University of Hargeisa

College of Education

Class 4 Senior Students Chemistry

Qualitative Organic Analysis



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Chapter one: Qualitative Organic Analysis

The analysis and identification of unknown organic compounds constitutes a very important aspect of experimental organic chemistry. Often, a common first step in the identification of an unknown substance is to determine what elements are present in the sample. The elemental analysis typically must be supplemented with other information about the compound: physical properties (melting point, boiling point, solubility, odour, colour, etc.), and confirmatory tests for functional groups.

	Test	Observation	Inference
1.	Preliminary Test and Physical Examination	ation	
А	State	i) Solid	Generally high molecular
			weight, usually having more
			than 6 carbon atom chain.
			Eg: Acids, Sugars, Amides, etc.
		ii) Liquid	Generally low molecular weight,.
			Eg: Alcohols, Ethers, Esters,
			Aliphatic amines, Aldehydes,
			Ketones, Hydrocarbons, etc.
		Pale Yellow	Nitro Compounds: nitrobenzene,
В	Colour		dinitrobenzene, and nitrophenol.
			Quinones and Iodoform.
		Yellow Orange	Nitro-aniline
		Pink	α -Naphthol, β -Naphthol, resorcinol,
		Red	Azo compounds, methyl orange
		Green	Nitroso compounds
		Greenish Yellow	nitrobenzaldehyde
		Brown-dark	Phenols, Amines, (darken due to oxidation)
		Colourless	Compounds not containing strong Chromophore.
			Eg: Acids, Hydrocarbons, ketones,
			esters, urea, thiourea, acetamide,
			acetanilide, benzamide, naphalene,
			etc

	Test	Observation	Inference
С	Odour	Pleasant	Alcohols (low mol. Wt.), Aromatic
			hydrocarbons, ethers, alkyl halides
			chloroform, chlorobenzene.
		Deep Sweet	Chloroform
		Fruity	Esters
		Phenolic / Carbolic	Phenols and cresols
		Fishy	Aromatic amines
		Kerosene	Hydrocarbons
		Moth Ball	Naphthalene
		Bitter Almond	Benzaldehyde, nitrobenzene
		Pungent/Irritating	Aliphatic acids, Acid chlorides,
			formaldehyde, and side chain
			halo hydrocarbons
	CAUTION:		
	Do not taste an unknown compound.		
	To note the odour, cautiously smell the cap	of the container and do it on	ly once. Never smell the contents of the
	container directly		

	Test	Observation	Inference
2.	Ignition Test		
	Flame Test: Take a small quantity of	Non-sooty Flame	Aliphatic compounds
	compound and put it on a metallic	Sooty Flame	Aromatic compounds
	spatula or in a porcelain dish and ignite it directly on the Bunsen burner	Ammonical odour	Urea, thiourea, amides may be present
		Chars and swells without melting	Sulphur containing compounds
		Melts and chars with a smell of burnt sugar	Carbohydrates may be present
		Produces coughing upon	Benzoic acid, salicylic acid etc may
		charring	be present
		Chars without melting	Sulphanilic acid, starch, uric acid may be present
	Beilstein's Test: Make one end of a copper wire in the	Burns with green flame	Urea, Chlorides, Bromides may be present
	form of a loop and heat it on a burner till flame is no longer coloured. Cool the wire and dip the loop in little of the sample and ignite the loop again in flame.	Burns without green flame	Flourides may be present Or other halides

3	Test for Unsaturation		
	a. Action of KMnO ₄ (Baeyers test): Sub (solid/Liquid) + Sodium carbonate solution + few drops of 2% KMnO ₄ solution – Shake vigorously	Decolorization of KMnO ₄	Unsaturated compounds may be present
		No Decolorization of KMnO ₄	Saturated compounds may be present
	 b. Action of Bromine Water (for freely or sparingly water soluble compounds): 	Decolorization	Unsaturated compounds may be present
	Sub (solid/Liquid) + Bromine water dropwise – Shake vigorously		
		No Decolorization	Saturated compounds may be present
	c. Action of Bromine Water (for water insoluble compounds):	Decolorization	Unsaturated compounds may be present
	Sub (solid/Liquid) + 2ml CCl ₄ or CHCL ₃ solution dropwise with shaking + Bromine in CCl ₄ dropwise – Shake vigorously.	No Decolorization	Saturated compounds may be present

General Qualitative Analysis Scheme

A. Preliminary Tests: In these tests, you can note all the physical characteristics of the compound that includes solid, liquid, color or odor. Also, performing an ignition test by heating a small amount of metal spatula helps in determining whether the compound is aromatic or aliphatic as aliphatic compounds produce luminous flame and aromatic compounds produce a sooty flame.

B. Physical Properties Detection: It can be made by determining the boiling point or melting point. In the case of liquids, it's better to go for distillation that serves the dual purpose for knowing the boiling point and also the purification of liquid that helps in performing subsequent tests.

C. Analysis of Elements: Analysis of Elements present in the compound can be performed with the help of various methods.

D. Solubility Tests: The test is performed using various reagents such as dil. HCl, dil. NaOH, sodium bicarbonate and hot or cold water. Useful information can be obtained by observing the compound's solubility.

E. Group Classification Tests: Various tests can help in deducing the functional groups in the unknown compound.

Chapter Two: Qualitative Analysis of Elements

Different Tests for Detection of Elements

1. Detection of Carbon and Hydrogen

Carbon and hydrogen are detected by heating the compound with CuO in a dry test tube. They are oxidized to CO_2 and H_2O respectively. If the CO_2 turns lime water milky, and H_2O turns **anhydrous CuSO**₄ blue, then the presence of carbon and hydrogen is confirmed.



Detection of Carbon and Hydrogen

2. Test for Phosphorous

The organic compound is heated with an oxidizing agent to oxidize phosphorous to phosphate. The solution is then boiled with **concentrated HNO₃** and treated with ammonium molybdate. Yellow precipitate confirms the presence of phosphorous.

The reaction is given below,

 $Na_3PO_4 + 3HNO_3 \rightarrow H_3PO_4 + 3NaNO_3$ $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O_3$

A very few organic compounds contain phosphorus. Its presence is detected by fusing the compound with an oxidizing mixture of sodium carbonate and potassium nitrate or with sodium

peroxide alone when an alkali phosphate is formed. The fused mass is extracted with water and filtered. The filtrate containing sodium phosphate is heated with cone. HNO3and an excess of ammonium molybdate solution is added. A yellow ppt. is formed if phosphorus is present. The yellow precipitate is ammonium phosphomolybdate, (NH4)3[PM012O40]

Detection of Halogens

Carius Method

A known mass of the compound is heated with Conc. HNO_3 in the presence of **AgNO_3** in a hard glass tube called Carius tube. Carbon and hydrogen are oxidised to CO_2 and H_2O . The halogen forms the corresponding AgX. It is filtered, dried and weighed.



The Beilstein test

The Beilstein test is a simple **qualitative chemical test** for organic **halides**. It was developed by **Friedrich Konrad Beilstein**.

A copper wire is cleaned and heated in a Bunsen burner flame to form a coating of copper(II) oxide. It is then dipped in the sample to be tested and once again heated in a flame. A positive test is indicated by a green flame caused by the formation of a copper halide.

This test is no longer frequently used. One reason why it is not widely used is that it is sometimes possible to generate the highly toxic chloro-dioxins if the test material is a polychloroarene (neoprene)

An alternative wet test for halide is the sodium fusion test — this test converts organic material to inorganic salts include the sodium halide. Addition of silver nitrate solution causes any halides to precipitate as the respective silver halide.

