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Qualitative Analysis of Organic Compounds

Class-F.Y.B.Sc.

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Qualitative Analysis of Organic Compounds

INTRODUCTION:-

- Qualitative analysis is deals with the determination of the nature, type, various elements and functional group present in chemical substances.
- Quantitative analysis is deals with determination of percent composition of various elements present in the sample.
- In organic qualitative analysis the elements or compounds are identified by chemical reaction.

TYPES OF ORGANIC COMPOUNDS:-

Organic compounds can be classified under four types

1. Acids

2. Phenols

3. Bases

4. Neutral

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS:-

For qualitative analysis of given organic compound following step wise procedure must be followed.

1. Determination of Nature
2. Determination of Type
3. Preliminary Test
4. Determination of Physical constant
5. Determination of elements
6. Functional group tests
7. To study the reaction

SYSTEMATIC ANALYSIS OF BINARY MIXTURE

1. Determination of Nature:-

The natures of binary mixture of organic compound are of three types.

(a) Solid-Solid, (b) Solid-Liquid and (c) Liquid-Liquid.

If the organic mixture containing liquid, the nature can be determine by following method.

Test	Observation	Inference
Take 2 drops of mixture on clean watch glass and blow air by mouth	If solid remains on watch glass	Nature is **Solid-Liquid**
	If Liquid remains on watch glass	Nature is **Liquid-Liquid**

Conclusion: The Nature of organic mixture is ……..

[Solid-Solid / Solid-Liquid / Liquid-Liquid]

2. **Determination of Type:-**

If the nature of binary mixture is solid-solid mixture it is necessary to find out first type then separate in to individual component using chemical method.

If the nature of binary mixture is solid-liquid or liquid-liquid the low boiling components is separated first by distillation and the type of individual component is then determined.

The types of organic mixtures are divided in following groups.

Group (A) Acid-Acid, Acid-Phenol, Acid-Base and Acid-Neutral

Group (B) Phenol -Phenol, Phenol -Base and Phenol –Neutral

Group (C) Base -Base and Base –Neutral

Group (D) Neutral-Neutral

Type determination for Solid-Solid mixture:-

(For Solid-Solid binary mixture the compounds are water insoluble)

Test	Observation	Inference
i) 10mg substance + 10 drops of 10% NaHCO3 shake well and filter cool the filtrate and acidify with conc. HCl	Partially soluble with Effervescence of CO2 1) Precipitate is obtained 2) No ppt obtained	Acid may present 1) Acid Present and confirmed 2) Acid is absent
ii) Residue + 10 drops of 10% NaOH shake well and filter cool the filtrate and acidify with conc. HCl	Partially or completely soluble 1) Precipitate or oily drops is Obtained 2) No ppt or oily drops	Phenol may present 1) Phenol present and Confirmed 2) Phenol is absent
iii) Residue + 10 drops of 1:1 HCl shake well and filter cool the filtrate and add 2N or 10% NaOH	Partially or completely soluble 1) Precipitate or oily drops is obtained 2) No ppt or oily drops	Base may present 1) Base present and confirmed 2) Base is absent
iv) if only one type is detected in above tests	then	Neutral compound is present

Conclusion: The type of organic mixture is ……

A) Acid-Phenol, Acid-Base, Acid-Neutral

B) Phenol-Base, Phenol-Neutral

C) Base-Neutral

(Hint: for solid-solid mixture same type should not be given)

Reactions:-

1) Acids:-

$$R\text{-}COOH + NaHCO_3 \rightarrow R\text{-}COONa + H_2O + CO_2\uparrow$$

Acid Base water soluble salt

$$R\text{-}COONa + \text{Conc. } HCl \rightarrow R\text{-}COOH\downarrow + NaCl$$

Salt Acid reappears

2) Phenols:-

$$Ar\text{-}OH + NaOH \rightarrow Ar\text{-}ONa + H_2O$$

Phenol Base water soluble salt

$$Ar\text{-}ONa + \text{Conc. } HCl \rightarrow Ar\text{-}OH\downarrow + NaCl$$

Salt Phenol reappears

3) Bases:-

$R\text{-}NH_2 + HCl \rightarrow R\text{-}NH_3Cl$

Base Acid water soluble quaternary salt

$R\text{-}NH_3Cl + NaOH \rightarrow R\text{-}NH_2\downarrow + NaCl$

Salt Base reappears

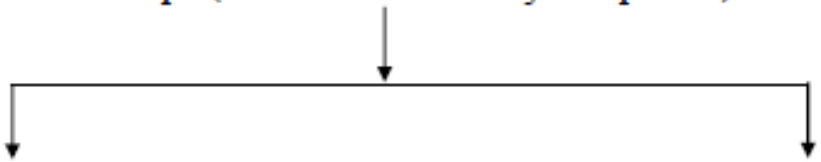
Separation of the mixture in to two components

(A) Separation of solid-solid mixture

The separation of Solid-Solid mixture is depends on the type of organic mixture as determined above.

Separation of group (A) Acid-Phenol, Acid-Base, Acid-Neutral

Take total mixture in a clean beaker and 10% $NaHCO_3$ is added in sufficient amount and stir the mixture till effervescence stops (Add more $NaHCO_3$ if required) then filter it.



Residue

(Wash with little NaHCO3

and then cold water)

it is either Phenol, Base or Neutral

Filtrate

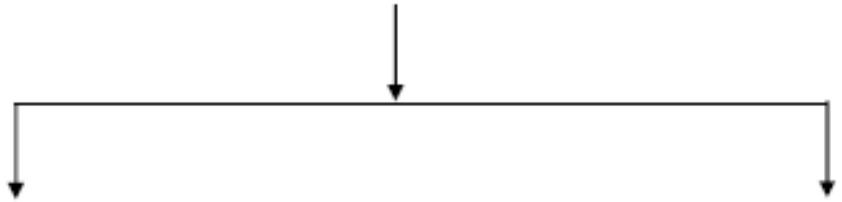
(It contains sodium salt of Acid)

Cool the filtrate and acidify with conc. HCl (till acidic to litmus), filter the precipitate, wash with little cold water and dry it.

Recrystalise two components separately using suitable solvents

Separation of group (B) Phenol-Base, Phenol-Neutral

Take total mixture of Phenol-Base, Phenol-Neutral in a clean beaker and 10% NaOH is added in sufficient amount and stir the mixture well (add more NaOH if required) then filter it.



Residue

(Wash with little NaOH and then cold water) it is either Base or Neutral

Filtrate

(It contains sodium salt of **phenol**) Cool the filtrate and acidify with conc. HCl (till acidic to litmus), filter the precipitate, wash with little cold water and dry it.

Recrystalise two components separately using suitable solvents

Separation of group (C) Base-Neutral

Take total mixture of Base-Neutral in a clean beaker and dil. HCl in sufficient amount, stir the mixture well (Add more dil HCl if required) then filter it.

Residue

(Wash with little 1:1 HCl and then cold water) it is Neutral compound

Filtrate

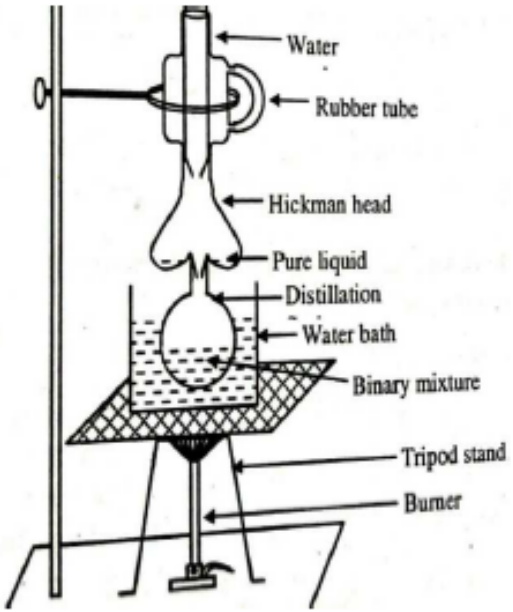
(It contains quaternary salt of **amine**) cool the filtrate and add 2N or 10% NaOH, filter the precipitate, wash with little cold water and dry it.

Recrystalise two components separately using suitable solvents

(B) Separation for Solid-Liquid & Liquid –Liquid mixture

The solid-liquid and liquid-liquid mixtures are separated by simple distillation using Hickman head apparatus.

