Chapter:
01

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AIM: TO PERFORM SYSTEMATIC QUALITATIVE ANALYSIS OF CARBOXYLIC ACID

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Requirements

Chemicals

1. $NaHCO_3$,
2. $FeCl_3$
3. Ethanol
4. Conc. H_2SO_4

Glass wares

1. Test-tube
2. Stands
3. Brush
4. Holder
5. Glass rod
6. Beakers

Theory: Carboxyl groups (-COOH) are the functional groups of carboxylic acids. Aliphatic and aromatic carboxylic acids are the two classes of carboxylic acids. In general, aliphatic carboxylic acids are depicted by formula RCOOH, while aromatic carboxylic acids are depicted by formula ArCOOH. When compared to other organic molecules of the same molecular weight, carboxylic acids have much higher boiling point. They are polar organic compounds that form extremely strong intermolecular hydrogen bonding. When compared to compounds of similar molecular weight, such as alcohols, ethers, aldehydes, and ketones; carboxylic acids have a higher solubility in water. Both the C=O and OH groups in them are capable of forming hydrogen bonds with water molecules. They

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are dissolving in Na_2CO_3, resulting in the release of CO_2, and they are also dissolving in NaOH.

A. Preliminary tests

Nature…… (Solid/liquid/semisolid, etc.)

Colour……..(colourless/transparent or specific colour, etc.)

Odour……..(odourless/pungent/fruity/sweet/bad, etc.)

Solubility: Solubility in H_2O, HCl, NaOH, and $NaHCO_3$. The solubility of a chemical in various solvents gives crucial information on its classification. Observe the solubility of 0.1 g or two to three drops of the given compound in 3 mL of a solvent after vigorous shaking (Class of compounds given in table).

Solvent/reagent & test	**Nature of compound**	**Class of compounds**
Compound soluble in hot/cold H_2O. Further solubility test not required if given sample is H_2O soluble	Neutral/Acidic/ Basic (Check with Litmus test)	Neutral-lower alcohols Acidic-Acids, phenols Basic-Amines
HCl soluble	Basic	Amines
NaOH soluble	Acidic	Acids and phenols
$NaHCO_3$ Solution Soluble	Strongly acidic	Carboxylic acids
Insoluble in above solvents	Neutral	Hydrocarbons, Alkyl or Aryl

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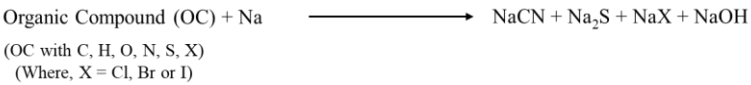
		Halides, Esters, Ethers, Greater Alcohols, Aldehydes, and Ketones

B. Ignition Test

Burn a small bit of the sample on a metal spatula to determine whether the substance is aliphatic or aromatic. A brilliant flame denotes an aliphatic component, whereas a sooty or smoky flame indicates an aromatic molecule.

C. Element Detection Test (Lassaigne Extract (LE))

In order to identify nitrogen, sulphur, and halogens (Cl, Br, I) in an organic compound, LE is made. These elements have formed covalent bonds with organic molecules. In order to identify these substances, their ionic forms must be transformed. This is achieved through the fusion of the organic molecule with Na metal. The ionic compounds produced during fusion are extracted in aqueous solution and may be identified using simple chemical investigations.. The sodium extract is also known as Lassaigne's extract.



Test for presence of Nitrogen: When combined with Na metal, the carbon and nitrogen in the organic complex give rise to NaCN, that is H_2O soluble. With the addition of sufficient quantities of $FeSO_4$, this is transformed into sodium Ferrocyanide. Ferric ions created during the procedure react with Ferro cyanide to yield a blue ferric Ferro cyanide precipitate.

$$Na + C + N \longrightarrow NaCN$$

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

Sodium Ferro cyanide

$$Na_4[Fe(CN)_6] + Fe^{3+} \longrightarrow Fe_4[Fe(CN)_6]_3$$

Ferric Ferro cyanide

Test for presence of sulphur: If the organic component contains sulphur, Na fusion will form Na_2S. Sulphide ions are easily recognized with sodium nitroprusside; a deep violet hue shows the presence of sulphur.