Lassaigne's Test (Sodium fusion test)

Place about a pea size of freshly cut sodium metal into a sodium fusion tube and heat the tube gently to melt the sodium to a shining globule. Add a small quantity of the sample (solid/liquid) into the fusion tube. Heat the tube carefully at first and then as strongly as possible until the bottom of the tube is glowing red, holding the tube at this heat for about 2 min. Quickly plunge the hot tube in a china dish containing about 8 ml of distilled water and cover the china dish immediately with a wire gauge. The tube crumbles into pieces and the mass comes out and dissolves in water. Boil the contents of the china dish thoroughly, filter the contents and collect the filtrate (which is also called Stock solution) in a test tube. Divide the filtrate into 3-4 portions and test each portion for the elements separately.

Test	Observation	Inference
1. Test for Nitrogen:		
a. Prussian Blue test	Blue colour	Nitrogen present
Stock solution + $FeSO_4$ solution – boil and cool. Add conc. H_2SO_4	No Blue colour	Nitrogen absent
2. Test for Sulphur:		
a. Sodium nitroprusside test	Pink colour	Sulphur present
Stock solution + Sodium nitroprusside	No Pink colour	Sulphur absent
b. Lead acetate Test	Black Ppt	Sulphur present
Stock solution + Acetic Acid + 2 ml Lead acetate (5%)	No Black Ppt	Sulphur absent
3. Test for Halogens:		
a. Silver Nitrate test Stock solution + dil. HNO ₃ – heat,	White ppt, which freely dissolves in 2 ml of ammonia solution	Chlorine present
boil and reduce to half the volume + a few drops of silver nitrate solution.	Pale yellow ppt, which is difficult to dissolve in 2 ml of ammonia solution	Bromine present
	Yellow ppt, which is insoluble in 2 ml of	lodine present
	No Ppt	Halogens absent

 $\begin{array}{rcl} & \underline{Test\ for\ Nitrogen:}\\ & 6\ NaCN & +\ FeSO_4 & \rightarrow & Na_4[Fe(CN)_6] & +\ Na_2SO_4\\ & Sodium\ cyanide & Sod.\ Ferrocyanide \\ & FeSO_4 & \rightarrow & 2Fe_2(SO_4)_3\\ & Na_4[Fe(CN)_6] & + & 2Fe_2(SO_4)_3 & \rightarrow & Fe_4[Fe(CN)_6] & + & Na_2SO_4\\ & & Ferricferrocyanide\\ & & prussian\ blue \end{array}$

Test for Sulphur: \rightarrow Na₄[Fe(CN)₅NOS] + Na, [Fe(CN), NO] Na,S + 2NaOH Sod. Ferric sulphocyanide Sod. nitroprusside (purple-violet colour) Na₂S + Pb(CH₃COO), \rightarrow PbS 2CH,COOH + Lead sulphide Test for Halogens: Dil. HNO3 $AgNO_3 + NaCl$ AgCl_(s) + NaNO₃ \rightarrow White ppt ↓2NH₄OH [Ag(NH_),]⁺ Cl⁻ + 2H,O Freely water soluble

Lassaigne's test is the general test for the detection of halogens, nitrogen and sulphur in an organic compound. In order to detect them, these have to be converted into their ionic forms.

Detection of Nitrogen

The presence of nitrogen in the organic compound is detected by **fusing organic compounds** with sodium metal to give sodium cyanide (NaCN) soluble in water.

 $\begin{array}{rcl} \underline{Test\ for\ Nitrogen:}\\ 6\ NaCN & +\ FeSO_4 & \rightarrow & Na_4[Fe(CN)_6] & +\ Na_2SO_4\\ Sodium\ cyanide & Sod.\ Ferrocyanide \\ FeSO_4 & \rightarrow & 2Fe_2(SO_4)_3\\ Na_4[Fe(CN)_6] & +\ 2Fe_2(SO_4)_3 & \rightarrow & Fe_4[Fe(CN)_6] & +\ Na_2SO_4\\ & & Ferricferrocyanide \\ & & prussian\ blue \end{array}$

Sodium fusion extract is boiled with ferrous sulphate and acidified with sulphuric acid. Sodium cyanide reacts with ferrous sulphate and forms sodium hexacyanoferrate (II). On heating with sulphuric acid, some ferrous is oxidized to ferric hexacyanoferate (II) Fe_4 [Fe (CN)₆]₃ which is Prussian blue in colour.

Q. How can nitrogen be detected in organic compounds?

A. The presence of nitrogen in the organic compound is detected by fusing organic compounds with sodium metal to give sodium cyanide (NaCN) soluble in water. This is converted into sodium ferrocyanide by the addition of sufficient quantities of ferrous sulphate. Ferric ions generated during the process react with ferrocyanide to form Prussian blue precipitate of ferric ferrocyanide.

Detection of Sulphur in Lassaigne's Test

1. Sodium nitroprusside test

During the preparation of Lassaigne's extract, sulphur from the organic compound reacts with sodium to form sodium sulphide. It gives a purple colour with sodium nitroprusside due to the formation of sodium thionitroprusside.

 $2Na + S \rightarrow Na_2S$ (From organic compound) $Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$ (From sodium extract) Sod. nitroprusside Violet colouration

2. Lead acetate test

Sodium sulphide formed during the preparation of Lassaigne's extract reacts with lead acetate to yield lead sulphide as black precipitate.

 $Na_2S + (CH_3COO)_2Pb \rightarrow PbS + 2CH_3COONa$ Black precipitate

Detection of halogens in Lassaigne's Test

1. Silver nitrate test

a. Chlorine

During the preparation of Lassaigne's extract, chlorine form the organic compound reacts with sodium to form sodium chloride. Sodium chloride gives a white precipitate of silver chloride with silver nitrate solution. The precipitate is soluble in ammonium hydroxide.

Na + Cl \rightarrow NaCl (From organic compound) NaCl + AgNO₃ \rightarrow AgCl + NaNO₃ Silver chloride (White ppt.)

AgCI + 2NH₄OH →
$$[Ag(NH_3)_2]CI + 2H_2O$$

(Soluble)

b. Bromine

Sodium bromide formed during the preparation of Lassaigne's extract reacts with silver nitrate to form pale yellow precipitate of silver bromide, which is sparingly soluble in ammonium hydroxide.

Na + Br \rightarrow NaBr (From organic compound) NaBr + AgNO₃ \rightarrow AgBr + NaNO₃ Silver bromide (Pale yellow ppt.)

c. lodine

Sodium iodide formed during the preparation of sodium fusion extract reacts with silver nitrate solution to form yellow precipitate of silver iodide, which is insoluble in ammonium hydroxide.

Na + I → Nal (From organic compound)

2. Carbon disulphide test

When sodium bromide and sodium iodide in the Lassaigne's extract is treated with chlorine water, the bromide and iodide are oxidized to the corresponding halogens. This halogen dissolves in carbon disulphide. Bromine imparts orange colour and iodine imparts violet colour in carbon disulphide layer.

 $Cl_2 + 2NaBr \rightarrow Br_2 + 2NaCl$ (From sod. extract) $\rightarrow l_2 + 2NaCl$ $Cl_2 + 2Nal \rightarrow l_2 + 2NaCl$ (From sod. extract)

Chapter 3: Qualitative Analysis of Functional Groups

Functional group

Functional group is an atom or group or group of atoms in a molecule that gives the molecule that gives the molecule its characteristic chemical properties.

