

ORGANOMETALLICS, BIOINORGANIC CHEMISTRY, POLYNUCLEAR HYDROCARBONS AND UV, IR SPECTROSCOPY: Lab

SECTION A

UNIT 1

Paper Chromatographic Separation and Identification of Metal Ions	5
Experiment 1: Separation and Identification of Cations of Analytical Group I	8
Experiment 2: Separation and Identification of Cations of Analytical Group II	11

UNIT 2

Inorganic Preparations and Measurement of their Conductivities	15
Experiment 3: Preparation of Tetraamminecarbonatocobalt(III) Nitrate	21
Experiment 4: Preparation of Tetraamminecopper(II) Sulphate Monohydrate	23
Experiment 5: Preparation of Potassium Trioxalatoferrate(III) Trihydrate	25
Experiment 6: Comparison of the conductance of the complexes (prepared by Experiments 3 to 5) with $M/1000$ solution of NaCl, $MgCl_2$ and $LiCl_3$	30

SECTION B

Experiment 7: Systematic Qualitative Analysis of Carboxylic Acids and Phenols and Preparation of their Derivatives	35
---	-----------

Experiment 8: Systematic Qualitative Analysis of Aldehydes and Ketones and Preparation of their Derivatives	51
--	-----------

Experiment 9: Systematic Qualitative Analysis of Amides, Nitro and Amino Compounds and Preparation of Their Derivatives	61
--	-----------

Experiment 10: Identification of Unknown Organic Samples	78
---	-----------

Course Design Committee

Dr Pritam Mukhopadhyay ,
Associate Professor, School of Physical
Sciences, Jawaharlal Nehru University,
New Delhi

Dr. Preeti Malhotra,
Department of Chemistry,
University of Delhi, Delhi

Dr. Sushmita Choudhury (Retd.),
Gargi College, University of Delhi
New Delhi

Dr. Sangeeta Pandita
Department of Chemistry
Zakir Husain Delhi College
University of Delhi, Delhi

**School of Sciences,
IGNOU, New Delhi 110068**

Prof. M.S. Nathawat
Prof. Sunita Malhotra
Prof. Bharat Inder Fozdar
Prof. Javed A. Farooqi
Prof. Sanjiv Kumar
Prof. Lalita S. Kumar
Prof. Kamalika Banerjee

Block Preparation Team

Prof. Kamalika Banerjee (Units 1 and 2)
School of Sciences, IGNOU

Prof. Bharat Inder Fozdar (Experiments 7, 8, 9 and 10)
School of Sciences, IGNOU

Course Coordinator: Prof. Kamalika Banerjee

Production

Mr. Rajiv Girdher
AR (P), MPDD, IGNOU

Mr. Hemant Kumar
SO(P), MPDD, IGNOU

Acknowledgements: Sh. Sarabjeet Singh and Sh. Deepak Kumar for word processing and Sh. Sarabjeet Singh for CRC preparation.

Unit 1 has been adapted from Experiment 4 of CHE-12L chemistry course, portions of Unit 2 of CHE-07L and Unit 18 of AEC-01 has been utilised in the writing of the four experiments of Unit 2. The utilisation of some content of Chemistry Lab III course (BCHCL 136) for developing Part B is gratefully acknowledged.

March, 2022

© Indira Gandhi National Open University, 2022

ISBN:

All rights reserved. No part of this work may be reproduced in any form, by mimeograph or any other means, without permission in writing from Indira Gandhi National Open University.

Further information on Indira Gandhi National Open University courses may be obtained from the University's office at Maidan Garhi, New Delhi-110 068 or IGNOU website www.ignou.ac.in.

Printed and published on behalf of Indira Gandhi National Open University, New Delhi by the Registrar, MPDD, IGNOU.

Printed at:

CHEMISTRY LAB: Organometallics, Bioinorganic Chemistry, Polynuclear Hydrocarbons and UV, IR spectroscopy

Welcome to the sixth Semester laboratory course in chemistry. This manual gives the procedural details of various experiments you are required to perform in the course of this lab work. Appropriate conceptual basis has also been laid for each experiment to make this manual complete in itself.

This Laboratory manual has two sections. **Section A** deals with experiments in inorganic chemistry and **Section B** with experiments in organic chemistry. There are six experiments in the Section A. First unit has two experiments based on paper chromatography. Thereafter the second unit, the first three experiments provide procedural detail for preparation and the purification of three inorganic compounds.. In the last experiment you will also compare the conductance of these prepared complexes with $M/1000$ solution of NaCl , MgCl_2 and LiCl_3 . , respectively.

Part B mainly deals with qualitative organic analysis. We shall study the experiment procedures for the qualitative classification tests and preparation of derivatives for organic compounds having commonly encountered functional groups such as phenolic, carbonyl, carboxylic, amino, and nitro.

All the experiments of this course are to be performed in about six days.

Expected Learning Outcomes

After studying this course and performing the given experiments, you will be able to:

- understand theoretical principle of chromatography and separate and identify cations of analytical group I and II with the help of paper chromatography;
- prepare and purify complexes and compare their conductances with those of standard solutions;
- describe the steps involved in the identification organic compounds by classical qualitative organic analysis;
- describe functional group tests and methods of the preparation of derivatives;
- identify the unknown organic compounds; and
- maintain laboratory records for the experiments performed during this course;

Study Guide

The general pattern of discussion of experiments in this course is similar to that of 1st, 2nd, 3rd and 4th semesters Chemistry Labs. In this lab course, you would be doing ten experiments. In this course, the performance of the experiments, recording the data, calculations and expression of result are to be done as in earlier chemistry lab course. The maintenance of Laboratory note book may be done as per the detail guidelines given for each Section. Some general guidelines for the maintaining Laboratory note book are given on next page. Remember that each experiment is going to be evaluated. Hence, read the Lab manual before going the laboratory for performing the experiments. This will help you in doing experiment in a proper way.

We want you to share the thrill of learning by doing. There is no better way to learn.

So, Best of Luck.

Laboratory Notebook

It is essential to keep a proper record of the work that has been done. The record should reflect all the observations at various stages of the experiment. The observations prove helpful in correct interpretation of an experimental result.

While preparing a laboratory note book, the following important points may be kept in mind.

- A bound note book should be used for laboratory record. You may use a laboratory record note book in which one side has ruled pages and other side is unruled.
- All entries must be made in ink. If you commit a mistake, it should be crossed and correct entry should be made.
- The first few pages in the note book should be left for making a list of contents.
- Graphs drawn should be attached to the laboratory note book.
- The laboratory note book is a complete record of all operations. Date, time, the number and the title of each experiment must be entered regularly.
- Record all observations and data in the note book at the time they are obtained. Never use scraps of paper for noting particulars like masses of substances weighed, melting points etc. They might get lost or mixed up.
- The record should be clearly written and well organised. On reading it, one should be able to understand what has been done.
- It may not be necessary to copy out the exact procedure, since this is given in your laboratory manual.
- The detailed calculations are to be shown.
- Results and conclusions drawn should be summarised for each experiment and explanation provided, if the results vary from those expected.

Certain marks have been allotted for maintaining a good laboratory note book too.

IMPORTANT

- **Attendance** is compulsory in the Laboratory Course work held generally at the Study Centre.
- The Laboratory Course is worth **2 credits** to be completed over **7 days** duration:
 - **6 days** of the **Guided** Laboratory work
 - **1 day** of the **Unguided** Laboratory work
- To successfully complete the laboratory course you will have to pass (at least **35% marks**) in the Guided and Unguided components separately.

UNIT 1

PAPER CHROMATOGRAPHIC SEPARATION AND IDENTIFICATION OF METAL IONS

Structure

1.1	Introduction	Requirements
	Expected Learning Outcomes	Procedure
1.2	Theory of Chromatography	Observations and Calculations
	Definition and Classification	Result and Discussion
	Principle	1.5
	The Concept of R_f Value	Experiment 2: Separation and Identification of Cations of Analytical Group II
1.3	Paper Chromatographic Separation of Metal Ions	Requirements
1.4	Experiment 1: Separation and Identification of Cations of Analytical Group I	Procedure
		Observations and Calculations
		Result and Discussion

1.1 INTRODUCTION

In this BCHEL-148 laboratory course, first two experiments are based on paper chromatography. Here we shall first discuss the basic theory of chromatography with some fundamental concepts. After that you will be introduced to the actual experiments in which you will perform paper chromatography of metal ions (Experiments 1 and 2).

Expected Learning Outcomes

After studying this unit and performing the given experiments you should be able to:

- ❖ define and classify chromatography;

- ❖ understand theoretical principle of chromatography;
- ❖ calculate the R_f values; and
- ❖ separate and identify cations of analytical group I and II.

1.2 THEORY OF CHROMATOGRAPHY

1.2.1 Definition and Classification

Chromatography is referred to any of a diverse group of techniques that effect a separation through a distribution of sample between two immiscible phases. One phase is stationary whereas the second is mobile which percolates through the first phase. The stationary phase may be a solid or a liquid while the mobile phase may be a liquid or a gas.

There are various ways to classify chromatography. On the basis of physical state of mobile phase the chromatography is classified into two broad groups.

- Liquid chromatography in which mobile phase used is in the form of a liquid.
- Gas chromatography in which mobile phase used is a gas.

1.2.2 Principle

Chromatography is essentially a separation process which affects a separation by distributing the sample into two phases. One phase is stationary and second is mobile and flows through the stationary phase. During the process of movement of mobile phase, small differences in adsorption-desorption or partitioning or ion-exchange behaviour of each component of a mixture are multiplied many fold and these parameters distinguish between the different solutes. The ability of chromatography to separate two solutes depends on the selectivity of the process and the degree to which the system can distinguish between the two solutes. The magnitude of the distribution is determined by the physico chemical nature of the solute and that of the mobile and stationary phases, beside various physical interaction (such as: hydrogen bonding, dipole moment etc.) of the solute with stationary-and mobile phases.

Some common steps used in different chromatographic techniques are: application of the sample onto a stationary phase, percolating a mobile phase over the stationary phase, obtaining the separation of components, collection of the different components for qualitative or quantitative purposes. Therefore, the principle of chromatography can be understood by taking a one kind of chromatography. For this purpose, let us consider a simple example of separation by column chromatography. This can be applied to other methods as well.

Let us suppose that we wish to separate a mixture of two (say coloured) components A and B. A small amount of the sample solution is introduced at the top of the column which is packed with suitable adsorbent (stationary phase). First a narrowband is formed at the top of the column. The developer (mobile phase) is now poured into the column and is allowed to flow through

the column. The two important steps are: (i) formation of the initial zone (ii) development of the initial zone and allowing the components to appear as separate zones. As soon as the solution comes in contact with the stationary phase (column material or adsorbent) and the mobile phase the following reversible reaction occurs:

Solute in the Stationary phase $\rightleftharpoons$ solute in the mobile phase

For which the equilibrium concentration are related as

$$K' = 1/K \frac{C_m}{C_s} \quad \text{or} \quad K = \frac{C_s}{C_m} \quad \dots (1.1)$$

where, $K' = 1/K$ and K' is equilibrium constant.

K is called as the distribution coefficient, C_s is the concentration of the solute in the stationary phase and C_m that in mobile phase.

For two solutes A and B there is competition of A and B (i) for the stationary phase and (ii) for the mobile phase.

If the stationary phase takes B more likely than A, the value of K_A will be less than K_B . Thus when the developer leaves the narrow band it is richer in A than B. The developer flowing downwards now comes in contact with fresh stationary phase and the solutes A and B face the new competition and when the mobile phase leaves this part of the stationary phase, each time it becomes richer and richer in A. Small differences in the interactions of A and B with stationary and mobile phases become exaggerated as the developer proceeds down the column, soon after the well separated bands of A and B are obtained.

If the development further proceeds (elution analysis) the components A and B of the mixture are elute out of the column. Solute A which has smaller K emerges first followed by B which has a larger K . The two fractions may be quantitatively analysed for A and B respectively.

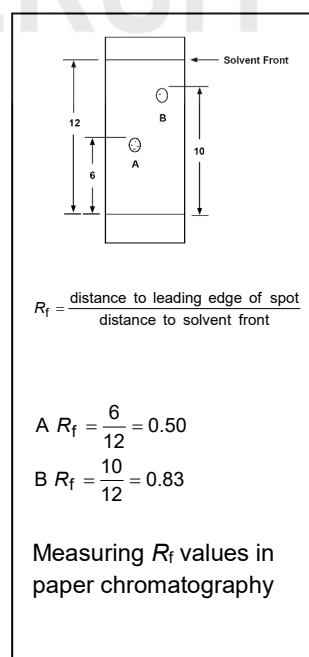
1.2.3 The Concept of R_f Value

R_f value of a solute is the ratio of the rate of movement of the solute peak to the rate of movement of the eluting solvent.

However, one can not readily detect the position of the solvent front or of the solute on the column chromatography. These are better measured now in terms of retention volume or retention time.

In paper chromatography R_f value is constantly quoted as a characteristic of the solute. It describes the migration of solute relative to that of developer and is given by

$$R_f = \frac{\text{distance moved by the centre of the solute zone}}{\text{distance moved by the solvent front}}$$



With this background, now we will take up experiment based on different types paper chromatography.

1.3 PAPER CHROMATOGRAPHIC SEPARATION OF METAL IONS

Paper chromatography (PC) is a simple technique to separate complex mixtures of metal ions, amino acids, sugars, dyes and drugs. A very small amount of sample is required for the analysis. PC has become a popular technique for the separation of metal cations. In this experiment, the use of PC will be illustrated to separate a mixture of cations of group I and group II.

1.3.1 Principle

In paper chromatography of cations, the principles of partition, adsorption and ion exchange may be exploited, out of these the most important is partition the involves the distribution of a solute between a mobile liquid phase and a gel (a kind of water cellulose complex) as the stationary phase. The different components of the sample are distributed across the paper depending on their partition coefficients.

Attempts have been to employ paper chromatography for the systematic qualitative analysis of metal cations. However, it is not possible to separate all the cations simultaneously and therefore, the separation of a group of cations can be handled. Most frequent of these is the preliminary separation into the current analytical groups, each of which is then subjected to a separate chromatographic analysis. In the Experiments (1 and 2) you will learn the use of paper chromatography for the separation of cations of analytical group I and group II, respectively.

1.4 EXPERIMENT 1: SEPARATION AND IDENTIFICATION OF CATIONS OF ANALYTICAL GROUP I

This experiment of an easy ascending paper chromatographic technique is rapid and requires no special apparatus or reagents. A very simple procedure for this separation has been employed with the use of only distilled water as the developer. However, other developers can also be utilised depending on the availability of the reagents and precautions in their use [e.g. butanol -1 + pyridine + water (15:1:9)]. In this experiment you will perform the separation of cations of group I.

1.4.1 Requirements

Apparatus		Chemical
Boiling tubes or chromatographic jar	5	Potassium chromate
Measuring cylinder	1	Lead nitrate
Pipette	1	Silver nitrate
Spotting capillaries	5	Mercurous nitrate
Small test tubes	5	Nitric acid
Whatman No. 1 filter paper		

Solution provided

- 1) Unknown solution: It can be prepared by dissolving any one or two nitrate of analytical group in water.
- 2) Detector: 0.25 M aqueous solution of potassium chromate $K_2Cr_2O_4$ is prepared by dissolving 24.25 g K_2CrO_4 in distilled water in 250 cm³ volumetric flask.

1.4.2 Procedure

Proceed according to the following steps:

1. Preparation of solutions

- i) Prepare 1 cm³ aqueous solutions of (i) lead nitrate (ii) silver nitrate (iii) mercurous nitrate by dissolving about .1g crystals in a small test tube. Add few drops of HNO_3 to prevent hydrolysis. For the preparation of mixture of cations, add few drops of each cation solutions in a test tube.
- ii) Developer: Distilled water.
2. Cut whatman No. 1 filter paper strips of the required size: 15 cm x 2 cm to fit usual boiling tube or 15 cm x 3 cm for chromatographic jar.
3. On each strip draw a line at about 1 cm of the one and put a dot in the centre of line. This end will be the bottom of the strip and development will take place from this end.
4. Apply the solutions of Pb^{2+} , Ag^+ and Hg_2^{2+} separately on 3 strips with the help of a fine capillary. Use a fresh capillary for each solution. The teacher is supposed to demonstrate the technique of application of the solution.
5. On the 4th paper strip apply the mixture of the three cations.
6. Apply the unknown solution (e.g., containing any one or two on the 5th paper strip.
7. Place 5 dry boiling tubes vertically in a stand.
8. Add distilled water, with the help of a pipette, to each of the boiling tubes so that the height of the developer (distilled water) in each of the boiling tubes is less than 1 cm. The sides of the boiling tube must be dry as far as possible.
9. Suspend the spotted and dried paper strips in the respective boiling tubes containing distilled water with the upper end pinned to the cork and the lower end touching the developer. Care is taken to see that this is done gently and the strip is vertical. The spot should always be above the developer level.
10. Allow the developer to rise along the paper and wait till the developer (solvent front) reaches near the upper end of the paper.

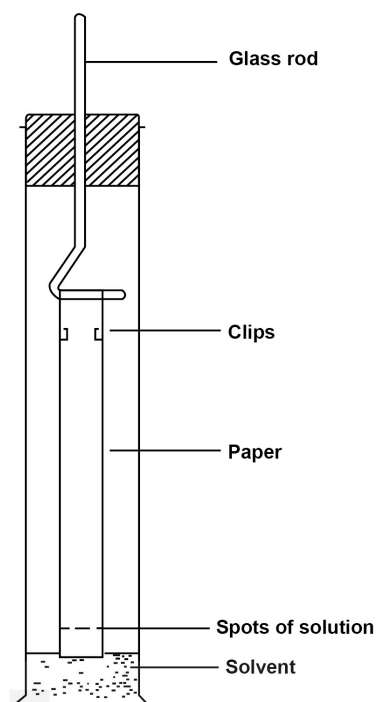
Application of the sample on the paper should be on a small area. Larger spots lead to poorer separations. Please indicate the name of test sample on the top of the paper strip.

The paper in the boiling tube or in the jar should be vertically changed and it should not touch the sides of the tube.

The spot of the solute (at the point of application) should always be above the level of the developer otherwise the solute will mix with the developer and error will be resulted.

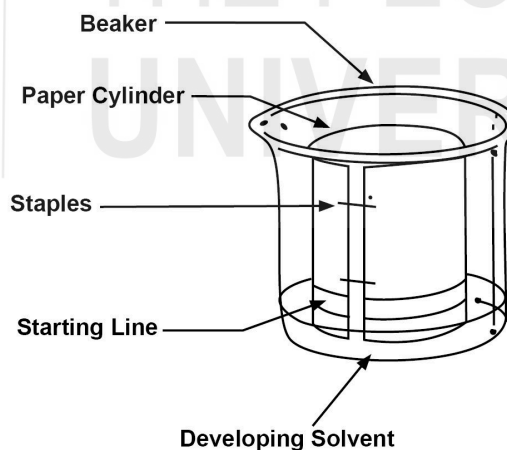
Ensure that the spot gets dried before placing the paper in the boiling tube.

Do not allow the paper to come in contact with impurities.



Apparatus for paper chromatography

11. Remove the paper from the boiling tube and mark the solvent front with the help of a pencil.
12. Get it dried to evaporate the developer.
13. Take potassium chromate solution in a pettri dish (or a watch glass) and dip the dried paper in the detector.



An alternate method for developing paper chromatogram by making paper cylinder. Beaker can be covered by aluminum foil.

14. Encircle the coloured zones with pencil and mark the centre of the zone.
15. Calculate the R_f values.
16. Compare the R_f values of individual cations with that of their R_f values in known mixture and in unknown.
17. Identify the cations present in the unknown on the basis of R_f values.

