

## Qualitative Analysis Test for and identify organic functional groups

| Functional group   | Test method   | Observation   | Comments   |
|--|---|---|--|
| <b>Alkene or Alkyne</b>  | Bubble gas through or add Bromine solution in hexane or water   | The orange /brown bromine rapidly decolourises, as a saturated colourless organic bromo-compound is formed  | $R_2C = CR_1 \rightarrow BrR_2C - CR_2BR$<br>$RC \equiv CR + 2Br_2 \rightarrow Br_2RC - CRBr_2$<br>Here R is H, alkyl or aryl<br>Saturated alkane do not reacts with bromine   |
| <b>Hydroxy group –OH</b><br>chemical test in alcohol and phenols ( in dry conditions)<br><br>The first 3 tests (i) (ii) (iii) given on right are quit general for most alcohol   | (i) Mix it with a few drops of ethanoyl chloride, test fumes with litmus and silver nitrate (* note ethanoyl chloride reacts with water, phenols and amines too!).<br><br>(ii) Mix it with a little phosphorus(V) chloride and test as above.<br><br>(iii) Warm with a little ethanoic acid and a few drops of conc. sulphuric acid. Pour into water. | (i) Litmus turns red and a white precipitate with silver nitrate <sub>(aq)</sub> (drop on end of glass rod), if the mixture is poured into water you may detect a 'pleasant' ester odour, can test for HCl but water and amines produce it too!<br><br>(ii) as for (1) but no ester smell!<br><br>(iii) You should get a 'pleasant' characteristic smell of an ester. | (i) $R-OH + CH_3COCl \rightarrow CH_3COOR + HCl$<br><br>An ester and hydrogen chloride are formed<br><br>(ii) $R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$<br><br>a chloro compound and hydrogen chloride are formed.<br><br>(i) and (ii)<br><br>$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ from the hydrogen chloride fumes dissolved in water.<br><br>(iii) $CH_3COOH + ROH \rightarrow CH_3COOR + H_2O$ |
| <b>Primary alcohol</b><br>chemical test $RCH_2OH$ , R = H, alkyl or aryl (NOT a phenol).<br><br>(ii) is not a good test on its own, since so many other readily reducible organic compounds will give the same reaction, though following it up by testing for an aldehyde gives it much more validity | (i) Lucas test – shake a few drops with cold zinc chloride in conc. $HCl_{(aq)}$<br><br>(ii) Distil with potassium dichromate(VI) and mod. conc. $H_2SO_{4(aq)}$  | (i) Solution remains clear.<br><br>(ii) If product distilled off immediately an aldehyde odour can be detected and the solution colour changes from orange to green.  | (i) Not usually reactive enough to form a primary halogenoalkane.<br>(ii) $R-CH_2OH + [O] \rightarrow R-CHO + H_2O$ or the full works!<br><br>$3R-CH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3R-CHO + 7H_2O$<br><br>The orange dichromate(VI) ion is reduced to the green chromium(III) ion. If the organic product is collected you could test for an aldehyde.  |