The same functional group will undergo the same or similar chemical reactions regardless of the rest of the molecule's composition

1) Alcoholic –OH group

We can detect the alcoholic group by the following tests:

Sodium Metal Test

We conduct this test on the basis of the appearance of effervescence due to the liberation of hydrogen gas in reactions of sodium with alcohol.

 $2R - OH + 2Na \rightarrow 2RONa + H_2$

Acetyl Chloride Test

Acetyl chloride reacts vigorously with primary and secondary alcohols with the evolution of hydrogen chloride. The hydrogen chloride gives white fumes of ammonium chloride with ammonium hydroxide.



 $HCI + NH_4OH \longrightarrow NH_4CI + H_2O$

Ceric Ammonium Test:

To the sample, we add a few drops of ceric ammonium nitrate and shake well. The appearance of pink or red colour indicates the presence of an alcoholic group.

 $2ROH + (NH_4)_2Ce(NO_3)_6 \rightarrow (ROH)_2Ce(NO_3)_4 + 2NH_4NO_3$

2) Carbonyls (Aldehydes and Ketones)

2,4-dinitrophenyl hydrazine test (Brady's Reagent)

• We add a small amount (2 drops or 0.05 – 0.1g) of the substance to 3 ml of 2,4dinitrophenyl hydrazine reagent and shake well. A crystalline precipitate indicates the presence of a carbonyl compound. Occasionally the precipitate is oily at first but this becomes crystalline upon standing.

What is Brady's Reagent?

• An aqueous solution of 2,4-dinitrophenyl hydrazine is known as *Brady's reagent*. It reacts with carbonyl compounds (aldehydes and ketone) to give a precipitate.

3) Differentiating Tests for Aldehydes

• Schiff's Test: We dissolve the given compound in alcohol and then add 1-2ml of Schiff's reagent. The appearance of pink, red or magenta colour confirms the presence of aldehyde group.

What is the Schiff's Test?

- Schiff's test is a chemical test used to check for the presence of aldehydes in a given analyte. This is done by reacting the analyte with a small quantity of a Schiff's reagent (colourless reagent)
- Tollen's Test (Silver Mirror Test): We add 3-4 drops of the liquid to the Tollen's reagent. We heat the container. A shining mirror precipitate confirms the presence of the aldehyde.

 $2Ag(NH_3)_2^+$ + RCHO + $3OH^- \rightarrow RCOO^-$ + $2Ag^-$ + $4NH_3$ + $2H_2O$

Tollen's' test, also known as silver-mirror test, is a qualitative laboratory test used to distinguish between an aldehyde and a ketone. It exploits the fact that aldehydes are readily oxidized, whereas ketones are not. Tollen's' test uses a reagent known as Tollen's' reagent, which is a colorless, basic, aqueous solution containing silver ions coordinated to ammonia Ag $(NH_3)_2^+$ It is prepared using a two-step procedure.

Step 1: Aqueous silver nitrate is mixed with aqueous sodium hydroxide.

 $2Ag^{+}(aq) + 2OH^{-}(aq) \rightarrow Ag_2 O(s) + H_2 O(l)$

Step 2: Aqueous ammonia is added drop-wise until the precipitated silver oxide completely dissolves.

$$\mathrm{Ag}_2\mathrm{O} + 4\,\mathrm{NH}_3 + \mathrm{H}_2\mathrm{O}
ightarrow 2\,\mathrm{Ag}(\mathrm{NH}_3)^+_2 + 2\,\mathrm{OH}^-$$

Tollen's' reagent oxidizes an aldehyde into the corresponding carboxylic acid.



Tollen's' test for aldehyde: left side positive (silver mirror), right side negative

The reaction of aldehyde is accompanied by the reduction of silver ions in Tollen's' reagent into metallic silver, which, if the test is carried out in a clean glass test tube, forms a mirror on the test tube

Ketones are not oxidized by Tollen's' reagent, so the treatment of a ketone with Tollen's' reagent in a glass test tube does not result in a silver mirror.

Tollen's' reagent is an alkaline solution of ammoniacal silver nitrate and is used to test for aldehydes or to differentiate between aldehydes and ketones. Silver ions in the presence of hydroxide ions come out of solution as a brown precipitate of silver (I) oxide, $Ag_2O(s)$. This precipitate dissolves in aqueous ammonia, forming the diamminesilver (I) ion, $[Ag(NH_3)_2]^+$. Ketones do not react with Tollen's' reagent. This test is also used to differentiate between aldose and ketose sugars

Test of Aldehydes with Fehling's Test

Fehling's solution is a complex compound of Cu^{2+} . When the aldehyde compound is treated with Fehling's solution Cu^{2+} is reduced to Cu^{+} and the aldehyde is reduced to acids. During the reaction, a red precipitate is formed.

 $\begin{array}{cccc} \mathrm{RCHO} &+& 2\mathrm{Cu}^{2+} + 5\mathrm{OH}^- &\longrightarrow & \mathrm{Cu}_2\mathrm{O}(s) \downarrow + \mathrm{RCOO}^- + 3\mathrm{H}_2\mathrm{O} \\ & & & & & & & & & \\ \mathrm{Aldehyde} & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\$

Note: The appearance of red precipitate confirms the presence of an aldehydic group.

4. Differentiating Tests for Ketones

Ketone Test with Sodium Nitroprusside Test:

Ketone responds to this test. Ketone reacts with alkali and forms an anion which further reacts with sodium nitroprusside and forms a coloured complex ion. Aldehydes do not respond to this test.

The chemical reaction is given below.

$CH_3COCH_3 + OH^- \rightarrow CH_3COCH_2^- + H_2O$

$[Fe(CN)_5NO]^{2-} + CH_3COCH_2^- \rightarrow [Fe(CN)_5NO.CH_3COCH_2]^{3-}$

Note: The appearance of red colouration shows the presence of ketone

1. m-Dinitrobenzene test

Place 0.5 ml of the given liquid (or 0.5 g of solid) in a clean test-tube and add about 0.1 g of finely powdered m-dinitrobenzene. Now add about 1 ml of dilute sodium hydroxide solution and shake.

Appearance of violet colour which slowly fades confirms ketonic group.

5) Carboxyl Group

We can identify Carboxylic acid by the following tests:

Litmus test

Carboxylic acids have a tendency to donate protons and act as acids. The carboxylic acid turns blue litmus red.

Sodium Bicarbonate test

We add Sodium bicarbonate (NaHCO₃) to the 1 ml of the sample. A brisk of effervescence indicates the presence of a carboxylic group.

 $RCO_2H + NaHCO_3 \rightarrow RCOONa + CO_2 + H_2O$

Procedure

- Prepare a saturated solution of sodium bicarbonate by dissolving sodium bicarbonate in 1ml of water.
- 2. Add the given organic compound to the saturated solution of sodium bicarbonate solution.

- 3. Shake the solution well.
- 4. If there is an evolution of brisk effervescence then it indicates the presence of carboxylic acid.

Ester Test

We warm a small amount of the acid with two parts of absolute ethanol and one part of concentrated sulphuric acid. We cool the solution and pour it continuously into aqueous Na_2CO_3 solution to neutralize the excess sulphuric acid. A sweet, fruity smell of an ester confirms the presence of ester.