The formation of a black precipitate, which is lead sulphide, following the addition of lead acetate is another method for determining whether or not sulphur is present.

$$(CH_3COO)_2Pb + Na_2S \longrightarrow 2CH_3COONa + PbS$$

Test for presence of both Nitrogen and

$$Na + S \longrightarrow Na_2S$$

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$$

Sod. nitroprusside — Sod. thio-nitroprusside (purple-violet colour)

Sulphur

In the presence of both nitrogen and sulphur, NaSCN is produced with sodium. The reaction between NaSCN and $FeCl_3$ produces a blood-red colour complex (ferric thiocyanate). Therefore, the emergence of a blood-red colour suggests the presence of both N and S.

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

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Test for presence of halogens (Cl, Br, I)

When halogens (X) combine with Na, sodium halide is produced (NaX). The silver halide (AgX) precipitate is made when sodium halide (NaX) reacts with silver nitrate (AgNO3). A white colour precipitates of AgCl that dissolves in NH_4OH indicates the presence of Cl. When there is an off-white precipitate of AgBr that is partially soluble in NH_4OH indicates presence of Br. Iodine is present when there is a yellow color precipitate of AgI is obtained that is not soluble in ammonium hydroxide.

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

Lassaigne's Extract (LE) Preparation Method

Take a little piece of the sodium metal and dry it between two layers of filter paper by placing it in between the spatula's notches. In an ignition tube, melt the piece of sodium metal, then add a little amount of the sample to the melting sodium metal in the ignition tube. Reheat the ignition tube over the fire until it reaches its previous high temperature. Put twenty millilitres of distilled water in a porcelain bowl and set it aside. Put four to five red-hot ignition tubes in the water and crush them. The mixture should be brought to a boil for five minutes before being filtered. This colourless liquid is known by its acronym, LE. When doing the various tests to determine whether or not an element is present, use 1-2 mL of the extract (s). If the filtrate is coloured, it indicates that the combination has not been entirely broken down, which implies that the entire fusion process needs to be repeated.

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Chemical Tests for Detection of Element (s)

Test for Nitrogen Observation

S. No.	Test for Element Detection	Observation	Inference
1	**Test for Nitrogen:** In a clean and dry test tube, mix 1-2 mL of LE with 2-3 crystals of $FeSO_4$ and bring to a boil. Put in a few drops of sodium hydroxide. The resulting ppt has a nasty green colour. Now add two to three drops of H_2O_2 solution to the walls of the test tube. The presence of nitrogen is indicated by the presence of the colour Prussian blue (ferriferrocyanide).	Prussian blue colour	
2	**Test for Sulphur:** 1. Add a 2-3 drops of sodium nitroprusside to 1-2 mL of LE, and if there is sulphur in the mixture, sodium thio-nitroprusside, which has a colour that is purple-violet, will be	Purple-violet in colour	

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	formed. 2. Add one to two ml of lead acetate containing acetic acid to one to two ml of LE. The formation of a dark precipitate is one way to establish whether or not sulphur is present in a substance. Dark colour is typically due to formation of lead sulphide or PbS.	Black precipitate	
3	**Test of Nitrogen and Sulphur present together:** 1. Take one to two ml of LE and add two to three crystals of $FeCl_3$. When nitrogen and sulphur are both present, a blood red colour compound known as ferric thiocyanate is produced.	Blood red colour	
4	**Test for halogens (Cl, Br, I):** 1. After adding 1-2 drops of HNO_3 to 1-2 mL of LE, add solution		

	containing $AgNO_3$ after that.		
	2. The production of a white precipitate (AgCl) that is soluble in NH_4OH is evidence that chlorine is present in the sample that was provided.	White precipitate	
	3. The presence of bromine can be verified by the production of a precipitate with a somewhat off-white colour that is only partially soluble in NH_4OH.	Off-white precipitate	
	4. The production of a yellow precipitate that is insoluble in NH_4OH is conclusive evidence that iodine is present in the sample that was provided, on the other hand.	Yellow precipitate	