1.4.3 Observations and Calculations

Observe the coloured spots of different cations. Pb^{2+} will appear as yellow; Ag^+ as orange-red and Hg_2^{2+} as orange zones. Measure the distance of the centre of each solute zone from the point of application. Call this distance d_s . Measure the distance between the solvent front and the starting line and call this distance as d_m . Calculate the R_f value of each solute by the relation:

$$R_f = \frac{\text{distance travelled by the centre of the solute zone}}{\text{distance travelled by the solvent front}} = \frac{d_s}{d_m}$$

Record your data in the following way:

Observation Table
PC of Metal Ions of Group I

Sample	d_s	d_m	$R_f = d_s/d_m$ Remark
Ag^+			
Hg_2^{2+}			
Pb^{2+}			
Mixture			
Unknown			
1.			R_f resembles with.....
2.			R_f resembles with.....

1.4.4 Result and Discussion

Metal ions present in the unknown sample are: .

1.....

2.....

The metal ions of analytical group I move along the paper in distilled water at different rates. On dipping in detector K_2CrO_4 solution the coloured precipitates of the chromates of lead, mercurous and silver appear as yellow, orange and orange-red zones on the paper. Sometimes, when the coloured spot of Hg_2^{2+} is not intense, the paper is exposed to ammonia vapours: the mercurous compound gives black spot. Lead migrates with the fastest rate and appears at the upper most area on the paper. Mercurous follows the lead. Silver migrates with the slowest rate and appears below the mercury zone.

1.5 EXPERIMENT 2: SEPARATION AND IDENTIFICATION OF CATION OF ANALYTICAL GROUP II

In this experiment you will perform the separation of bismuth (III), copper (II), cadmium (II), lead (II) and mercury (II) using paper chromatography. This

separation is achieved by 1-butanol saturated with 3M HCl as developer. However, another simple developer containing ethanol + water + 1M HCl (18:1:1) can also be used to separate Pb^{2+} , Cu^{2+} , Cd^{2+} (excluding Hg^{2+} from Group II).

1.5.1 Requirements

Apparatus		Chemical
Boiling tubes	5	1-Butanol
Measuring cylinder	1	3M HCl
Pipette	1	bismuth chloride
Cupric chloride		Lead chloride
Spotting capillaries	7	Mercuric chloride
Small test tubes	7	
Petridish		
Whatman No. 1 filter paper sheets		

Solution provided

1. **Unknown Solution:** It can be prepared by dissolving any one or two chlorides of analytical group II in water.
2. **Preparation of Detector 1:** H_2S water. It is prepared by passing H_2S gas in water and add a few drops of ammonia to it. Keep it in a covered container.
3. **Preparation of Detector 2:** Dithizone. Prepare a conc. solution of dithizone in chloroform or carbon tetrachloride.

1.5.2 Procedure

Proceed according to the following steps.

1. i) Preparation of Solution:

Sample Preparation: prepare 1 cm³ concentrated aqueous solutions of (i) bismuth chloride (ii) cadmium chloride (iii) cupric chloride (iv) lead chloride and (v) mercuric chloride. Add 1-2 drops of hydrochloric acid to prevent hydrolysis. For the preparation of the mixture of their cations, add few drops of each cation solutions in a test tube.

- ii) Preparation of Developer: Developer (1-butanol saturated with 3M HCl): Prepare this developer by taking equal volumes of 1-butanol and 3M hydrochloric acid in a separatory funnel. Shake well and allow to stand to separate the layers clearly. Reject the lower aqueous layer and use the upper (organic) layer as the developer.

2. Cut whatman No. 1 filter strips of about 15×2 cm to be placed in usual boiling tubes (or chromatographic jars).
3. On each strip draw a line with pencil at about 1 cm of one end and mark a point in the centre of line. This point is the point of application of the solute/sample solution.
4. Apply the test solution to the point of application with the help of a fine capillary. Apply bismuth, cadmium, copper, lead and mercury solutions separately on 5 strips. Use a fresh capillary for each solution.
5. Apply the mixture solution and unknown solution separately on other strips. Application of solution can be repeated twice or thrice if the solutions are dilute.
6. Take the clean and dry boiling tube and place (10-15 cm³ of) the developer in each of these boiling tube.
7. Suspend the spotted and dried paper strips in the respective boiling tubes containing distilled water with the upper end pinned to the cork and the lower end touching the developer. Care is taken to see that this is done gently and the strip is vertical. The spot should always be above the developer level.
8. Allow the developer to rise along the paper and wait till the developer (solvent), reaches near the upper end of the paper.
9. Remove the paper strip and mark the solvent front with the help of a pencil.
10. Leave the paper for some time to get it dried.
11. Hold the paper in an atmosphere of H₂S gas until the zones of metallic sulphides are seen. An alternative way is to use H₂S water in which the paper is dipped to locate the zones. Another alternative method is use dithizone for detecting the zones of metal ions. Spray the paper (or dip in) with a concentrated solution of dithizone in chloroform.
12. Encircle the coloured zones and mark the centre of each zone. Calculate the R_f values of individual cations with that of their R_f values in mixture to identify the cations in the mixture and unknown sample solution.

1.5.3 Observations and Calculations

Observe the colour of the spots of various cations of group II. With H₂S bismuth (III) will appear as dark brown: cadmium (II) as yellow: copper (II) as chocolate brown: lead (II) as black and mercury (II) as black zones.

Measure the distance travelled by the centre of the solute zone (d_s) and the distance travelled by the solvent front (d_m) on the paper chromatogram.

Calculate the R_f values of each solute by the relation. $R_f = \frac{d_s}{d_m}$.

Record your data in the following way:

Observation Table

PC Separation of Pb^{2+} , Cu^{2+} , Cd^{2+} , Bi^{3+} and Hg^{2+}

Sample cation	d_s	d_m	$R_f = d_s/d_m$	Remark
Hg^{2+}				
Cd^{2+}				
Bi^{3+}				
Pb^{2+}				
Cu^{2+}				
Mixture				
Unknown				
1.			R_f resembles with.....	
2.			R_f resembles with.....	

1.5.4 Result and Discussion

Metal ions present in the unknown sample are:

1.
2.

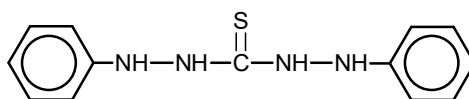
The rate of migration of group II metal ions in butanol saturated with 3M HCl appears in the order $\text{Hg}^{2+} < \text{Cd}^{2+} < \text{Bi}^{3+} < \text{Pb}^{2+} < \text{Cu}^{2+}$.

When H_2S is used as detector the coloured zones of metallic sulphides are seen: HgS black, CdS yellow, Bi_2S_3 dark brown, PbS black and CuS Chocolate brown.

When dithizone is used as detector, coloured complexes of metal ions are formed with dithizone. Dithizone is the commercial name of diphenyl-1-thiocarbazon (see formula in below).

Metal ion + Dithizone $\rightarrow$ coloured complex

Colours of the complexes of metal ions are: mercury-pink, cadmium- purple, bismuth-purple and copper brown. Lead is not clearly detected for which rhodizonic acid may be used.



Diphenylthiocarbazon
(dithizone)

UNIT 2

INORGANIC PREPARATIONS AND MEASUREMENT OF THEIR CONDUCTIVITIES

Structure

- | | | | |
|-----|---|-----|---|
| 2.1 | Introduction | 2.5 | Experiment 5: Preparation of Potassium Trioxalatoferrate (III) Trihydrate |
| | Expected Learning Outcomes | | Principle |
| 2.2 | Conductance and Conductometry | | Requirements |
| 2.3 | Experiment 3: Preparation of Tetraamminecarbonatocobalt (III) nitrate | | Procedure |
| | Principle | | Observations |
| | Requirements | | Calculations |
| | Procedure | | Result |
| | Observations | 2.6 | Experiment 6: Comparison of the conductance of the complexes (prepared by Experiments 3 to 5) with $M/1000$ solution of NaCl , MgCl_2 and LiCl_3 |
| | Calculations | | Principle |
| | Result | | Requirements |
| 2.4 | Experiment 4: Preparation of Tetraamminecopper(II) Sulphate Monohydrate | | Procedure |
| | Principle | | Observations |
| | Requirements | | Calculations |
| | Procedure | | Result |
| | Observations | 2.7 | Summary |
| | Calculations | 2.8 | Answers |
| | Result | | |

2.1 INTRODUCTION

In Unit 1, we discussed the use of paper chromatography to separate a mixture of cations of group I and group II. In this unit, we will discuss the

preparation and the purification of three inorganic compounds. You will have to prepare and purify these compounds during the laboratory practicals of this course. You will also compare the conductance of these prepared complexes with $M/1000$ solution of NaCl , MgCl_2 and LiCl_3 .

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ prepare and purify tetraamminecarbonatocobalt (III) nitrate, tetraamminecopper(II) sulphate and potassium trioxalatoferrate(III) trihydrate;
- ❖ perform various laboratory operations involved in these preparations;
- ❖ calculate percentage yield of these compounds;
- ❖ explain the principles involved in the preparation of these compounds;
- ❖ measure the conductance of these compounds; and
- ❖ compare their conductance with that of $M/1000$ solution of NaCl , MgCl_2 and LiCl_3 .

2.2 CONDUCTANCE AND CONDUCTOMETRY

Some Basic Concepts of Conductance

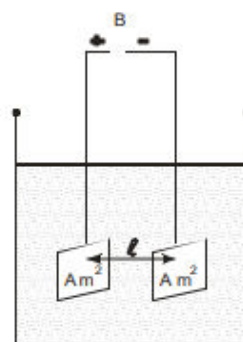
The ease of flow of electric current through a body is called its conductance. In metallic conductors it is caused by the movement of electrons, while in electrolytic solutions it is caused by applied electrical field. The electrolytic **conductance**, G ; of a medium is equal to the reciprocal of its electrical resistance R in ohms:

$$G = \frac{1}{R} \quad \dots (2.1)$$

The flow of current through an electrolytic solution is due to the charge carried-out by - ions and causes electrolytic conduction. We thus expect movement of ions in aqueous' solutions of electrolytes and also in molten electrolytes.

Specific Conductance

Since a solution is a three dimensional conductor, the 'exact resistance will depend on the spacing (l) and area (A) of the electrodes.



The resistance of a solution is proportional, to the distance between the electrodes and inversely proportional to the electrode surface area. If two electrodes having a cross sectional area of $A \text{ m}^2$ and separated by $l \text{ m}$ are dipped in a solution of some electrolyte, the resistance (R) of the solution present between the two electrodes is:

$$R \propto l$$

$$R \propto \frac{1}{A}$$

and $R \propto \rho \frac{l}{A} \quad \dots (2.2)$

where ρ (Rho) is proportionality constant and is called as **specific resistance** or **resistivity**.

Reciprocal of specific resistance is known as **specific conductance** or **conductivity** designated by κ (kappa):

$$\kappa = \frac{1}{\rho} \quad \dots (2.3)$$

Hence Eq. (2.2) can be written as

$$R = \frac{1}{\kappa} \times \frac{l}{A}$$

$$\kappa = \frac{1}{R} \times \frac{l}{A} \quad \dots (2.4)$$

The ratio (l/A) is known as **cell constant**, K_{cell} and $(1/R) = G$ (from Eq. 2.1).

Now we can summarise as, $\kappa = 1/\rho = (1/R) (l/A) = GK_{\text{cell}} \quad \dots (2.5)$

Conductivity = observed conductance $\times$ cell constant

Since the resistance is expressed in ohm, Ω (omega) the reciprocal ohm (Ω^{-1}) was earlier used as the unit for conductance. However, in SI system, the unit for conductance is 'Siemens' and, given the symbol 'S'. Hence, the unit for conductivity will be S m^{-1} ($1\text{S} = 1\Omega^{-1}$) or S cm^{-1} . It may be remembered that $\text{S m}^{-1} = 100 \text{ S cm}^{-1}$. However specific conductance is customarily reported in smaller units as milli Siemens per meter (mS m^{-1}) and micro Siemens per cm ($\mu\text{S cm}^{-1}$).

Molar Conductivity

In order to compare quantitatively the conductivities of electrolytes, a quantity called **molar conductivity** is frequently used. The molar conductivity, Λ_m , (capital lambda) is the conductivity per unit molar concentration of dissolved electrolyte. It is related to conductivity, κ by the relation:

$$\Lambda_m = \frac{\kappa}{c} \quad \dots (2.6)$$

where c is the concentration in mol m^{-3} . The molar conductivity is usually expressed in $\text{S m}^2 \text{mol}^{-1}$ or $\text{S cm}^2 \text{mol}^{-1}$. It may be remembered that $\text{S m}^2 \text{mol}^{-1} = 10,000 \text{ S cm}^2 \text{mol}^{-1}$.

Conductivity increases with:

- (i) Concentration of the solution and
- (ii) Speed of the ions concerned.

It is to be remembered that c in Eq. 2.6 is to be expressed in mol m^{-3} unit. If the concentration is given in terms of molarity (mol dm^{-3}), then the following conversion is to be carried out

$$c(\text{mol m}^{-3}) = \text{Molarity} \times 1000 \quad \dots (2.7)$$

Earlier equivalent conductivity (Λ_{eq}), which is given by the following expression, was in use

$$\Lambda_{\text{eq}} = \frac{1000 \times \kappa}{c} \quad \dots (2.8)$$

where c is the concentration expressed in terms of normality of the solution. However, IUPAC recommends the use of molar conductivity only.

For example, consider equimolar solutions of sodium chloride and magnesium chloride. The concentration of chloride ions in the solution of magnesium chloride is double the concentration of chloride ions in the solution of sodium chloride. The amount of charge carried by one magnesium ion is double the amount of charge carried by sodium ion. Molar conductivity will therefore change with the number of ions produced per mole of solute.

Thus, the number of ions in ionic salts relate to molar conductivity Λ_m , as shown below.

Table 2.1: Molar Conductivity Values of Some Ionic salts

Number of ions	$\Lambda_m (\text{S cm}^2 \text{ mol}^{-1})$
2	118-131
3	235-275
4	408-435
5	~560

In conductometry we examine the transport of electricity in solution and application of this phenomenon to chemical analysis. The principle advantage of this technique is its simplicity and relatively good sensitivity. The behaviour of electrolytic solutions, determining the purity of water, acid-base, precipitation, determination of ionization constants, solubilities and complex formation, all these can be studied with the help of conductometry.

Now we will see how conductance is measured.

Measurement of Conductance

Principle of Wheatstone Bridge is used to measure the conductance of solution. Therefore, before taking up the measurement of conductance of solution, let us study the principle of Wheatstone Bridge.

The Wheatstone Bridge Principle

A Wheatstone bridge (Fig. 2.1) is employed to measure the resistance of an electronic conductor. It works on the principle of obtaining balance between two arms with the help of a balance indicator (e.g. a galvanometer) at the condition of potential being equal.

Let R_x be an unknown resistor, R_1 and R_2 two standard resistors, R_3 an adjustable resistor and G a galvanometer. The bridge is connected to a source of power S , a battery, and a tapping key K is placed in the path to control the connections.

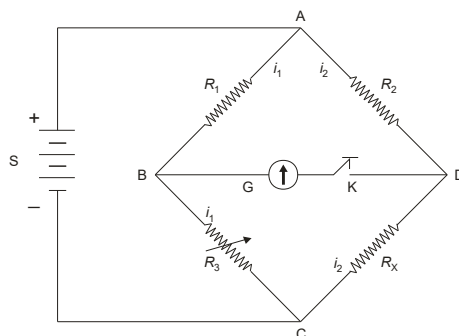


Fig. 2.1: A DC Wheatstone Bridge circuit.

To measure the resistance R_x , the tapping key K is held down momentarily and the bridge is balanced by adjusting R_3 to get no deflection in galvanometer under these conditions.

In the bridge the total current is divided into two paths: i_1 through R_1 and R_3 , and i_2 through R_2 and R_x . Under the balancing conditions, the potential at points B and D must be the same, i.e. the ohmic voltage drop through the resistors R_1 and R_2 must be the same. Hence, the potential at B (E_B) must be equal to potential at D (E_D).

$$E_B = E_D \quad \dots (2.9)$$

$$\text{or} \quad i_1 R_1 = i_2 R_2 \quad \dots (2.10)$$

$$\text{Similarly } i_1 R_3 = i_2 R_x \quad \dots (2.11)$$

Dividing Eq. (2.10) by Eq. (2.11) we get,

$$\frac{R_1}{R_3} = \frac{R_2}{R_x}$$

$$\text{and} \quad R_x = \frac{R_2 R_3}{R_1} \quad \dots (2.12)$$

Thus, we can calculate R_x as R_1 , R_2 and R_3 are all known. Conductance G , being the reciprocal of resistance will be,

$$G = \frac{R_1}{R_2 R_3} \quad \dots (2.13)$$

Alternatively, the conductometric cell can be incorporated into operational amplifier control circuit, as shown in. Fig. 2.2. The amplifier balances the potential of two inputs. The current from the input potential, E_i , is balanced by the current from amplifier output which passes through a feedback resistor (R_f). The output potential, E_o is in terms of resistance:

$$E_o = E_i \left(\frac{R_f}{R_x + 1} \right)$$

where R_x is the resistance of conductometric cell.

With respect to the solution conductance, G , above equation becomes

$$E_0 = E_i(R_f G + 1)$$

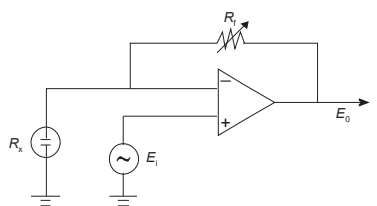


Fig.2.2: An operational amplifier control circuit for conductometric measurement. R_x is the solution resistance and R_f is the feedback resistance.

Measurement of Conductance of a Solution

The Principle of the Wheatstone bridge can be used to measure the conductance of solutions. However, the following considerations must also be kept in mind:

- (i) since a direct current would polarize the electrodes in the conductivity cell by electrolyzing the solution to avoid polarization an alternating current (ac) source of power must be used in place of a dc Source (battery) usually ac voltages of 3-6 volts with frequency of 50 Hz or 1000 Hz used across points A and C of Fig. 2.3.
- (ii) A suitable conductivity cell (with electrodes dipped in the solution) is located between points C and D. Thus R_x represents the resistance of the conductivity cell.
- (iii) Since, the cell also acts like a small capacitor (C_x), and to balance its capacitive resistance a variable capacitor, C_B , must be inserted into the bridge.

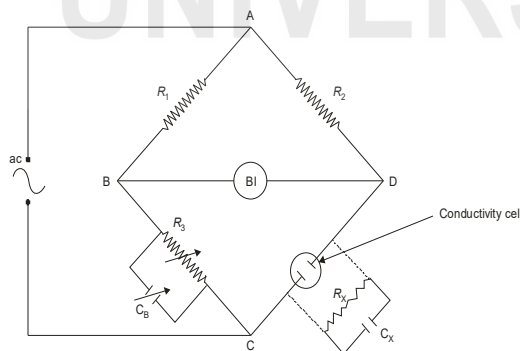


Fig. 2.3: A conductivity bridge circuit.

- (iv) The balance inductor (BI) may be an ac galvanometer, but some other devices are also be used:
 - An earphone can act as a balance indicator if the frequency of the ac source is in audio-range.
 - A magic eye, which gives a green fluorescence as a result of electrons striking a phosphor coating inside the glass tube, is used in several commercial instruments.