Carboxylic acid reacts with alcohol in the presence of concentrated sulphuric acid and forms a pleasant smelling ester. This reaction is known as esterification. The chemical reaction is given below.

$\text{RCOOH} + \text{R-OH} + \text{H}_2\text{SO}_4 \rightarrow \text{RCOO-R} \text{ (Ester)} + \text{H}_2\text{O}$

Formation of a sweet smelling compound (ester) indicates the presence of carboxylic group in the given organic compound

Procedure

- Mix the given compound with ethyl alcohol and concentrated sulphuric acid.
- Heat the mixture in a dry test tube in a water bath.
- Pour the reaction mixture into a beaker carefully containing water.
- Neutralize the excess sulphuric acid.
- If a sweet smelling substance is sensed then it indicates the presence of acid

6) Amino Group

The most important basic nitrogen compounds are the primary, secondary and tertiary amines and they dissolve in mineral acids and change red litmus to blue.

Chemical classification of the amine function: The classification of primary, secondary or tertiary amines is done by means of the reaction with nitrous acid.

Nitrous Acid Test:

• We add 2g of the substance to 5 ml of 2 M HCl acid. Then, we cool it and add 2 ml of icecold 10% aqueous NaNO₂ solution slowly by means of a dropper. If we obtain a clear solution, with a continuous evolution of nitrogen gas, the substance is a primary amine.

 $RNH_2 + HNO_2 \rightarrow ROH + H_2O + N_2$

7) Aromatic amines and esters Aromatic amines and esters test with 20% NaOH m/v

Take a little of organic substance in a test tube. Add 2 ml 20% NaOH solution and reflux for 30 minutes



Instead heat the reaction in water bath for 30 minutes



Then cool and acidify with concentrated HCl. The formation of white precipitate aromatic acid indicates the presence of aromatic amides and aromatic esters.

Aromatic amides and esters undergo alkaline hydrolysis to alkali salt of the aromatic acid.

$\textbf{Ar-COOR} + \textbf{NaOH} \rightarrow \textbf{Ar-COONa} + \textbf{ROH}$

$\text{Ar-COONH}_2 + \text{NaOH} \rightarrow \text{Ar-COONa} + \text{NH}_3$

This alkali salt reacts with concentrated hydrochloric acid to give free aromatic acid.

$\textbf{Ar-COONa + HCI} \rightarrow \textbf{Ar-COOH + NaCI}$

White ppt



The white precipitate is due to the presence of aromatic acid

Note: Most aromatic acids exist in solid state.

8) Detection of Carbohydrates Carbohydrates test with concentrated Sulphuric acid

Take a little of the substance in a clean test tube. Carefully add a few drops of concentrated sulphuric acid and heat it.



If you could observe a black colour that is charring with the smell of burnt sugar, it is an indication that the compound is carbohydrate.

The black colour is due to the formation of carbon by the dehydration of the carbohydrate on heating with the concentrated sulphuric acid.

Carbohydrates undergo dehydration:

 $\textbf{C}_{12}\textbf{H}_{22}\textbf{O}_{11} \quad \underline{\textbf{conc.H}_2\textbf{SO}_4} \rightarrow \textbf{6H}_2\textbf{O} + \textbf{6C}$



The organic compound melts and chars with a smell of burnt sugar

Note: If you add very concentrated sulphuric acid to the table sugar without heating, the black colour will also appear immediately. The hydrogen and the oxygen are removed as water by the concentrated sulphuric acid

9) Aromatic Hydrocarbons

Instead, if the organic compound dissolves gradually on heating with concentrated sulphuric acid, it shows the presence of aromatic hydrocarbon, it is due to the formation of corresponding sulphonic acid.





The organic compound dissolves gradually on heating with concentrated sulphuric acid.

Sulfonic acids

In **organic chemistry**, **sulfonic acid** (or **sulphonic acid**) refers to a member of the class of organosulfur compounds with the general formula $R-S(=O)_2-OH$, where R is an organic alkyl or aryl group and the $S(=O)_2(OH)$ group a sulfonyl hydroxyl. As a substituent, it is known as a **sulfo group**.



Benzene sulfonic acid

Chapter 4: Solubility Tests

Like dissolves like; a substance is most soluble in that solvent to which it is most closely related in structure. This statement serves as a useful classification scheme for all organic molecules.

The solubility measurements are done at room temperature with 1-2 drop of a liquid, or 5 mg of a solid (finely crushed), and 0.2 to 1 mL of solvent. If a very small amount of the sample fails to dissolve when added to some of the solvent, it can be considered insoluble; and, conversely, if several portions dissolve readily in a small amount of the solvent, the substance is obviously soluble.

If an unknown seems to be more soluble in dilute acid or base than in water, the observation can be confirmed by neutralization of the solution. The original material will precipitate if it is less soluble in a neutral medium.

If both acidic and basic groups are present, the substance may be amphoteric and therefore soluble in both acid and base. Aromatic aminocarboxylic acids are amphoteric, like aliphatic ones, but they do not exist as zwitterions. They are soluble in both dilute hydrochloric acid and sodium hydroxide, but not in bicarbonate solution. Aminosulfonic acids exist as zwitterions; they are soluble in alkali but not in acid.

Zwitterion

Zwitterion is **an ion that contains two functional groups**. In simple terms, it is an ion possessing both positive and negative electrical charges. Therefore, zwitterions are mostly electrically neutral (the net formal charge is usually zero). In the solid state, amino acids exist as dipolar ions called zwitterions /ZwItə,rAIən/.



Amino acid



Zwitterion form

A monofunctional molecule **possesses one functional group**, a difunctional two, a trifunctional three, and so on. Compounds which contain two or more are also termed as polyfunctional compounds

Notes to Solubility Tests

- 1. Groups I, II (soluble in water). Test the solution with pH paper. If the compound is not easily soluble in cold water, treat it as water insoluble but test with indicator paper.
- 2. Take small amount of the unknown in a clean test tube add a little amount of ether. If it is soluble in ether, the substance is a group one. If it is insoluble, it is group 2.
- 3. HCl + a substance that is insoluble with water. If it is insoluble, it is group 3.
- 4. 5% NaOH : If the substance is insoluble in water but dissolves in 5% sodium hydroxide, it is group IV (carboxylic acids and phenols)



5. Sodium Hydrogen carbonate

Add approximately 1 mL of 5% NaHCO $_3$ to if it is soluble, it is carboxylic acid and if not it is Phenolic.



a. Sub + Water	Soluble	Group 1 or 11 present
Sub + Ether	Soluble	Group 1
		Low molecular weight compounds
		like acids, esters etc. present
	Insoluble	Group II present
		Sugars, amides (urea) present
b. Sub + Dil HCl	Soluble	Group III present
		1°, 2° or 3° Amine present
c. Sub + Dil NaOH	Soluble	Group IV present
		Acids, Phenols or phenolic acids
		present
If Nitrogen is Absent		
d. Sub + Conc. H ₂ SO ₄ (In a dry test tube)	Soluble	Group V present
	Insoluble	Group VI present
If Nitnesson is Abcomt	1	1

Systematic qualitative analysis of unknown organic compounds



Procedure for Determining Solubility of Organic Compounds

1) Water Solubility

Add approximately 6 drops of water to the test tube containing your unknown. Shake the tube or stir with a glass stirring rod. A soluble unknown will form a homogeneous solution with water, while an insoluble liquid will remain as a separate phase. A liquid which is soluble in water may be either a low molecular weight polar compound of up to 5 carbon atoms or less. You may add additional water, up to 1 mL, if your compound does not completely dissolve with the smaller amount.