1) Take total mixture in to a 25ml clean and dry R.B. flask.
2) A small piece of porcelain is added to avoid the bumping.
3) Attach a Hickman head to R.B. flask fitted with water condenser.
4) Keep the round bottom flask in to water bath and fit the total assembly to a stand as shown in figure.
5) Heat the flask on boiling water bath, the mixture boils and the vapours go up in the condenser which after cooling get collected in Hickman head in the form of pure liquid.
6) When maximum liquid is collected in Hickman head stop the heating, keep the burner off.
7) Now loosen the clamp and first remove water condenser. Take out the Hickman head and R.B. flask together from water bath and slowly disconnect.



8) With the help of rubber teat pipette take out volatile liquid in small clean test tube.

9) Repeat the same procedure and collect maximum volatile liquid in the Hickman head and collect in test tube and kept in ice bath to avoid loss of volatile liquid.

10) After sufficient amount of liquid collected in test tube detach the R.B. flask and pour the content on clean watch glass.

11) The solid will remain present on watch glass.

12) If liquid-liquid mixture is present, remove the Hickman head and condenser and heat it again on boiling water bath to remove traces of volatile component.

12) Find out type for each component separately as per procedure given below.

Type determination for Solid / Liquid compound:-

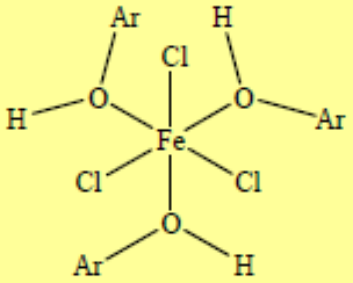
For type determination organic substances are mainly classified in to two groups on the basis of their solubility in cold water.

10mg substance + cold water and shake well	Compound is completely soluble/ miscible	(A) Water soluble/ Miscible compound present
	Compound is completely insoluble/ immiscible	(A) Water insoluble/ immiscible compound present

[A] Type determination for water soluble (Miscible) substances.

Test	Observation	Inference
i) Add few crystals or 2 drops of liquid on wet litmus papers.	a) Blue litmus turns red	a) Acid or Phenol Present
	b) Red litmus turns blue	b) Base is present
	c) No change on either litmus papers	c) Neutral substance present
Separation of Acid / Phenol (If present)		
ii) 10mg substance + 10 drops of 10% $NaHCO_3$	a) effervescence of CO_2	Acid is present
	b) No effervescence of CO_2	Phenol is present
$R\text{-}COOH + NaHCO_3 \rightarrow R\text{-}COONa + H_2O + CO_2\uparrow$		
iii) 10mg substance + 2 drops of $FeCl_3$	Blue coloration	Phenol is present

$$3Ar\text{-}OH + FeCl_3 \longrightarrow$$



[B] Type determination for water insoluble (immiscible) substances.

Test	Observation	Inference
i) 10mg substance + 10 drops of 10% $NaHCO_3$	Soluble with Effervescence of CO_2 and reprecipitated by conc. HCl	Acid is Present and confirmed
ii) 10mg substance + 10 drops of 10% NaOH shake	Completely Soluble and reprecipitated by conc. HCl	Phenol is Present and confirmed
iii) 10mg substance + 10 drops of 1:1 HCl shake	Completely Soluble and reprecipitated with 10% NaOH	Base is present and confirmed
iv) if all test i), ii) and iii) are negative	Then	Substance is Neutral

Note: Once a particular type is determined do not take further test.

Conclusion: The type of organic solid / liquid is ……..

Reactions: please refer reactions on slide no. 8

Purification of organic compounds

1. Crystallization:

- After separation of solid-solid or solid-liquid mixture it is essential to recrystalise solid component separately.
- It is assume that impurities present in comparatively small portion even less than 5% in the substances.
- The technique crystallization is used remove the impurities from the compound.
- The purification of solids by crystallization is based upon differences in their solubility in a given solvent or mixture of solvents.
- In simplest form crystallization process consist of (a) dissolving impure substance in some suitable solvent at or near boiling point (b) filtering the hot solution from insoluble particle (c) allowing cool the solution of dissolved substance to crystallize out and (d) separating the crystals from mother liquor.

The following condition should be full fill while choosing solvent for crystallization.

1) Substance must be insoluble at room temperature.

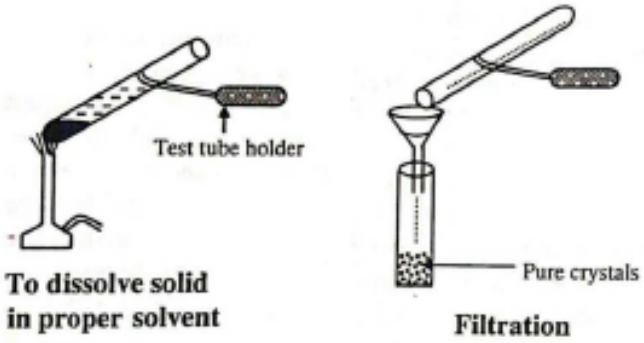
2) Substance should be completely soluble at hot condition.

3) Substance should be reappears after cooling.

The solvent used for recrystallisation must be easily available, cheap and should not react with organic compound. The common solvents used for crystallization are

A) Water, B) ethyl alcohol and C) water + ethyl alcohol mixture.

Procedure for crystallization:



1) Take about 0.5 gm solid substance in test tube fitted with test tube holder.

2) Add about 2-3 ml water / ethyl alcohol / water + alcohol (depends on solubility) in the test tube.

3) A piece of porcelain is added to avoid bumping of solvent.

4) Heat the content on low flame (on water bath for compounds soluble in ethyl alcohol / water + alcohol) till a clear solution is obtained (add more water if compound does not dissolves).

5) Rapidly filter the hot solution through dry fluted filter paper in to another test tube.

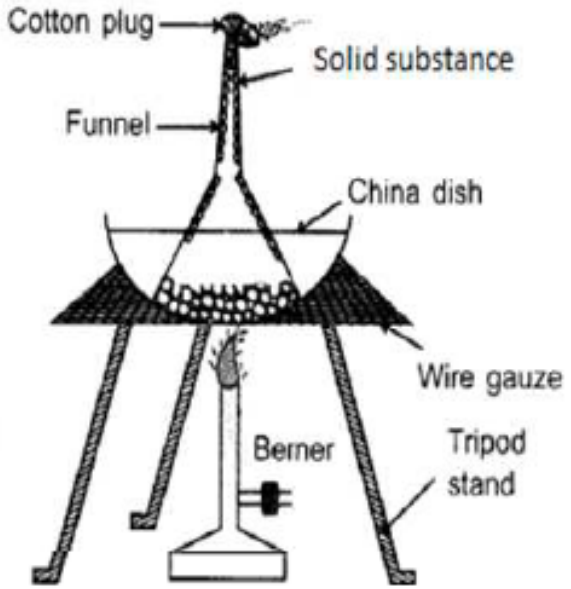
6) Allow the solution to cool at room temperature and then in ice.

7) Crystals are slowly developed after cooling (After cooling if crystals are not obtained, concentrate the filtrate on wire gauge and then cool it again).

8) Filter these crystals on Buchner funnel, wash with distilled water and dry at suitable temperature. Find its melting point.

2. Sublimation

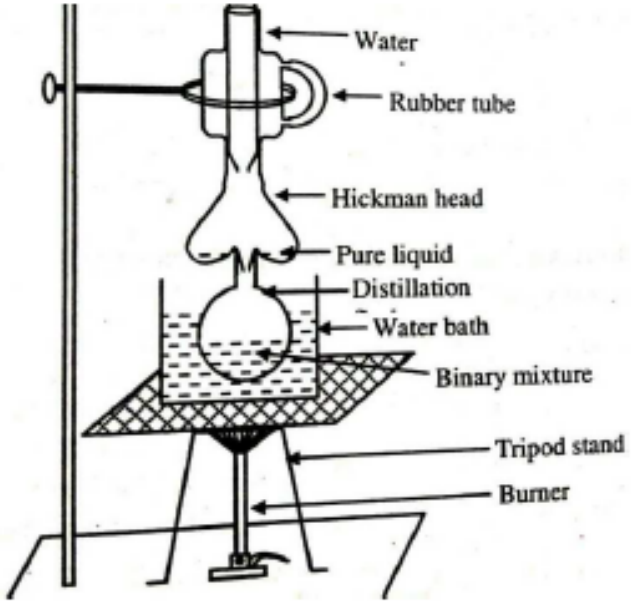
The direct conversion from solid state to vapor without the intermediate formation of liquid state is called sublimation. The number of compounds which can be purify by sublimation method under normal pressure. (eg. Naphthalene, Anthracene, Benzoic Acid, Camphor, Quinones etc.)