- For much precise conductance measurements a cathode ray oscilloscope is used as the balance indicator.
- (v) Conductance ($G = 1/R_x$) can be read directly on commercially available instruments as a panel mounted meter. Now several digital instruments are also available, such instruments give the conductance directly as the numerical value.

SAQ 1

At 298 K, the resistance of 2.00×10^{-2} M KCl is 195.96Ω and that of 2.50×10^{-3} M K_2SO_4 is 775.19Ω . The conductivity (κ) of 2.00×10^{-2} M KCl at 298 K is 0.2768 S m^{-1} . Calculate molar conductivity of K_2SO_4 solution.

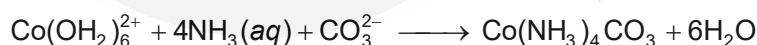
2.3 EXPERIMENT 3: PREPARATION OF TETRAAMMINECARBONATOCOBALT(III) NITRATE

In this experiment you will learn how to prepare tetraamminecarbonatocobalt (III) nitrate.

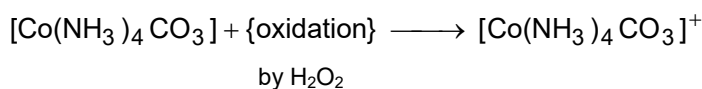
2.3.1 Principle

Cobalt(III) forms kinetically inert coordination complexes. In comparison with other transition metals they have slower ligand exchange. The slow reactivity of this octahedral complex has made the chemists to further investigate it in great detail. In this experiment, we will prepare the coordination compound of cobalt, i.e. $[\text{Co}(\text{NH}_3)_4 \text{CO}_3] \text{NO}_3$ with the help of ligand substitution reaction.

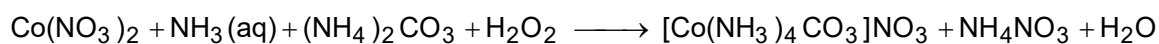
Cobalt nitrate $[\text{Co}(\text{NO}_3)_2]$ is deliquescent and therefore tends to absorb water vapours from atmosphere and forms $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Since Co(II) complexes react very rapidly by ligand exchange, therefore in the first step following reaction takes place:



The intermediate tetraamminecarbonato cobalt(II) when formed, is oxidized by addition of hydrogen peroxide (H_2O_2) to form $[\text{Co}(\text{NH}_3)_4 \text{CO}_3]^+$.



Reaction involved:



This sort of intermediate which has a carbonato ligand is a useful in the synthesis of coordination complex. The carbonate ion is easily removed by the additional of HCl and the carbonate forms carbon dioxide. The carbonate ion is a bidentate ligand and leaves two open coordination sites. Water molecules or chloride ions may occupy the open coordination sites. Water is not a strong ligand and addition of ions such as X^- , NH_3 or NO_2 leads to the replacement of these coordinated water molecules.

2.3.2 Requirements

Chemical	Apparatus	
Cobalt nitrate hexahydrate	Beakers 150 cm ³	2 No.
	Bunsen burner	1 No.
Ammonia	Evaporating dish	1 No.
Ammonium carbonate	Funnel glass	1 No.
Hydrogen peroxide	Funnel stand	1 No.
Distilled water	Glass rod	1 No.
	Measuring cylinder	1 No.
	Porous plate	1 No.
	Tripod stand	1 No.
	Watch glass	1 No.
	Wire gauze	1 No.
	Filter paper	Few circles

2.3.3 Procedure

Weigh 10.0 g ammonium carbonate. Transfer to a 150 cm³ beaker. Dissolve in 25 cm³ distilled water and add 25 cm³ of concentrated aqueous ammonia. To this, add around 4 g of cobalt nitrate (in 10 cm³ water) with continuous stirring. After that add 3 cm³ of 30% hydrogen peroxide with stirring. Heat the solution and reduce the volume to about 30 cm³. During the evaporation, add 1.25 g of ammonium carbonate slowly. Filter the solution while hot if it is not fully dissolved. Cool the dark purple coloured solution (or filtrate) in ice bath and then allow the red precipitate of [Co(NH₃)₄CO₃] NO₃ to settle. Filter the red crystalline product by washing with cold distilled water. Dry the crystals by pressing them gently between pads of filter papers. Allow to dry on a porous plate. Weigh the crystals and record the yield. Calculate the percentage yield.

Structure

The tetraamminecarbonato cobalt(III) nitrate complex is having octahedral geometry in which carbonate ligand is acting as a bidentate ligand.

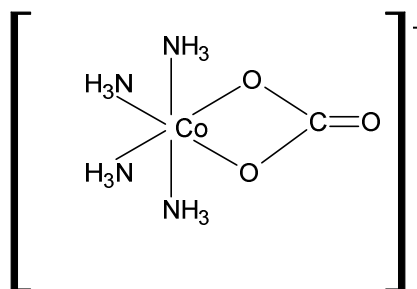


Fig. 2.4: Structure of [Co(NH₃)₄CO₃]⁺ ion.

2.3.4 Observations

Weight of cobalt nitrate taken = g

Weight of tetraamminecarbonatocobalt(III) nitrate = g

(experimental yield)

The reactant that is completely consumed in a chemical reaction is called limiting reagent.

2.3.6 Calculation of Percent Yield

Your objective should be to prepare as high a yield of tetraamminecarbonatocobalt(III) nitrate as possible. To measure the efficiency of the procedure, you should calculate the percent yield, where

$$\text{Percent yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

The theoretical yield is the calculated maximum amount of product which might be obtained under ideal conditions from the starting materials. In an experiment, the theoretical yield is seldom, if ever, reached.

2.3.7 Result

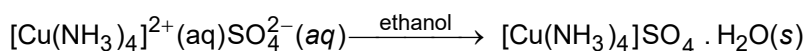
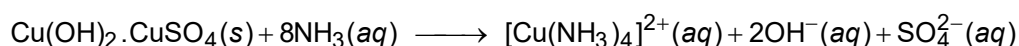
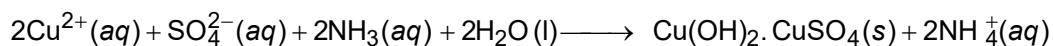
The percent yield of tetraamminecarbonatocobalt(III) nitrate = %

2.4 EXPERIMENT 4: PREPARATION OF TETRAAMMINECOPPER(II) SULPHATE MONOHYDRATE

In this experiment you will synthesise a complex compound, tetraamminecopper(II) sulphate monohydrate, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$.

2.4.1 Principle

When aqueous ammonia is added to a solution containing copper(II) sulphate, a pale blue precipitate of basic copper(II) sulphate is first formed. This dissolves in excess of aqueous ammonia solution giving a deep blue solution containing the complex ion, tetraamminecopper(II). Addition of ethanol to this solution results in precipitation of a deep blue coloured complex, tetraamminecopper(II) sulphate monohydrate:



The names and gram molecular weights of important compounds involved in this experiment are listed below:

Name	Formula	Gram Formula Weight g/mole
Copper(II) sulphate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	249.5
Ammonia	NH_3	17
Tetraamminecopper(II) sulphate monohydrate	$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$	245.74

2.4.2 Requirements

Chemical	Apparatus
Copper(II) sulphate	Beakers 250 cm ³ 1 No.
Ammonia(aq), Sp. gr. 0.88 (15 M)	Bunsen burner 1 No.
Ethanol	Buchner funnel 1 No.
Distilled water	Filtration apparatus 1 No.
	Glass rod 1 No.
	Measuring cylinder 1 No.
	Tripod stand 1 No.
	Watch glass 1 No.
	Water bath 1 No.
	Filter paper Few circles

2.4.3 Procedure

Weigh out 2.0 g copper(II) sulphate and powder it. Add powdered crystals to a 250 cm³ beaker. Prepare ammonia solution by adding 10 cm³ ammonia (aq) to 5 cm³ distilled water. Slowly add ammonia solution to the powder with stirring until all the copper(II) sulphate dissolves resulting in a deep blue solution. Add 1-2 cm³ of ammonia solution in excess. Add ethanol dropwise and with stirring till a deep blue precipitate is formed. Heat the beaker on a water bath at 60°C, stir and wait till the blue precipitate just dissolves. Cover the beaker with a watch glass and set aside to crystallise. Beautiful dark blue needle like crystals separate after 1 hour. Filter off the crystals using a Buchner funnel and wash with 2-3 cm³ ethanol at the pump. Allow the air to pass for 5 minutes. Transfer the product to a watch glass and dry in a desiccator. Store the crystals in a weighed weighing bottle.

Weigh the dry crystals. Calculate the percent yield.

2.4.4 Observations

Weight of copper(II) sulphate taken = g

Weight of tetraamminecopper(II) sulphate monohydrate (experimental yield) = g

2.4.5 Calculations

$$\begin{aligned}\text{No. of moles of copper(II) sulphate} &= \frac{\text{g of CuSO}_4 \cdot 5\text{H}_2\text{O taken}}{\text{gram molecular weight}} \\ &= \frac{2.0}{249.5} \text{ moles}\end{aligned}$$

No. of moles of complex formed = No. of moles of copper(II) sulphate taken

$$= \frac{2.0}{249.5} \text{ moles}$$

Theoretical yield in gram = No. of moles $\times$ gram molecular weight

$$= \frac{2.0}{249.5} \times 245.74 = 1.97 \text{ g}$$

$$\text{Percent yield} = \frac{\text{Explained yield}}{\text{Theoretical yield}} \times 100\%$$

2.4.6 Result

The percent yield of the tetraamminecopper(II) sulphate monohydrate = %

2.4.7 Structure of the Complex

Tetraamminecopper(II) sulphate is an example of a complex, in which copper(II) ion is bound to four unidentate ammonia molecules. The coordination number of copper(II) is 4. The complex has a square planar structure (Fig. 2.5) and possesses one unpaired electron.

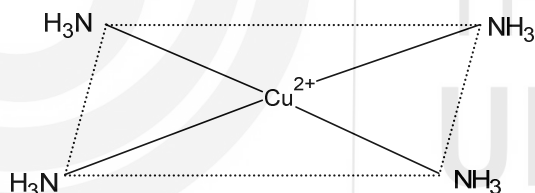


Fig. 2.5: Structure of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion.

This can be explained on the basis of dsp^2 hybridisation of Cu^{2+} ion, which you might have studied in Units 4 and 5 of the BCHCT 137 course.

2.5 EXPERIMENT 5: PREPARATION OF POTASSIUM TRIOXALATOFERRATE(III) TRIHYDRATE

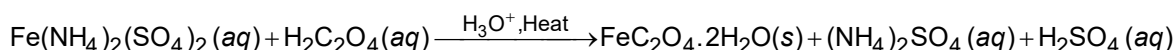
In this experiment, you will synthesis the complex compound potassium trioxalatoferrate(III) trihydrate.

2.5.1 Principle

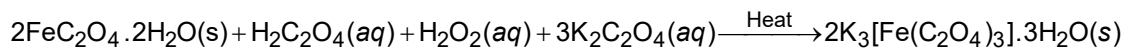
The synthesis of potassium trioxalatoferrate(III) is achieved in two steps. The first step consists in the preparation of the yellow iron (II) oxalate from ammonium iron(II) sulphate by reaction with oxalic acid in the presence of dilute sulphuric acid.

The second step involves the oxidation of iron(II) oxalate with H_2O_2 in the presence of excess oxalate ions when emerald green crystals of potassium trioxalatoferrate(III) are obtained.

Step 1



Step 2



The names and gram formula weights of important compounds involved in this experiment are listed below:

Name	Formula	Gram Formula Weight g/mole
Ammonium iron(II) sulphate	$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	392.13
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	126.07
Potassium oxalate	$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	184.25
Hydrogen peroxide	H_2O_2	34.02
Potassium trioxalatoferrate(III)	$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	491.25

2.5.2 Requirements

Chemical

Ammonium iron(II) sulphate
Oxalic acid
Potassium oxalate
Dilute sulphuric acid (5 M)
Hydrogen peroxide (3%)
Acetone
Ethanol
Distilled water

Apparatus

Beakers 250 cm³ 1 No.
Beaker 100 cm³ 1 No.
Buchner funnel 1 No.
Bunsen burner 1 No.
Desiccators 1 No.
Filtration apparatus 1 No.
Glass rod 1 No.
Measuring cylinder 1 No.
Tripod stand 1 No.
Watch glass 1 No.
Water bath 1 No.
Wire gauze 1 No.
Filter paper Few circles

2.5.3 Procedure

Step 1: Preparation of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

Weigh 5.0 g ammonium iron(II) sulphate and transfer to a 250 cm³ beaker. Add 15-20 cm³ distilled water and 1 cm³ dil. H_2SO_4 . Stir to dissolve.

Add 10% oxalic acid (25 cm^3) solution to the above iron(II) solution and heat to boiling with continuous stirring. **[Caution: Do not leave it unattended as this solution is susceptible to spillover and there can be bumping once the solid starts separating].** Add more oxalic acid, if necessary to get the maximum yield of the yellow iron(II) oxalate, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Allow the yellow product to settle. Carefully decant the hot supernatant liquid and repeatedly wash the precipitate with hot water. Retain the solid in the beaker for the next step.

Step 2: Synthesis of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$

Add a warm solution of potassium oxalate (5.0 g in 15 cm^3 distilled water) to the iron(II) oxalate precipitate in the beaker. Suspend a thermometer in the solution. Take 3% H_2O_2 (20 cm^3) in a measuring cylinder. Stir the solution and add hydrogen peroxide very slowly a few drops at a time with the help of a dropper so as to maintain the temperature around 40°C . In all 20 cm^3 of 3% H_2O_2 is added. The addition may take up to 30 minutes.

Heat to boiling. Add 10% $\text{H}_2\text{C}_2\text{O}_4$ solution, first $4\text{--}5\text{ cm}^3$ in one lot and later dropwise until the precipitate just dissolves. In all about 10 cm^3 solution will be required. Keep the solution boiling till a green colour is obtained. Heat for another 5 minutes. Filter the solution in a 100 cm^3 beaker and allow to cool to room temperature in a dark cupboard since the product is photosensitive. Add 10 cm^3 ethanol to the beaker and redissolve any crystals formed by gentle warming on a water bath and put the solution in a dark cupboard to crystallise. Cover with a watch glass. Slower evaporation encourages the development of larger and purer crystals.

Filter the crystals on a Buchner funnel by suction. Wash with ethanol-water (1: 1) mixture and finally with acetone. Dry in a desiccator over calcium chloride. Weigh the crystals and record the yield.

2.5.4 Observations

- | | | |
|------|--|-----|
| i) | Weight of ammonium iron(II) sulphate taken | = g |
| ii) | Weight of oxalic acid taken | = g |
| iii) | Weight of potassium oxalate taken | = g |
| iv) | Weight of complex formed | = g |
| | (Experimental yield) | |

2.5.5 Calculation of Percent Yield

$$\text{No. of moles of } \text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} = \frac{\text{g of } \text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}}{\text{gram molecular weight}}$$

$$= \frac{5.0}{392.13} = 0.013 \text{ mole}$$

$$\text{No. of moles of } \text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O} \text{ formed} = 0.013 \text{ mole}$$

$$\text{Theoretical yield in gram} = \text{No. of moles} \times \text{gram molecular weight}$$

$$= 0.013 \times 491.25 = 6.40 \text{ g}$$

$$\text{Percent yield} = \frac{\text{Explained yield}}{\text{Theoretical yield}} \times 100\%$$

$$= \frac{\text{Explained yield}}{6.40} \times 100\%$$

2.5.6 Result

Percent yield of potassium trioxalatoferrate(III) trihydrate = %

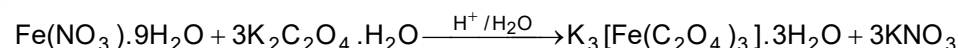
2.5.7 Alternate Procedure for the Synthesis of Potassium Trioxalatoferrate(II) Trihydrate

There are two more procedures, which are straight forward, less time consuming and involve more cost efficient method of synthesis. These require the use of iron(III) nitrate or chloride instead of ammonium iron(II) sulphate.

Procedure A: Use iron(III) nitrate

Requirements

Chemical	Apparatus	
Potassium oxalate, $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	Beakers 150 cm ³	2 No.
Iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Buchner funnel	1 No.
Distilled water	Desiccators	1 No.
Ethanol	Filtration apparatus	1 No.
Acetone	Glass rod	1 No.
Ice	Watch glass	1 No.
	Water bath	1 No.



Prepare a solution of iron(III) nitrate (4.0 g in 20 cm³ distilled water) in a 150 cm³ beaker. Add this solution slowly to a stirred hot solution of potassium oxalate (containing 6.0 g of the salt in 40 cm³ of distilled water) taken in another 150 cm³ beaker. A clear green coloured solution is obtained. Heat for 2-3 minutes more.

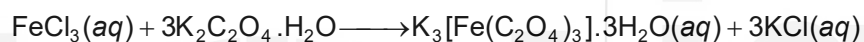
Cool in an ice bath. Filter the crystals using a Buchner funnel. Wash with ice cold water, followed by ethanol and acetone.

The emerald green product may be redissolved in warm water (15-20 cm³) and reprecipitated by cooling in ice bath at 0°C. Collect the crystals by filtration. Wash with ethanol-water (1: 1) mixture and finally with acetone.

Dry in a desiccator in a dark cupboard. Weigh the crystals and calculate the percent yield.

Procedure A: Use iron(III) chloride**Requirements**

Chemical	Apparatus	
Iron(III) chloride (anhydrous)	Beakers 150 cm ³	1 No.
Potassium oxalate K ₂ C ₂ O ₄ . H ₂ O	Buchner funnel	1 No.
Distilled water	Desiccators	1 No.
Ethanol	Filtration apparatus	1 No.
Acetone	Glass rod	1 No.
Ice	Watch glass	1 No.
	Water bath	1 No.



Take 6.0 g of potassium oxalate in a 150 cm³ beaker. Add 20-25 cm³ of distilled water. Heat using a wire gauze to get a clear solution. Add 1.6 g iron(III) chloride in small lots to hot solution of K₂C₂O₄. Heat again till a green coloured solution is obtained.

Cool the solution in ice bath at 0°C. Keep at this temperature until crystallisation is complete. Filter the crystals using a Buchner funnel. Collect the product after washing with ethanol and acetone. Recrystallise the complex as in procedure A. Dry the complex in a desiccator in a dark cupboard. Weigh the complex and calculate the percent yield.

2.5.8 Structure

Potassium trioxalatoferrate(III) is an example of a complex compound, in which iron(III) is chelated to three bidentate oxalate groups forming six bonds. Coordination number of iron is six. It is octahedrally surrounded by six oxygen atoms, two each from each oxalate group as shown in Fig. 2.6.

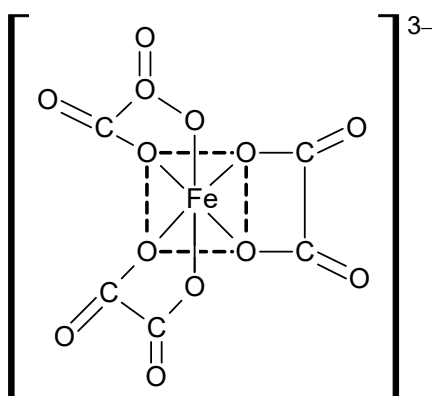


Fig. 2.6: Structure of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ ion.

2.6 EXPERIMENT 6: COMPARISON OF THE CONDUCTANCE OF THE COMPLEXES (PREPARED BY EXPERIMENTS 3 TO 5) WITH *M*/1000 SOLUTION OF NaCl, MgCl₂ AND LiCl₃

In this experiment you will compare the conductance of the complexes (prepared by Experiments 3 to 5) with *M*/1000 solution of NaCl, MgCl₂ and LiCl₃.

