Reactions and Identification of organic Compounds:

A Knowledge of the Elementry Constituents is essential for the chracterisation of any unknown organic Compound. In general, all organic Compounds are expected to Contain Carbon and hydrogen. The Elements which Commonly occure in organic Compound along with Carbon, hydrogen and oxygen, and with which we are Primarily Concerned are: nitrogen, Sulphur and the halogens (Cl, Br, I).

The method for the detection of nitrogen, Sulphur and halogens depends upon the fact that fusion with Sodium, of an organic Compound containing these elements, converts them to easily identifiable ions

$$C, H, O, N, S, X \xrightarrow[\text{with Sodium}]{\text{Fusion}} \begin{array}{l} NaCN \\ NaCNS \\ Na_2S \\ NaX. \end{array}$$

This method is introduced by J. L. Lassaigne in 1843, which, after his name, is known as Lassaigne's test.

The Lassaigne's Test (Sodium Extract Solution)

Wear Safety-glasses before you proceed for the Preparation of Sodium extract. Introduce a small Piece (about half the size of Pea) of freshly cut, clean and dry Sodium, into the ignition-tube, held in a vertical Position, with a Pair of tong. Heat the lower part of the tube in a Bunsen flame gently, till Sodium melts to form a shining globule. Remove the ignition tube from the flame and then insert a small amount of the organic Compound under identification. If organic Compound is liquid, add the Sodium Carbonate to reduce its loss by Evaporation. Keep it in the Red-hot condition for 1-2 minutes. (until the Compound has Completely

reacted) and then plung into about 8-10ml of distilled water kept in a Porcelin basin. Boil the Contents of the Porcelain basin for 2-3 minutes and filter. (Immediately cover the dish with a wire-gauge, to prevent any unreacted sodium or of the broken glass pieces from flying of the dish.)

Use the filtrate known as Lassaigne's Extract for testing the Extra Elements.

The filtrate should be clear like water, if it is coloured than it indicates incomplete fusion and the entire Process should be repeated.

Precautions → (1.) Do not touch the Sodium with your fingers, handle it with forceps.

2. There may be a slight Explosion with Compounds like nitroalkanes, azides, diazonium salts, chloroform and Carbontetrachloride. Safety goggles should be worn to avoid accidents.

(3.) Unreacted Sodium should be Carefully decomposed by reacting with a small amount of ethyl alcohol.

Test for Nitrogen →

(1.) Reaction with Ferrous Sulphate - Take 1-2 ml Sodium Extract (L.E), add freshly prepared ferrous sulphate. A dark greenish grey PPt (Precipitate) of ferrous hydroxide is obtained. Boil the mixture gently for one minutes and acidify with dilute Sulphuric acid (3-4ml). A blue precipitate (Prussian blue) colour indicates the Presence of nitrogen in the compound.

$$6NaCN + FeSO_4 \longrightarrow Na_4Fe(CN)_6 + Na_2SO_4$$

$$3Na_4Fe(CN)_6 + 2Fe_2(SO_4)_3 \longrightarrow \cancel{Fe_4[Fe(CN)_6]_3}$$

$$Fe_4[Fe(CN)_6]_3$$

Prussian blue.

Boil the resulting mixture gently for one or two minutes to facilitate aerial oxidation of ferrous ions into ferric ions.

$$6NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$

Prussian blue

$$3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 6Na_2SO_4.$$

Benzidine Copper Sulphate Test (For Nitrogen)

Sod. Extract + Acetic acid (3-4 drops) → Add Freshly prepared benzidine + shake the mixture + Copper Sulphate Solution (1-2 drops.). Appearance of a blue colour indicates the Presence of nitrogen.

Test for Sulphur →

① **Lead Acetate test** → Acidify 2 ml of Sodium Extract with dilute Acetic acid (2ml) and add 5-6 drops of lead Acetate Solution. A black precipitate of lead Sulphide indicate the presence of Sulphur.

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

or

$$(CH_3COO)_2Pb$$

black

Sodium Nitroprusside test → To 2ml of Sodium Extract, add a few drops of a freshly prepared dilute solution of sodium nitroprusside, $Na_2[Fe(CN)_5NO]2H_2O$. A brilliant Purple coloration confirms Sulphur.

