
UNIT 3 PRELIMINARY QUALITATIVE ANALYSIS

Structure

- 3.1 Introduction
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- 3.2 Classical Qualitative Organic Analysis for Identification of a Pure Compound
- 3.3 Physical Examination
- 3.4 Elemental Analysis
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- 3.6 Determination of Physical Constants
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3.1 INTRODUCTION

In the first block of this course we learnt how the organic synthesis are carried out. We also exposed you to simple laboratory techniques. The compounds isolated from a reaction mixture or from some natural source may be unknown. Identification and characterization of the structure of unknown substances constitute vital part of organic chemistry. Introduction into this area is provided by a study of qualitative organic analysis, which is an essential part of the training of the organic chemist.

In this unit we shall describe the stepwise procedures that may be followed to identify a monofunctional and pure unknown compound using classical methods. In recent years, the development of chromatographic methods of separation and analysis by spectroscopic techniques has revolutionised the qualitative organic analysis. These techniques are discussed in chemistry Lab-12 and 'Spectroscopy' courses.

Objectives

After studying this unit and performing the experiments set in it, you should be able to :

- describe the steps involved in the identification of unknown compounds by classified qualitative organic analysis,
- carry out the physical examination of organic compounds
- determine nitrogen , sulphur, and halogens,
- determine the solubility of a organic compound,
- describe the method of the identification of a unknown organic compound,
- describe how to prepare a notebook for the experiments of qualitative organic analysis,

3.2 CLASSICAL QUALITATIVE ORGANIC ANALYSIS FOR IDENTIFICATION OF A PURE COMPOUND

The classical qualitative organic analysis consists of a series of steps that helps to establish the identity of the unknown compound. These steps are

- i) Physical examination
- ii) Elemental analysis to determine the presence of elements other than carbon, hydrogen, and oxygen
- iii) Solubility test in water, dilute bases and dilute acid
- iv) Determination of physical constants
- v) Functional group analysis using classification tests
- vi) Preparation of derivatives

While analysing organic compounds, we can follow first four steps in any order, but before performing the qualitative test for functional groups. Our final step must always be the preparation of one or more solid derivatives. For performing this steps you are again going to use laboratory techniques which we have already mentioned in Unit 1 of block 1. Let us discuss these steps one by one.

3.3 PHYSICAL EXAMINATION

In the physical examination we consider following points:

Check of Sample Purity: In this lab course we are providing unknown organic compound in pure form so it is not necessary for you to check the sample purity. Otherwise, first step of qualitative organic analysis is the purity check by boiling point or melting point or tlc or gas or paper chromatography. This we have already mentioned in Unit 1 of Block 1.

Note the physical state: The physical state of the compound whether it is solid or liquid should be indicated.

Note the colour: The colour is also informative. Common coloured compounds include nitro and nitroso compounds (yellow), α -diketones (yellow), quinones (yellow to red), azo compounds (yellow to red). Phenols and amines are often brown to dark- purple because of traces of air oxidation products.

Note the odour: The odour of many organic compounds is highly distinctive. Amines are recognisable by their fishy odour, esters are often pleasantly fragrant. Alcohols, ketones, aromatic hydrocarbons and aliphatic alkenes have characteristic odours. Thiols, isonitriles and low-molecular weight carboxylic acids possess unpleasant odours.

Make an ignition test: Take a small amount of given sample on a spatula and heat the spatula on a burner to see if it solid melts normally and then burns. Observe the flammability and nature of the flame. A yellow, sooty flame is indicative of an aromatic or a highly unsaturated aliphatic compound, a yellow but nonsooty flame is characteristic of aliphatic hydrocarbons. Halogenated or highly oxygenated compounds often burn with difficulty or not at all (for example carbontetrachloride is used as fire-extinguisher).

Caution: Do not taste an unknown compound. To note the odour cautiously smell the compound. Many organic compounds are intensely lachrymatory or worse.

The characteristic odour of sulphur dioxide indicates the presence of sulphur in the compound. Certain compounds like sugars char and leave a black residue on the spatula and emit a characteristic odour.

If a white, nonvolatile residue is left after ignition, add a drop of water and test the solution with litmus or pH paper. A sodium (or other metal) salt is indicated by an alkaline test.

Experiment No.1

Carry out Physical Examination of Some Organic Compound

For this experiment we are providing six organic compounds.