Check the pH of the water to determine if the unknown is partially or completely soluble in water and whether your compound has changed the pH of the water.

- pH paper turns red: water soluble acidic compound
- pH paper turns blue: water soluble basic compound
- pH paper does not change color: water soluble neutral compound or insoluble compound

2) Solubility in Ether

Ethers are regarded as excellent solvents for a wide range of organic compounds.

3) 5% HCl Solubility

Add approximately 1 mL of 5% HCl; in small portions of about 6 drops each to the test tube containing your unknown. Shake test tube vigorously after the addition of each portion of solvent. Solubility will be indicated by the formation of a homogeneous solution, a color change, or the evolution of gas or heat. If your compound is HCl-soluble, then it is an organic base. Amines are the most common organic base.

4) 5% NaOH Solubility

Add approximately 1 mL of 5% NaOH in small portions of about 6 drops each to the test tube containing your unknown. Shake test tube vigorously after the addition of each portion of solvent. Solubility will be indicated by the formation of a homogeneous solution, a color change, or the evolution of gas or heat. If soluble, then your unknown is behaving as an organic acid. The most common organic acids are carboxylic acids and phenols. Carboxylic acids are usually considered stronger acids than phenols, but both of these acids will react with NaOH (a strong base).

5) 5% NaHCO₃ Solubility

Add approximately 1 mL of 5% NaHCO₃ in small portions of about 6 drops each to the test tube containing your unknown. Shake test tube vigorously after the addition of each portion of solvent. Solubility will be indicated by the formation of a homogeneous solution, a color change, or the evolution of gas or heat. If soluble, then it is a carboxylic acid. If not, then it a weaker organic (phenols). Typically, only a carboxylic acid will react with NaHCO₃.

If insoluble in all solutions, then your unknown is not an acidic or basic organic compound.

Chapter 5: Derivatives

Preparation of Derivatives

Before an organic compound can be identified with certainty, it is necessary that it be converted to at least one other sharp-melting solid compound called a 'derivative'; liquid derivatives are not considered suitable. A derivative which melts above 80° should be chosen wherever possible because of the reluctance of some low-melting compounds to crystallize especially if traces of solvent are present. The compound is identified by cross reference of its melting or boiling point with the melting point of one of its derivatives.

Purification of Derivatives

When preparing a derivative, it is necessary that the product be obtained in a pure form, thus ensuring an accurate melting point. The procedure for recrystallisation is as follows: the crude material is dissolved in the minimum of hot solvent, filtered if necessary *without* suction, and the solution obtained allowed cooling slowly. The crystalline product is collected in a Buchner funnel, washed with a small volume of ice-cold solvent, dried thoroughly and the melting point determined. This procedure should be repeated until no further increase in melting point is observed.

If the crude material is badly discolored, it is often advantageous to add a little activated charcoal to the solution which should then be boiled gently for up to 5 minutes. The hot solution is filtered without suction and the filtrate allowed cooling slowly.



Recrystallisation

The procedure of preparation

Aim: To prepare suitable solid derivatives from given organic compound and confirmation of unknown compound by melting point.

Principle/ Theory:

- The preliminary examination and group classification tests indicate the particular class (functional group) to which an unknown organic compound may belong.
- It is always better to identify the unknown compound with certainty when its converted to sharp meting solid compound.
- This conversion of solid/ liquids compounds to sharp melting solid compounds is refereed as derivative.
- Liquid derivatives are not considered suitable.
- A derivative which melts above 80°C should be chosen wherever possible (best, between 80 - 150 ° C).
- The compound is identified by cross reference of its melting or boiling point with the melting point of one of its derivatives.
- When preparing a derivative, it is necessary that the product be obtained in a pure form, thus ensuring an accurate melting point.
- For purification of derivatives recrystallization is done.

The following table lists some of the classes of organic compounds and a selection of derivatives that may be prepared to characterize them.

Class of compound	Derivatives
Alcohols	3,5-dinitrobenzoate
Phenols	Benzoate, acetate, bromo-derivative
Aldehydes and ketones	Semicarbazone, 2,4-dinitrophenyl-hydrazone, oxime
Acids	Anilide, amide, p-toluidide.
Amines	Benzoyl, acetyl and sulphonamide derivatives

Converting Alcohol to 3,5-Dinitrobenzoate



3,5-dinitrobenzoic acid phosphorus pentachloride

3,5-Dinitrobenzoyl chloride

- Heat gently a mixture of 3,5-dinitrobenzoic acid (1 g) and phosphorus pentachloride (1.5 g) in a dry test tube, until it liquifies (5 min).*
- The liquid is poured on a dry watch glass and allowed to solidify. The phosphoryl chlorides are removed by
 pressing the solid with a spatula on a wad of filter paper.
- The residual acid chloride is suitable for immediate use in the preparation of the derivatives.

*Work under fume hood. Fumes are irritating to the eyes and nose.



- The 3,5-dinitrobenzoyl chloride is mixed with the alcohol (0.5 1 mL) in a loosely corked dry test tube and heated on a steam bath for about 10 min. (2° and 3° alcohols require up to 30 min)
- On cooling add 10 mL sodium hydrogen carbonate solution, stir until the ester crystallizes out, and filter at the pump.

Summary

Qualitative analysis of organic compounds is done to detect the presence of various elements such as phosphorus, nitrogen, sulfur and halogen elements..

Carbon and hydrogen are detected by heating the compound with copper (II) oxide. In this way, the carbon that is present in the compound will be oxidized to carbon dioxide and hydrogen to water. Carbon dioxide is tested by limewater which develops turbidity, and hydrogen is tested with anhydrous copper sulphate, which turns blue.

The phosphorous present in the organic compound is oxidized to phosphate by the **oxidizing agent sodium peroxide.** This solution is then boiled with nitric acid and treated with ammonium molybdate. As a result, a yellow precipitate is formed, indicating the presence of phosphorous. The yellow precipitate is ammonium phosphomolybdate, (NH₄)₃[PMo₁₂O₄₀]

The reaction is given below,

 $Na_3PO_4 + 3HNO_3 \rightarrow H_3PO_4 + 3NaNO_3$

H₃PO₄ + 12(NH₄)₂MoO₄ + 21HNO₃ →(NH₄)₃PO₄. Mo₁₂O₄₀ + 21NH₄NO₃ + 12H₂O

Note: sodium carbonate and potassium nitrate can be also used as oxidizing agents

Lassaigne's test extract is called as sodium fusion extract. The cyanides, sulphides and halides of sodium will be formed. These will be extracted from the fused mass by boiling it with distilled water. Hence, the name of the extract is sodium fusion extract.

Halogen elements are detected by Lassaigne's test. Fluorine cannot be detected by Lassaigne's test. Even though Lassaigne's test is used for the detection of halogens, all halogens except fluorine can be detected. This is because, in Lassaigne's test, the sodium extract is treated with silver nitrate. Only in the case of fluorine, the silver fluoride formed is soluble, unlike the others which is insoluble. Thus, the precipitate will not be formed and so, this method cannot be used for fluorine detection.

In the test for nitrogen, sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate (II). On heating with concentrated sulphuric acid, some iron (II) ions are oxidized to iron (III) ions which react with sodium hexacyanoferrate (II) to produce iron (III) hexacyanoferrate (II), which is Prussian blue in color. Moreover, nitrogen atoms are soluble in concentrated sulphuric acid.