Procedure: Take the given compound in porcelain evaporating dish which kept on sand bath, supported on tripod stand. The dish is covered with filter paper which has been perforated with number of small holes. A funnel of same size is placed on filter paper with stem on up side. The stem of funnel is fitted with small cotton to avoid loss of vapors. Heat the evaporating dish on low flame or on sand bath. The solid is converted in to vapor and passes through hole and deposits pure crystals on the inner side of the funnel. Remove the flame and cool the evaporating dish. Remove the funnel and collect the crystals on glaze paper. Repeat the same procedure till the sufficient amount of substance collected on glaze paper. Find out the melting point of crystalline substance.

3. Distillation

After separation of liquid-liquid mixture, it is essential to purify the separated liquids. The volatile liquid collected in Hickman head need not necessary to purify, but the non volatile liquids are purified by following method.



Procedure:

1) Take about 1 ml non volatile liquid in 10ml round distillation flask.
2) A small piece of porcelain is added to avoid the bumping.
3) Attach a Hickman head to round distillation flask fitted with water condenser.
4) Keep the round bottom flask on wire gauge and slowly heat the distillation flask.
5) As the liquid boils the vapours go up in the condenser which after cooling get collected in Hickman head in the form of pure liquid.
6) When maximum liquid is collected in Hickman head stop the heating, keep the burner off. Let the whole assembly to cooled.
7) Now loosen the clamp and first remove water condenser. With the help of rubber teat pipette take out non volatile liquid in small clean test tube.
8) Repeat the same procedure to collect maximum non volatile liquid in Hickman head and collect in test tube.
9) Find out the Belting point of distilled liquid.

Individual Analysis of organic compound:-

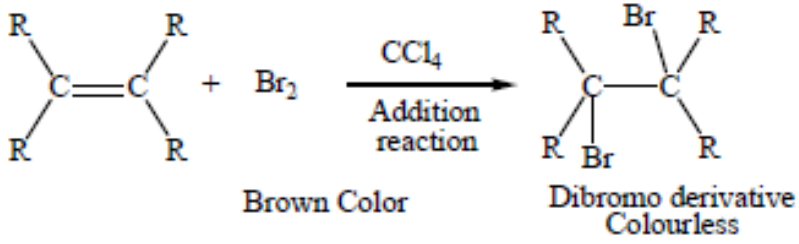
3. Preliminary Test:-

Test	Observation	Inference
a) Colour	**A) Solid**	
	i) Colourless, crystalline white solids	Benzoic, Cinnamic, Salicylic, Oxalic, Phthalic acids, Naphthalene, Urea, Thiourea etc. may be presnet
	ii) Coloured solid	
	a) Yellow	Nitro Amines, Nitro Phenols, m-dinitrobenzene etc. are present
	b) Orange	O-nitroaniline
	c) Brown	B-Naphthol
	d) Pinkish	P-toluidine, Resorcinol
	B) Liquids	
	i) Colourless liquid	Acetone, Chlorobenzene, Methyl Acetetate, Acetophenone Chloroform, etc. are present
	ii) Yellow Liquid	Aniline, Nitrobenzene, Dimethyl Aniline etc. present

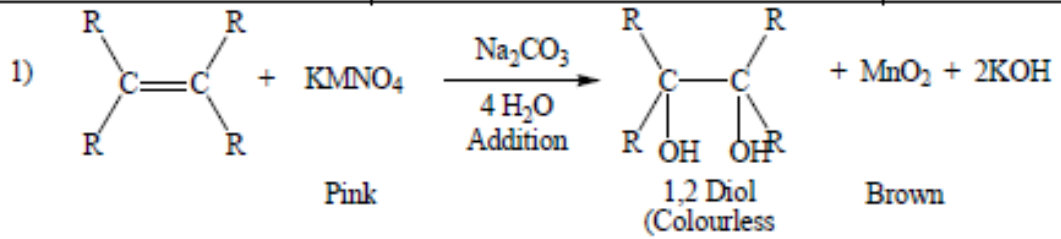
b) Odour	a) pleasant odour b) Phenolic odour	Ketones, Alcohols, Chloroform etc. α- Naphthol, β- Naphthol, Nitrophenol etc.
	c) Fishy smell d) Odour of bitter almond e) Odour of naphthol ball f) Irritating odour g) odourless	Aniline, Dimethylaniline, P-Toluidine etc. Nitrobenzene Napthalene Acetic acid Glucose, fructose, Urea, Thiourea, Acetanilide acids etc.
c) Action of Na_2CO_3 10mg substance + 10 drops of 10% Na_2CO_3	i) Effervescence of CO_2 ii) No effervescence of CO_2	i) Acid is Present ii) Acid is absent
$2R\text{-}COOH + Na_2CO_3 \rightarrow 2R\text{-}COONa + CO_2 \uparrow + H_2O$		
d) Action of 10% NaOH 10mg substance + 10 drops of 10% NaOH shake	i) Yellow color changes to orange red ii) No orange red colour iii) Completely soluble	i) Nitrophenol is present ii) Nitrophenol is absent iii) Acid or phenol is present

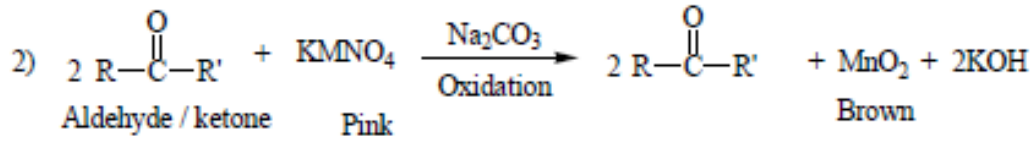
e) Determination of saturation / Unsaturation:

Test	Observation	Inference
i) Br_2/ CCl_4 test 10 mg substance + CCl_4+ 2-3 drops of Br_2 in CCl_4	i) Brown color of Br_2 disappears without ppt ii) No decolourisation iii) Decolourisation with ppt	i) Unsaturated substance is present ii) Saturated substance is present iii) Reactive aromatic and saturated substance is present



ii) Baeyer / $KMnO_4$ Test 10 mg substance + 1 ml 10% Na_2CO_3 + 2-3 drops of very dilute $KMnO_4$ shake well	i) Pink colour of $KMnO_4$ disappear ii) No decolourisation	i) Unsaturated or easily oxidisable substance is present ii) Saturated substance is present





f) Determination of Aliphatic / Aromatic nature:

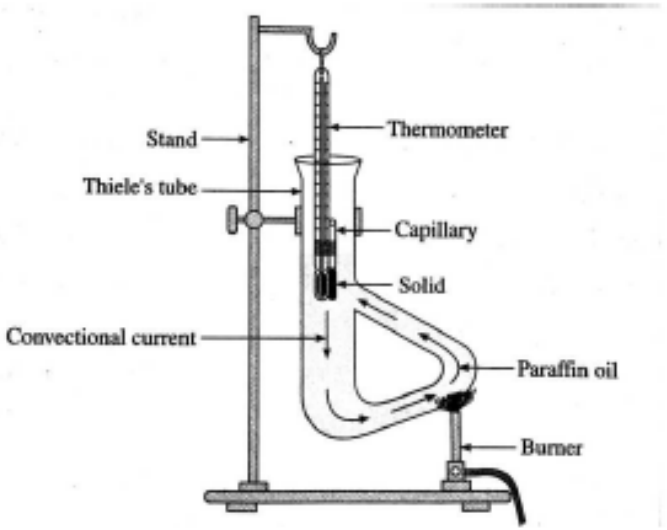
Test	Observation	Inference
Take 10 mg substance on clean copper gauze and heat on blue flame	i) Sooty flame ii) No sooty flame iii) Green flame	i) Aromatic substance is present ii) Aliphatic substance is present iii) Halogen is presnet

Conclusion: Given organic substance is

1) Acidic / Phenolic / Basic / Neutral
2) Saturated / Unsaturated
3) Aliphatic / Aromatic

4. Determination of Physical constant:-

Melting point: it is define as the temperature at which solid in condition of equilibrium passes in to liquid state.