Requirement:

Chemicals

Samples

Apparatus

Burner

Spatula

Procedure

Take six organic samples from your counsellor and follow the procedure as mentioned above for physical state, colour, odour and ignite test for each sample. Report your results in the Table given below:

Table 3.1 : Physical Examination of Organic Compounds

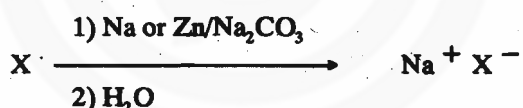
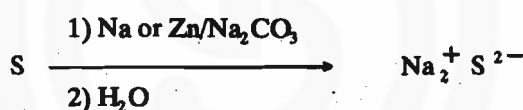
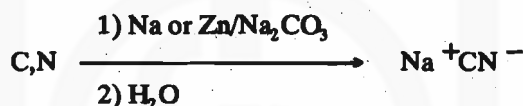
Sample No.	Physical State	Colour	Odour	Ignite test	Conclusive (Aromatic or aliphatic)
1					
2					
3					
4					
5					
6					

Discuss your results with your counsellor.

3.4 ELEMENTAL ANALYSIS

The technique of elemental analysis involves the determination of which elements may be present in a compound. The halogens, sulphur, oxygen, and nitrogen are the elements other than carbon and hydrogen that are most commonly found in organic molecules. There is no direct method for the detection of oxygen. Its presence as a part of functional group will become apparent later. Presence of other hetero atoms, may be detected using the Lassaigne fusion technique where the organic compound heated with metallic sodium, or by Middleton's fusion using sodium carbonate and zinc in place of sodium.

In both methods analysis is based on the conversion of the hetero atoms to inorganic salts such as cyanide, sulphide or halide.



Bonding in organic compound are generally covalent, therefore, like inorganic compound, no direct method available for the detection of elements. In sodium fusion method covalent bonds of hetero atoms are broken by heating of organic compounds with sodium metal. This results in the formation of inorganic ions involving these elements: X⁻ ions from halogens, S²⁻ ion from sulphide, CN⁻ ion from nitrogen. These ions can in turn be readily identified by inorganic qualitative methods.

Organic
Compounds

Though Middleton's method is less hazardous and also considered to be superior to Lassaigne fusion for the analysis of volatile compounds, but for this method very pure zinc powder is required. In this course we shall consider only the Lassaigne fusion method.

Experiment No. 2

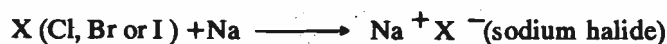
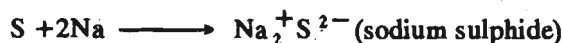
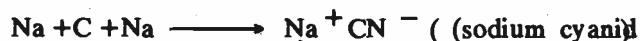
Determination of Nitrogen, Sulphur and Halogens by Lassaigne Sodium Fusion Method

For this experiment, we are providing six compounds.

Introduction

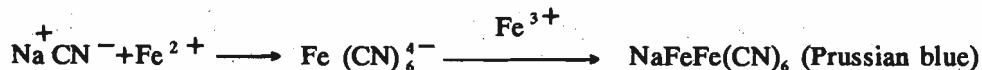
The basis of the sodium fusion procedure is as follows. On fusion with sodium the elements present in organic compounds are converted to ionic forms involving nitrogen, sulphur and halogens if they were present in the organic compound. As mentioned above nitrogen containing organic compound gets converted to cyanide ions, sulphur containing organic compounds to sulphide ion and halogen containing organic compound to halide ion. After the organic compound has been heated with sodium metal, the residue is hydrolysed with distilled water to destroy the excess sodium and dissolve the inorganic ions that are formed as a result of fusion reactions.

Owing to its potentially hazardous nature, the fusion operation should be carried out very carefully. The face should be kept away from the mouth of the test tube at all time. Acid pointing the fusion tube in the direction of anybody else.

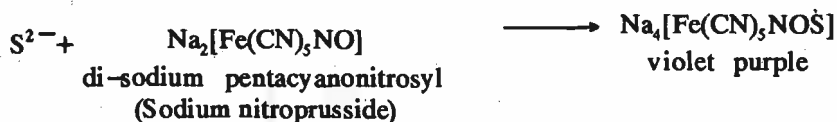
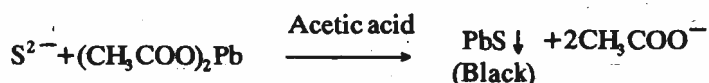


The aqueous solution of these ions are divided into five portions and each can be analysed by using following qualitative tests:

- i) **Detection of nitrogen:** First portion of the aqueous solution is carefully acidified, followed by addition of ferrous ion, Fe^{2+} , and ferric ion, Fe^{3+} . This converts the cyanide ion into sodium ferric ferrocyanide, which precipitate as an intense blue solid called 'Prussian blue'.