 $\begin{array}{rcl} \underline{Test\ for\ Nitrogen:}\\ 6\ NaCN & +\ FeSO_4 & \rightarrow & Na_4[Fe(CN)_6] & +\ Na_2SO_4\\ Sodium\ cyanide & Sod.\ Ferrocyanide \\ FeSO_4 & \rightarrow & 2Fe_2(SO_4)_3\\ Na_4[Fe(CN)_6] & +\ 2Fe_2(SO_4)_3 & \rightarrow & Fe_4[Fe(CN)_6] & +\ Na_2SO_4\\ & & Ferricferrocyanide \\ & & prussian\ blue \end{array}$

In case, both nitrogen and sulphur are present in an organic compound, sodium thiocyanate is formed. The color formed is blood red and not Prussian blue. This is because, in this case, there are no free cyanide ions.

Na + C + N+ S \rightarrow NaSCN Fe³⁺ + SCN⁻ \rightarrow [Fe (SCN)] ²⁺ (blood red)

1. Sodium nitroprusside test

During the preparation of Lassaigne's extract, sulphur from the organic compound reacts with sodium to form sodium sulphide. It gives a purple colour with sodium nitroprusside due to the formation of sodium thionitroprusside.

 $2Na + S \rightarrow Na_2S$ (From organic compound)

 $\begin{array}{cccc} Na_2S & + & Na_2[Fe(CN)_5NO] \rightarrow & Na_4[Fe(CN)_5NOS] \\ (From sodium extract) & Sod. nitroprusside & Violet colouration \end{array}$

In the test for sulphur, the sodium fusion extract is acidified with acetic acid and lead acetate is added to it. Once this reaction takes place, a black precipitate is formed. This black precipitate is lead sulphide, indicating the presence of sulphur.

 $Na_2S + (CH_3COO)_2Pb \rightarrow PbS + 2CH_3COONa$ Black precipitate

Detection of halogens in Lassaigne's Test

1. Silver nitrate test

a. Chlorine

During the preparation of Lassaigne's extract, chlorine form the organic compound reacts with sodium to form sodium chloride. Sodium chloride gives a white precipitate of silver chloride with silver nitrate solution. The precipitate is soluble in ammonium hydroxide.

Na + CI
$$\rightarrow$$
 NaCI
(From organic compound)
NaCI + AgNO₃ \rightarrow AgCI + NaNO₃
Silver chloride
(White ppt.)
AgCI + 2NH₄OH \rightarrow [Ag(NH₃)₂]CI + 2H₂O
(Soluble)

b. Bromine

Sodium bromide formed during the preparation of Lassaigne's extract reacts with silver nitrate to form pale yellow precipitate of silver bromide, which is sparingly soluble in ammonium hydroxide.

Na + Br → NaBr (From organic compound)

c. lodine

Sodium iodide formed during the preparation of sodium fusion extract reacts with silver nitrate solution to form yellow precipitate of silver iodide, which is insoluble in ammonium hydroxide.

Nal + AgNO₃ → Agl + NaNO₃ Silver iodide (Yellow ppt.)

Note: Nitric acid is added to sodium fusion extract before adding for testing halogens **because nitric acid decomposes** sodium cyanide, NaCN and sodium sulphide Na₂S

Carius Method

Carius Method is also used to detect or estimate the halogens in organic compounds. The compound is heated with Conc. HNO₃ in the presence of <u>AgNO₃</u> in a hard glass tube called Carius tube. Carbon and hydrogen are oxidised to CO_2 and H_2O . The halogen forms the corresponding AgX.

The Beilstein test is a simple qualitative chemical test for organic **halides**. It was developed by Friedrich Konrad Beilstein.

A <u>copper</u> wire is cleaned and heated in a Bunsen burner flame to form a coating of **copper (II) oxide.** It is then dipped in the sample to be tested and once again heated in a flame. A positive test is indicated by a green flame caused by the formation of a copper halide.

This test is no longer frequently used. One reason why it is not widely used is that it is sometimes possible to generate the highly toxic <u>chloro-dioxins</u> if the test material is a **polychloroarene** (neoprene).

Chapters 3-5

Functional group is an atom or group or group of atoms in a molecule that gives the molecule that gives the molecule its characteristic chemical properties.

The same functional group will undergo the same or similar chemical reactions regardless of the rest of the molecule's composition.

A monofunctional molecule **possesses one functional group**, a difunctional two, a trifunctional three, and so on. Compounds which contain two or more are also termed as polyfunctional compounds

We can detect the alcoholic group by the following tests:

- Sodium Metal Test
- Acetyl Chloride Test
- Ceric Ammonium Test
- Iodoform test

Reagent + alcohol	If the test is positive, this is how to know it
Sodium Metal Test	the appearance of effervescence due to the liberation of hydrogen
	gas
Acetyl Chloride Test	the evolution of hydrogen chloride gas
	The hydrogen chloride gives white fumes of ammonium chloride
	with ammonium hydroxide
ceric ammonium nitrate	The appearance of pink or red colour

Carbonyls (Aldehydes and Ketones) test

What is Brady's Reagent?

An aqueous solution of **2,4-dinitrophenyl hydrazine(DNP)** is known as **Brady's reagent**. It reacts with carbonyl compounds (aldehydes and ketone) to give a **precipitate**.

Both aldehydes and ketones are carbonyl compounds.

Reagent + aldehyde or ketone	If the test is positive, this is how to know it
2,4-dinitrophenyl hydrazine	A crystalline precipitate indicates the presence of a
	carbonyl compound either aldehyde, ketone or both

Note: 2,4-dinitrophenyl hydrazine teat, we **cannot distinguish** between aldehydes and ketones. The following tests are carried out to distinguish between them.

Tests that can distinguish aldehydes from ketones:

- Tollen's Test (Silver Mirror Test
- Fehling's Test
- The Schiff's Test
- Tollen's Test: Tollen's' test, also known as silver-mirror test, Tollen's' reagent is an alkaline solution of ammoniacal silver nitrate and is used to distinguish aldehydes from ketones. We add 3-4 drops of the liquid to the Tollen's reagent. We heat the container. A shining silver mirror precipitate confirms the presence of the aldehyde.

 $2Ag(NH_3)_2^+$ + RCHO + $3OH^- \rightarrow RCOO^-$ + $2Ag^-$ + $4NH_3$ + $2H_2O$

Tollen's' reagent oxidizes an aldehyde into the corresponding carboxylic acid. Ketones are not oxidized by Tollen's' reagent, so the treatment of a ketone with Tollen's' reagent in a glass test tube does not result in a silver mirror

2. Schiff's Test:

We dissolve the given compound in alcohol and then add 1-2ml of Schiff's reagent. The appearance of **pink, red or magenta colour** confirms the presence of aldehyde group

Test of Aldehydes with Fehling's Test

Fehling's solution is a complex compound of Cu^{2+} . When the aldehyde compound is treated with Fehling's solution Cu^{2+} is reduced to Cu^{+} and the aldehyde is reduced to acids. During the reaction, a **red precipitate of copper (I) oxide (Cu₂O)** is formed.

 $\begin{array}{ccc} \mathrm{RCHO} & + & 2\mathrm{Cu}^{2+} + 5\mathrm{OH}^- & \longrightarrow & \mathrm{Cu}_2\mathrm{O}(s) \downarrow + \mathrm{RCOO^-} + 3\mathrm{H}_2\mathrm{O} \\ & & \\ \mathrm{Aldehyde} & & & \\ & &$

Note: The appearance of red precipitate confirms the presence of an aldehydic group.