Procedure for determining melting point:

1) Fill the fine capillary whose one end is sealed, with powdered sample by gently tapping the capillary on the table.

2. Repeat this procedure till sufficient quantity is present in the capillary.

3. Attach the capillary to the thermometer with the help of a thread such that the lower end of the capillary and the thermometer bulb are at the same level.

4. Insert the thermometer in the Thiele's tube such that only the thermometer bulb is dipped inside the paraffin oil. (as shown in figure-3.5)

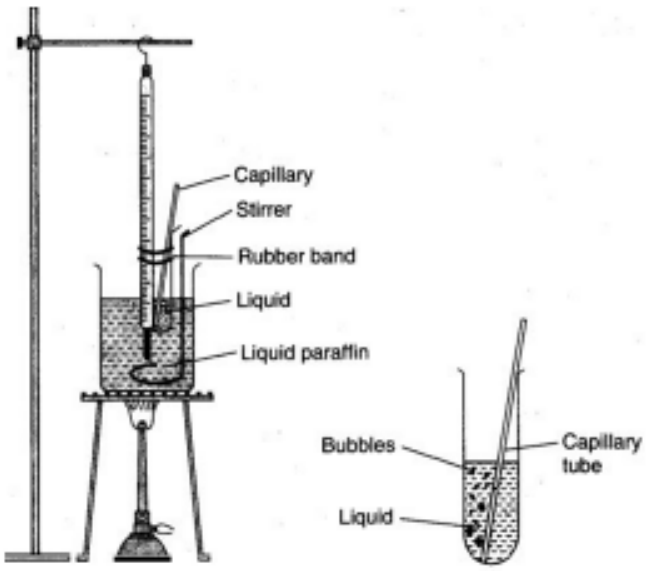
5. Heat the lower side arm of the Thiele's tube with the help of the burner (blue flame) slowly back and forth. If the heating is too fast remove the burner for few seconds, and then resume heating.

6. The rate of heating should be low near the melting point (about 1°C/min).

7. Record the exact melting point of the compound.

Boiling point:

It is define as the temperature at which the vapour pressure becomes equal to atmospheric pressure.



Procedure for determining boiling point:

1 Take a sodium fusion tube and add few drops of the liquid sample into it.

2. Seal one end of the capillary and insert it in the fusion tube with its open end dipped in the liquid.

3. Tie this assembly to the thermometer with the help of a thread such that the lower end of the sodium fusion tube and the thermometer bulb are at the same level.

4. Insert the thermometer in the Thiele's tube such that only the thermometer bulb is dipped inside the paraffin oil.

5. Heat the lower side arm of the Thiele's tube with the help of the burner (blue flame) slowly back and forth. If the heating is too fast remove the burner for few seconds, and then resume heating.

6. Stop heating and record the temperature when vigorous, continuous bubbling starts (If the bubbling is not continuous then continue heating). Continue looking at the fusion tube till the last bubble comes out. At this point the liquid rises in the capillary. Record this temperature as the boiling point

7. Repeat this procedure till constant boiling point is recorded.

5. Determination of Elements:-

The organic substances also contain N, S and Halogens as extra elements. It is often valuable to determine the existence of other element N, S and Halogens.

Detection of Carbon and Hydrogen:

The presence of carbon and hydrogen is directly determined by heating a small quantity (0.1 g) of pure and dry compound with excess of cupric oxide or lead chromate in a dry hard glass tube fitted with cork and delivery tube immersed in lime water. The hard glass tube is heated strongly. The carbon present in the organic compound is oxidized to carbon dioxide and hydrogen to water. The oxygen required for oxidation is taken from cupric oxide or lead chromate. The formed carbon dioxide turns lime water milky which is indicating the presence of carbon in the organic compound. The appearance of small drops of water on the cooler part of the test tube indicates the presence of hydrogen in the organic compound

Reactions:

(i) $C + 2\,CuO \xrightarrow{\Delta} 2\,Cu + CO_2,$

(ii) $H_2 + 2\,CuO \xrightarrow{\Delta} 2\,Cu + H_20$

Detection of Nitrogen, Sulphur and Halogen

The organic compounds are covalent compounds and are insoluble in water. These compounds are converted in to ionic form, which ionize in water and appear in easier form to detect the Nitrogen, Sulphur and Halogen in the organic compound. To obtain elements Nitrogen, Sulphur and Halogen in the ionic form, the organic compound is fused with sodium metal, so that it forms sodium cyanid, sodium sulphide and sodium halide respectively.

Lassaigene's Test (Sodium fusion test):

A freshly cut small piece of sodium metal is melted in a hard glass ignition tube (or sodium fusion tube) small amount of the substance is then added to the molten metal and the mass is gradually heated to redness. (If vigorous reaction occurs, remove from flame to allow the reaction to stop). The red hot tube is plunged into 10 distilled water (do not use tap water) taken in a porcelain dish. Similarly one more tube ignited and plunged in to above water. Then solution is concentrated by boiling and filtered. The filtrate is then used for detection of Nitrogen, Sulphur and Halogen.

The Organic Compounds are not fused with potassium because it is too reactive and dangerous and the reaction cannot be controlled. Similarly the organic compounds not fused with magnesium or calcium metals as they are much less reactive and hence only sodium metal is used for fusion with organic substances.

Test	Observation	Inference
1) Detection of Nitrogen		
To 1 ml portion of sodium fusion extract freshly prepared saturated solution of $FeSO_4$ + drop of $FeCl_3$ solution + drop of NaOH The mixture is then boiled for few minutes, cooled in Ice and acidified with concentrated HCl or dilute H_2SO_4	Blue or Green colouration	Nitrogen is present

$$Na + C + N \rightleftharpoons NaCN \text{ (Sodium Fusion Extract)}$$

$$FeSO_4 + 2\,NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$Fe(OH)_2 + 6\,NaCN \longrightarrow \underset{\text{Sodium hexacyano ferrate (II)}}{Na_4Fe(CN)_6} + 2\,NaOH$$

OR $$3Na_4Fe(CN)_6 + 2\,Fe_2(SO_4)_3 \longrightarrow \underset{\text{Ferric Ferrocyanide}}{Fe_4[Fe(CN)_6]_3} + 6Na_2SO_4$$

2) Detection of Sulphur		
i) Sodium Nitro-prusside Test To 1 ml portion of sodium fusion extract freshly prepared solution of sodium nitro-prusside is added + 2 drops of dilute NaOH is added.	Intense purple colour	Sulphur is present
ii) Lead Acetate 1 ml of the sodium fusion extract is acidified with CH_3COOH + few drops of lead acetate solution is added	A black ppt of PbS	Sulphur is present

i) Sodium Nitro-prusside Test

$$2\,Na + S \rightleftharpoons Na_2S$$

$$Na_2S + \underset{\text{Sodium Nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Purple colour}}{Na_4[Fe(CN)_5NOS}$$

ii) Lead Acetate

$$Na_2S + Pb(CH_3COO)_2 \longrightarrow PbS\downarrow + 2\,CH_3COONa$$

3) Detection of Nitrogen and Sulphur together		
1 ml of sodium fusion extract is neutralized by dil. HCl and few drops of $FeCl_3$ solution are added	Deep red colour discharged by $HgCl_2$	Nitrogen and Sulphur present together

$$Na + C + N + S \rightleftharpoons NaCNS$$

$$3\ NaCNS + FeCl_3 \longrightarrow \underset{\text{Deep Red}}{Fe(CNS)_3} + 3\ NaCl$$

4) Detection of Halogens		
i) To 1 ml portion of sodium fusion extract, 2 ml concentrated nitric acid is added and the solution is boiled to remove cyanide (if the original compound contains nitrogen). Then few drops of silver nitrate solution is added.	A curdy white or yellow precipitate	Halogen is present

$$Na + X \rightleftharpoons NaX$$

$$NaX + AgNO_3 \longrightarrow AgX\downarrow + NaNO_3$$

ii) Separation of Halogen 1 ml portion of sodium fusion extract is treated with chloroform and chlorine water (freshly prepared) and shaken well	(a) If chloroform layer becomes violet (b) If chloroform layer becomes Brown (C) If chloroform layer becomes colourless	(a) Iodide is present (b) Bromine is present (C) Chlorine is present

$$NaCl + Cl_2 \xrightarrow{CHCl_3} NaCl + Cl_2 \quad \text{(Colourless)}$$

$$NaBr + Cl_2 \xrightarrow{CHCl_3} NaCl + Br_2 \quad \text{(Brown)}$$

$$NaI + Cl_2 \xrightarrow{CHCl_3} NaCl + I_2 \quad \text{(Violet)}$$

Conclusion:

Given organic compound containing ……elements

According to elemental analysis the organic substance can be classified in to four groups as,

1) Substance containing C, H (O) elements,
2) Substance containing C, H (O) and N elements,
3) Substance containing C, H (O), N and S elements,
4) Substance containing C, H (O) and X (halogen) elements.