- ii) **Detection of Sulphur:** In second portion of aqueous solution the sulphur can be detected by precipitation as black lead sulphide with lead acetate solution and acetic acid or by the violet or purple colour produced by addition of di-sodium pentacyanonitrosyl ferrate (sodium nitro-prusside) in third portion.



- iii) **Detection of Halogens:** Fourth portion of aqueous solution is acidified with dilute nitric acid and boiled to remove any sulphide or cyanide ions that are expelled as hydrogen sulphide or hydrogen cyanide, respectively. Sulphide and cyanide must be removed because they interfere with the test for halogens. In this portion silver nitrate solution is added, and the presence of halide is detected by the formation of a precipitate of silver halide.



The colour of the precipitate provide a tentative indication of the halogen present:

AgCl (White solid)

AgBr (light yellow)

AgI (dark yellow solid)

Positive identification of halide ions can be made by the following inorganic qualitative test. Carbon tetrachloride or chloroform and chlorine water added to fifth portion of aqueous solution. Shake the solution and check the colour of chloroform or carbon tetrachloride layer (lower layer).

Violet colour is due to iodide ion, orange or brown colour is due to bromide ion and no colour and positive test with AgNO_3 indicate the presence of chloride ion.

Requirements

Chemicals

Samples

Sodium metal (4mm cube)

Iron (II) sulphate (Ferrous sulphate); Iron (III) chloride, (Ferric Chloride) (5%).

Dilute sulphuric acid (5%).

Solution of disodium pentacyanonitrosylferrate (0.1%) (sodium nitroprusside)

Dilute nitric acid (5%).

Silver nitrate solution (5%).

Chlorine water.

Carbon tetrachloride or chloroform.

Acetic acid

Lead acetate solution (0.15 M)

Apparatus

Burner

Six fusion tube

Six test tubes

China dish

Tongs

Wire gauze

Tripod

Apparatus for filtration.

Procedure

Add 15 cm³ of distilled water into a clean china dish and place it near to your burner. Place about 20 mg of your sample in the bottom of a small fusion tube or in case of liquid take one or two drops of liquid in a fusion tube with the help of pipet or dropper. Use tongs to hold the fusion tube. Put a piece of sodium roughly a 4 mm cube into the mouth of the test tube, without allowing it to come into contact with the substance at the bottom. Heat the sodium gently over a small burner flame until it melts and runs down into the sample. There may be a very vigorous reaction when the molten sodium touches the sample. Heat the tube gently for 1 min; and then heat more strongly until the bottom of the tube glows red hot. Holding the gauze with tongs in your free hand drop the red hot fusion tube into the water of china dish and cover it immediately with gauze.

If the fusion tube does not break when it comes in contact with water, crush it with the help of a glass rod. Allow any excess sodium to react and when the reaction has subsided, place the china dish on the gauze on a tripod and boil the solution for 2 min. Filter the solution whilst hot, to remove the broken glass and charred material and divide this aqueous solution in five equal portions in five test tubes.

Caution : Manipulate sodium with a knife and tongs or forceps : never touch it with the fingers. Wipe it free of kerosene with dry filter paper.

1. Detection of Nitrogen

Add 200 mg of iron (II) sulphate to the first portion heat the solution to boiling and add 2 drops of ferric chloride solution add sufficient dilute sulphuric acid to dissolve any precipitate and make the solution acidic. The formation of a deep blue precipitate or colouration (Prussian Blue) indicates the presence of nitrogen in the original organic compound. If the solution is green or blue-green, filter it; washing the filter paper with distilled water, and examine the residue for the blue colouration.

Red hot fusion tube will shatter on contact with the water, releasing any unreacted sodium, and the gauze stop the loss of any material.