Qualitative Analysis Test for and identify organic functional groups

| Functional group  | Test method   | Observation  | Comments  |
|---|---|--|---|
| <p><b>Secondary alcohol</b> chemical test</p> <p><math>R_2CHOH</math>, R = alkyl or aryl.</p> <p>(ii) is not a good test on its own, since so many other reducible organic compounds will give the same reaction, though following it up by testing for a ketone gives it much more validity.</p> | <p>(i) Lucas test.</p> <p>(ii) Distil with <math>K_2Cr_2O_7/H_2SO_{4(aq)}</math></p>                  | <p>(i) Solution may cloud very slowly or remains clear (hit and miss)</p> <p>(ii) If product distilled off immediately ketone odour can be detected and the solution colour changes from orange to green</p> | <p>(i) May be reactive enough to slowly form an insoluble secondary halogenoalkane: <math>R_2CHOH + HCl \rightarrow R_2CHCl + H_2O</math></p> <p>(ii) <math>R_2CHOH + [O] \Rightarrow R-CO-R + H_2O</math> or the full works!</p> <p><math>3R_2CHOH + Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3R-CO-R + 7H_2O</math></p> <p>The orange dichromate(VI) ion is reduced to the green chromium(III) ion. If the organic product is collected you could test for an aldehyde.</p> |
| <p><b>Tertiary alcohol</b> chemical test</p> <p><math>R_3COH</math>, R = alkyl or aryl.</p>   | <p>(i) Lucas test.</p> <p>(ii) Distil with <math>K_2Cr_2O_7/H_2SO_{4(aq)}</math></p>                  | <p>(i) Goes cloudy very quickly.</p> <p>(ii) No aldehyde or ketone readily formed</p>  | <p>(i) Reactive enough to immediately form an insoluble tertiary halogenoalkane <math>R_3COH + HCl \Rightarrow R_3CCl + H_2O</math></p> <p>(iii) Stable to modest oxidation.</p>  |
| <p><b>Phenols</b>(OH group is attached directly to aromatic ring)chemical test. R-OH, where R is aryl e.g. <math>C_6H_5OH</math></p>  | <p>Add a few drops of iron(III) chloride solution to little of the phenol in water</p>                | <p>Usually gives a purple colour</p>   | <p>( See also test for primary aromatic amines –use it in reverse starting with a known primary aromatic amine)</p>   |
| <p><b>Carboxylic acids</b> chemical test</p> <p><math>RCOOH</math></p>  | <p>Mix the carboxylic acid with water and add a little sodium hydrogencarbonate solid or solution</p> | <p>Fizzing, colourless gas gives white precipitate with lime water</p>   | <p><math>RCOOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2</math></p> <p>(see also salts of aliphatic carboxylic acids below)</p>  |

Qualitative Analysis Test for and identify organic functional groups

| Functional group   | Test method  | Observation  | Comments   |
|--|--|--|--|
| <b>Salts of aliphatic carboxylic acids</b> e.g. $\text{RCOO}^-\text{Na}^+$ or $(\text{RCOO}^-)_2\text{Mg}$ etc.                              | Add a little hydrochloride/ sulphuric acid to a suspected salt of an aliphatic carboxylic acid   | The solid or solution have no stronger odour, but after adding the mineral acid you should get a pungent odour of the original aliphatic acid. If it's the salt of an aromatic carboxylic acid, you get little odour and maybe white crystalline precipitate | The stronger acid, $\text{HCl}/\text{H}_2\text{SO}_4$ displaces the weaker aliphatic carboxylic acid which have strong-pungent characteristic odours e.g. ethanoic acid from an ethanoate salt ( <i>smell of acetic acid, vinegar</i> ) and butanoates release butanoic acid ( <i>butyric acid, rancid odour</i> ).  |
| <b>Acid or Acyl Chloride chemical test</b><br><br>$\text{RCOCl}$<br><br>Fumes in air forming $\text{HCl}_{(g)}$                              | (i) Add a few drops to water, test with litmus and silver nitrate solution.<br><br>(ii) Add to a little ethanol and pour the mixture into water.   | (i) Litmus turns red and a white precipitate with silver nitrate.<br><br>(ii) As above and you may detect a 'pleasant' ester odour.  | (i) $\text{RCOCl} + \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{HCl}$<br><br>The acid chloride is hydrolysed to form $\text{HCl}$ acid (chloride ions) and the original carboxylic acid.<br><br>(ii) $\text{CH}_3\text{CH}_2\text{OH} + \text{RCOCl} \rightarrow \text{RCOOCH}_2\text{CH}_3 + \text{HCl}$<br><br>an ethyl ester and hydrogen chloride are formed |
| <b>Acid Amide chemical test</b><br><br>$\text{RCONH}_2$  | Boil the suspected amide with dilute sodium hydroxide solution, see in inorganic for ammonia tests   | Ammonia evolved on boiling (no heat required to form ammonia, if it was an ammonia salt)   | $\text{RCONH}_2 + \text{NaOH} \rightarrow \text{RCOONa} + \text{NH}_3$   |
| <b>Aliphatic amines</b> (primary, where R = alkyl) chemical test $\text{R-NH}_2$<br><br>e.g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{-NH}_2$ | (i) Lower members soluble in water but a very fishy smell! test with red litmus and conc. $\text{HCl}(\text{aq})$ fumes.<br>(ii) If a suspected salt of an amine, then add sodium hydroxide solution to free the amine | (i) A fishy odour, litmus turns blue, white clouds with $\text{HCl}$ .<br><br>(ii) The above is not observed until after adding the alkali.  | (i) Unless its a liquid or solid, only the more fishy odour distinguishes it from ammonia. (ii) The reaction is e.g. $\text{R-NH}_3^+ + \text{OH}^- \rightleftharpoons \text{R-NH}_2 + \text{H}_2\text{O}$   |