2.6.1 Principle

The high sensitivity of the conductometric measurements makes it an important analytical tool for environmental analysis and certain other applications. A continuous or spot check measurement of conductance is employed, usually, with a dip electrode cell and meter. In certain cases continuous recording of conductance is also employed.

Since conductance depends on ionic concentrations, the purity of steam distillate, demineralized water, and the ionic contents of raw water can be checked with measuring conductance directly. Metal industries, electroplating baths and rinse baths are monitored by conductance methods.

Perhaps the most common application of direct conductometry has been for estimating the purity of distilled water. Kohlrausch with a painstaking work after 42 successive distillations of water in vacuum obtained a conductivity water with specific conductance, $\kappa = 4.3 \times 10^{-8} \text{ S cm}^{-1}$ at 18°C. Traces of an ionic impurity will increase the conductance appreciably. Ordinary distilled water in equilibrium with the carbon dioxide of the air has a conductivity of about $7.0 \times 10^{-7} \text{ S cm}^{-1}$. The sea water has much higher value of conductivity and the conductometric measurements are widely used to check the salinity of water in oceanography.

Measuring conductance of soil helps in finding the moisture content of soils at various places with portable instruments. All soils contain varying amount of water soluble salts upto 0.1% or even more. These salts are usually present as sulphate, chloride, carbonate or bicarbonate of sodium, potassium, calcium and magnesium and contribute to the conductance of the soil. The soil may be classed as saline and non-saline depending on the nature and quantity of the salts present. Conductivity of a saturated extract with water of saline soil at 25°C has conductivity greater than 4 mS cm^{-1} .

Conductivity of coordination compounds (or complex) gives the degree to which a given coordination compound (or complex) can conduct electricity. They are different for different compounds. Based on the values of their conductivities, the compounds may be classified as electrolytes and non-electrolytes. You have learnt about Werner's theory of coordination compounds in your previous courses (BCHCT 137, unit 4). This theory may be supported from the conductivity data and help in determining the structure of a compound. Werner introduced primary and secondary valence to support his postulates. (Recapitulate the terms ligands, coordination number, coordination compounds)

2.6.2 Requirements

Chemical	Apparatus	
M/1000 solution of NaCl	Beakers 250 cm ³	1 No.
M/1000 solution of MgCl ₂	Beaker 100 cm ³	4 No.
M/1000 solution of LiCl ₃	Measuring cylinder	1 No.
Distilled water	Conductivity meter	1 No.

2.6.3 Procedure

Let us now discuss the experimental measurement of conductance.

Conductance is reciprocal of resistance and the resistance of a cell can be measured by placing it in an arm of a Wheatstone bridge. The inverse of the resistance gives the conductance and can be directly read on a conductivity measuring instrument, known as “Conductometer”.

A typical conductometer consists of an ac source, a Wheatstone bridge circuit, a null detector or direct reading display and a conductivity cell. .

To avoid the effects of polarization, i.e. the change in composition of the measuring cell, alternating current (ac) is used. The instrument has an arrangement to convert the supply of 50 Hz to higher frequency, say 1000 Hz. For measuring low conductance solutions, the lower frequency is preferable and for high conductive solutions higher frequencies are preferably used.

Several inexpensive conductometers are commercially available. The instruments come as a line-operated unit with and without digital readout. For spot checking on a process stream or tank, a dip-type of conductivity cell is used. For titration work conductivity cells of varied designs are available. In some titrations on open beaker with fixed electrodes is sufficient. However, for fairly dilute solutions an open beaker would not be satisfactory because atmospheric CO₂ may alter the conductance.

Fig. 2.7 gives the view of a typical conductometer, which can be operated as with given instructions.

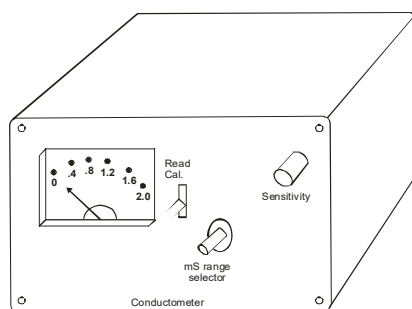


Fig.2.7: Conductometer.

1. Plug the instrument to an ac supply.
2. Put the frequency selector switch to required frequency (say 1000 Hz).

3. Set the mode selector on CAL and set the range selector on the desired setting e.g., 2, 20 or 200. These figures refer to the full scale meter value in milli Siemens (mS). With the help of sensitivity knob keep the pointer roughly midway between the lowest and highest sensitivity say at 1 position.
4. Connect the conductivity cell electrodes to the appropriate terminals of the instrument. Clean the conductivity cell with distilled water (Conductivity water).
5. Take the standard KCl solution (say 0.1M) in a clean beaker. Introduce a stirring rod (to be used for magnetic stirring) in the solution and put the solution beaker on a magnetic stirrer plate.
6. Insert the conductivity cell in the solution. Ensure that the platinum plate electrodes are completely immersed in the solution and they do not touch the stirring rod or the sides or the bottom of the beaker.
7. Switch on the instrument and allow it to warm up for 2-5 minutes.
8. Measure the conductance, G_s , of the standard KCl solution by putting meter switch to READ position.
9. Remove the KCl solution from the beaker; wash the conductivity cell properly with distilled water. Take the unknown solution in the beaker and measure its conductance, G_u , in the manner as for standard KCl solution.
10. Calculate the cell constant, from the conductance and conductivity values of the standard,

$$K_{\text{cell}} = \frac{\text{Conductivity (specific conductance)}}{\text{Observed conductance of the standard}}$$

$$= \frac{\kappa_s}{G_s} \text{ cm}^{-1}$$

11. Calculate the conductivity (specific conductance) of the unknown solution = cell constant $\times$ observed conductance
- $$\kappa_u = K_{\text{cell}} \cdot G_u$$
12. For titration work, the value of cell constant, K_{cell} is not required to be calculated, since the cell constant will remain unchanged during the course of any given titration.

Notes:

When the range selector is switched to a new position, it is essential to check the calibration again. Set the meter again to read one with the sensitivity control, if any deviation is observed.

The conductivity cell, when not in use, should be kept in distilled water to prevent drying the platinum electrodes.

In case of fouling the conductivity cell electrode plates, clean them by keeping in dilute $K_2Cr_2O_7$ containing H_2SO_4 solution (i.e. dilute chromic acid) for 24 hours and then washing with running water followed by rinsing with distilled water.

Prepare 0.001 M solutions of (a) Tetraamminecarbonatocobalt (III) nitrate, (b) tetraamminecopper(II) sulphate monohydrate and (c) potassium trioxalatoferrate(III) trihydrate complex in 100.00 ml volumetric flask. Measure the electrical conductivity κ of freshly prepared (a) Tetraamminecarbonatocobalt (III) nitrate, (b) tetraamminecopper(II) sulphate monohydrate and (c) potassium trioxalatoferrate(III) trihydrate complex. Calculate the molar conductivity, and relate to the number of ions, in order to conclude the formula of complex. Compare values with that of 0.001 M solution of NaCl, $MgCl_2$ and $LiCl_3$. Be sure to rinse the cell with distilled water before and after use.

Precautions

- Rinse the cell with distilled water before and after use.
- Stirring is required constantly to prevent bumping.

2.6.4 Observations

Observation Table I

Molar Conductivity Values

Sl. No.	Sample	Conductance, Siemen (S)	Conductivity, κ ($S\ cm^{-1}$)	Molar Conductivity, Λ_m ($S\ cm^2\ mol^{-1}$)
1.	NaCl (0.001 M)			
2.	$MgCl_2$ (0.001 M)			
3.	$LiCl_3$ (0.001 M)			
4.	$[Co(NH_3)_4CO_3] NO_3$ (0.001 M)			
5.	$Cu(NH_3)_4SO_4 \cdot H_2O$ (0.001 M)			
6.	$K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ (0.001 M)			

Result:

1. The molar conductivity of tetraamminecarbonatocobalt(II) nitrate is found to be and is comparable with molar conductivity value of $M/1000$ solution of.....
2. The molar conductivity of tetraamminecopper(II) sulphate is found to be and is comparable with molar conductivity value of $M/1000$ solution of
3. The molar conductivity of potassium trioxalatoferrate(II) trihydrate is found to be and is comparable with molar conductivity value of $M/1000$ solution of

2.7 SUMMARY

In this unit we discussed the preparation of the following three inorganic compounds:

1. Tetraamminecarbonatocobalt(III) nitrate
2. Tetraamminecopper(II) sulphate
3. Potassium trioxalatoferrate(III) trihydrate

We also described the calculation of percentage yield of the prepared complexes. At the end we have compared the conductance of these prepared complexes with $M/1000$ solution of NaCl, $MgCl_2$ and $LiCl_3$.

2.8 ANSWERS

Self Assessment Questions

1. From Eq. 2.5 for KCl solution:

$$\begin{aligned} K_{\text{cell}} &= \kappa \times R \\ &= 0.2768 \text{ S m}^{-1} \times 195.96 \Omega \\ &= 54.24 \text{ m}^{-1}. \end{aligned}$$

Conductivity of K_2SO_4 solution can be given by,

$$\begin{aligned} \kappa &= \frac{K_{\text{cell}}}{R} = \frac{54.24 \text{ m}^{-1}}{775.19 \Omega} \\ &= 0.06997 \text{ S m}^{-1}. \end{aligned}$$

concentration of K_2SO_4 in mol m^{-3} unit:

$$\begin{aligned} c &= 1000 \times 2.50 \times 10^{-3} \text{ mol m}^{-3} \\ &= 2.50 \text{ mol m}^{-3} \end{aligned}$$

Molar conductivity of K_2SO_4 can be calculated using Eq. 2.6

$$\begin{aligned} \Lambda_m &= \frac{\kappa}{c} = \frac{0.06997}{2.50} \text{ S m}^2 \text{ mol}^{-1} \\ &= 0.028 \text{ S m}^2 \text{ mol}^{-1} \end{aligned}$$

EXPERIMENT 7

SYSTEMATIC QUALITATIVE ANALYSIS OF CARBOXYLIC ACIDS AND PHENOLS AND PREPARATION OF THEIR DERIVATIVES

Structure

7.1	Introduction		Procedure
	Expected Learning Outcomes		Observations and Results
7.2	Functional Group Identification	7.4	Experiment 7b: Identification of Phenols and Preparation of their Derivative
7.3	Experiment 7a: Identification of Carboxylic Acids and Preparation of their Derivatives		Functional Group Tests
	Solubility Test		Preparation of Characteristic Derivatives
	Functional Group Test of Carboxylic Acids		Requirement
	Characteristic Derivatives		Procedure
	Requirements	7.5	Observation and Result
			Answers

7.1 INTRODUCTION

Organic compounds are classified into different classes based on the presence of functional groups. In the previous course, BCHCL-134 you have studied elementary analysis of organic compounds, e.g., physical examination, elemental analysis and determination of physical constants etc. In this Experiment and Experiments 9 and 10, you will learn some basic concepts of functional group analysis and perform qualitative tests for identification of some important functional groups. Along with this, you will also prepare their derivatives.

Both carboxylic acids and phenols are acidic in nature. Phenols are less **acidic** than **carboxylic acids** and do not react with NaHCO_3 to form water-soluble salts. As a result, phenols are insoluble in 5% NaHCO_3 but most of phenols are soluble in 5% NaOH . In this experiment, our focus will be on qualitative tests used in identification of carboxylic acids and phenols. For the confirmation of the presence of these functional groups, we will also prepare some derivative of carboxylic acid and phenols.

Expected Learning Outcomes

After performing the experiment given, you should be able to:

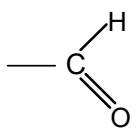
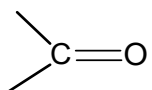
- ❖ explain the meaning of functional group of an organic compound;
- ❖ identify the carboxylic acids by sodium bicarbonate test;
- ❖ identify the phenol by ferric chloride test and Liebermann's test;
- ❖ prepare characteristic derivatives of carboxylic acids; and
- ❖ prepare characteristic derivatives of phenols.

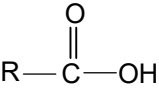
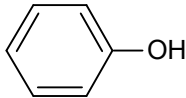
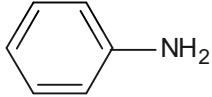
7.2 FUNCTIONAL GROUP IDENTIFICATION

Organic compounds are classified into different classes based on the presence of functional groups. You can recall from your theory course that the functional groups are the sites of chemical reactions. The identification of functional groups depends on their specific features of structure and reactivity.

Somehow identification of functional group depends basically on the correct determination of the elements, which you have studied in BCHCL-134 Course. 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. Some common classes of monofunctional organic compounds are listed in Table 7.1

Table 7.1: Common monofunctional organic compounds

Sr. No.	Functional Group	Class	Nature
1.		Aldehydes	Neutral
2.		Ketones	Neutral

3.		Carboxylic acids	Acidic
4.		Phenols	Weakly acidic
5.	-NO ₂	Nitro compounds	Neutral
6.	-CONH ₂	Amides	Neutral
7.		Amines	Neutral

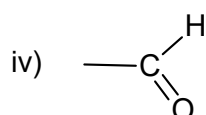
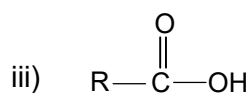
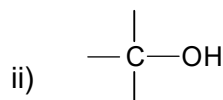
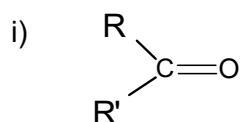
For the identification of the functional group, we generally follow the following steps;

1. Physical examination
2. Elemental analysis
3. Solubility test
4. Identification of functional groups using chemical tests
5. Preparation of derivatives

In your earlier course (BCHCL 134), we have covered steps 1 and 2. In this experiment and in next two experiments (Experiments 9 and 10), our focus will be on the remaining three steps. Our classical scheme for identification of functional group involves performing a number of chemical tests on a substance, each of which is specific for a type of functional group. After confirming the presence of the functional group in an organic compound, we prepare crystalline derivative to identify the actual compound by comparison of melting point with literature value of the compound. The ideal derivative should be able to be simply and quickly prepared with good yield. It should also be easily purified and identified. These should also have sharp and definite melting points preferably between 50°C and 250°C. In this work, you are advised not to jump to premature conclusions about the identity of the compound. Always prepare one derivative and check that its properties agree with those expected values before leaping into the preparation of the second confirmatory derivative. The methods for preparing derivatives for different functional groups will be discussed in this experiment and also in Experiments 9-11.

SAQ 1

Identify the functional group present in the following compounds.



So far in this experiment, we have discussed different steps that are evolved to establish the identity of the unknown compound. Now, we will apply them in identification of carboxylic acids and phenols.

7.3 EXPERIMENT 7a: IDENTIFICATION OF CARBOXYLIC ACIDS AND PREPARATION OF THEIR DERIVATIVES

Before going in detail of chemical tests used for the identification of carboxylic acids and phenols, we would like to discuss solubility test as it plays an important role in the identification of the carboxylic acid functional groups.

7.3.1 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

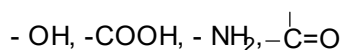
The solubility tests are done at room temperature. Take 100 mg of a solid (finely crushed) or 0.2 cm³ liquid and 3.0 cm³ of solvent in small test tubes. The mixture should be shaken vigorously. It is recommended that the solubility tests to be done in the order presented below:

Solubility in Water

Weight 100 mg of the finely crushed solid or measure 0.2 cm³ of liquid with the help of graduated pipette or burette and 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 touching it with pH paper.

The solubility of the compound in distilled water suggests that the compound is a low molecular weight organic compound having 4-5 carbon atoms, which contain a polar group such as

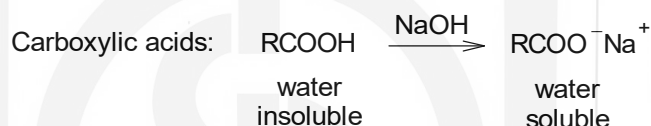


If higher molecular weight compound soluble in water, it must be polyfunctional, for example carbohydrates. On the other hand, alkanes, alkenes, alkynes and alkyl halides are water-insoluble.

If the organic compound is water soluble and gives a positive acidic test with pH paper, it 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.

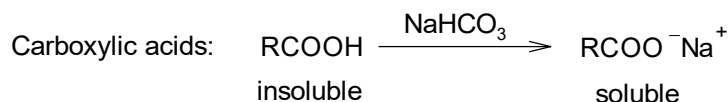


NaOH soluble organic compound should then be tested for solubility in the weaker base, 5% NaHCO_3 solution, which may permit distinction between carboxylic and phenolic functional groups.

Solubility in 5% Sodium hydrogencarbonate (Sodium bicarbonate) Solution

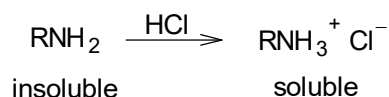
Similar to the procedure adopted for the solubility of water, the solubility of the compound is checked with 5% aqueous solution of sodium hydrogencarbonate. If it is soluble, the presence of a carboxylic acid group may be tentatively concluded, owing to the formation of the water-soluble sodium salt.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

Highly acidic phenols are soluble in 5% sodium bicarbonate.



Solubility in 5% Hydrochloric Acid

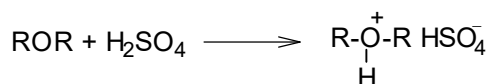
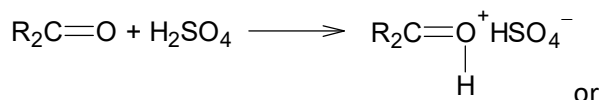
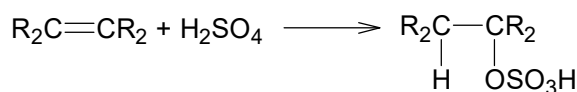
The solubility in 5% aqueous hydrochloric acid is evidence for an amino compound or a heteroaromatic base.



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

Solubility in Concentrated Sulphuric Acid

Take 3 cm³ 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 sulphuric acid indicates the presence of oxygenated and unsaturated aliphatic compound.



The general solubility behaviour of common classes of organic compound is shown schematically in Fig. 7.1.