2. Detection of Sulphur

- i) Acidify second portion of aqueous solution with acetic acid, and add a few drops of lead acetate solution. A black precipitate of PbS indicates the presence of sulphur in the original organic compound.
- ii) In third portion of aqueous solution add 2 cm³ of the disodium pentacyanonitrosyl ferrate solution. The purple colouration which fades slowly on standing confirms that sulphur is present.

3. Detection of Halogens

To the fourth portion of aqueous solution, add sufficient nitric acid to render the solution acidic and boil the mixture until its volume has been halved.

Add 1 cm³ of the silver nitrate solution to this mixture. The observation of a white or yellowish thick precipitate indicates the presence of halogen in the original organic compound. A faint turbidity should not be interpreted as a positive test. Tentative identification of the particular halogen may be made on the basis of colour: Silver chloride is white, silver bromide is pale yellow, and silver iodide is yellow.

To further distinguish the halogen present, add 0.5 cm³ of carbon tetrachloride or chloroform to the fifth test tube. Add chlorine water dropwise to the mixture with gentle shaking. The appearance of a brown colouration in the bottom layer indicates bromine, whereas a purple or violet colouration indicates iodine. By the

The heating of aqueous solution with HNO₃ has the effect of removing any HCN or H₂S if cyanide or sulphides are present which would interfere with this test. It may be omitted if nitrogen and sulphur have been shown to be absent.

process of elimination, a sample which gives a white precipitate with silver nitrate, but no colouration on treatment with chlorine water must contain chlorine. Repeat above mentioned procedure for all given six organic compound and report your results in the Table given below:

Table 3.2 : Elemental analysis of organic samples

Sample No.	Element present
1	
2	
3	
4	
5	
6	

Discuss your result with your counsellor.

3.5 SOLUBILITY TEST

Solubility test of an organic compound in water, dilute acid or dilute base can provide useful, but not definitive, information about the presence or absence of certain functional groups.

Procedure for solubility tests

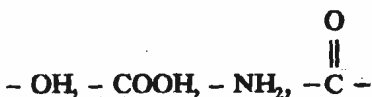
The solubility tests are done at room temperature. With 100 mg of a solid (finely crushed) or 0.2 cm³ liquid and 3.0 cm³ of solvent in small test tubes. The mixture should be shaken vigorously. It is recommended that the solubility tests be done in the order presented below:

Solubility in Water

Weight out 100 mg of the finely produced solid or measure 0.2 cm³ of liquid with the help of graduated pipette or burette treat it with successive 1.0 cm³ portion of distilled water, shake vigorously after each addition until 3.0 cm³ have been added. If the compound does not dissolved completely in 3.0 cm³ of water, it may be regarded as insoluble in water.

Now test the contents of the test tube with pH paper. This test can be done by taking one drop of solution with the help of glass rod and touch it with pH paper.

The solubility of the compound with distilled water suggests the presence of a low molecular weight organic compound (4-5 carbon), which contain a polar group such as

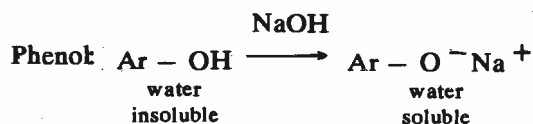
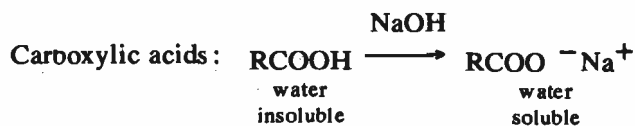


If higher molecular weight compound, it must be polyfunctional, for example carbohydrates. On the other hand, alkanes, alkenes, alkynes and alkyl halides are water-insoluble.

If the organic compound is water soluble and give positive acidic test with pH paper, the compound is likely to be a low molecular weight carboxylic acid such as acetic acid. If compound gives positive basic test with pH paper the compound is a low molecular weight organic base such as diethylamine. A neutral solution suggests the presence of a neutral polar compound such as ethanol or acetone.

Solubility in 5% Sodium Hydroxide

If the compound is insoluble in distilled water, it should be similarly tested for solubility in 5% aqueous sodium hydroxide solution. This solubility indicates the presence of a carboxylic acid, sulphonic acid, or phenol. Because they are converted into their water - soluble sodium salts.

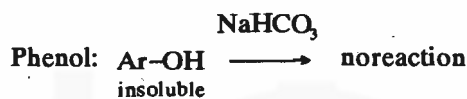


NaOH soluble organic compound should then be tested for solubility in the weaker base, 5% NaHCO₃, which may permit distinction between carboxylic and phenolic functional groups.