Detection of Phosphorus: The presence of phosphorus in an organic compound can be detected by fusing the compound with a mixture of sodium carbonate and potassium nitrate or with sodium peroxide. During this the phosphorus from the organic compound is converted into a phosphate. The phosphate can be tested as usual by nitric acid and ammonium molybdate solutions, which gives a canary yellow precipitate.

Test	Observation	Inference
10mg substance + $Na2CO_3$ + KNO_3(Or H_2O_2) fuse the mixture + HNO_3 + $(NH_4)_2MoO_4$	Canary yellow precipitate	Phosphorus is present

$$P + Na_2CO_3 + KNO_3 \longrightarrow PO_4^{3-}$$

$$PO_4^{3-} + HNO_3 \longrightarrow H_3PO_4$$

$$H_3PO_4 + 21\ HNO_3 + 12\ (NH_4)_2MoO_4 \longrightarrow (NH_4)_3(PMo_{12}O_{40})\downarrow + 21\ NH_4NO_3 + 12\ H_2O$$

Canary yellow ppt

6. Functional Group Tests:-

The atom or group of atom that defines the structure of particular family of organic compound and at the same time determines their properties is called functional group. It is also possible that a compound contains two or more identical or different functional group which are said to be poly-functional groups. Some of the important functional groups and their characteristic tests and reactions for their identification are discussed below.

1) Substance containing C, H (O) elements

A) ACIDS

Test	Observation	Inference
1) $NaHCO_3$ Test 10mg substance + dropwise 10% $NaHCO_3$	Effervescence of CO_2 Reprecipitated with Conc. HCl	Carboxylic group (-COOH) Present and confirmed

$$R\text{-}COOH + NaHCO_3 \rightarrow R\text{-}COONa + H_2O + CO_2\uparrow$$

$$R\text{-}COONa + \text{Conc. } HCl \rightarrow R\text{-}COOH\downarrow + NaCl$$

2) Esterification Test 10mg substance in dry test tube + 10 drops of ethyl alcohol + 2 drops of Conc. H_2SO_4 warm gently	Fruity smell of ester	Carboxylic group (-COOH) Present and confirmed
$R\text{-}COOH + C_2H_5OH \xrightleftharpoons{H_2SO_4} R\text{-}COO\,C_2H_5 + H_2O$		
3) $AgNO_3$ Test 10mg substance in dry test tube + 10 drops of ethyl alcohol shake well to get clear solution + 2 drops of alcoholic $AgNO_3$ solution	White precipitate of silver salt of Carboxylic acid	Carboxylic group (-COOH) Present and confirmed
$R\text{-}COOH + AgNO_3 \xrightarrow{Alcohol} R\text{-}COOAg\downarrow + HNO_3$		

B) PHENOLS

Test	Observation	Inference
1) NaOH Test 10mg substance + 10 drops of 10% NaOH shake well	Completely Soluble and reprecipitated by conc. HCl	Phenol is Present and confirmed

$$Ar\text{-}OH + NaOH \rightarrow Ar\text{-}ONa + H_2O$$

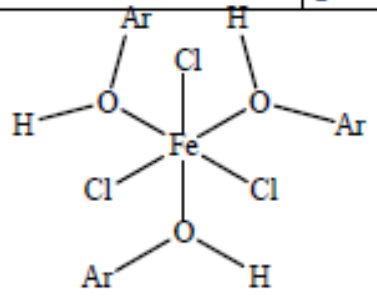
Phenol Base ater soluble salt

$$Ar\text{-}ONa + \text{Conc. } HCl \rightarrow Ar\text{-}OH\downarrow + NaCl$$

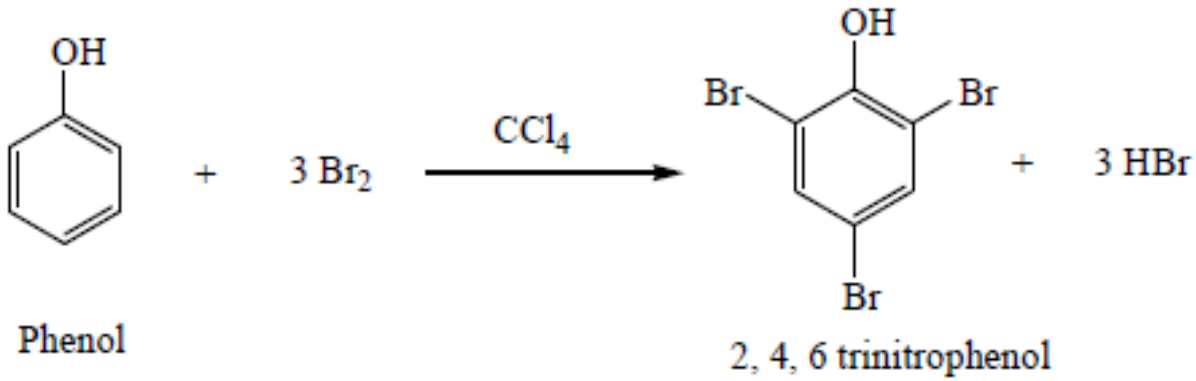
Salt Phenol reappears

2) $FeCl_3$ Test iii) 10mg substance + 10 drops of ethyl alcohol + 2 drops of $FeCl_3$	a) Blue/ Green / Violet coloration b) No Blue/ Green / Violet coloration	a) Simple Phenol is present b) Nitrophenols are present

$$3Ar\text{-}OH + FeCl_3 \xrightarrow{\text{Alcohol}}$$



3) Br_2 in CCl_4 Test		
10mg Substance + 10 drops of CCl_4 + 2-3 drops of Br_2 in CCl_4	Brown color of bromine disappear	Phenol is Present and confirmed