Qualitative Analysis Test for and identify organic functional groups

| Aliphatic amines  | Test method  | Observation   | Comments  |
|---|--|---|---|
| (Primary, secondary and tertiary)   | (i) Sub+dil.HCl+NaNO <sub>2</sub> cool to 0 <sup>0</sup> -5 <sup>0</sup> C<br><br>(ii) Sub+dil.HCl+NaNO <sub>2</sub> cool to 0 <sup>0</sup> -5 <sup>0</sup> C+NaOH<br><br>(iii) Sub+dil.HCl+NaNO <sub>2</sub> cool to 0 <sup>0</sup> -5 <sup>0</sup> C+ β-naphthol in NaOH | Yellow ppt<br><br>Green ppt<br><br>Red azo dye  | (i) Secondary amine<br><br>(ii) Tertiary amine<br><br>(iii) primary amine   |
| <p><b>Aldehydes</b> chemical test (R-CHO, R = H, alkyl or aryl) to distinguish from ketones (R<sub>2</sub>C=O, R = alkyl or aryl) and also reducing sugars.</p> <p>Note</p> <p>(1) Test (b)(i) and (ii) can be used to distinguish aldehydes (reaction) and ketones (no reaction).</p> <p>(2) Aromatic aldehydes do NOT give a positive result with (b)(ii) Benedict's or Fehling's reagent).</p> <p>(3) Reducing sugars may also give a positive test with (b)(i)/(ii) reagent e.g. glucose (aldohexose) but not fructose? (ketohexose)?</p> | (a) Add a few drops of the suspected carbonyl compound by Brady's reagent (2,4-dinitrophenylhydrazine solution)  | (a) A yellow – orange precipitate forms with both types of carbonyl compound  | <p>The aldehyde or ketone 2,4-dinitrophenylhydrazone is formed</p> $R_2C=O + (NO_2)_2C_6H_3NHNH_2 \Rightarrow (NO_2)_2C_6H_3NHN=CR_2 + H_2O$ <p>(R = H, alkyl or aryl)</p> <p>This tells you its an aldehyde or ketone, but can't distinguish them, read on below!</p>  |
|   | (b)(i) warm a few drops of the compound with Tollens' reagent [ammoniacal silver nitrate]<br><br>(b)(ii) simmer with Fehling's or Benedict's solution [a blue complex of Cu <sup>2+</sup> <sub>(aq)</sub> ]  | (b) Only the aldehyde produces (i) A silver mirror on the side of the test tube.<br><br>(ii) A brown or brick red ppt | <p>Aldehydes are stronger reducing agents than ketones and reduce the metal ion and are oxidised in the process</p> $i.e. RCHO + [O] \rightarrow RCOOH$ <p>(i) reduction of silver(I) ion to silver metal<br/> <math display="block">RCHO + 2Ag^+ + H_2O \rightarrow RCOOH + 2Ag + 2H^+</math></p> <p>(ii) reduction of copper(II) to copper(I) i.e. the blue solution of the Cu<sup>2+</sup> complex changes to the brown/brick red colour</p> |