Solubility in 5% Sodium Bicarbonate

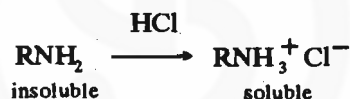
Similar to the procedure adopted for the solubility of water, the solubility of compound is checked with 5% aqueous solution of sodium bicarbonate. If it is soluble, the presence of a carboxylic acid group may be tentatively concluded, owing to the formation of the water-soluble sodium salt. Phenols are insoluble in sodium bicarbonate.

Highly acidic phenols are soluble in 5% sodium bicarbonate



Solubility in 5% Hydrochloric Acid

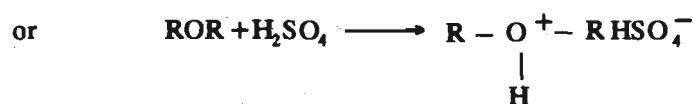
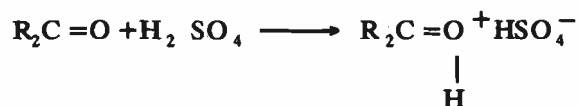
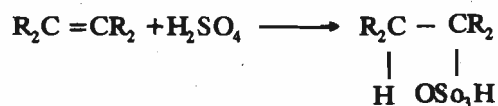
The solubility in 5% aqueous hydrochloric acid is evidence for an amino compound or a heteroatomic base.



Any unknown insoluble in all the reagents so far should also be checked for solubility in concentrated sulphuric acid.

Solubility in Concentrated Sulphuric Acid

Place 3 ml of concentrated sulphuric acid with the help of graduated pipette in a dry test tube and add 100 mg of solid or 0.2 cm³ of liquid. The solubility of organic compound in H₂SO₄ indicate the presence of oxygenated and unsaturated aliphatic materials.



The general solubility behaviour of common classes of organic compound is shown schematically in Fig. 3.1.

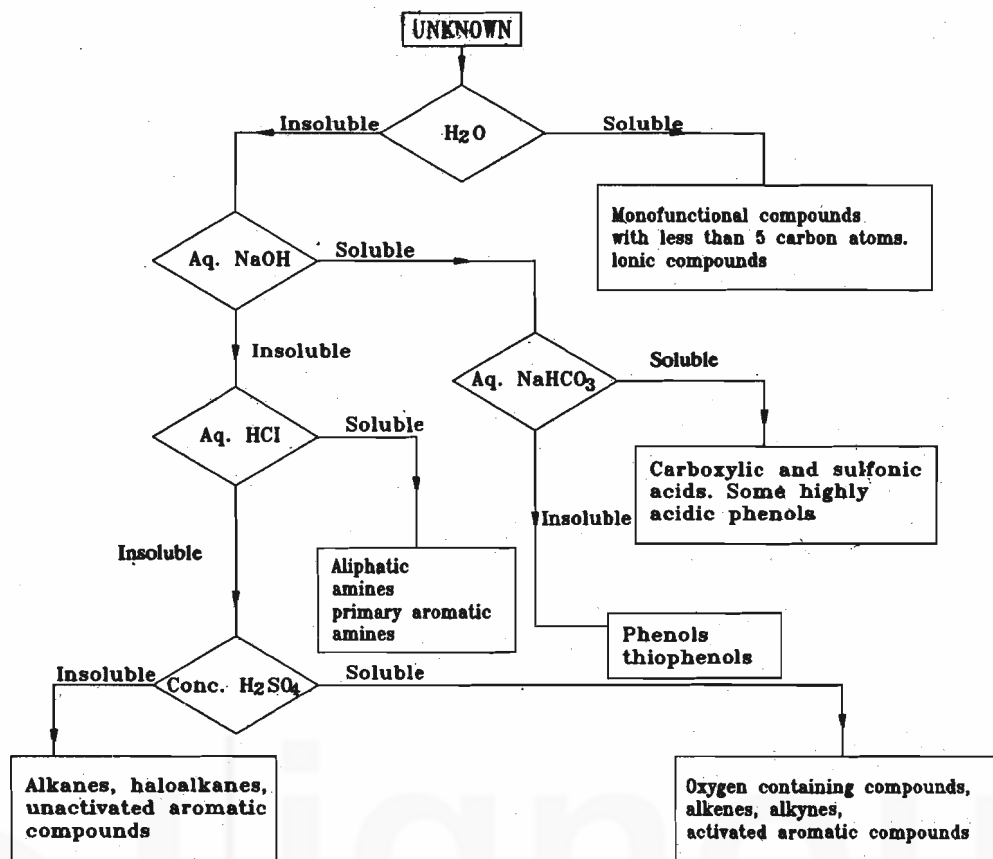


Fig. 3.1 : Solubility behaviour of common classes of organic compounds

Experiment 3

Determination of Solubility of Some Organic Compound

For this experiment we are providing six organic compound.