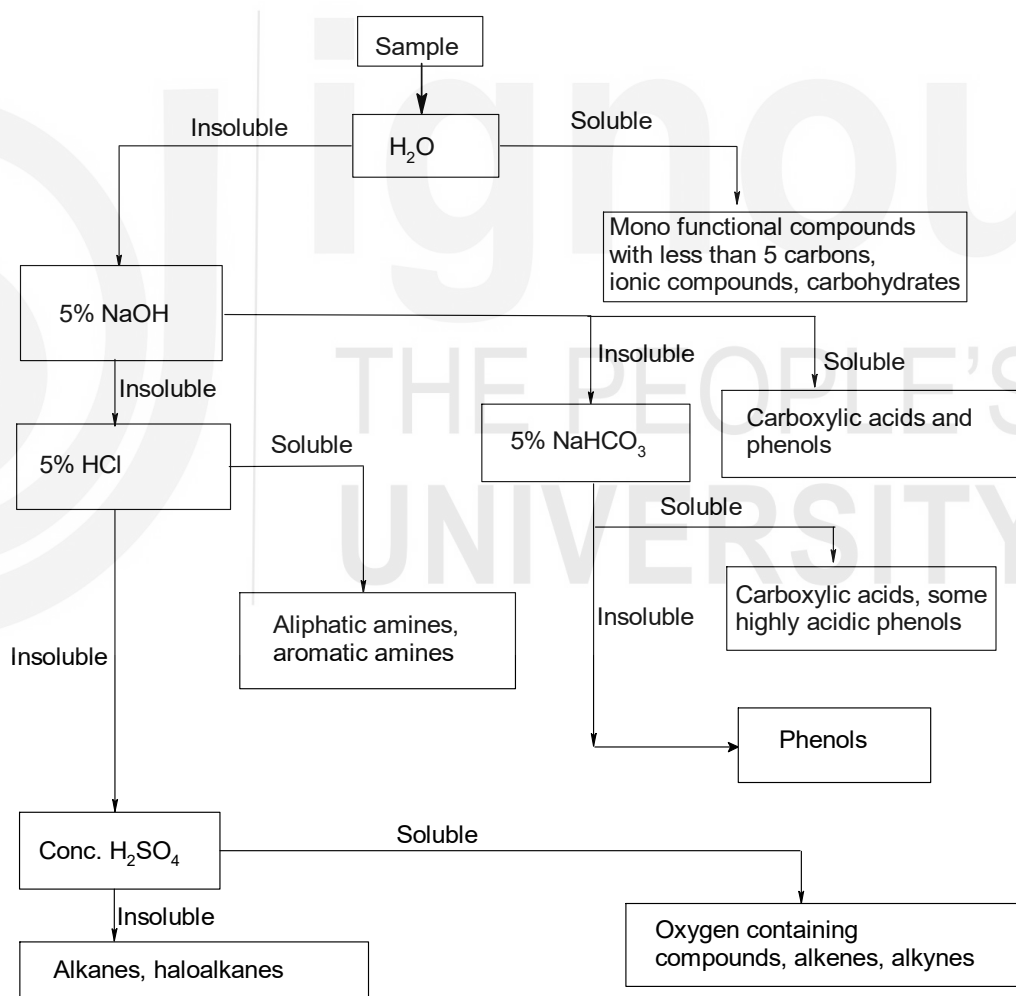


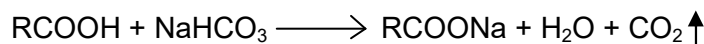
Fig.7.1: Solubility behaviour of common classes of organic compounds.

7.3.2 Functional Group Test for Carboxylic Acids

Carboxylic acids are represented by general formula RCOOH. The –COOH group is known as carboxylic group. The presence of carboxylic group in the compound is ascertained by following test:

Sodium Bicarbonate Test

One of the best tests for the carboxylic group is solubility in basic solution. Carboxylic acids liberate carbon dioxide from sodium bicarbonate.



Take 0.2 g of the unknown compound in a test tube and add 1 cm³ of 5% aqueous sodium bicarbonate. Vigorous evolution of carbon dioxide with effervescence indicates the presence of carboxylic group.

7.3.3 Characteristic Derivatives

Common derivatives prepared for identification of carboxylic acids are: amides, anilides and *p*-toluidides. Amides, anilides and *p*-toluidides are prepared from the corresponding acid chloride by treatment with ammonia, aniline or *p*-toluidine, respectively. It is considered that the method for the preparation of anilides and *p*-toluidides has advantage over amide. This is because amides are more soluble in water and as a result are harder to isolate. The acid chloride is prepared from the acid or its salt, and thionyl chloride.



or



Be very careful while adding conc. NH₄OH, the reaction is quite vigorous.

Acid chloride can be used to make the amide, anilides or *p*-toluidides.

Therefore, let us first study the method for preparation of acid chloride. Then, we will learn the method for preparation derivative of carboxylic acids.

Preparation of Acid Chloride

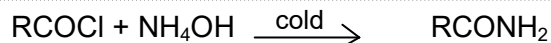
Take the sample of carboxylic acid (1 g), thionyl chloride (2 cm³) and dimethylformamide (DMF) (5 drops) in a small round bottom flask. Attach a reflux condenser and reflux for about 30 minutes. Precipitate of acid chloride will appear at the bottom of the flask. This mixture, containing acid chloride, can be used to prepare amide, anilide or *p*-toluidide derivative as described below:

Procedure for Preparing Derivatives

Common derivatives used for identification of carboxylic acids are Amides, *p*-Toluidides and Anilides Derivatives. Let us discuss the method of preparation for these derivatives individually.

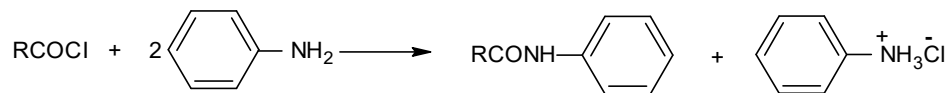
i) Amide Derivative

To about 2 gm of the above mixture, containing acid chloride, and add 15 cm³ of ice-cold conc. NH₄OH. A vigorous reaction takes place. Filter off the solid formed as the result of the reaction. Recrystallise it from water or aqueous ethanol. The reaction involved in this process is:



ii) *p*-Toluidides and Anilides Derivatives

Take about 2 g of the crude acid chloride in a 100 cm³ conical flask and dissolved it in 5 cm³ of acetone. To this add 1 g *p*-toluidine (dissolved in acetone). Shake the mixture for few minutes and add 50 cm³ of NaOH to the flask. Filter off the solid *p*-toluidide which formed during the reaction. Wash the *p*-toluidide with water and recrystallised from ethanol. The reaction involved in this process is:



If you want to prepare anilide, use aniline in place of *p*-toluidine and you will get anilides.

After drying the derivative, determine its M.P and compare it with theoretical value.

SAQ 2

Fill in the blanks.

- Carboxylic acids liberate from sodium bicarbonate.
- Reaction of acid chloride with ammonia yields
- Reaction of carboxylic acid with yields anilides.

SAQ3

Complete the following reactions

- $\text{RCOOH} + \text{NaHCO}_3 \longrightarrow \dots + \dots + \dots$
- $\text{RCOOH} + \text{SOCl}_2 \longrightarrow \dots + \dots + \dots$
- $\text{RCOCl} + \text{NH}_4\text{OH} \longrightarrow \dots$

7.3.4 Requirements

S. No.	Apparatus	S. No.	Chemicals
1.	Beakers	2	1. NaOH
2.	Conical flask	1	2. Acetone
3.	Droppers	1	3. Carboxylic acid
4.	M.P. apparatus	1	4. Ethanol
5.	Reflux condenser	1	5. conc. H ₂ SO ₄
6.	Round bottom flask	1	6. HCl
7.	Test tubes	1	7. conc. NH ₄ OH
8.	Thermometers	3	8. <i>p</i> -Toluidine
9.	Water bath	1	9. Pyridine
			10. Sodium bicarbonate

10	pH paper	1	11. Thionyl chloride
			12. 2,4-Dimethylformamide (DMF)
			13. 2-3 Samples of Carboxylic acid

7.3.5 Procedure

1. Collect sample(s) of carboxylic acid from your counsellor and carry out physical examination of the sample as discussed in BCHCL 134 course.
2. Carry out solubility test as discussed in Sec. 7.3.1. If your compound is soluble in water, check the pH of solution using pH paper.
3. Carry out functional group test (class determination test) as discussed in Sec. 7.3.2.
4. Prepare at least one derivative using procedure discussed in 7.3.3
5. Dry the prepared derivative and take the m.p. of both derivative and sample if it is solid. Predict the actual compound by comparison of melting point of sample and its derivative with literature values. Use appendix A for this purpose.

7.3.6 Observations and Result

1. Physical Examination

- a) Physical state :
- b) Colour :
- c) Odour :
- d) Ignition test :

Comment: This suggests that the unknown 'A' is either aromatic or aliphatic compound

2. Elemental Analysis: Not necessary at this point

3. Solubility test

H ₂ O	5% NaOH	5% NaHCO ₃	5% HCl	Conc. H ₂ SO ₄	Expected Class

4. Test with pH paper :

5. Melting point/Boiling point observed :

5. Class determination :

Sodium bicarbonate Test

6. Preparation of derivatives

(a) Derivative chosen:

M.P. observed

(b) Derivative chosen

M.P. observed

7. Examination of literature

Possible Compound	M.P. in Literature	Derivative(s)/ M.P. in Literature	M.P. of Sample	M.P. of Derivative(s)

8. The unknown compound is

9. The structure of this compound is.....

7.4 EXPERIMENT 7b: IDENTIFICATION OF PHENOLS AND PREPARATION OF THEIR DERIVATIVES

The aromatic compounds in which hydroxyl (OH) group is directly attached to benzene ring are called phenols. Phenols are mildly acidic. These require careful handling, especially in laboratories, because these can cause chemical burns. There are few laboratories tests which confirm the presence phenolic group in organic compounds.

In this section, we shall study the method for carrying out functional group test of phenols and preparation of their characteristic derivatives.

7.4.1 Functional Group Test

There are following three main functional group tests for identification of phenols.

- Ferric Chloride Test
- Liebermann's Test
- Ceric Ammonium Nitrate Test

Following apparatus and chemicals are required for these test;

i) Ferric Chloride Test

Most phenols react with ferric chloride and give colour. Some phenols, that do not give colour in aqueous or alcoholic solution, but they do so in chloroform especially after addition of a drop of pyridine. Some phenols do not give colour at all. So a negative test must not be taken as significant without supporting further information.

Procedure

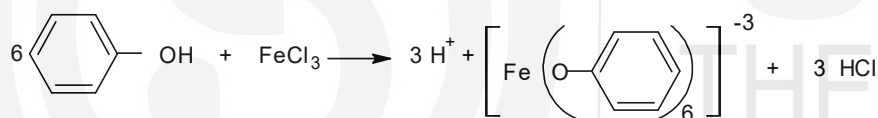
Dissolve 0.5 g of the unknown compound in 1-2 cm³ of water (or a mixture of water and 95% ethanol if the compound is not water soluble) and add a few drops of very dilute (1%) ferric chloride solution. Wide range of colours given below, show the presence of phenolic -OH.

Compound	Colour
Phenol, o-Cresol	Violet
<i>p</i> -Cresol, quinol	Blue
<i>m</i> -Cresol, 1-Naphthol(alcoholic)	Blue-violet
Resorcinol	--
1- Naphthol	Pink
2- Naphthol (alcoholic)	Green

Following compounds do not respond with ferric chloride test,

- Picric acid
- Naphtholsulphonic acid

The reaction involved in this test is,



There are mainly to functional group tests for identification of phenols which are given below:

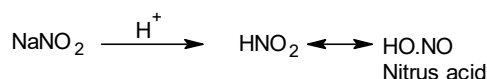
ii) Liebermann's Test

Phenols in which *para* position is free, give positive Liebermann's test, although few exception are noted. For example, *p*- substituted phenols and nitrophenols do not respond to Liebermann's test. Dihydroxyphenols, except resorcinol, do not give satisfactory result with this test.

Procedure

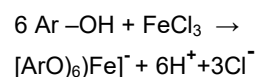
Take few crystals of sodium nitrite and compound (0.5 g) in a dry test tube. Heat the mixture gently for about 30 seconds, allow it to cool and add 0.5 cm³ of conc. sulphuric acid. On shaking the contents a deep green or blue colour develops. Dilute the content with water, the colour changes to red. Now add excess of dilute sodium hydroxide solution, the green or blue again reappears. Colour formation is observed due to the production of salt of indophenols.

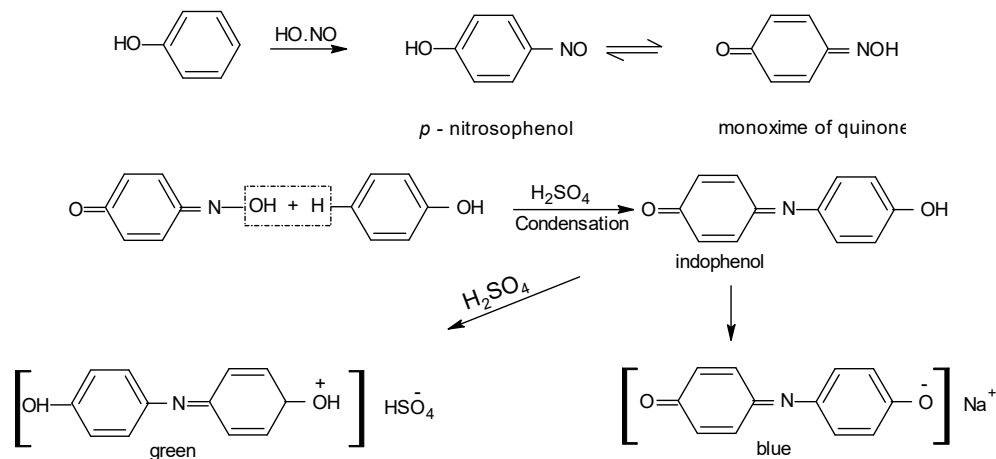
The reactions of the test are:



Enols ($\text{R}'\text{C}(\text{OH})=\text{CHR}'$) also give a wide range of colour with FeCl_3 .

The phenol complexes are probably coordination compounds in which iron is hexavalent.





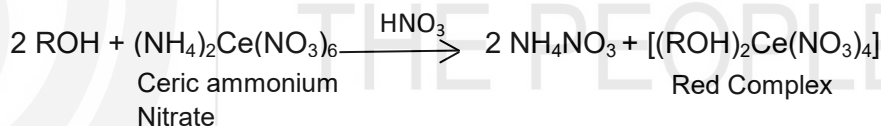
iii) Ceric Ammonium Nitrate Test

Ceric ammonium nitrate can also be used as a qualitative test for phenols. You carry out the test at room temperature because hot solutions of the reagent oxidise many of organic compounds.

Procedure

Prepare the solution of the unknown compound (0.2 g or 1 cm³) in water, (or dioxane for water insoluble compounds) add few drops of ceric ammonium nitrate. A red colour is obtained. This indicates the presence of primary, secondary and tertiary alcohols. Alcohols replace nitrate ions in complex cerate anions, resulting in a change from a yellow to red solution.

The preliminary reaction for phenol/alcohols is,



7.4.2 Preparation of Characteristic Derivatives

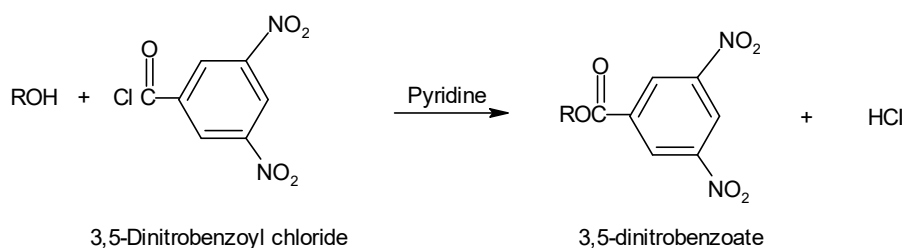
Some common derivatives which are used to identify the phenols are:

- i) 3,5- Dinitrobenzoate Derivatives
- ii) 1-Naphthyl Urethane Derivative

Let us discuss each of them separately

i) 3,5- Dinitrobenzoate Derivatives

The reaction between 3,5-dinitrobenzoyl chloride and alcohol gives the corresponding ester (3,5-dinitrobenzoate). 3,5-Dinitrobenzoate esters are suitable derivatives for both alcohols and phenols. The reaction involved in this preparation is as under:

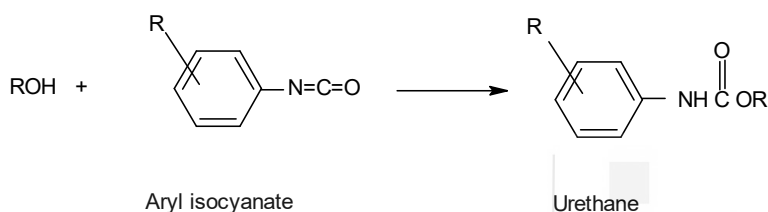


Procedure

Dissolve the alcohol (2 cm^3) in dry pyridine (5 cm^3) and add 3,5-dinitrobenzoyl chloride (1.2 g) in a 100 cm^3 round-bottomed flask. Reflux the reaction mixture for about 30 minutes and pour it into 40 cm^3 of hydrochloric acid. Separate the solid or oily product and stir with 15 cm^3 sodium carbonate solution (1M) to remove any 3,5-dinitrobenzoic acid formed. Filter the solid and recrystallised from petroleum ($60\text{--}80^\circ\text{C}$), ethanol or aqueous ethanol.

ii) 1-Naphthyl Urethane Derivative

This derivative is also suitable for both alcohols and phenols. When aryl substituted isocyanate, $\text{ArN}=\text{O}$, react with alcohols, it gives a urethane.



A major side reaction is that of water with isocyanate. To avoid the side reaction, take precautions to ensure that the alcohol is **anhydrous**.

Procedure

Place the phenol (0.5 g), dry pyridine (1 cm^3) and 1-naphthylurea (0.5 cm^3) in a dry test tube. Shake the mixture for few minutes. If no precipitate forms, warm gently on a water bath for 5 minutes and then cool the mixture in ice. Filter off the solid product. Recrystallise the crude derivative from petroleum ether ($40\text{--}60^\circ\text{C}$). (Remove 1-naphthylurea by filtration which is insoluble in petroleum).

SAQ 4

Which of the following would give colour with FeCl_3 ?

- i) *p*-Cresol
 - ii) Phenol
 - iii) Resorcinol
 - iv) 2-Naphthol (alcoholic)
-

SAQ 5

Which one of the following compounds does not show colour with FeCl_3

- i) Picric acid
 - ii) *o*-cresol
 - iii) Quinol
 - iv) 2-Naphthol (alcoholic)
-

SAQ 6

Give the three main functional group tests for identification of phenols.

7.4.3 Requirements

S. No.	Apparatus	S. No.	Chemicals
1.	Beakers	2	1. conc. NH_4OH
2.	Conical flask		2. pH Paper
3.	Droppers	1	3. Carboxylic acid
			4. Ethanol
4.	M.P. Apparatus	1	5. Pyridine
5.	Reflux condenser	1	6. Acetone
6.	Round bottom flask	1	7. Sodium nitrite
7.	Test tubes	3	8. 3,5-Dinitrobenzoyl chloride
8.	Thermometers	1	9. Ceric ammonium nitrate
9.	Water bath	1	10. H_2SO_4
			11. HCl
			12. NaOH
			13. Ferric chloride
			14. Sodium carbonate
			15. petroleum ether (40-60°C)
			16. 1-naphthylurea
			17. Samples of Phenols

7.4.4 Procedure

1. Collect sample(s) of phenol from your counsellor and carry out physical examination of the sample as discussed in BCHCL-134 course.
2. Carry out solubility test as discussed in Sec. 7.3.1. Check the pH of water solution using pH paper.
3. Carry out class determination test as discussed in Sec. 7.4.1.
4. Prepare at least one derivative using procedure discussed in 7.4.2
5. Dry the prepared derivative and take the m.p. of both the derivative and sample if your sample is solid. Predict the actual compound by comparison of melting point of sample and its derivative with literature values.