Phenol

2, 4, 6 trinitrophenol

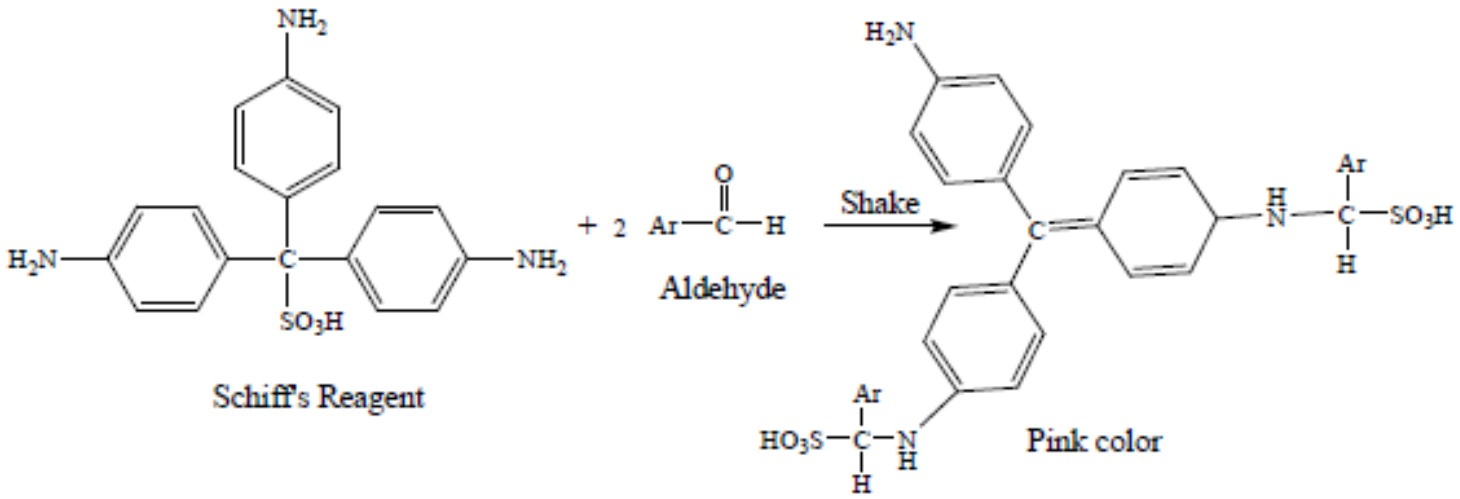
C) NEUTRALS

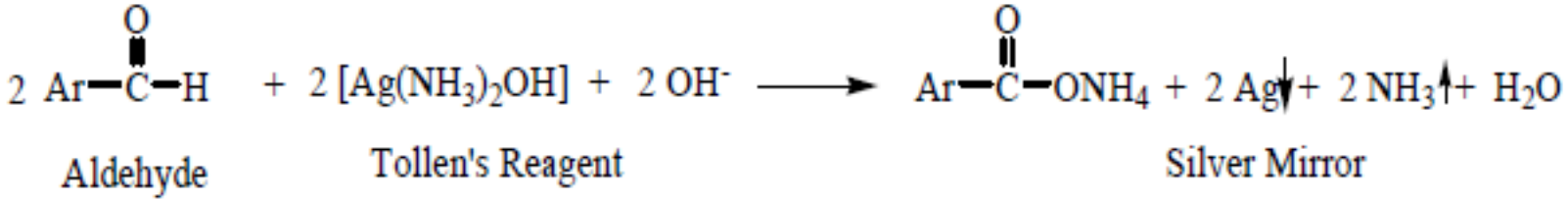
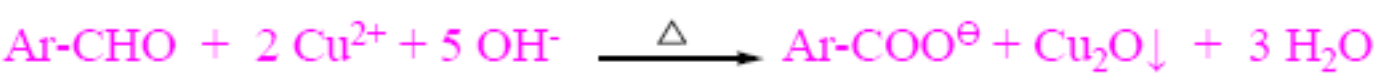
Neutrals containing C,H (O) elements are classified in to six groups

1) Aldehyde 2) Ketones 3) Carbohydrates 4) Esters 5) Alcohols and 6) Hydrocarbons.

1) Aldehyde (Liquids)

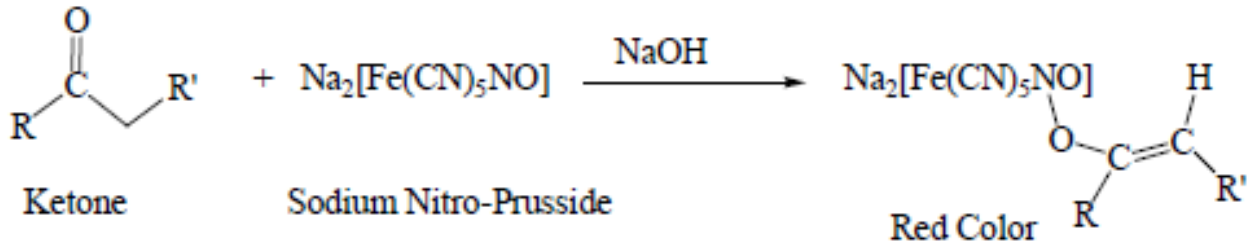
Test	Observation	Inference
a) Caro's Test 4 drops of Schiff's reagent in test tube + 4 drops of substance shake well and keep it for some times.	Pink color slowly develop at the bottom of test tube	Aromatic aldehyde (Ar-CHO) group is present



b) Tollen's Test 1 ml Tollen's reagent + 4 drops of substance shake well and warm carefully	Silver mirror is deposited on inner wall test tube	Aldehyde (Ar-CHO) group is present
Tollen's reagent- take 4 drops of $AgNO_3$ solution add dil NaOH, a white precipitate forms and the add NH_4OH till precipitate dissolves.		
		
c) Fehling Solution Test/ Benedicts Test 10 mg Substance + 10 drops of water + 10 drops of Fehling's solution and warm	Red ppt of cupric oxide obtained	Aldehyde (Ar-CHO) group is present
		

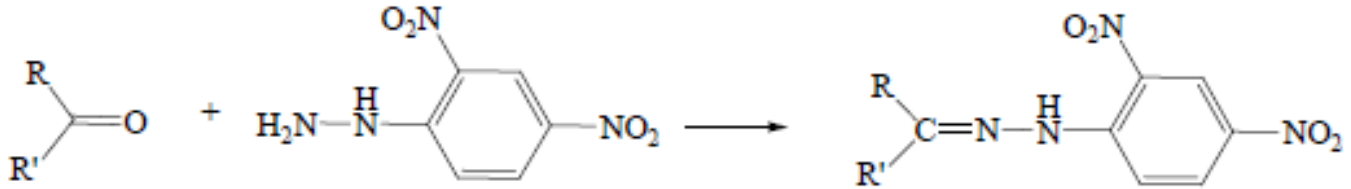
2) Ketones (Solid/Liquid)

1) Sodium Nitro-prusside Test 10mg Substance + 4 drops of Sodium Nitro-prusside + 4 drops NaOH shake well	Red color	Ketone (R-CO-R') is present



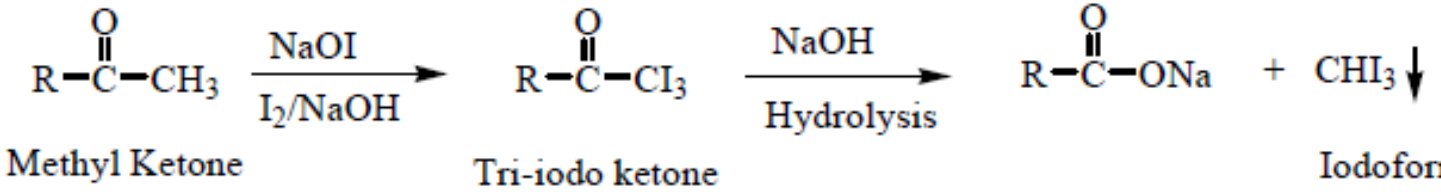
Ketone — Sodium Nitro-Prusside — Red Color

2) 2:4 DNP Test 10 mg substance + 10 drops of ethyl alcohol + 10 drops 2:4 DNP reagent Shake well	Yellow or Red ppt	Ketone (R-CO-R') is present



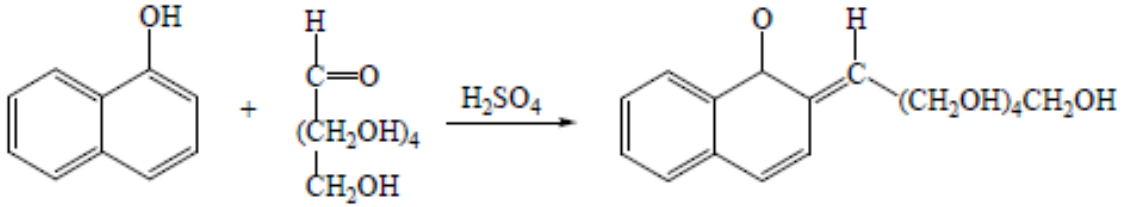
Ketone — 2: 4 DNP reagent — 2: 4 DNP derivative

3) Iodoform Test (given by only Methyl Ketone) 10 mg substance + 10 drops of NaOH + 3 ml dil I_2 solution and then warm	Yellow ppt of Iodoform obtained	Methyl ketone (CH_3-CO-R') Present



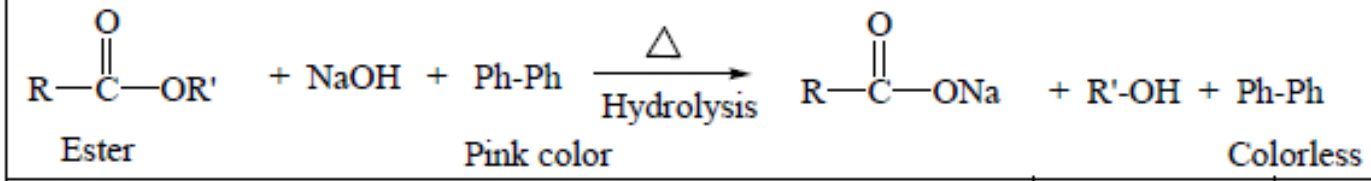
3) Carbohydrates (Water soluble Solids)