Requirement

Chemical

Samples

Distilled water

NaOH solution (5%)

NaHCO₃ solution (5%)

HCl solution (5%)

Conc. H₂SO₄

pH paper

Apparatus

Small test tubes (4)

Burettes (5)

Push

Balance

Procedure

Follow the procedure for solubility as discussed earlier for each sample and report your results in the Table 3.3 given below:

Table 3.3 : Solubility test of Organic Samples.

Preliminary Qualitative Analysis

Sample No.	Solubility				Conc. H ₂ SO ₄	pH test	Remark
	H ₂ O	NaOH	NaHCO ₃	HCl			
1							
2							
3							
4							
5							
6							

On the basis of these analysis make preliminary proposals as the nature of your samples. Discuss your results with your counsellors.

3.6 DETERMINATION OF PHYSICAL CONSTANTS

Procedural details for the determination of melting point and boiling point of organic compound is given in Unit 1 of Block 1 of this course. When looking for candidate structures on the basis of the melting point or boiling point which we have recorded for our unknown, it is necessary to include for consideration compounds which have values within 5°C. For this purpose we are giving tables of organic compound with their melting or boiling points in Appendix. We can select our probable compounds from the tables on the basis of the melting point or boiling point of unknown compound. Discard those compounds which do not fit with results obtained from physical examination, elemental test and solubility test. But still these informations generally lead to many positive substances for the unknown. It is now necessary to pinpoint the actual compound from our list of candidates structures. This will involve the functional group identification and the preparation of atleast two derivatives. These information together with the informations of physical examination, elemental analysis, solubility, confirm the actual substance.

3.7 FUNCTIONAL GROUP IDENTIFICATION

Though it is rare for an unknown to possess just one functional group, but in this laboratory course we will provide you only monofunctional compounds. Our classical scheme involves performing a number of chemical tests on a substance, each of which is specific for a type of functional group. Table 3.4, indicates the common classes of monofunctional organic compounds which we are going to discuss. The detail of these tests will be discussed in Units 4 and 5. The results of these tests usually allow the assignment of the unknown to a structural class such as alkene, aldehyde, ketone or ester, etc.

Table 3.4 : Common classes of monofunctional organic compounds

Neutral compounds	Acidic compounds	Basic compounds
C, H, O compounds	C, H, O compounds	C, H, N compounds
Aldehydes	Carboxylic acids	Amines
Ketones		
Esters	Phenols (weakly acidic)	
Alcohols		
Ethers	C, H, O, halogen compounds	
	Acyl halides	
C, H compounds		
Alkenes		
Alkynes		

Neutral compounds	Acidic compounds	Basic compounds
Arenes		
C, H, halogen compounds		
Halides		
C, H, N, O compounds		
Nitro-compounds		
Amides		

The results obtained from the elemental analysis and solubility tests can be used to advantage in deciding which functional group tests should be performed initially or which should not be done at all. The following examples illustrate the use of the preliminary work in making these decisions:

- i) If a compound is found to contain nitrogen and to be soluble in dilute HCl, a classification test for an amine should be applied first.
- ii) The test for a phenol should be performed on an unknown that is soluble in dilute sodium hydroxide but insoluble in dilute sodium bicarbonate.
- iii) If the elemental analysis indicates the absence of halogen, the test for alkyl or aryl halides can be omitted.
- iv) The absence of nitrogen means that tests for amines, amides, nitriles and nitro compounds need not be performed.

3.8 PREPARATION OF DERIVATIVES

After confirming the presence of the functional group in the unknown sample, we prepare crystalline derivatives to identify the actual substance by comparison of melting points with literature values. The ideal derivative should be simply and quickly prepared by a high yielding. It should also be easily purified and identified. These also have sharp and definite melting points preferably between 50°C and 250°C. In this work, you would be well advised not to jump to premature conclusions about the likely identity of your compound always prepare one derivative and check that its properties agree with those expected before leaping into the preparation of the second confirmatory derivative. The detail discuss to prepare derivatives for different functional groups will be discussed in Units 4 and 5.