7.4.5 Observations and Result**1. Physical Examination**

- a) Physical state :
 b) Colour :
 c) Odour :
 d) Ignition test :

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

2. Elemental Analysis: Not necessary at this point.**3. Solubility test**

H ₂ O	5% NaOH	5% NaHCO ₃	5% HCl	Conc. H ₂ SO ₄	Expected Class

4. Test with pH paper :**5. Melting point/Boiling point observed :****5. Class determination**

Ferric Chloride Test

Liebermann's Test

Ceric Ammonium Nitrate Test

6. Preparation of derivatives

(a) Derivative chosen

M.P. observed

M.P. in literature

(b) Derivative chosen

M.P. observed

M.P. in literature

7. Examination of literature

Possible compound..... M.P..... Derivatives

8. The unknown compound is**9. The structure of this compound is.....**

7.5 ANSWERS

Self Assessment Questions

1.
 - i) Ketones
 - ii) Alcohols
 - iii) Carboxylic Acids
 - iv) Aldehydes
2.
 - i) Carbon dioxide
 - ii) Amide
 - iii) Aniline
3.
 - i) $\text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2\uparrow$
 - ii) $\text{RCOCl} + \text{SO}_2 + \text{HCl}$
 - iii) RCONH_2
4. All four
5. i)
6.
 - i) Ferric Chloride Test
 - ii) Liebermann's Test
 - iii) Ceric Ammonium Nitrate Test

EXPERIMENT 8

SYSTEMATIC QUALITATIVE ANALYSIS OF ALDEHYDES AND KETONES AND PREPARATION OF THEIR DERIVATIVES

Structure

8.1 Introduction

Expected Learning Outcomes

8.2 Aldehydes and Ketones

Functional Group Tests

Preparation of Characteristic Derivatives

Requirement

Procedure

Observation and Result

8.3 Answers

8.1 INTRODUCTION

In the last experiment, we have learnt some basic concepts of functional group chemistry and performed qualitative tests for identification of carboxylic acids and phenols and methods of preparation of their derivatives. In this experiment, you will carry out tests for the identification of aldehydes and ketones using Brady's test, Tollen's test, Schiff test and Iodoform test. You will also perform tests to differentiate these two categories of compounds. Once your functional group has been determined, you will prepare a derivative of your compound to establish actual identity of your given sample.

Expected Learning Outcomes

After performing the experiment, you should be able to:

- ❖ identify the aldehydes and ketones by Brady's test, Tollen's test and Schiff test.
- ❖ prepare characteristic derivatives of aldehydes and ketones.

8.2 EXPERIMENT 8: IDENTIFICATION OF ALDEHYDES AND KETONES AND PREPARATION OF THEIR DERIVATIVES

Both aldehydes and ketones have carbonyl group ($>C=O$). You have studied the reactions of carbonyl group in organic chemistry course (BCHCT-133). In this experiment you will perform the tests for detecting aldehydes and ketones. In the last section, you will learn the methods of preparation of derivatives of aldehydes and ketones.

8.2.1 Functional Group Test

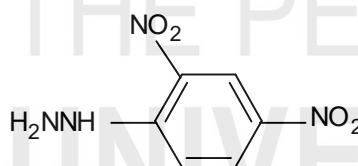
There are four main following functional group tests for identification of aldehyde and ketones. They are:

- i) Brady's Test
- ii) Tollen's Test
- iii) Schiff Test
- iv) Iodoform Test

Let us discuss each of these separately.

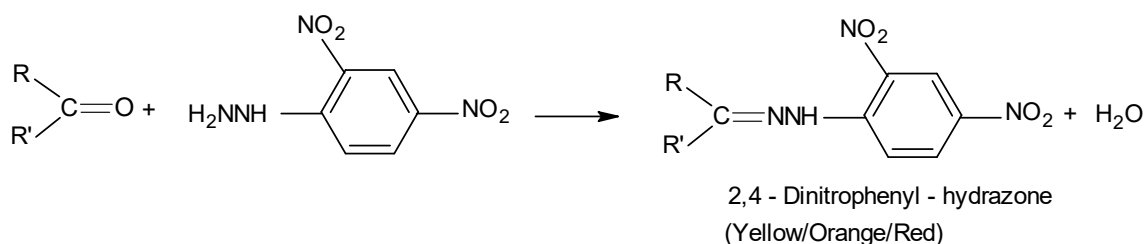
i) Brady's Test

2,4-Dinitrophenylhydrazine (2,4-DNP) is known as Brady's reagent. It is a red-orange solid, usually supplied wet to reduce the risk of explosion. The structure of 2,4-Dinitrophenylhydrazine is given below.



2,4-Dinitrophenylhydrazine derivatives offer a convenient way of separating the components of a mixture of aldehydes and ketones.

The carbonyl compounds (aldehydes/ketones) react with 2,4-dinitrophenylhydrazine (DNP) and give crystalline 2,4-dinitrophenylhydrazone product having orange/ yellow/ red colour. The reaction involved in the Brady's test is given:



This test is carried out as given below:

Procedure

Take 0.5 g of the unknown compound in a test tube and dissolve it in few drops of water or ethanol. Add 1 cm³ of Brady's reagent. Heat the reaction

mixture on water bath for few minutes and then cool it in ice. The appearance of yellow/orange/red crystalline precipitate indicates the presence of aldehydes or ketones.

The colour of the precipitate gives some idea of the type of carbonyl compounds.

Colour of Precipitate	Compound
Yellow	Saturated carbonyl compounds
Orange	α , β -Unsaturated carbonyl compounds
Red	Aromatic carbonyl compounds

SAQ 1

Write the structural formula of 2,4-Dinitrophenylhydrazine.

ii) Tollen's Test

If Brady's test is positive, then aldehydes and ketones are differentiated through Tollen's test. A positive Tollen's test is indicated by the or sometimes precipitation of elemental silver, often producing a characteristic "silver mirror" on the inner surface of the reaction vessel.

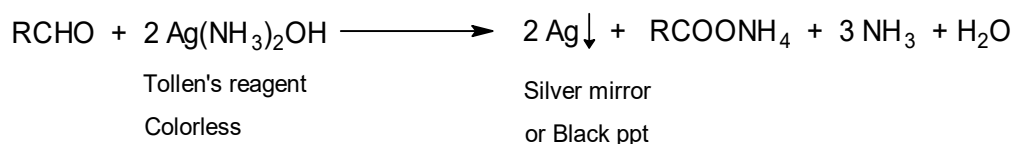
Tollens' reagent is used to determine the presence of aldehydes in organic compounds. The reagent consists of a solution of silver nitrate, ammonia and sodium hydroxide (to maintain a basic pH of the reagent solution). It was named after its discoverer, the German chemist Bernhard Tollens. A positive Tollens test indicates the presence of an aldehyde. Normally, ketones do not give Tollen's test but there are few exceptions, for example acetophenone and cyclohexanone. Some easily oxidisable compounds (e.g., certain phenols, 2-naphthol; and amines) also give positive Tollen's test but these compounds do not give positive test with DNP.

Silver ammonium ion $[\text{Ag}(\text{NH}_3)_2]^+$ is present in Tollen's reagent. In this test, aldehyde is oxidised to carboxylic acid and silver ion reduced to free silver.

Procedure

Place the unknown compound (2 drops of liquid or 0.05 g of solid) and add 1 cm³ of freshly prepared Tollen's reagent in a clean test tube. Shake the test tube and place it in the stand for about 10 minutes. If black precipitate or silver mirror on the wall of test tube is not appeared, warm the test tube for few minutes on a water bath. Formation of black precipitate of silver or silver mirror indicates the presence of aldehydic group.

The reaction can be given as:

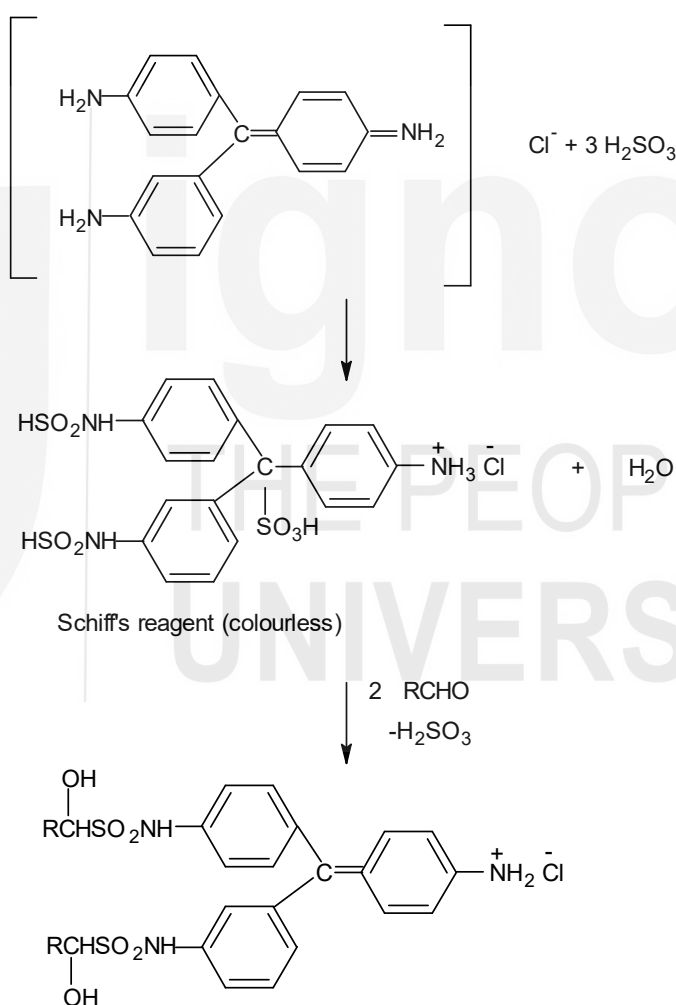


SAQ 2

Name the chemist who discovered the Tollens Test.

iii) Schiff's Test

Another method for distinguishing between aldehyde and ketone is Schiff Test. Aldehydes give positive Schiff's test whereas ketones do not react with Schiff's reagent. In this test, an aldehyde reacts with Schiff's reagent to form a characteristic magenta colour. Some aromatic aldehydes (e.g., vanillin), give a negative result with the Schiff's reagent. Methyl ketones ($\text{CH}_3\text{CO}-$) may restore the colour of Schiff's reagent very slowly. Your test tube should be free from alkali and the salts of weak acids because these also redden the Schiff's reagent like an aldehyde. The reaction sequence of this is:



Perform this test as given below:

Procedure

Take 2 cm^3 of unknown compound or 2 cm^3 of aqueous or alcoholic solution of the unknown compound in a test tube. Then add 2 cm^3 of Schiff's reagent in the test tube and shake it for 2 minutes. **Do not warm or heat** the Schiff's reagent because pink colour develops on heating even in the absence of aldehyde. The appearance of wine-red or purple colour indicates the presence of an aldehyde group.

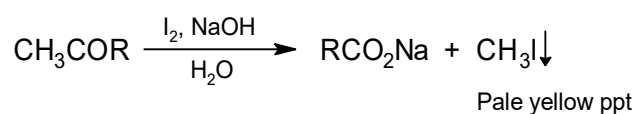
SAQ 3

What are the compounds involved in the preparation of Schiff 's reagent?

iv) Iodoform Test

Iodoform test is useful for the identification of methyl ketones (CH_3COR) and secondary methyl carbinols $\text{CH}_3\text{CH}(\text{OH})\text{R}$. Since this test is positive for $\text{CH}_3\text{CH}(\text{OH})$ - groups, it is advised that you should perform iodoform test after confirming the presence of carbonyl group. Ethanol, acetaldehyde (ethanol), CH_2ICO - also gives positive iodoform test. The test is negative for acetic acid and some other similar compounds.

Reaction involved in the test is given by,



Carry out the test as given below:

Procedure

Dissolve 0.5 cm^3 of the unknown liquid or 0.2 g of the solid in water (3 cm^3) or aqueous dioxane (2 cm^3 water + 2 cm^3 dioxane) in a boiling tube. Add iodine-potassium iodide solution (1 cm^3) and then few drops of 3 M sodium hydroxide solution with shaking until the brown colouration vanishes. A positive test is indicated by immediate formation of pale yellow precipitate of iodoform (iodoform), melting point. 119°C , without heating.

SAQ 4

Write the reaction involved in the Iodoform test.

SAQ 5

Which of the following compounds will give a positive haloform test?

- a) $\text{C}_6\text{H}_5\text{COCH}_3$; b) CH_3COOH ; c) CH_3CHO ;
d) CH_2ICOR ; e) $\text{CH}_3\text{COCH}_2\text{COOR}$
-

8.2.2 Preparation Characteristic Derivatives

For the preparation of derivatives, carbonyl group of aldehydes and ketones are converted into another groups such as $> \text{C} = \text{NNHR}$, oximes, etc. Some important derivatives which help in the identification of aldehyde and ketones are:

- i) 2,4-Dinitrophenylhydrazone

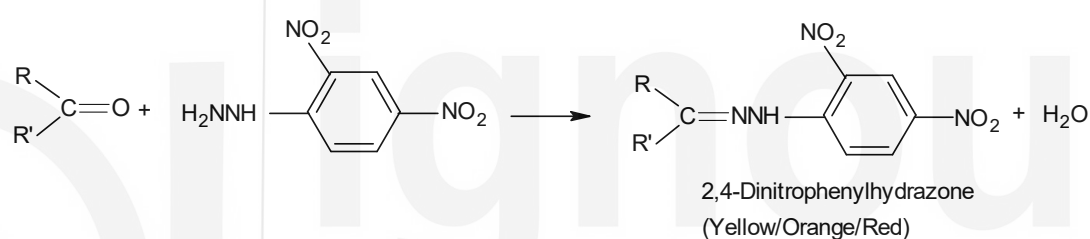
ii) Semicarbazone

iii) Oximes

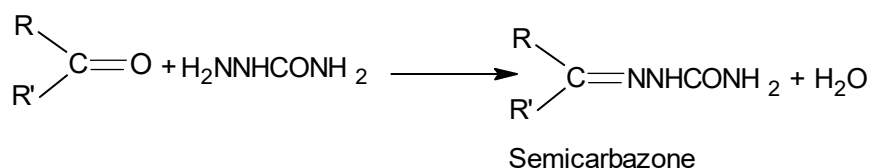
Methods for the preparation of some common derivatives are given below this section.

i) **2,4-Dinitrophenylhydrazone****Procedure**

Dissolve 0.5 g of the unknown carbonyl compound in a small volume of ethanol and add 2-3 cm³ of the 2,4-dinitrophenylhydrazine reagent. Heat the mixture on water bath for 15-20 minutes, if no solid separates immediately, cool it and if a precipitate still does not form, add water dropwise until precipitate forms. Filter off the resulting solid, wash it with aqueous methanol (equal volumes of water) and methanol and recrystallise the solid from ethanol or ethyl acetate. Take the melting point. Reaction involve in the process is given below:

ii) **Semicarbazone****Procedure**

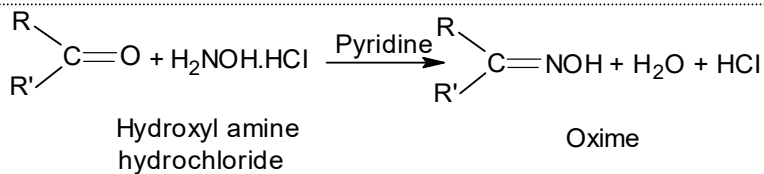
Dissolve the semicarbozide hydrochloride (0.5 g) and sodium acetate (0.8 g) in 5 cm³ of water in a test tube and then add the carbonyl compound (0.5 g). Add minimum amount of ethanol dropwise to get a clear solution if the solution is not clear. Heat the mixture for 10-20 minutes on a water bath, cool in the ice and filter. Recrystallise the product from ethanol, aqueous ethanol, water or benzene.

iii) **Oximes**

This is used for higher molecular weight aldehydes and ketones.

Procedure

Place a mixture of 0.5 g of carbonyl compound, 0.5 g of hydroxylamine hydrochloride, 3 cm³ of pyridine and 3 cm³ of absolute ethanol in a small round bottom flask. Fit reflux condenser to the round bottom flask and reflux the mixture for 2 hours on water bath. Evaporate the recrystallised the residue from ethanol or aqueous ethanol. The reaction involved in the preparation of oxime is given below:



SAQ 6

What are the main derivatives used to for identification of aldehyde an ketones?

SAQ 7

Write the chemical formula of the following compounds.

- i) 2,4-Dinitrophenylhydrazone
 - ii) Semicarbazone
 - iii) Oximes
-

8.2.3 Requirements

S. No.	Apparatus	Qty.	S. No.	Chemicals
1	Beakers	2	1	Alcohol
2	Boiling tube	1	2	2,4-Dinitrophenylhydrazine (2,4-DNP)
3	Conical flask	1	3	Dioxane
4	Droppers	1	4	Ethanol
5	M.P. Apparatus	1	5	Hydroxylamine hydrochloride
6	Reflux condenser	1	6	Iodine- potassium iodide solution
7	Round bottom flask	1	7	Methanol
8	Test tubes	3	8	Pyridine
9	Thermometers	1	9	Schiff 's reagent
10	Water bath	1	10	Semicarbazide hydrochloride
			11	Sodium acetate
			12	Tollen's reagent
			13	Samples of aldehydes and ketones

Solution Provided

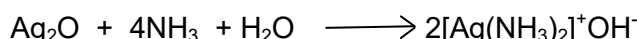
Brady's reagent: Dissolve 1 g of DNP in 5 cm³ concentrated sulphuric acid. Add this solution slowly with shaking and cooling to a mixture of water (7 cm³) and ethanol (25 cm³). Filter it to remove any suspended solid and store as a stock solution.

Tollen's reagent:

Solution A: Dissolve silver nitrate (2.5) g in distilled water (40 cm³).

Solution B: Dissolve potassium hydroxide (3 g) in distilled water (40 cm³).

Mix equal volumes of solutions A and B. A white precipitate (Ag₂O) is obtained. Now add concentrated ammonia solution (30%) drop by drop until the mixture is almost clear.



Tollen's reagent should be prepared immediately before the experiment because on long standing it decomposes to yield a potentially explosive solid, silver nitride (Ag₃N).

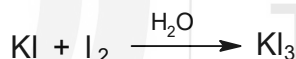
Schiff 's reagent

Dissolve *p*-rosaniline hydrochloride (0.2 g) in saturated solution (20 cm³) of sulphur dioxide in water. Shake and allow it to stand for few hours until becomes colourless or pale yellow. Dilute with water (180 cm³) and separate the clear solution by filtration.

Iodine-potassium iodide reagent: It is prepared by adding 50 g of potassium iodide and 25 g of iodine to distilled water (200 mL). A clear solution is obtained after stirring. Deep brown colour of the solution is due to the formation of triiodide anion (I₃).

Schiff's reagent tends to acquire colour on storage. Therefore, it is necessary to use only colourless Schiff's reagent.

Keep the Schiff's reagent in a well stopped bottle in dark.



8.2.4 Procedure

1. Collect sample(s) of aldehyde and ketone from your counsellor and carry out physical examination of the sample as discussed in BCHCL 134 course.
2. Carry out solubility test as discussed in Sec. 8.3.1. If your compound is soluble in water, check the pH of solution using pH paper.
3. Carry out functional group test (class determination test) as discussed in Sec. 8.2.1.
4. Prepare at least one derivative using procedure discussed in 8.2.2
5. Dry the prepared derivative and take the m.p. of both derivative and sample if it is solid. Predict the actual compound by comparison of melting point of sample and its derivative with literature values. Use appendix A for this purpose.

8.2.5 Observations and Result

1. Physical Examination

- a) Physical state :
- b) Colour :

c) Odour :

d) Ignition test :

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

2. **Elemental Analysis:** Not necessary at this point.

3. **Solubility test**

H ₂ O	5% NaOH	5% NaHCO ₃	5% HCl	Conc. H ₂ SO ₄	Expected Class

4. **Test with pH paper:**

5. **Melting point/Boiling point observed:**

5. **Class determination:**

Brady's Test

Tollen's Test

Schiff Test

Iodoform Test

6. **Preparation of derivatives**

a) Derivative chosen

M.P. observed

M.P. reported in literature

b) Derivative chosen

M.P. observed

M.P. reported in literature

7. **Examination of literature**

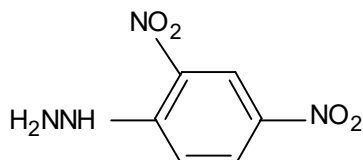
Possible compound.....M.P.....Derivatives

8. The unknown compound is

9. The structure of this compound is

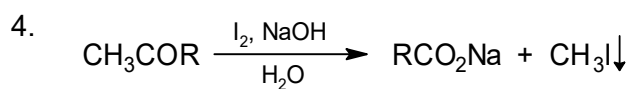
8.3 ANSWERS

1.