Test	Observation	Inference
Molisch's Test 10mg substance + 4 drops of 10% α – Naphthol in alcohol shake well and add conc. H_2SO_4 from inner side of test tube	Reddish violet coloration at the junction of two layers	Carbohydrate is ($C_nH_{2n}O_n$)present

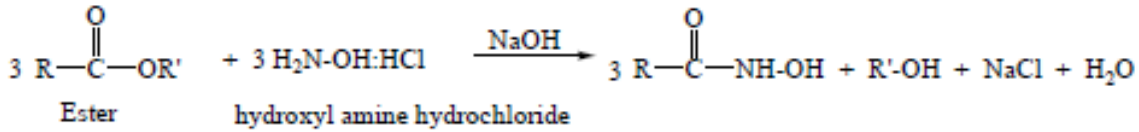


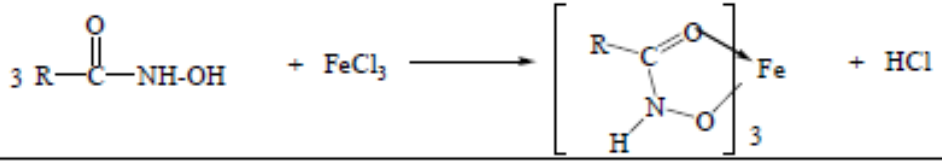
4) Esters (Water immiscible liquids)

Test	Observation	Inference
1) Phenolphthalein Test 5 drops substance + 1 ml water + 2 drops of Phenolphthalein indicator + very dilute NaOH drop by drop till pink color persists, then heat the solution	Pink color slowly disappears	Ester group (R-COOR') present



Test	Observation	Inference
2) Hydroxamic Test 2 drops substance + 4 drops of hydroxyl amine hydrochloride in alcohol + NaOH till alkaline + 10 drops of dil HCl + 1-2 drops of 5% $FeCl_3$ solution and observe the color	Blue / Violet / Red / Orange color	Ester group (R-COOR') present





5) Alcohols (R-OH)

Test	Observation	Inference
a) Dry Sodium Metal Test 10 drops of substance in dry test tube + a small piece of dry sodium metal and close the mouth of test tube with thumb	Evolution of hydrogen gas	Alcoholic (R-OH) group present
$2\ R\text{-}OH + 2\ Na \longrightarrow 2\ R\text{-}ONa + H_2\uparrow$		
b) Lucas Reagent Test 10 drops of Lucas reagent (Zinc Chloride + Conc. HCl) + 10 drops substance and shake well	a) Cloudy Ppt immediately formed b) Cloudy Ppt formed after 5 min. c) No cloudy Ppt formrd at all	a) Tertiary alcohol Present b) Secondary alcohol Present c) Primary alcohol Present

6) Hydrocarbons:

i) If all above tests are absent ⟶ Hydrocarbon is Present

ii) Confirm the hydrocarbon by its physical constant (M.P. /B. P.)

2) Substance containing C, H (O) and N elements

A) ACIDS (Nitro Acids)

Test	Observation	Inference
1) $NaHCO_3$ Test 10mg substance + dropwise 10% $NaHCO_3$	Effervescence of CO_2 Reprecipitated with Conc. HCl	Carboxylic group (-COOH) Present and confirmed
R-COOH + $NaHCO_3$ → R-COONa + H_2O + $CO_2\uparrow$		
2) Neutral Reduction Test 10 mg substance + 10 drops of 50 % ethyl alcohol + 6 drops of $CaCl_2$ solution + Pinch of Zn dust + heat to boiling and filter in to Tollen's reagent	Black / Gray Precipitate	Nitro ($-NO_2$) group Present

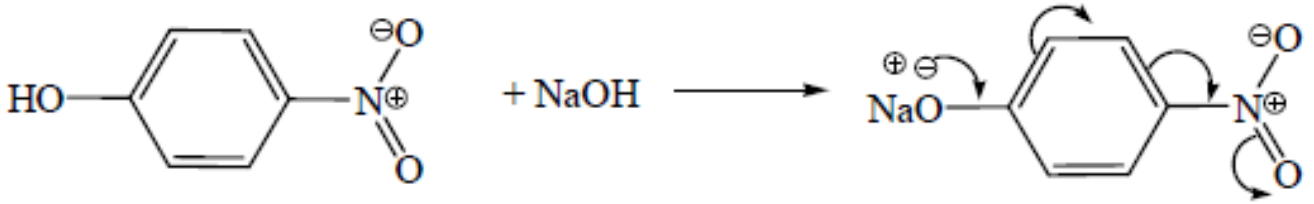
i) $Ar\text{-}NO_2 + CaCl_2 + Zn \xrightarrow[\text{Ethanol}]{\Delta} Ar\text{-}NH\text{-}OH + H_2O$

Nitro Group — Clear solution (Filtrate)

ii) $Ar\text{-}NH\text{-}OH + [Ag(NH_3)_2OH] + 2OH^- \longrightarrow Ar\text{-}N{=}O + 2Ag\downarrow + 2NH_3 + 4\,H_2O$

Filtrate — Tollen's Reagent — Black/ Gray Ppt

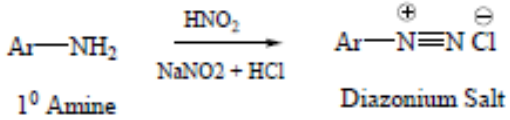
B) PHENOLS (Nitro Phenols)

Test	Observation	Inference
1) NaOH Test 10mg substance + 10 drops of 10% NaOH shake well	Yellow color solution changes Orange / red	Nitro phenol is Present
 Yellow Red Color		
2) Neutral Reduction Test 10 mg substance + 10 drops of 50 % ethyl alcohol + 6 drops of $CaCl_2$ solution + Pinch of Zn dust + heat to boiling and filter in to Tollen's reagent	Black / Gray Precipitate	Nitro ($-NO_2$) group Present

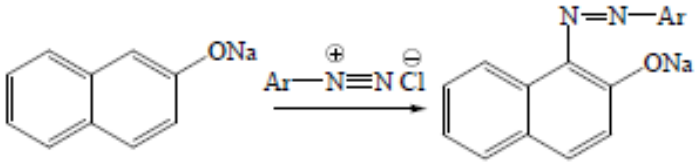
C) BASES

Test	Observation	Inference
i) HCl Test 10mg substance + 10 drops of 1:1 HCl shake	Completely Soluble and reprecipitated with 10% NaOH	Base is present and confirmed
$R\text{-}NH_2 + HCl \rightarrow R\text{-}NH_3^{\oplus}Cl^{\ominus}$ Base Acid water soluble quaternary salt $R\text{-}NH_3^{\oplus}Cl^{\ominus} + NaOH \rightarrow R\text{-}NH_2\downarrow + NaCl$ Salt Base reappears		
ii) Diazotisation Test a) 10 mg substance + 10 drops of Conc. HCl boil and cool in water + 2-3 drops of $NaNO_2$ Solution b) If observation (i) and (ii) are absent then add above solution dropwise in to ice cold solution of β-Naphthol in NaOH	(i) If yellow solid separates out (ii) If red color and on addition of NaOH gives Green solids Orange Dyestuff	(i) Secondary amine (Ar_2NH)is present (ii) Tertiary amine (Ar_3N) is present Primary amine (Ar-NH_2) is Present