So far in this unit we have discussed different steps that are evolved to establish the identity of the unknown compound. In next section, we will discuss how we prepare laboratory note- books of classical qualitative analysis.

3.9 QUALITATIVE TYPE OF EXPERIMENT AND LABORATORY NOTE BOOK

In Section 1.7 of Unit 1 (Block 1), we have discussed what important points one may keep in mind while preparing a laboratory note book for organic experiments. Here we will discuss a possible format for qualitative type experiments.

Each experiment should start on a fresh page, which should contain a title and experiment number at the top.

A sample note book format for qualitative experiment is given here. Identification of 2-naphthol (β -naphthol) is taken as our example.

Experiment No. 'A'

Identification of an Unknown Organic Compound

1. Physical Examination

- | | |
|-------------------|-----------------------------------|
| a) Physical state | solid |
| b) Colour | white |
| c) Odour | moth balls like |
| d) Ignition test | luminous, sooty flame, no residue |

Comment: This suggests that the unknown 'A' is aromatic compound.

2. Elemental Analysis

N, S, Cl, Br, I None

3. i) Solubility test

H ₂ O	5% NaOH	5% NaHCO ₃	5% HCl	Conc. H ₂ SO ₄	Expected Class
–	soluble	soluble	–	–	Acidic phenols, carboxylic acids

iii) Reaction to pH paper neutral

4. Physical Constants

Melting point observed 122 - 124°C

5. Class determination

- i) with aq. FeCl₃ no colour
 ii) with alcoholic FeCl₃ green solution

Comment: These tests indicate the presence of phenolic compound.

6. Examination of literature

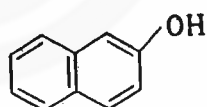
Possible compound	M.P.	Derivatives Benzoate	1-Naphthyl Urethane
2-Naphthol	123°C	107°C	157°C

Comments: Picric acid also have M.P. 122°C. Elemental analysis shows negative test for nitrogen element. That's why it is not selected.

7. Preparation of derivatives

- (a) Derivative chosen Benzoate
 M.P. observed 106 - 107°C
 M.P. in literature 107°C
 (b) Derivative chosen 1-Naphthyl urethane
 M.P. observed 156-158°C
 M.P. in literature 157°C

8. The unknown compound is 2-naphthol. The structure of this compound is



UNIT 4 QUALITATIVE CLASSIFICATION TESTS AND PREPARATION OF DERIVATIVES-I

Structure

- 4.1 Introduction
 - Objectives
- 4.2 Functional Group Identification
- 4.3 Aldehydes and Ketones
 - Functional Group Test
 - Characteristic Derivatives
- 4.4 Alcohols
 - Functional Group Test
 - Characteristic Derivatives
- 4.6 Phenols
 - Functional Group Test
 - Characteristic Derivatives
- 4.6 Carboxylic Acids
 - Functional Group Test
 - Characteristic Derivatives
- 4.7 Esters
 - Functional Group Test
 - Characteristic Derivatives
- 4.8 Answers

4.1 INTRODUCTION

In the last Unit you have studied elementary analysis methods of organic compounds, e.g., physical examination, elemental analysis, solubility test and determination of physical constants etc. In this unit first you will learn the identification of organic compounds having carbon, hydrogen and oxygen elements (aldehydes, ketones, alcohols, phenols, carboxylic acids and esters) and then you will study the methods for the preparation of their derivatives.

Objectives

After studying this unit, you should be able to test and derivatise the following compounds :

- Aldehydes and Ketones
- Alcohols
- Phenols
- Carboxylic acids
- Esters

4.2 FUNCTIONAL GROUP IDENTIFICATION

Organic compounds are classified into different classes based on the presence of functional groups. Except in the teaching laboratory, it is rare for an unknown compound to possess just one functional group. You must always be aware of the possibility that more than one functional group may be present. However, here we will examine only monofunctional compounds.

You can recall from your theory course that the functional groups are the sites of chemical reactions. The determination of functional groups depends on their specific features of structure and reactivity. The identification of functional group depends basically on the correct determination of the elements. Common monofunctional organic compounds are