2. A German chemist Bernhard Tollens discovered. Tollens test

3. *p*-rosaniline hydrochloride, ii. sulphur dioxide, iii. water



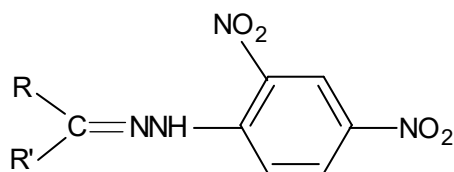
5. a, c and d

6. i) 2,4-Dinitrophenylhydrazone

ii) Semicarbazone

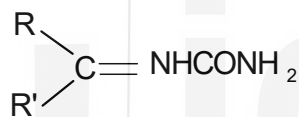
iii) Oximes

7. i)



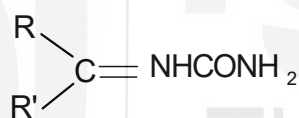
2,4-Dinitrophenyl-hydrazone

ii)



Semicarbazone

iii)



Semicarbazone

EXPERIMENT 9

SYSTEMATIC QUALITATIVE ANALYSIS OF AMIDES, NITRO AND AMINO COMPOUNDS AND PREPARATION OF THEIR DERIVATIVES

Structure

9.1	Introduction	Requirement
	Expected Learning Outcomes	Procedure
9.2	Experiment 9A: Identification of Amines	Observation and Result
	Functional Group Tests	9.4 Experiment 9C: Identification of Amides
	Preparation of Characteristic Derivatives	Functional Group Tests
	Requirement	Preparation of Characteristic Derivatives
	Procedure	Requirement
	Observation and Result	Procedure
9.3	Experiment 9B: Identification of Nitro Compounds	Observation and Result
	Functional Group Tests	9.7 Answers
	Preparation of Characteristic Derivatives	

9.1 INTRODUCTION

In the last experiment we have discussed the qualitative analysis of aldehydes and ketones. In this experiment we shall test the functional group of compounds having i) carbon, hydrogen and nitrogen atoms (amines) and ii) carbon, nitrogen and oxygen atoms (nitro compounds and amides).

First we will learn how to identify amines by i) Hinsberg test ii) Nitrous acid test iii) Diazotisation and iv) Gabriel phthalimide test. In the next section we will discuss

Use caution in handling amines. Many are toxic.

the methods of identification of nitro compounds by i) ferrous hydroxide test and ii) by reduction process.

In the last section we will learn how to identify the amide by i) ammonia evaluation test and ii) hydroxamic acid test. We will also learn the method for preparation of derivatives of these compounds.

Expected Learning Outcomes

After performing the experiment given, you should be able to:

- ❖ identify the amines by Hinsberg, nitrous acid, diazotisation and Gabriel phthalimide tests;
- ❖ prepare characteristic derivative of amines by Schotten-Baumann method;
- ❖ identify the nitro compounds by ferrous hydroxide test and by reduction process;
- ❖ prepare characteristic derivatives of nitro compounds by reduction to amine;
- ❖ identify the amide by ammonia evaluation test and hydroxamic acid test; and
- ❖ prepare characteristic derivatives of amides by hydrolysis.

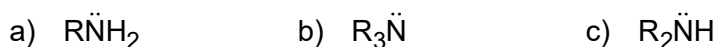
9.2 EXPERIMENT- 9a: IDENTIFICATION OF AMINES AND PREPARATION OF THEIR DERIVATIVES

Compounds that contain a basic nitrogen atom with a lone pair are called amines. The substituent -NH_2 is called an amino group. They are formally derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl groups (these may respectively be called alkylamines and arylamines). Amines in which both alkyl and aryl of substituents are attached to one nitrogen atom may be called alkylarylamines.

Amines can be classified according to the nature and number of substituents on nitrogen. There are three types of amines i.e. Primary (1°) amines, Secondary (2°) amines and Tertiary (3°) amines

- **Primary (1°) amines:** In primary amines one of three hydrogen atoms in ammonia is replaced by an alkyl or aromatic group.
- **Secondary (2°) amines:** In secondary amines nitrogen atom has one hydrogen atoms and two organic substituents (alkyl, aryl or both).
- **Tertiary (3°) amines:** In tertiary amines, nitrogen has three organic substituents (alkyl, aryl or both) without any hydrogen atom.

Classify the following as Primary (1°) amines, Secondary (2°) amines and Tertiary (3°) amines.



9.2.1 Functional Group Test

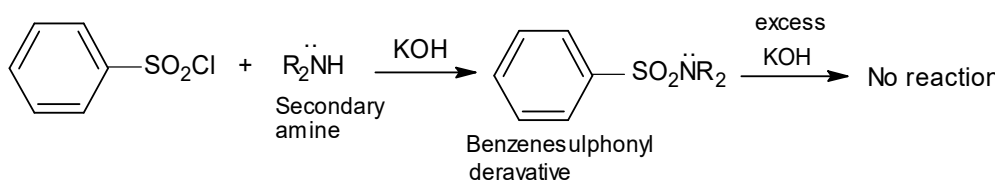
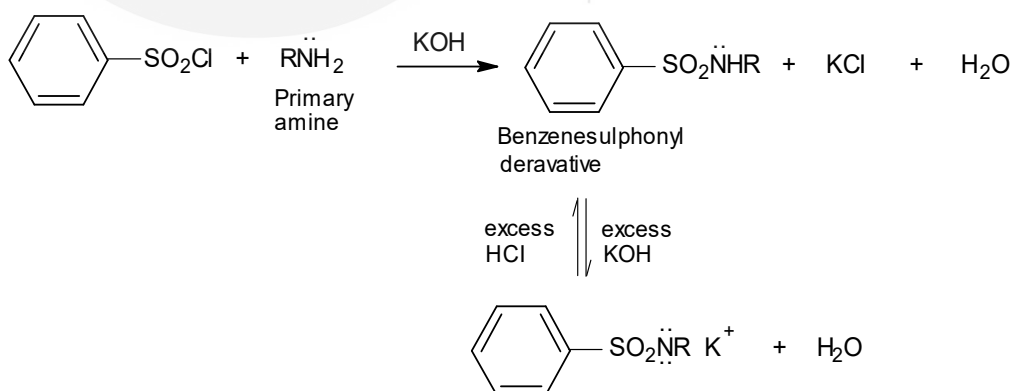
In this section we shall study about the test used for the characterisation of amines. The amines can be mainly identified by (i) Hinsberg Test (ii) Nitrous Acid Test (iii) Diazotisation and Coupling and (iv) Carbylamine test (Positive for primary amines).

i) Hinsberg Test

Primary, secondary and tertiary amines can be identified by Hinsberg test. These three amines can be distinguished by this test. The reaction between primary or secondary amines and benzenesulfonyl chloride gives the corresponding substituted benzenesulfonamide. The reaction is carried out in excess base. Sulfonamides, of primary and secondary amines, are distinguishable because sulphonamides from primary amine have acidic amino hydrogen, which make the product soluble in alkali. On the other hand, the benenesulfonamide secondary amines bear no acidic aminmo hydrogen and they are insoluble in both acid and base. Tertiary amines lack the necessary acidic hydrogen for formation of benzenesulfonyl derivatives.

Thus, with few exceptions, primary amines react with benzenesulfonyl chloride to provide homogeneous reaction mixtures and secondary amines react to yield heterogeneous reaction mixtures.

Do you allow benzenesulphonyl chloride to come in contact with skin. Use caution in handling amines. Many of these are toxic.



Procedure

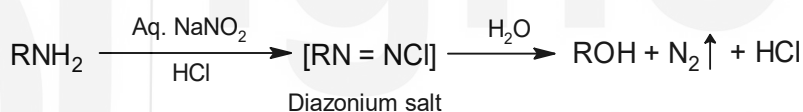
In a test tube take 3-4 drops (or 0.1 g) of the unknown compound, 0.2 g of benzenesulfonyl chloride 1 cm³ of methanol and 5 cm³ of 10% sodium hydroxide. Heat the mixture for few minutes. Just below its boiling point, till order of benzenesulfonyl chloride is gone. Then cool the reaction mixture in ice. On cooling, if no precipitate appears than the substance is probably a tertiary amine. If precipitate appears, the amine is either primary or secondary.

If a precipitate is present, filter it, wash it with 2 cm³ of water and transfer it to a test tube. Add 2 cm³ of 5% sodium hydroxide solution and warm the reaction mixture to 50° C and shake it well. If the precipitate dissolves, the amine is primary. If the precipitate does not dissolve it indicates a secondary amine.

ii) Nitrous Acid Test

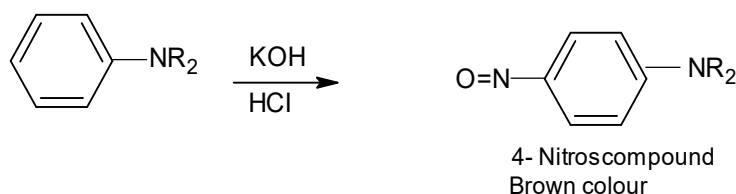
The nitrous test is useful to differentiate between primary aliphatic, primary aromatic, secondary and tertiary amines.

Primary amines react with nitrous acid to yield diazonium ion. The aliphatic amines yield unstable diazonium ion which decomposes to give nitrogen gas and alcohol. On the other hand aromatic amines give stable diazonium salt (stable in solution at 0° C).

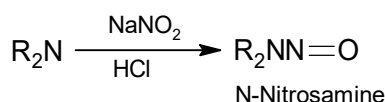
**Procedure**

Take 0.5 g of the compound in a test tube and dissolve it in 2 cm³ 2 M hydrochloride acid (Note: few weakly basic amines require conc. Hydrochloric acid). Cool it to 5°C in ice and add 4 or 5 drops of 5% aqueous sodium nitrite. Note which of the following is observed:

- i) There is effervescence (nitrogen gas is evolved) and clear solution is obtained. This shows the presence of primary aliphatic amine or amide (RCONH₂).
- ii) No effervescence and formation of a clear solution indicates the presence of primary aromatic amine or tertiary amine.
- iii) Formation of dark brown solution indicates the presence of tertiary aromatic amine.



- iv) No effervescence but the formation of cloudy solution or emulsion (generally yellow) indicates the presence of secondary amine.



iii) Diazotisation and Coupling

The **diazo** group is an organic moiety consisting of two nitrogen atoms (azo) at the terminal position. The general structural formula is $\text{R}_2\text{C}=\text{N}^+=\text{N}^-$. They are called diazo compounds or diazoalkanes. The process of conversion of primary aromatic amines into its diazonium salt is called diazotization or diazotation. Diazonium salts are important synthetic intermediates that can undergo coupling reactions to form azo dyes. Reaction between primary aromatic amine and nitrous acid give a diazo compound. This reaction is known as diazotization. It was first given by Peter Griess. Diazonium salt is used at very low temperature because of the fact that at the higher temperature they are unstable. Secondary and tertiary amines do give this test. Secondary amine has only have one hydrogen atom on the nitrogen and hence they cannot complete the diazotization reaction and gives yellow oily nitrosamine products. Tertiary amines do not have any hydrogen atom on nitrogen; simply undergo an acid–base reaction with nitrous acid giving soluble salts. Many diazonium salts are highly explosive and decompose violently on heating. One must be very careful while using them.

Destroy the isocyanide by adding excess of hydrochloric acid and throw it outside.

Anilides ($\text{C}_6\text{H}_5\text{NHCOR}$) also give positive carbylamines test.

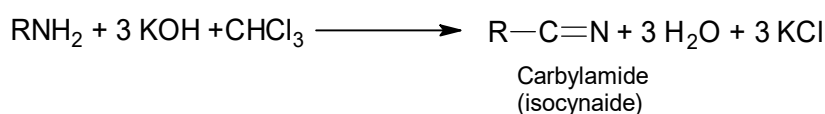
Procedure

If nitrous acid test gives a clear solution, then to this solution add 5% 2-naphthol dissolved in sodium hydroxide (2M) and note which of the following is observed:

- Formation of bright red to dark brown precipitate indicates the presence of primary aromatic amine.
- If no colour appears (ignore white to yellow precipitate) and test (ii) (a) is positive then perform carbylamines test for primary amines.

iv) Carbylamine test: Positive for primary amines

The carbylamine reaction is used for the identification of primary amines. This is also known as Saytzeff's isocyanide test. In this reaction, the analyte is heated with alcoholic potassium hydroxide and chloroform. Formation of isocyanide (carbylamine) indicates the presence of a primary amine, the presence of an amine being indicated by the characteristic foul smell of an isocyanide. Secondary and tertiary amines do not give carbylamine test, since they have more than one alkyl group which hinders the approach of $-\text{NH}_2$ group. The carbylamines reaction, also known as Hoffman's isocyanide test



Procedure

Place a small quantity of organic compound, alcoholic KOH (caustic potash) solution (1 cm³) and chloroform (few drops) in a test tube. Shake the contents

of tube and heat gently. A bad smell of isocyanide indicates the presence of a primary amine.

SAQ 2

Fill in the following blanks.

- The reaction between primary and benzenesulfonyl chloride gives
- Nitrous Acid test is useful to differentiate between, ... and amines.
- Primary amine on reaction with alcoholic caustic potash in presence of chloroform gives
- Cabylamine test gives positive for amines

9.2.2 Characteristic Derivatives

The most common derivatives of primary and secondary amines are benzoate and toluene -4- sulphonate. Acetyl derivative is also quite common. However, tertiary amines do not undergo same reactions. Solid derivatives suitable for characterisation of tertiary amines are the picrate and methiodes.

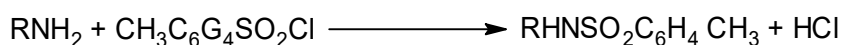
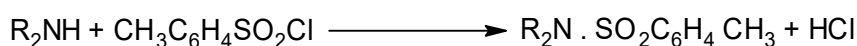
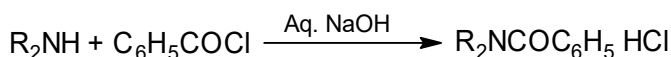
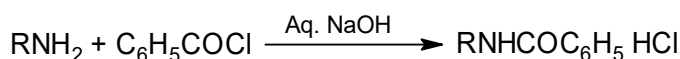
Experimental procedures for the preparation of these derivatives are given below:

Procedure

i) Benzoate and Toluene-4 sulphonate (Scotten-Baumann Method)

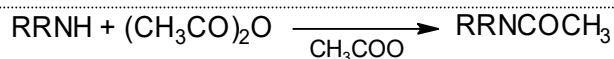
Place the compound (0.5 g), 2 M sodium hydroxide (10 cm³) and benzoylchloride (1 cm³) in a boiling tube. If the mixture is not homogenous, add sufficient amount acetone. Shake the contents vigorously until a solid is obtained. Sometimes few drops of water is added in order to get the precipitate. Filter off the precipitate, wash with cold water and recrystallise from alcohol.

If you want to prepare toluene -4- sulphonate, use toluene -4- sulphonyl in place of benzoylchloride.



ii) Acetyl Derivative

Primary and secondary amines are best acetylated with acetic anhydride.



R = alkyl, aryl or H

Procedure

Place amine (0.5 g), acetic acid (1 cm³) and acetic anhydride (1 cm³) in a conical flask. Heat the reaction mixture for about 20 minutes, cool and pour the contents into ice-water. Filter the solid and crystallise from water or aqueous ethanol.

Some *ortho* substituted derivatives of aromatic amines are difficult to derivatise because of steric hindrance. Such derivatives can be prepared by adding a few drops of concentrated sulphuric acid, which acts as a catalyst, and by use of an excess of acetic anhydride.

iii) Picrates

Procedure

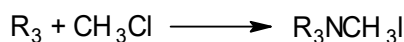
Dissolve the amine (0.5 g) in ethanol (10 cm³) and add saturated ethanolic solution of picric acid (5 cm³). Heat the reaction mixture on water bath for 3 minutes and allow it to cool. Filter the solid product and recrystallize from ethanol.



iv) Methiodides

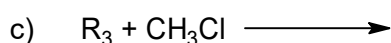
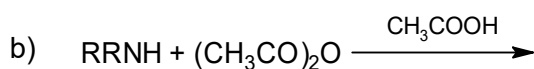
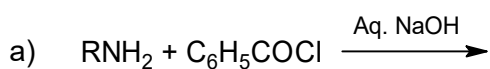
Procedure

Gently Warm a mixture of the amine (0.5 g) with methyl iodide (0.5 g cm³) on a water bath for several minutes. Then cool it in an ice and recrystallise the product from ethanol or methanol or ethyl acetate.



SAQ3

Complete the following reactions;



SAQ 4

Tick the correct answer from the following choices given below:

a) Carbylamine test is responded by:

- i) $\text{CH}_3\text{CH}_2\text{NH}_2$
- ii) $\text{CH}_3\text{NHC}_2\text{H}_5$
- iii) $(\text{CH}_3)_3\text{N}$
- iv) $(\text{C}_6\text{H}_5)_2\text{NH}$

b) Nitrosoamines are formed by

- i) Primary amine
- ii) secondary amine
- iii) tertiary amine
- iv) none of above

9.2.3 Requirements

S. No.	Apparatus	Qty.	S. No.	Chemicals
1	Beakers	1	1	HCl
2	Boiling tube	1	2	KOH
3	Burner	1	3	NaOH
4	Conical flask	1	4	Acetic acid
5	Droppers	1	5	Acetic anhydride
6	M.P. Apparatus	1	6	Aqueous sodium nitrite
7	Reflux condenser	1	7	Benzenesulfonyl chloride
8	Round bottom flask	1	8	Benzoylchloride
9	Test tubes	3	9	Chloroform
10	Thermometers	1	10	Ethanol
11	Water bath	1	11	Ethyl acetate
			12	ice
			13	Methanol
			14	Methyliodide
			15	2-Napthol
			16	Picric acid
			17	Toluene -4- sulphonyl
			18	Samples of amines

9.2.4 Procedure

1. Collect sample(s) of amine from your counsellor and carry out physical examination and also elemental test of the sample as discussed in BCHCL 134 course.
2. Carry out solubility test as discussed in Sec. 8.3.1. If your compound is soluble in water, check the pH of solution using pH paper.
3. Carry out functional group test (class determination test) as discussed in Sec. 9.2.1.
4. Prepare at least one derivative using procedure discussed in 9.2.2
5. Dry the prepared derivative and take the m.p. of both derivative and sample if it is solid. Predict the actual compound by comparison of melting point of sample and its derivative with literature values. Use appendix A for this purpose.

9.2.5 Observations and Result**1. Physical Examination**

- a) Physical state :
- b) Colour :
- c) Odour :
- d) Ignition test :

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

2. Elemental Analysis: Nitrogen test:**3. Solubility test**

H ₂ O	5% NaOH	5% NaHCO ₃	5% HCl	Conc. H ₂ SO ₄	Expected Class

4. Test with pH paper:**5. Melting point/Boiling point observed:****6. Class determination:**

- (i) Hinsberg Test
- (ii) Nitrous Acid Test
- (iii) Diazotisation and Coupling and
- (iv) Cabylamine test

7. Preparation of derivatives

- a) Derivative chosen
M.P. observed
M.P. reported in literature

b) Derivative chosen

M.P. observed

M.P. reported in literature

8. Examination of literature

Possible compound.....M.P.....Derivatives

9. The unknown compound is

10. The structure of this compound is

9.3 EXPERIMENT 9b: IDENTIFICATION OF NITRO COMPOUNDS AND PREPARATION OF THEIR DERIVATIVES

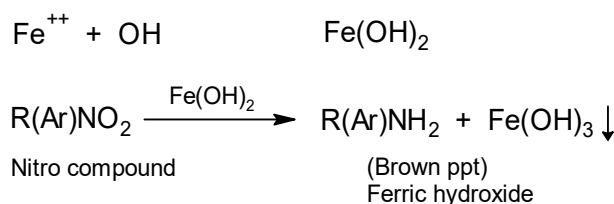
Organic compounds having $-\text{NO}_2$ as a functional group are known as nitro compounds. They may be aliphatic ($\text{R}-\text{NO}_2$) or aromatic ($\text{Ar}-\text{NO}_2$) compounds. Both aliphatic and aromatic compounds are oxidising agents.

