogen bond with water molecules, thus increasing miscibility.
(b) The nitric acid neutralises the excess sodium hydroxide. This is essential because the silver nitrate used in stage (c) would react with hydroxide ions to form a brown precipitate of silver(I) hydroxide

$$Ag^+(aq) + OH^-(aq) \rightarrow AgOH(s)$$

mixed with black silver(I) oxide resulting from the decomposition of some of the silver hydroxide. These precipitates would mask any precipitates formed in stage (C).

$$2Ag(OH)(s) \rightarrow Ag_2O(s) + H_2O(l)$$

(c) The halide ions produced in stage (a) combine with the added silver ions to form precipitates of insoluble white silver chloride, cream silver bromide or yellow silver iodide.
(d) Silver chloride, bromide and iodide show a decreasing solubility in ammonia solution. When the precipitate does dissolve, the silver ion is converted to the silver(I) diammine complex ion $[Ag(NH_3)_2^+]$ which is colourless and water soluble.

Note 1
This test is not applicable to fluoroalkanes because silver fluoride is water soluble and would not form a precipitate at stage (c).

Note 2
This test is not applicable to halobenzenes (e.g. chlorobenzene, C_6H_5Cl) because the C-X bond is much stronger in halobenzenes due to extended delocalisation. This means the hydrolysis required in stage (a) will not occur.

Equations
X = Cl, Br or I
(a) $RX + OH^- \rightarrow ROH + X^-$
(b) $NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$
(c) $Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$
(d) $AgX(s) + 2NH_3 \rightarrow Ag(NH_3)_2^+(aq) + X^-(aq)$

Q2 Write equations for these reactions being applied to 2-bromopropane. Name the organic product.

Test 4 : Sodium metal test for OH groups

Method
Add a small, fresh piece of sodium metal to a $2cm^2$ test sample. Test any gaseous product by applying a lighted splint.

Observations
A molecule containing an OH group (alcohol, carboxylic acid or phenol) will cause an effervescence of a colourless gas. This will "pop" when exposed to a lighted splint.

Explanation
Sodium atoms are oxidised to sodium ions (Na^+) by electron loss resulting in the reduction of the H atom in an OH group to hydrogen gas (H_2) which creates the effervescence and "pop". Alcohols form alkoxides, carboxylic acids form salts and phenols from phenates.

Equation
$C—OH + Na \rightarrow C—O^-Na^+ + \frac{1}{2} H_2$

Note 1
This reaction will occur for *any* wet sample! Water must be absent from the test sample when using this test.
$Na(s) + 2H_2O(l) \rightarrow NaOH + H_2(g)$

Note 2
This test can be used in conjunction with tests 5, 6, 7 and 11 to distinguish alcohols from carboxylic acids from phenols.

Note 3
Not required in AQA specification.

Q3 Write equations for this reaction being applied to (a) methylpropan-2-ol (b) propanoic acid (c) phenol (hydroxybenzene).

Test 5 : Acidified potassium dichromate solution test

Method	Heat a small sample of the test compound with a mixture of sulphuric acid and potassium dichromate(VI) [$K_2Cr_2O_7$].
Observations	Aldehydes, primary alcohols and secondary alcohols will cause the orange solution to change to green.
Explanation	(a) An aldehyde is oxidised to a carboxylic acid by the dichromate oxidising agent, resulting in the reduction of orange dichromate to green chromium(III) [Cr^{3+}]. (b) Primary alcohols are oxidised to aldehydes and then carboxylic acids, along with the same dichromate reduction. (c) Secondary alcohols are oxidised to ketones, along with the same dichromate reduction.
Equations	(a) $3RCHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 3RCOOH + 2Cr^{3+} + 4H_2O$ (b) $3RCH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3RCHO + 2Cr^{3+} + 7H_2O$ then $3RCHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 3RCOOH + 2Cr^{3+} + 4H_2O$ (c) $3R_1CH(OH)R_2 + Cr_2O_7^{2-} + 8H^+ \rightarrow 3R_1COR_2 + 2Cr^{3+} + 7H_2O$
Note 1	Tertiary alcohols are not oxidised by this reaction. This is because there is no H atom bonded to the same C as the OH.
Note 2	This test can be used in conjunction with tests 8 or 9 to distinguish primary from secondary alcohols and in conjunction with test 4 to distinguish primary and secondary alcohols from tertiary alcohols.
Note 3	Simplified equations are often used for these reactions. [O] represents oxygen provided by the oxidising agent. (a) $RCHO + [O] \rightarrow RCOOH$ (b) $RCH_2OH + [O] \rightarrow RCHO + H_2O$ then $RCHO + [O] \rightarrow RCOOH$ (c) $R_1CH(OH)R_2 + [O] \rightarrow R_1COR_2 + H_2O$