Qualitative Analysis Test for and identify organic functional groups

|   |  |   |   |
|---|--|---|---|
|   |  |   | <p>of insoluble copper(I) oxide <math>\text{Cu}_2\text{O}</math>.</p> $\text{RCHO} + 2\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{Cu}_2\text{O} + 4\text{H}^+$ <p>With (b)(i)/(ii) no reactions with ketones.</p>   |
| <p><b>Aromatic amines</b><br/>chemical test (where R = aryl with the amine or amino group directly attached to an aromatic ring) <math>\text{R-NH}_2</math></p> <p>e.g. <math>\text{C}_6\text{H}_5\text{-NH}_2</math></p>   | <p>(i) Dissolve the primary aromatic amine in dilute hydrochloric acid at <math>5^\circ\text{C}</math> and mix with sodium nitrite solution.</p> <p>(ii) Add a phenol dissolved in dilute sodium hydroxide.</p>  | <p>(i) It should be a clear solution with few, if any, brown fumes.</p> <p>(ii) A coloured precipitate [red – brown – yellow etc.]</p>  | <p>(i) If a primary aromatic amine, a 'stable' diazonium salt is formed. Diazonium salts from aliphatic amines decompose rapidly evolving colourless nitrogen.</p> <p>(ii) An azo dyestuff molecule is formed in a coupling reaction e.g.</p> $\text{C}_6\text{H}_5\text{-N=N-C}_6\text{H}_4\text{-OH}$   |
| <p><b>Halogenoalkanes</b><br/>(haloalkanes)chemical test <math>\text{R-X}</math> where R = alkyl, X = Cl, Br or I</p> <p>The halide is covalently bound (C-X bond), so the halogen X cannot react with the silver ion to form the ionic <math>\text{Ag}^+\text{X}^-</math> (s)precipitate until it is converted to the 'free' <math>\text{X}^-</math> ionic form. Note that aromatic halogen compounds where the X is directly attached to the ring, do NOT readily hydrolyse in this way and no <math>\text{AgX}</math> ppt. will be seen. Aromatic C-X is a stronger bond than aliphatic C-X.</p> | <p>(i) Warm a few drops of the haloalkane with aqueous ethanolic silver nitrate solution, the ethanol increases the solubility of the immiscible haloalkanes.</p> <p>(ii) Gently simmering a few drops with aqueous NaOH (may need to add ethanol to increase solubility and reaction rate). Add dilute nitric acid followed by aqueous silver nitrate solution.</p> | <p>(i) Observe colour of precipitate and the effect of ammonia solution on it (for rest of details see the (i) notes for chloride bromide and diiodide tests above in inorganic)</p> <p>(ii) see the (i) notes as above for more details.</p> | <p>i) <math>\text{AgNO}_3 + \text{RX} \rightleftharpoons \text{R-NO}_3? + \text{AgX}_{(s)}</math></p> <p>(ii) The sodium hydroxide converts the halogen atom into the ionic halide ion in a hydrolysis reaction.</p> $\text{RX}_{(aq)} + \text{NaOH}_{(aq)} \rightleftharpoons \text{ROH}_{(aq)} + \text{NaX}_{(aq)}$ <p>then</p> $\text{Ag}^+_{(aq)} + \text{X}^-_{(aq)} \rightarrow \text{AgX}_{(s)}$ <p>The addition of dilute nitric acid prevents the precipitation of other silver salts or silver oxide (e.g. <math>\text{Ag}_2\text{O}</math> forms if solution alkaline)</p> |

Qualitative Analysis Test for and identify organic functional groups

| Functional group  | Test method   | Observation  | Comments  |
|---|---|--|---|
| <p><b>Esters chemical test</b> RCOOR'</p> <p>R = H, alkyl or aryl</p> <p>R' = alkyl or aryl</p> <p>There is no simple test for an ester. Usually a colourless liquid with a pleasant 'odour'.</p> | <p>The ester can be reacted with saturated ethanolic hydroxylamine hydrochloride + 20% methanolic KOH and gently heated until boiling. Then mixture acidified with 1M HCl<sub>(aq)</sub> and FeCl<sub>3(aq)</sub> added dropwise.</p> | <p>Deep red or purple colour formed. The test depends on the formation of a hydroxamic acid R-C(=NOH)OH which forms coloured salts with Fe<sup>3+</sup><sub>(aq)</sub> ion</p> | <p>The reaction is also given by acid chlorides and acid anhydrides and phenols gives a purple colour with iron(III) chloride, so frankly, the test is not that good. This test is not to be expected .</p>   |
| <p><b>Iodoform test</b></p> <p>The formation of CHI<sub>3</sub>, triiodomethane(or old name '<i>iodoform</i>').</p>   | <p>NaOH<sub>(aq)</sub> is added to a solution of iodine in potassium iodide solution until most of the colour has gone. The organic compound is warmed with this solution</p>   | <p>A yellow solid is formed with the smell of an antiseptic CHI<sub>3</sub>, tri-iodomethane melting point 119°C</p>   | <p>This reaction is given by the alcohol ethanol CH<sub>3</sub>CH<sub>2</sub>OH and all alcohols with the 2-ol structure -CHOH-CH<sub>3</sub> and</p> <p>the aldehyde ethanal CH<sub>3</sub>CHO and all ketones with the 2-one structure R-CO-CH<sub>3</sub> (<i>'methyl ketones'</i>)</p> <p>It's a combination of halogenation and oxidation and is not a definitive test for anything, it just indicates a possible part of a molecules structure.</p> |