$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4Fe(CN)_5NOS$

Sodium nitroprusside — Purple colour

Note – Sodium nitroprusside is unstable in aqueous solution and therefore, the should be freshly prepared on each occasion.

Combined test for Nitrogen and Sulphur →

(1) Test with $FeCl_3$ → Acidify the sodium Extract 2ml with dilute hydrochloric acid 5–6 drops and treat with Ferric chloride solution (3–4 drops). The appearance of blood red colour indicates the presence of nitrogen and sulphur

$$3NaSCN + FeCl_3 \longrightarrow Fe(SCN)_3 + 3NaCl$$

Ferric thiocyanat

Blood red

2. Cobaltinitrate test →

Sodium Extract 2ml with dil HCl (1ml) Add alcohol (2ml) and treat with Cobalt nitrate solution (4-5 drops). Appearance of a blue colour indicates the presence of both nitrogen and sulphur.

$$NaSCN + HCl \longrightarrow HSCN + NaCl$$

$$4\,HSCN + Co(NO_3)_2 \longrightarrow H_2Co(SCN)_4 + 2HNO_3$$

Cobalt thiocyanic acid.
Blue.

Test for Halogens →

(1) Beilstein Test →

(2) Silver nitrate test - Take 2ml Sodium Extract add 2-3 ml dil. HNO_3. Boil the solution gently for 1-2 minutes to expel any hydrogen cyanide

Systamatic Analysis of Simple Monofunctional Organic Compounds.

Function groups Qualitative Analysis

Aim - To identify a ~~organic~~ function gp in the given organic compounds.

(A) Preliminary Investigations.

1. Physical State → Compound is a Solid or liquid if Solid Compound is crystalline or amorphous

2. Colour - Note the Colour of Compound. The Colour of Compound gives informations for Compound's identification.

Colourless Compounds or white compound - Carbohydrates, aldehydes, Ketones, Carboxyl acids, esters, alcohols, ethers and Some Simple hydrocarbons, Phenols, amines, aminophenols etc

Colourless turning - Phenols, amines, aminophenols reddish or Pinkish due to oxidation by air

Yellow - Nitro Compounds, quinones, iodoform

Greenish yellow - P-nitroso Compounds

Odour - Some organic Compounds have (Possess) a very characteristic odour.

Bitter almond odour - Nitrobenzene, benzaldehyde, benzonitrile etc.

Pungent Odour → Acetic Acid, acetylchloride, acetic anhydride, Benzoyl Chloride, Benzyl chloride, benzoquinone, formic acid

Cucumber like odour – chloral hydrate | Offensive odour → Isocyanide
Odour of Moth balls – Naphthalene
Mouse like odour – Acetamide and Acetonitrile
Cinnamon-like – Cinnamaldehyde.
Pleasent fruity – Esters, ethers, Acetate.
Sweet odour – chlorooform, alcohols.
Garlic-like – Thiophenols, thioalcohols.
Phenolic odour – Phenols
Irritating Pungent odour – Lower acid, aldehydes and acid halides etc
Vinegar like – Acetic acid.
Pyridine like – Heterocyclic bases.
Fish like – Aliphatic amines, Side chain aromatic amines.

Do not inhale the vapours of the compound directly.

Flametest → Heat the Organic Compound 50 mg on a nickel spatula over a low flame, raising the temperature gradually.

Non Sooty flame.	Aliphatic Compounds.
Sooty flame	Aromatic Compounds
Ammonical odour,	urea, thiourea etc
charring with smell of burnt sugar.	Carbohydrates, tartrate citrates etc

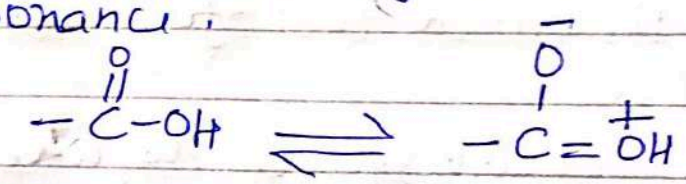
Action of Alkali – Take 100mg organic compound and add aqueous sodium hydroxide (2-ml.) and heat for 1-2 minutes.