Precautions

- The metal sodium is particularly reactive; when it is exposed to air, it interacts with the moisture that is present in the air. Additionally, it reacts with the sweat on the hands. As a consequence of this, you SHOULD NOT hold it in your

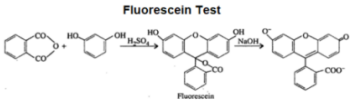
hands. When working with sodium metal, it is imperative to always use dry forceps.

- It is necessary to remove any oil from the sodium metal by pressing it between two layers of folded filter paper before using it in any experiment.
- When you are fusing sodium, you should use dry ignition tubes. The reaction between sodium and water is rather violent.
- Put the bit of sodium metal back in the original container it came in. DO NOT throw it out in the garbage or put it in the sink.
- Repeat the technique for fusing sodium with at least three ignition tubes this time. This is to ensure that the fusion has taken place successfully.
- After you have submerged the red-hot ignition tube in water, you should use a glass rod to delicately splinter it. To extract the sodium salts that are water-soluble, bring the mixture to a boil and let it simmer for two to three minutes.

Functional Group Test for Carboxylic Acids

S. No.	Identification Test	Observation	Inference
1	**Litmus test:** Samples are dissolved in water or alcohol. Submerge a blue litmus paper and observe the change in colour.	Blue litmus turns red	Acidic group may be present
2	**Sodium Bicarbonate Test:** It is also known as effervescence test. Observe for effervescence after	Effervescence of CO_2 is	-COOH may be present

	dissolving a sample in water, adding a pinch of sodium bicarbonate. 	observed	
3	**Neutral ferric chloride test:** Neutralize the $FeCl_3$ solution with NaOH, and then add it to the sample solution. Observe for colour changes.	Red colour complex	-COOH is confirmed
4	**Ester formation test:** On a water bath, a combination of 0.2 g of the given sample, 0.4 mL of C_2H_5OH, and 0.2 mL of conc. H_2SO_4 is heated for two minutes. Slowly pour the mixture into a dish holding 2 mL of $NaHCO_3$ solution in an evaporating dish. 	Fruity/sweet smell	-COOH is confirmed
5	**Fluorescein Test:** This identification test is performed with dicarboxylic acid. When dicarboxylic acid is heated, acid anhydride is produced. This reaction is known as the fluorescein test because a fluorescent dye is generated when anhydride is reacted with resorcinol in the presence of conc. H_2SO_4. 1. In a test tube, place the organic component to be	Green colour fluorescent solution	-COOH is confirmed

	evaluated. 2. Combine with 100 mg of resorcinol and 0.5 mL of conc. H_2SO_4. 3. The test tube is slowly heated on a Bunsen burner. 4. Transfer the solution to a beaker containing dil. NaOH. 5. Remark: The resulting solution must be alkaline 		
6	**Ammonium $AgNO_3$ test:** When two or three drops of ammoniacal $AgNO_3$ solution are introduced to a neutral solution, the solution becomes acidic. Rapidly forming a white precipitate of Ag and reducing it to metallic silver upon heating.	Black precipitate or mirror	-COOH is confirmed
7	**Mercuric chloride test $HgCl_2$:** When two or three drops of $HgCl_2$ solution are introduced to a neutral solution, a white precipitate of Hg_2Cl_2 forms, which is reduced to Hg by heating with excess format. When NH_4OH is added to the precipitate, it turns white.	It turns grey	-COOH is confirmed

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8	**Potassium permanganate test $KMnO_4$**: When a few drops of Na_2CO_3 and then a few drops of $KMnO_4$ are added to a solution, the colour is destroyed.	The colour is destroyed	-COOH is confirmed

Result: The qualitative systemic assays of carboxylic acids have been identified and reported.

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