Q4 Write simplified equations for this reaction being applied to (a) butanal (b) propan-1-ol (c) propan-2-ol.

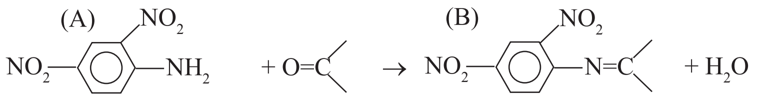
Test 6 : Universal indicator solution test

Method	Add 2 or 3 drops of Universal Indicator solution to the test sample in $2cm^3$ of water.
Observations	Carboxylic acids and phenols will give a weakly acidic result. Acyl chlorides will give a strongly acidic result. Amines will give a weakly alkaline result.
Explanation	(a) Carboxylic acids and phenols are weak acids since they are only slightly ionised in aqueous solution. (b) Acyl chlorides are completely hydrolysed in the water producing carboxylic and hydrochloric acids. The latter is a strong acid since it is fully ionised in aqueous solution. (c) Amines are able to accept a proton via the lone pair on the N atom but this ionisation is only partial
Equations	(a) $RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$ $C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$ (b) $RCOCl + H_2O \rightarrow RCOOH + H^+ + Cl^-$ (c) $NR_3 + H_2O \rightleftharpoons [NHR_3]^+ + OH^-$

Test 7 : Sodium hydrogen carbonate solution test

Method	Add $5cm^3$ of dilute sodium hydrogen carbonate solution to a $2cm^2$ test sample. Test any gaseous product by bubbling it through lime water.
Observations	(a) Carboxylic acids will cause a slow effervescence of a colourless gas. This will cause the lime water to change from colourless to "milky". (b) Acyl chlorides will cause a similar set of observations but the reaction will be very vigorous.
Explanation	Weak carboxylic acids generate a low concentration of hydrogen ions resulting in a slow displacement of CO_2 from the hydrogen carbonate.
Equations	(a) $RCOOH + H_2O \rightarrow RCOO^- + H_3O^+$ then $H_3O^+ + HCO_3^- \rightarrow 2H_2O + CO_2$ (b) $RCOCl + H_2O \rightarrow RCOOH + HCl$ then $HCl + NaHCO_3 \rightarrow NaCl + H_2O + CO_2$
Note	The acidity of phenols is too low to cause this reaction.

Test 8 : Brady's test for aldehydes and ketones

Method	Add a few drops of Brady's reagent (2,4-dinitrophenylhydrazine [2,4-DNPH - see (A)] dissolved in methanol and concentrated sulphuric acid) to $2cm^3$ of test sample.
Observations	An aldehyde or a ketone will produce a yellow, orange or red precipitate.
Explanation	The C=O bond of an aldehyde or ketone condenses with the NH_2 group in 2,4-dinitrophenylhydrazine to form an insoluble coloured 2,4-dinitrophenylhydrazone – see (B).
Equations	
Note 1	Alkane based aldehydes and ketones tend to produce a more yellow precipitate whereas aryl aldehydes and ketones tend to produce a more red precipitate.
Note 2	This test is specific for aldehydes and ketones. Acids, esters, amides etc., which also contain a C=O bond, do not react.
Note 3	Following a positive result for this test, the compound can be distinguished as an aldehyde or a ketone using either test 9 or 10.
Note 4	This reaction is often used to *identify* a particular aldehyde or ketone. The phenylhydrazone precipitate is filtered off and purified by recrystallisation. Its melting point is then determined and the aldehyde or ketone identified by comparison of this with the melting points of known hydrazones.