1) Primary Amine

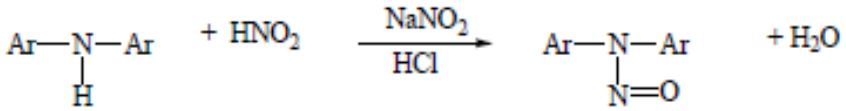


1^0 Amine — Diazonium Salt



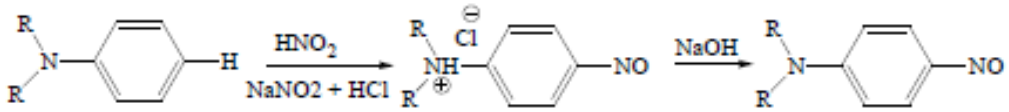
B-Naphthol in NaOH — Orange Dyestuff

2) Secondary Amine



2^0 Amine — Nitroso Amine, Yellow solid / Oil

3) Tertiary amine



3^0 Amine — Nitroso Amine, Red Color — Nitroso Amine, Green Color

iii) Neutral Reduction Test 10 mg substance + 10 drops of 50 % ethyl alcohol + 6 drops of $CaCl_2$ solution + Pinch of Zn dust + heat to boiling and filter in to Tollen's reagent	Black / Gray Precipitate	Nitro ($-NO_2$) group Present

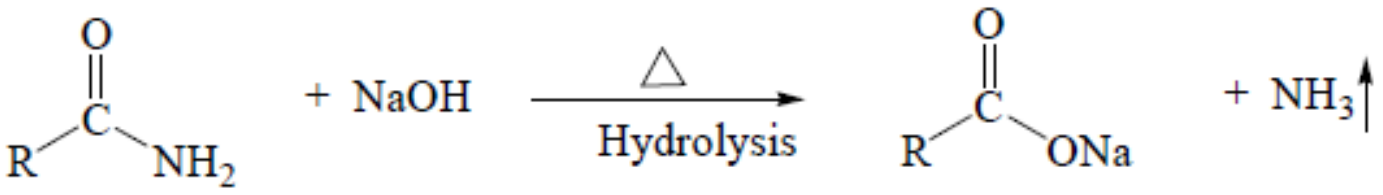
D) NEUTRAL

Neutral containing C,H (O) and N elements are of three types.

1) Amides, 2) Anilides and 3) Nitrohydrocarbons

1) Amides

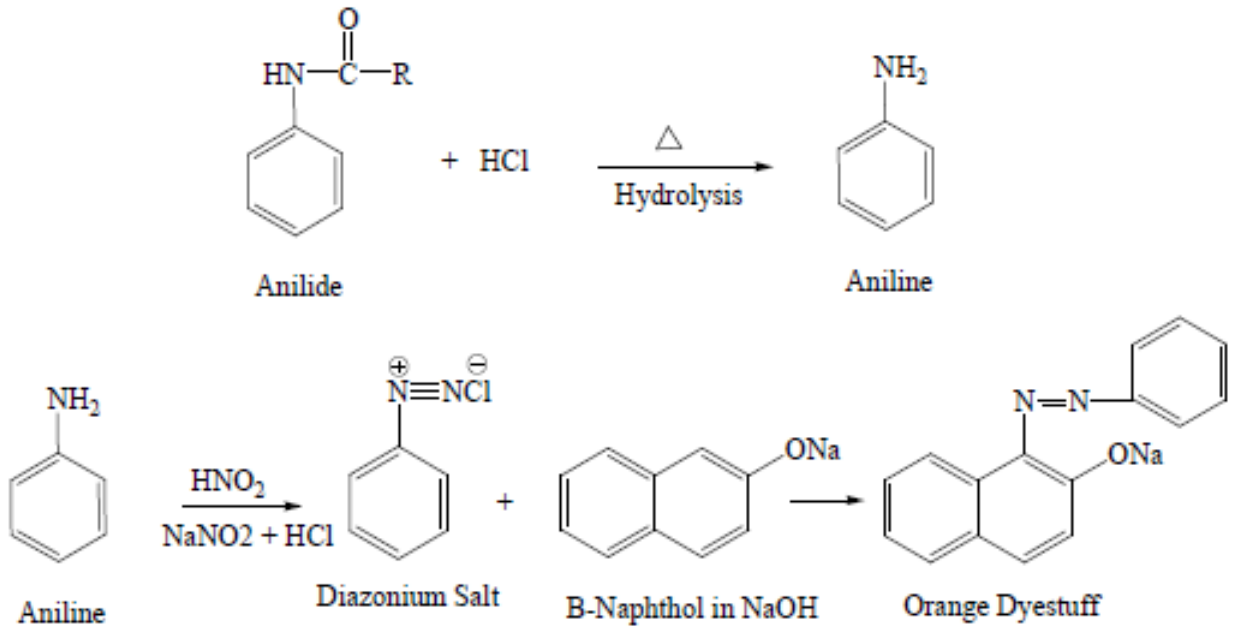
Test	Observation	Inference
NaOH Test 10 mg substance + 10 drops NaOH solution and boil	Evolution of ammonia which turns moist turmeric paper red	Amide ($R\text{-}CONH_2$) Present



Amide Salt

2) Anilides

Test	Observation	Inference
i) Hydrolysis and Diazotisation Test a) 10 mg substance + 10 drops of Conc. HCl boil and cool in ice water + excess of $NaNO_2$ Solution then add this solution dropwise in to ice cold solution of β-Naphthol in NaOH	Orange Dyestuff	Anilide group (Ar-NHCOR) Present



3) Nitro Hydrocarbons

Test	Observation	Inference
i) Neutral Reduction Test 10 mg substance + 10 drops of 50 % ethyl alcohol + 6 drops of $CaCl_2$ solution + Pinch of Zn dust + heat to boiling and filter in to Tollen's reagent	Black / Gray Precipitate	Nitro hydrocarbon ($Ar\text{-}NO_2$) Present

i) $Ar\text{-}NO_2 + CaCl_2 + Zn \xrightarrow[\text{Ethanol}]{\Delta} Ar\text{-}NH\text{-}OH + H_2O$

Nitro Group — Clear solution (Filtrate)

ii) $Ar\text{-}NH\text{-}OH + [Ag(NH_3)_2OH] + 2OH^- \longrightarrow Ar\text{-}N{=}O + 2Ag\downarrow + 2NH_3 + 4\,H_2O$

Filtrate — Tollen's Reagent — Black/ Gray Ppt

ii) Ferrous Hydroxide Test 10mg Substance + freshly prepared 5% ferrous Ammonium Sulphate solution + 1 drops dil H_2SO_4 + excess of KOH solution, Shake the test tube	Red brown ppt.	Nitro hydrocarbon ($Ar\text{-}NO_2$) Present

$Ar\text{-}NO_2 + 6\,Fe(OH)_2 + 4H_2O \longrightarrow Ar\text{-}NH_2 + 6\,Fe(OH)_3\downarrow$

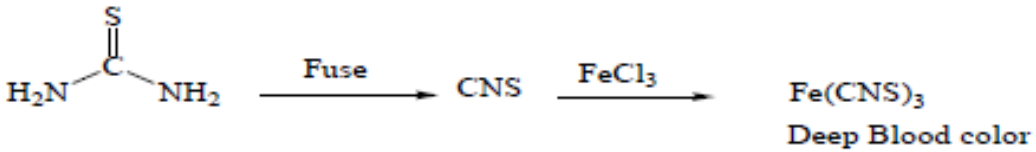
Bluish green — Brown ppt

3) Substance containing C, H (O), N and S elements

D) NEUTRAL

Thiourea

Test	Observation	Inference
10 mg substance fused in test tube, cool + 1 ml water + 2 drops of $FeCl_3$ solution	Blood red coloration	Thiourea present

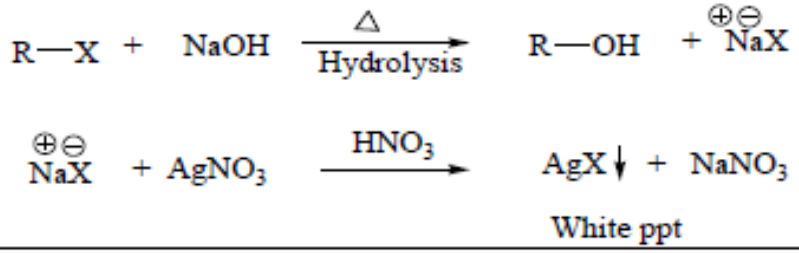


4) Substance containing C, H (O) and X (halogen) elements

D) NEUTRAL

Halo-Hydrocarbons

Test	Observation	Inference
4 drops of substance + 10 drops of NaOH boil well and cool, Acidify with Conc. HNO_3, then add 2 drops of $AgNO_3$ solution and shake well	a) White ppt settle at bottom b) No White ppt settle at bottom	a) Aliphatic halide present b) Aromatic halide present




Thank you!