Tests that can distinguish ketones from aldehydes :

- Sodium Nitroprusside Test
- m-Dinitrobenzene test

Ketone Test with Sodium Nitroprusside Test:

Ketone responds to this test. Ketone reacts with alkali and forms an anion which further reacts with sodium nitroprusside and forms a red *colouration* complex ion that *shows the presence of ketone*. Aldehydes do not respond to this test.

The chemical reaction is given below.

 $CH_3COCH_3 + OH^- \rightarrow CH_3COCH_2^- + H_2O$

 $[Fe(CN)_5NO]^{2-} + CH_3COCH_2^- \rightarrow [Fe(CN)_5NO.CH_3COCH_2]^{3-}$

M-dinitrobenzene test

Place 0.5 ml of the given liquid (or 0.5 g of solid) in a clean test-tube and add about 0.1 g of finely powdered m-dinitrobenzene. Now add about 1 ml of dilute sodium hydroxide solution and shake. Appearance of **violet** colour confirms ketonic group.

Carboxyl Group: We can identify Carboxylic acid by the following tests:

- Litmus test
- Sodium Bicarbonate test
- Ester Test

Sodium Bicarbonate test

We add **Sodium bicarbonate** (NaHCO₃) to the 1 ml of the sample. A brisk of effervescence indicates the presence of a carboxylic group.

 $RCO_2H + NaHCO_3 \rightarrow RCOONa + CO_2 + H_2O$

Ester Test

Carboxylic acid reacts with alcohol in the presence of concentrated **sulphuric acid** and forms a pleasant smelling ester. **The sweet, fruity smell of an ester confirms** the presence of ester.

 $\textbf{RCOOH} + \textbf{R-OH} + \textbf{H}_2\textbf{SO}_4 \rightarrow \textbf{RCOO-R} \text{ (Ester)} + \textbf{H}_2\textbf{O}$

Amino Group

The classification of primary, secondary or tertiary amines is done by means of the reaction with **nitrous acid.**

Nitrous Acid Test:

Preparation of Nitrous acid

Nitrous acid (HNO₂) is a weak acid. It is prepared by starting with solid sodium nitrate and using cold dilute hydrochloric acid.

We add 2g of the substance to 5 ml of 2 M HCl acid and 10% aqueous NaNO₂ solution. If we obtain a clear solution, with a continuous **evolution of nitrogen gas**, the substance is a primary amine.

 $RNH_2 + HNO_2 \rightarrow ROH + H_2O + N_2$

Aromatic amines and esters test with 20% NaOH

Take a little of organic substance in a test tube. Add 2 ml 20% NaOH solution and reflux for 30 minutes

Then cool and acidify with concentrated HCl. The **formation of white precipitate aromatic acid** indicates the presence of aromatic amides and aromatic esters

Refluxing

The process of heating a mixture for a chemical reaction to occur while condensing vapors and returning to the mixture as a liquid is known as **refluxing.**

Carbohydrates test with concentrated Sulphuric acid

Take a little of the substance in a clean test tube. Carefully add a few drops of concentrated **sulphuric acid** and heat it.

If you could observe a **black colour that is charring with the smell of burnt sugar**, it is an indication that the compound is carbohydrate.

The black colour is due to the formation of **carbon** by the dehydration of the carbohydrate on heating with the concentrated sulphuric acid.

$\textbf{C}_{12}\textbf{H}_{22}\textbf{O}_{11} \xrightarrow{\textbf{conc.H}_2\textbf{SO}_4} \rightarrow \textbf{6H}_2\textbf{O} + \textbf{6C}$

Aromatic Hydrocarbons

Aromatic Hydrocarbons **dissolves** gradually on heating with **concentrated sulphuric** acid; it shows the presence of aromatic hydrocarbon, it is due to the formation of corresponding **sulphonic acid**.

Notes to Solubility Tests

- Groups I, II (soluble in water). Test the solution with pH paper.
- Take small amount of the unknown in a clean test tube add a little amount of ether. If it is soluble in ether, the substance is a group one. If it is insoluble, it is group 2.
- HCl + a substance that is insoluble with water. If it is insoluble, it is group 3.
- 5% NaOH: If the substance is insoluble in water but dissolves in 5% sodium hydroxide, it is group IV (carboxylic acids and phenols).
- Add approximately 1 mL of 5% NaHCO₃ to if it is soluble, it is carboxylic acid and if not it is Phenolic.

Preparation of Derivatives

Before an organic compound can be identified with certainty, it is necessary that it be converted to at least one other sharp-melting solid compound called a 'derivative'; liquid derivatives are not considered suitable. A derivative which melts above 80° should be chosen

Purification of Derivatives

Recrystallisation is how to purify the derivatives



Preliminary Test and Physical Examination

Test		Observation	Inference	
Ignition Test				
Flame Test: Take a small quantity of compound and put it on a metallic spatula or in a porcelain dish and ignite it directly on the Bunsen burner	Non-sooty Flame		Aliphatic compounds	
	Sooty Flame because high percentage of carbon		Aromatic compounds	
	Ν	Melts and chars with a smell of burnt sugar		
	C	Carbohydrates may be present		
Test for Unsaturation				
a. Action of alkaline KMnO ₄ (Baeyers test):		Decolorization of	Unsaturated compounds may	
Sub (solid/Liquid) + Sodium carbonate		KMnO₄	be present	
solution + few drops of 2% $KMnO_4$ solution –				
Shake vigorously				
		No Decolorization of	Saturated compounds may	
		KMnO ₄	be present	
b. Action of Bromine Water (for freely or		Decolorization	Unsaturated compounds may	
sparingly water soluble compounds):			be present	
Sub (solid/Liquid) + Bromine water dropwise –				
Shake vigorously				

Beilstein's Test: Make one end of a copper wire in	Burns with green flame	Urea, Chlorides, Bromides may be present
the form of a loop and heat it on a burner till flame is no longer coloured. Cool the wire and dip the loop in little of the sample and ignite the loop again in flame.	Burns without green flame	Flourides may be present Or other halides

Questions

1. Carbon and hydrogen are detected by heating the compound with which of the following?

- A) Copper (II) oxide
- B) Iron (II) oxide
- C) Iron (III) oxide
- D) Copper (I) oxide

Answer: A

Explanation: Carbon and hydrogen are detected by heating the compound with copper (II) oxide. In this way, the carbon that is present in the compound will be oxidized to carbon dioxide and hydrogen to water. Carbon dioxide is tested by limewater which develops turbidity, and hydrogen is tested with anhydrous copper sulphate, which turns blue.

2. Which compound gets precipitated in the detection of carbon and hydrogen?

- a) Copper
- b) Carbon dioxide
- c) Calcium carbonate
- d) Copper sulphate
- View Answer

Answer: c

Explanation: Calcium carbonate (CaCO₃) gets precipitated during the detection of carbon and hydrogen. Firstly carbon will react with copper (II) oxide to form copper and carbon dioxide. Then, hydrogen will react with the same copper (II) oxide to form copper and water. After this, the presence of carbon dioxide is tested by reacting it with calcium hydroxide and the product obtained is calcium carbonate, which gets precipitated and water.