Note 5	Not required in AQA specification.

Q5 Write the equation for this reaction applied to propanal.

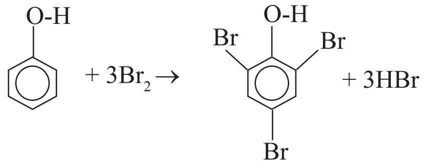
Test 9 : Tollens test for aldehydes

Method	Ammoniacal silver nitrate (Tollens reagent) is made by adding dilute ammonia drop-wise to silver nitrate solution until the initial precipitate of silver(I) oxide just dissolves to form a colourless solution. Mix equal volumes of the test sample and this reagent and warm the mixture in a hot water bath.
Observations	Aldehydes will produce a coating of silver on the inside wall of the test-tube – a “silver mirror”.
Explanation	Ammoniacal silver nitrate contains silver(I) diammine complex ions, $Ag(NH_3)_2^+$. These are reduced by any aldehyde to form metallic silver. The aldehyde is oxidised to the corresponding carboxylic acid.
Equations	$RCHO + 2Ag(NH_3)_2^+ + 2OH^- \rightarrow RCOOH + 2Ag + H_2O + 4NH_3$
Note	Ketones do not reduce Tollens which gives a method for distinguishing aldehydes from ketones.

Test 10 : Fehling’s test for aldehydes

Method	Fehling’s solution is made by mixing Fehling’s A and Fehling’s B solutions. Fehling’s A is a blue aqueous solution of copper(II) sulphate, while Fehling’s B is a colorless solution of aqueous potassium sodium tartrate and a sodium hydroxide. Mix equal volumes of the test sample and this reagent and warm the mixture in a hot water bath.
Observations	Aldehydes cause a brick-red precipitate to form and the blue solution will fade.
Explanation	Copper(II) ions are reduced by any aldehyde to form brick-red, insoluble copper(I) oxide. The aldehyde is again oxidised to the corresponding carboxylic acid.
Equations	$RCHO + 2Cu^{2+} + 4OH^- \rightarrow RCOOH + Cu_2O + 2H_2O$
Note 1	Ketones do not reduce Fehling’s which gives another method for distinguishing aldehydes from ketones.
Note 2	The “tartrate” is present to prevent the precipitation of copper(II) hydroxide when Fehling’s A and B are mixed. It forms a soluble complex with the copper(II) ions.
Note 3	Fehling’s test is also used to distinguish reducing sugars from non-reducing sugars. This is because reducing sugars contain a potential aldehyde group.

Test 11: Bromine water test for phenol

Method	Add an aqueous bromine solution drop-wise to $2cm^3$ of the test sample in aqueous solution, shaking the mixture as the drops are added.
Observations	The orange bromine solution is decolourised and a white precipitate is formed.
Explanation	The benzene ring undergoes electrophilic substitution by bromonium ions (Br^+) provided by the bromine which is consumed, causing the decolourisation. 2,4,6-tribromophenol is formed which is the white precipitate.
Equations	
Note	Not required in AQA specification.