Smell of Ammonia	Primary amides
Smell of Chloroform	chloral
Smell of amine on Prolonged heating	Anilides

Organic Compound + Water

- Soluble in water (the compound is also soluble in ether)
  - Acidic → Acid Phenols
  - Basic → Amines
  - Neutral → Aliphatic alcohols, Aldehyde, ketones, nitriles, esters.
- Soluble in water (the compound is insoluble in ether)
  - Acidic → Hydroxy Acids, Sulphonic acids, Salts of Amine, Amino acid
  - Basic → Amino Alcohols
  - Neutral → Carbohydrates, Polyhydric alcohols
- Insoluble in water
  - $NaHCO_3$ → Soluble in $NaHCO_3$. Carboxylic Acids.
  - 5% NaOH → Insoluble in $NaHCO_3$ but Soluble in dil NaOH. Phenols
  - dil HCl → Insoluble in $NaHCO_3$ & NaOH but Soluble in dil HCl. Amines
  - Conc H_2SO_4 → Insoluble in $NaHCO_3$, NaOH & dil Acid. Soluble in H_2SO_4
    - Soluble: ethers, esters, aldehydes, ketones
    - Insoluble Compounds: Benzene, Chlorobenzene, toluene etc.

Carboxylic acids → The acids do not show the typical reaction of carbonyl groups because of the following resonance.



However, they have a tendency to donate protons and act as acids. It is this property which is helpful in the identification of a $-COOH$ gp

(i.) Litmus Test →

Procedure → Add blue litmus solution (1 drop) to an aqueous solution of acid 1 ml. Appearance of a red colour indicates the presence of a carboxylic acid.

(ii.) Sodium Bicarbonate test → Carboxylic acids react with a solution of sodium bicarbonate with effervescence evolving CO_2.

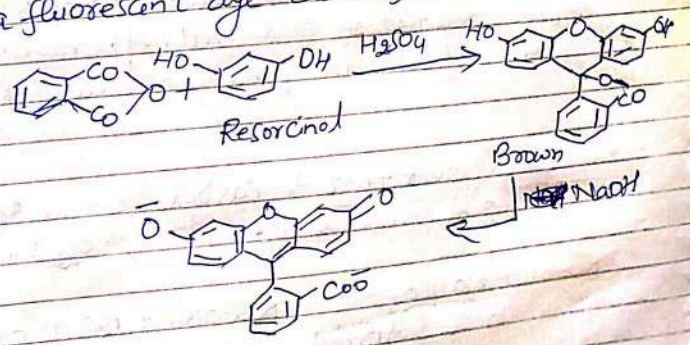
$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2 \uparrow$$

Procedure - To a saturated solution of sodium bicarbonate in water (1 ml) add the given compound (solid or 2-3 drops of liquid or an aqueous or an alcoholic solution of compound) Effervescence indicates the presence of a carboxylic acid

Note - use acid free alcohol for the test.

(iii) Fluorescein Test → This test should be performed only if the above test of for -COOH gp. i and ii are positive.

This test given by dicarboxylic acids which can form an anhydride on heating (e.g. Pthalic ; Succinic acid etc) when a dicarboxylic acids or its ~~derivative~~ anhydride is heated with Resorcinol in presence of Conc. H_2SO_4, a fluorescent dye called fluorescein is obtained.



Fluorescein.

Procedure → Take organic compound and add Resorcinol 100mg. and Conc Sulphuric acid. in a dry test tube, Heat gently for 2 minute on bunsen burner. Pour the mixture into a beaker containing Sodium hydroxide solution. Appearance of a green fluorescent solution is a Positive test.

Carbonyl Compounds Functing groups

Aldehydes and Ketones.

Identification of aldehydes and ketones is based on two types of reactions of the $>C=O$ gp. i.e (a) addition to $>C=O$ and (b) oxidation of the addition reactions, the addition of NH_3 and substituted ammonias are more important. The addition is generally followed by elimination resulting into an unsaturated compound.

$$>C=O + ZNH_2 \longrightarrow >C\begin{matrix}OH \\ NHZ\end{matrix} \xrightarrow{-H_2O} >C=NZ$$

These reactions are acid or base catalyzed and do not occur in strongly acidic or basic solutions. For each reaction there is an optimum PH, and hence maintenance of PH while carrying out the reaction is very important

Aldehydes can be easily oxidised to carboxylic acids. Ketones, on the other hand are difficult to oxidise.