3. Identify the element that cannot be detected by Lassaigne's test.

- a) Nitrogen
- b) Fluorine
- c) Sulfur
- d) chlorine

View Answer

Answer: b

Explanation: Fluorine cannot be detected by lassaigne's test. Even though lassaigne's test is

used for the detection of halogens, all halogens except fluorine can be detected. This is because, in lassaigne's test, the sodium extract is treated with silver nitrate. Only in the case of fluorine, the silver fluoride formed is soluble, unlike the others which is insoluble. Thus, the precipitate will not be formed and so, this method cannot be used for fluorine detection.

4. Potassium can replace sodium in lassaigne's test.

a) True

b) False

Answer A

Explanation: Potassium, like sodium is electropositive in nature. In lassaigne's test, the elements present in the compound are converted from their covalent form to their ionic form by fusing the compound with sodium metal. Since, potassium has similar characteristics of electro positivity as sodium and since potassium is highly reactive, it can be used instead of sodium in lassaigne's test.

5. What is Lassaigne's test extract called as?

- a) Fusion extract
- b) Sodium fusion extract
- c) Lassaigne extract

d) Sodium extract

View Answer

Answer: b

Explanation: Lassaigne's test extract is called as sodium fusion extract. The cyanides, sulphides and halides of sodium will be formed. These will be extracted from the fused mass by boiling it with distilled water. Hence, the name of the extract is sodium fusion extract.

6. In the test for nitrogen, the sodium fusion extract is acidified with which of the following?

- a) Dilute sulphuric acid
- b) Dilute hydrochloric acid
- c) Concentrated hydrochloric acid
- d) Concentrated sulphuric acid

View Answer

Answer: d

Explanation: In the test for nitrogen, sodium cyanide first reacts with iron (III) sulphate and forms sodium hexacyanoferrate (II). On heating with concentrated sulphuric acid, some iron (II) ions are oxidized to iron (III) ions which react with sodium hexacyanoferrate (II) to produce iron (III) hexacyanoferrate (II), which is Prussian blue in color. Moreover, nitrogen atoms are soluble in concentrated sulphuric acid.

7. What is the color of the precipitate obtained in the test for sulphur?

- a) White
- b) Black
- c) Violent

d) Blue View Answer

Answer: b

Explanation: In the test for sulphur, the sodium fusion extract is acidified with acetic acid and lead acetate is added to it. Once this reaction takes place, a black precipitate is formed. This black precipitate is lead sulphide, indicating the presence of sulphur.

8. In case of both nitrogen and sulphur existence, Prussian blue is still the color of the end product.

a) True b) False

, View Answer

Answer: b

Explanation: In case, both nitrogen and sulphur are present in an organic compound, sodium thiocyanate is formed. The color formed is blood red and not Prussian blue. This is because, in this case, there are no free cyanide ions.

Na + C + N+ S → NaSCN Fe³⁺ + SCN⁻ → [Fe (SCN)] ²⁺ (blood red)

9) A X color precipitate, which is Y in ammonium hydroxide indicates presence of chlorine. Identify X and Y:

a) X = yellowish, Y = soluble

- b) X = yellow, Y = insoluble
- c) X = white, Y = insoluble
- d) X = white, Y = soluble View Answer

Answer: d

Explanation: During the detection of chlorine, when the organic compound reacts with sodium, it forms sodium chloride. This sodium chloride gives the white precipitate of silver nitrate with silver nitrate solution. This white precipitate is also soluble in ammonium hydroxide.

10. Which is the oxidizing agent used in the test for phosphorous?

- a) Hydrogen peroxide
- b) Potassium nitrate
- c) Sodium peroxide Answer: c

d) Nitric acid

Explanation: The phosphorous present in the organic compound is oxidized to phosphate by the oxidizing agent sodium peroxide. This solution is then boiled with nitric acid and treated with ammonium molybdate. As a result, a yellow precipitate is formed, indicating the presence of phosphorous.

11) Nitric acid is added to sodium extract before adding silver nitrate for testing halogens because

A) Nitric acid reduces sulphide

B) Nitric acid decomposes NaCN and Na₂S Answer B

C) Nitric acid oxidizes the organic compounds

D) Nitric acid acts as dehydrating agent

12) The Prussian blue colour obtained during the test of nitrogen by Lassaigne's test is due to the formation

- A) $Fe_4[Fe(CN)_6]_3$
- B) Na₃[Fe(CN)₆]
- _{C)} [Fe(CN)₃
- D) Na₄[Fe(CN)₅ NOS]

Answer A

13) Aromatic compounds burn with sooty flame because

- A) They have a relatively high percentage of hydrogen
- B) They have a relatively high percentage of carbon
- C) They have a ring structure
- D) They are reluctant to react with atmospheric oxygen.

Answer B

14) What is the significance of qualitative analysis in organic compounds?

Qualitative analysis of the organic compound **helps in determining the presence or absence** of a particular compound or element.

15) What is Qualitative Analysis of organic compounds in Chemistry?

Qualitative analysis of organic compounds is a method to detect the presence of various elements such as phosphorus, nitrogen, sulfur and halogen elements.

16. How is the Test of Halogens done for its Detection in an Organic Compound?

It is performed by acidifying a portion of the fusion solution with dilute nitric acid. Further, excess silver nitrate solution is added where a precipitate formed indicates the halogen presence

17. Which method is used to estimate carbon and hydrogen?

Liebig's combustion method is used to detect or estimate carbon and hydrogen. The hydrogen present is oxidized to water and the carbon present is oxidized to carbon dioxide

18) State how aliphatic compounds burn?

They burn non-sooty flame

19) Why aromatic compounds burn with sooty flame?

Because they have a relatively high percentage of carbon

20) Why fluorine element that cannot be detected by Lassaigne's test? The silver fluoride formed is soluble, unlike the others which is insoluble. Thus, the precipitate will not be formed and so, this method cannot be used for fluorine detection.

21) How can you identify the presence of alcoholic functional group in a given organic compound?

Any of the following tests can be carried out to detect the alcoholic functional group.

- 1. Sodium metal test
- 2. Ester test
- 3. Ceric ammonium nitrate test
- 4. Acetyl chloride test
- 5. Iodoform test
- 22. What is used for Ceric Ammonium Nitrate Test?
 - It is carried out to detect the alcoholic functional group
- 23. What is the colour of the precipitate that is formed in ceric ammonium nitrate test?
- 24. Write down the steps of ceric ammonium nitrate test
 - 1. Take 1ml of given compound in a dry test tube.
 - 2. Add a few drops of ceric ammonium nitrate reagent and shake the solution well.
 - 3. Observe the solution.
 - 4. If red precipitate appears then the presence of alcoholic group is conformed.
- 25. Why the given alcohol is dried completely before carrying out sodium metal test?

Alcohol is dried completely before carrying out sodium metal test because sodium itself reacts with water vigorously.

26. Give the names of any four functional groups? Some functional groups are:

- Hydroxyl group (-OH)
- Amino group (-NH₃)
- Acid group (-COOH)
- Aldehyde group (-CHO)

26. Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

The added nitric acid decomposes NaCN to HCN and Na2S to H2S.

$$\label{eq:acnor} \begin{split} &\mathrm{NaCN} + \mathrm{HNO}_3 \rightarrow \mathrm{NaNO}_3 + \mathrm{HCN} \\ &\mathrm{Na}_2\mathrm{S} + 2\mathrm{HNO}_3 \rightarrow 2\mathrm{HNO}_3 + \mathrm{H}_2\mathrm{S} \end{split}$$

This removes all the nitrogen and sulphur present. Hence, only halogen is available for testing