Test 12: Testing for an acyl chloride

Method	Add water drop-wise to a $2cm^3$ test sample. Then add 2-3 drops of Universal Indicator.
Observations	On adding water, an acyl chloride will react very vigorously producing white fumes and a colourless solution. On adding the indicator, a strongly acidic solution will be detected.
Explanation	An acyl chloride is immediately hydrolysed by water by a very exothermic reaction producing a colourless solution of the carboxylic acid and fumes of hydrogen chloride. The carboxylic acid and some dissolved HCl cause the solution to be strongly acidic.
Equations	$RCOCl + H_2O \rightarrow RCOOH + HCl$

Summary of test applications

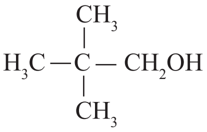
Functional Group	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10	Test 11	Test 12
Alkene	√	√									√	
Haloalkane	√		√									
Primary Alcohol	√			√	√							
Secondary Alcohol	√			√	√							
Tertiary alcohol	√			√								
Aldehyde	√				√			√	√	√		
Ketone	√							√				
Carboxylic acid	√			√		√	√					
Acyl chloride	√					√						√
Amine	√					√						
Phenol	√	√		√		√					√	

Phenyl	√											

Further Questions

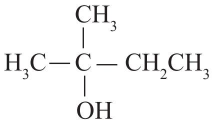
Q6 Describe how you could distinguish between the compounds in the following pairs (A&B ; C&D ; E&F) using **one** simple test-tube reaction in each case.
For each pair, identify a reagent and state what you would observe when both compounds are tested separately with this reagent.

(a) A



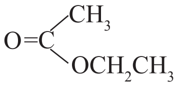
$$H_3C-C(CH_3)_2-CH_2OH$$

B

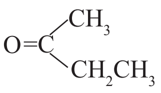


$$H_3C-C(CH_3)(OH)-CH_2CH_3$$

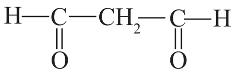
(b) C



D

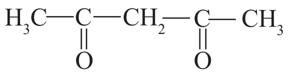


(c) E



$$H-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-H$$

F

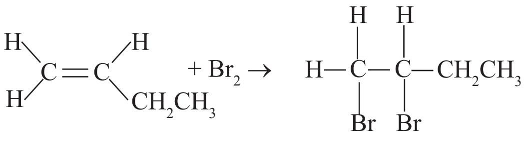


$$H_3C-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

Q7 A chemist has discovered that the labels have fallen off four bottles each of which contains a different organic liquid. These liquids are known to be propan-1-ol, propanal, hexane and 1-bromopropane. Suggest a series of test-tube reactions which a chemist could use to confirm the identities of the four compounds. State the reagents used and the observations expected.

Answers to Questions

Q1



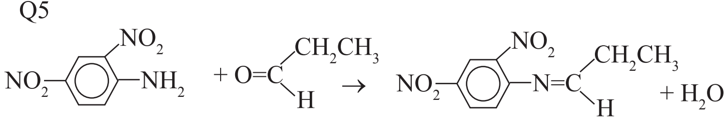
1,2-dibromobutane

Q2 (a) $CH_3CHBrCH_3 + OH^- \rightarrow CH_3CH(OH)CH_3 + Br^-$
(b) $NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$
(c) $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
(d) $AgBr(s) + 2NH_3 \rightarrow Ag(NH_3)_2^+(aq) + Br^-(aq)$

Q3 $R—OH + Na \rightarrow R—O^-Na^+ + \frac{1}{2} H_2$
(a) $R = (CH_3)_2CH—$ (b) $R = CH_3CH_2CO—$ (c) $R = C_6H_5–$

Q4 (a) $CH_3CH_2CH_2CHO + [O] \rightarrow CH_3CH_2CH_2COOH$
(b) $CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$
then $CH_3CH_2CHO + [O] \rightarrow CH_3CH_2COOH$
(c) $CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$

Q5



Q6 (a) A is a primary alcohol while B is a tertiary alcohol.
→ apply test 5 → A causes orange to green ; B remains orange.
(b) C is an ester while D is a carboxylic acid.
→ apply test 4, 6 or 7 → C negative for all ; D positive for all.
(c) E has an aldehyde group but F does not
→ apply test 9 or 10 → E positive for both ; F negative for both.

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