9.3.1 Functional Group Test

The most common functional group tests for nitro compound are

- i) Ferrous hydroxide test and
 - ii) Reduction to amines and Dye Test
- i) **Ferrous Hydroxide Test**

Organic compounds that are oxidizing agents will oxidize ferrous hydroxide (blue) to ferric hydroxide (brown). The most common oxidizing agents are **nitro compounds**. Practically this test is given by all nitro-compounds in about one minute. During the reaction Fe (II) is oxidised to Fe (III) in the presence of nitro compounds. The reaction involved is:



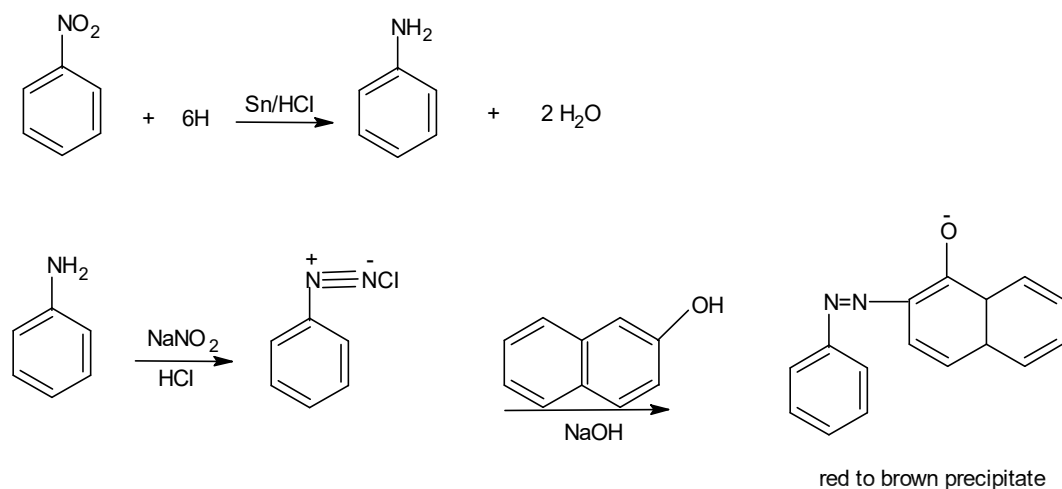
Procedure

A slight darkening or greenish colouration of the blue precipitate should not be considered a positive test.

To a freshly prepared solution of 2 cm³ of 5% aqueous ferrous ammonium sulphate, add 2 drops of sulphuric acid (1 M), 1 cm³ of ethanolic sodium potassium hydroxide (2 M) and unknown compound (2 drops of liquid or 0.5 g of solid). Warm the solution with continuous shaking on a water bath for few minutes. The positive test is indicated by blue precipitate turning rust brown within a minute. Prepare a similar mixture without unknown compound (Blank test). There will be no change in initially, formed blue precipitate in the blank test.

ii) Reduction to Amines and Dye Test

Nitro compounds can identify by reduction of nitro group. The reaction involved is:

**Procedure**

Take about 0.5 g of the unknown compound and 3 cm^3 of 7 M hydrochloride acid in a boiling tube. Add 1 g of stannous chloride to it and warm with continuous shaking for 15 minutes. Filter the mixture, cool it in ice (5°C) and add 5% aqueous sodium nitrite (5-6 drops). To this add 2 cm^3 of 5% solution of 2-naphthol in 2 M sodium hydroxide and note which of the following happens:

- A red to brown precipitate forms which indicates the presence of aromatic nitro compounds.
- No coloured precipitate formation which indicates the presence of aliphatic nitro compounds. (Ignore white to yellow precipitate).

9.3.2 Characteristic Derivatives

Preparation of derivatives of nitro compounds depends on the type of nitro compounds detected. Nitro compounds are reduced to amines and derivatized as primary amines. This method can be utilized for both aliphatic and aromatic nitro compounds.

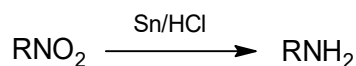
Reduction of Nitro compounds to Primary Amines

Preparation of derivatives of nitro compounds depends on the type of nitro compounds. Nitro compounds are reduced to amines and derivatised as primary amines. This method can be utilised for both aliphatic and aromatic nitro compounds. Nitro compounds can be converted to primary amines by the following method.

Procedure

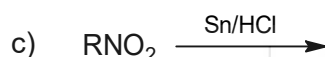
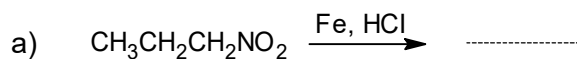
Place the nitro compound (1 g) and concentrated hydrochloric acid (10 cm^3) into a small round bottom flask and add ethanol (2 cm^3) and tin (3 g). Cool the reaction mixture until initial reaction subsides and then heat under reflux for 25 minutes. Decant the supernatant liquid, cool it and basify with 40% sodium hydroxide with stirring and cooling in ice (use excess of 40%

Sodium hydroxide to dissolve tin (II) hydroxide formed). Extract the alkaline mixture with diethyl ether and, dry on anhydrous sodium sulphate, filter and then evaporate ether. Crystallize the solid from aqueous ethanol.



SAQ 5

Fill up the blanks:



9.3.3 Requirements

S. No.	Apparatus	Qty.	S. No.	Chemicals
1.	Test tubes	3	1.	NaOH
2.	Droppers	1	1.	H ₂ SO ₄
3.	Water bath	1	2.	HCl
4.	Thermometers	1	3.	Sodium nitrite
5.	Beakers	2	4.	Ethanol
6.	M.P. Apparatus	1	5.	Diethyl ether
7.	Round bottom flask	1	6.	Phenolphthalein
8.	Reflux condenser	1	7.	Ferrous ammonium sulphate
9.	Conical flask		8.	Sodium potassium hydroxide
10.	Burner	1	9.	Stannous chloride
11.	Boiling tube	1	10.	Tin
12.	Erlenmeyer flask.		11.	Samples of nitro compound

9.3.4 Procedure

1. Collect sample(s) of nitro compound from your counsellor and carry out physical examination and also elemental test of the sample as discussed in BCHCL 134 course.

2. Carry out solubility test as discussed in Sec. 8.3.1. If your compound is soluble in water, check the pH of solution using pH paper.
3. Carry out functional group test (class determination test) as discussed in Sec. 9.3.1.
4. Prepare at least one derivative using procedure discussed in 9.3.2
5. Dry the prepared derivative and take the m.p. of both derivative and sample if it is solid. Predict the actual compound by comparison of melting point of sample and its derivative with literature values. Use appendix A for this purpose.

9.3.5 Observations and Result

1. Physical Examination

- a) Physical state :
- b) Colour :
- c) Odour :
- d) Ignition test :

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

2. Elemental Analysis: Nitrogen test:

3. Solubility test

H ₂ O	5% NaOH	5% NaHCO ₃	5% HCl	Conc. H ₂ SO ₄	Expected Class

4. Test with pH paper:

5. Melting point/Boiling point observed:

6. Class determination:

- (i) Ferrous hydroxide test and
- (ii) Reduction to amines and Dye Test.

6. Preparation of derivatives

- a) Derivative chosen
M.P. observed
M.P. reported in literature
- b) Derivative chosen
M.P. observed
M.P. reported in literature

7. Examination of literature

Possible compound.....M.P.....Derivatives

8. The unknown compound is

9. The structure of this compound is

9.4 EXPERIMENT 9c: IDENTIFICATION OF AMIDES AND PREPARATION OF THEIR DERIVATIVES

Amides are represented by the general formula RCONH_2 . The qualitative test generally used for amides are ammonia evolution test and hydroxamic acid test.

9.4.1 Functional Group Test

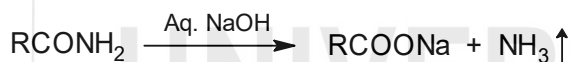
There are two main functional group tests for identification of amides.

- i) Ammonia Evolution Test and
- ii) Hydroxamic Acid Test.

i) Ammonia Evolution Test

Amides are hydrolysed with aqueous sodium hydroxide to carboxylic acid salt and ammonia. The evolution of ammonia is indicative of amide.

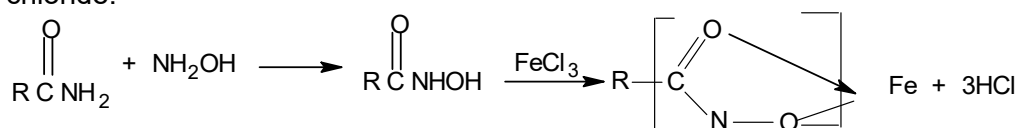
This test fails if hydrogen at the nitrogen atom is replaced by an alkyl or aryl group, then amines are produced.

**Procedure**

Heat about 0.2 g of the compound with 2 cm³ of 2 M aqueous sodium hydroxide. Evolution of ammonia indicates the presence of an amide group. Detect the evolution of ammonia by its smell and/or by its action on moist red litmus paper (red → blue).

ii) Hydroxamic Acid Test

Amides, give a coloured solution on treatment with hydroxylamine and ferric chloride.

**Procedure**

Take 2-3 drop or 0.02 g of sample compound in a boiling tube and add 0.2 g of solid hydroxylamine hydrochloride and 5 cm³ 10% NaOH solution. Heat the mixture on a boiling water bath. Cool and acidify the reaction mixture with dilute hydrochloric acid and add 2-3 drops of 5% aqueous ferric chloride.

Purple or deep red colour due to formation of ferric complex of hydroxamic acid indicates the presence of amide.

9.4.2 Characteristic Derivatives

Primary amide (RCONH_2) on hydrolysis furnishes carboxylic acid. Carboxylic acid is identified to characterize the amide.



i) Hydrolysis of Amide-Isolation of Acid

Place the unknown compound (0.5 g) and 2 M aqueous sodium hydroxide (10 cm^3) into a conical flask and heat the reaction mixture on water bath for about 30 minutes. The reaction mixture is cooled and acidified with dilute sulphuric acid. The precipitated acid is filtered, washed with water and recrystallize from water or ethanol. If on acidification no precipitate is formed, use it for the preparation of acid derivatives.

ii) Picrate Derivatives

Some amides form picrates. Prepare picrate derivatives as described under 9.3.2 (iii).

SAQ 6

Fill in the blanks:

- Benzamide upon hydrolysis with alkali followed by acidification furnished and
- Ethanoic acid on reaction with ammonia afforded

9.4.3 Requirements

S. No.	Apparatus	Qty.	S. No.	Chemicals
1.	Test tubes	3	1.	Ethanol
2.	Droppers	1	2.	Sulphuric acid
3.	Water bath	1	3.	Sodium hydroxide
4.	Thermometers	1	4.	Potassium hydroxide
5.	Beakers	2	5.	Ferric chloride
6.	M.P. Apparatus	1	6.	Hydroxylamine hydrochloride
7.	Round bottom flask	1	7.	Hydrochloric acid
8.	Reflux condenser	1	8.	

9.	Conical flask	9.
10.	Burner	10.
11.	Boiling tube	11.
12.	Erlenmeyer flask.	12.

9.4.4 Procedure

1. Collect sample(s) of nitro compound from your counsellor and carry out physical examination and also elemental test of the sample as discussed in BCHCL 134 course.
2. Carry out solubility test as discussed in Sec. 8.3.1. If your compound is soluble in water, check the pH of solution using pH paper.
3. Carry out functional group test (class determination test) as discussed in Sec. 9.3.1.
4. Prepare at least one derivative using procedure discussed in 9.3.2
5. Dry the prepared derivative and take the m.p. of both derivative and sample if it is solid. Predict the actual compound by comparison of melting point of sample and its derivative with literature values. Use appendix A for this purpose.

9.3.5 Observations and Result

1. Physical Examination

- a) Physical state :
- b) Colour :
- c) Odour :
- d) Ignition test :

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

2. Elemental Analysis: Nitrogen test:

3. Solubility test

H ₂ O	5% NaOH	5% NaHCO ₃	5% HCl	Conc. H ₂ SO ₄	Expected Class

4. Test with pH paper:

5. Melting point/Boiling point observed:

6. Class determination:

- i) Ammonia Evolution Test
- ii) Hydroxamic Acid Test

7. Preparation of derivatives

- a) Derivative chosen
M.P. observed
M.P. reported in literature
- b) Derivative chosen
M.P. observed
M.P. reported in literature

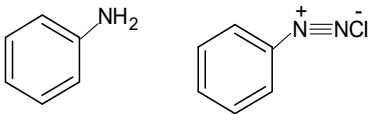
8. Examination of literature

Possible compound.....M.P.....Derivatives

9. The unknown compound is

10. The structure of this compound is

9.4 ANSWERS**Self Assessment Questions**

1. a) primary amine, b) tertiary amine, c) secondary amine
2. a) benzenesulfonamide, b) primary, secondary, tertiary
c) isocyanide d) primary
3. a) $\text{RNHCOC}_6\text{H}_5 + \text{HCl}$
b) RRNCOCH_3
c) $\text{R}_3\text{NCH}_3\text{I}$
4. a) i b) ii
5. a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
b) 
c) RNH_2
6. a) benzoic acid; ammonia
b) ethanamide

IDENTIFICATION OF UNKNOWN ORGANIC SAMPLES

Structure

10.1	Introduction	10.4	Reporting Results for Qualitative Analysis of Unknown Organic Compounds
	Expected Learning Outcomes		
10.2	Requirements		
10.3	Procedure	10.5	APPENDIX

10.1 INTRODUCTION

After having good practice with the known functional group compound collect few samples (at least six samples) for the identification of unknown compounds from the category of functional group discussed in this course.

Expected Learning Outcomes

After performing the given experiments you should be able to:

- ❖ describe functional group tests and methods of the preparation of derivatives of a unknown sample;
- ❖ identify the unknown organic compounds

10.2 REQUIREMENTS

1. The requirements for unknown organic samples will be remain same as for earlier experiments which you have conducted for known organic sample.
2. Six unknown organic samples

10.3 PROCEDURE

Follow the steps given below:

1. Physical examination

- a) Physical State
- b) Colour
- c) Odour
- d) Ignition test

2. Physical constants

Melting point/Boiling point

3. Element detection

(N,S, halogen)

4. Solubility test

5. Functional Group test

6. Preparation of derivatives

Prepare suitable derivatives of the proposed compound and compare the melting point with the literature report.

7. Examination of literature

Compare the information obtained so far (1-6) with the literature report.

8. Write correct name and structure of the compound

Various experimental steps may be recorded in systematic way for the identification of compound. This may be illustrated by taking the example of 2-Naphthol.

10.4 REPORTING RESULTS FOR QUALITATIVE ANALYSIS OF UNKNOWN ORGANIC COMPOUNDS

Here we will discuss some important points one should keep in mind while reporting results in a laboratory note book for qualitative analysis of organic compounds.

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.....Faint phenol-like odor
- d) Ignition test luminous, sooty flame, no residue

Comments: This suggest that the compound 'A' aromatic compound.

2. Physical Constants

Melting point observed 122-124°C

3. Elemental Analysis

N,S,Cl,Br, I.....None

4. i) Solubility test

H ₂ O	Aq. NaOH	Aq. NaHCO ₃	HCl	Conc. H ₂ SO ₄	Expected class
	Soluble phenols	Slightly soluble	-	-	Aromatic
	No bubbles				

5. Reaction to pH paper not visible colour change

6. Functional Group Test

- i) With alcoholic FeCl₃.....Green solution.

Comment: The above tests indicated the presence of phenolic compound

7. Preparation of Derivatives

- a) Derivatives chosen 3,5-Benzoate

M.P. Observed 208-210°C

M.P. reported 210°C

- b) Derivative chosen 1-Naphthylurethane

M.P. observed 156-158°C

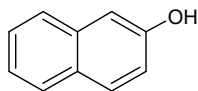
M.P. in literature 157°C

8. Examination of literature

M.P. of Derivatives			
Possible compound	M.P	3,5-benzoate	1-Naphthylurethane
2-Naphthol		M.P.	M.P.
	123°C	210°C	157°C

Comment: The above data correspond to 2-naphthol

9. Result: The unknown compound is 2-naphthol. The structure of this compound is



10.5 APPENDIX: Tables for B.P./M.P. of Organic Compounds and their Derivatives

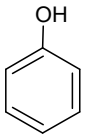
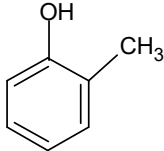
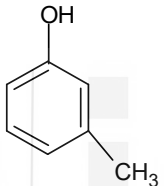
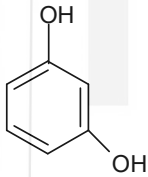
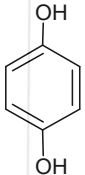
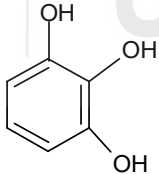
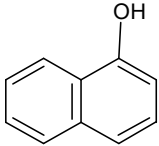
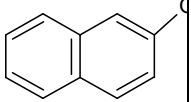
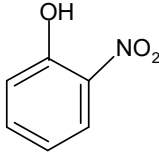
Aldehyde and their derivatives

Compound	Formula	B.P./ M.P.* (°C)	B.P./ M.P. of Derivatives (°C)		
			2,4-Dinitrophenyl hydrazone	Semicabazone	Oxime
Formaldehyde	HCHO	-21	166	169 with decomposition	
Acetaldehyde	CH ₃ CHO	20	168	169	47
Propionaldehyde	CH ₃ CH ₂ CHO	49	150	89	40
Benzaldehyde		179*	236	222	35
Salicylaldehyde		196*	252 Decomposed	231	63

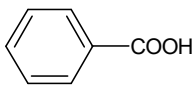
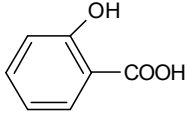
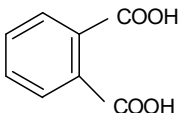
Ketones and their Derivatives

Compound	Formula	B.P./ M.P.* (°C)	M.P. of Derivatives (°C)		
			2,4-Dinitrophenyl hydrazone	Semicarbazone	Oxime
Acetone	CH ₃ COCH ₃	56	128	190	59
Ethylmethyl ketone	CH ₃ COC ₂ H ₅	80	115	145	
Acetophenone		202	240	199	60
Benzophenone		48*	239	165	143

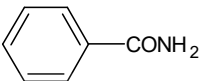
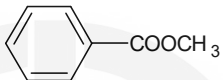
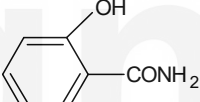
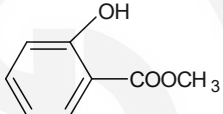
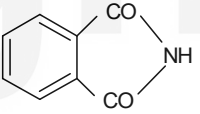
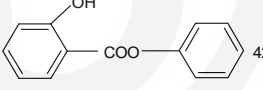
Phenols and their Derivatives

Compound	Formula	B.P./ M.P.* (°C)	M.P. of Derivatives (°C)	
			3,5- Dinitrobenzoate	1-Naphthyl urethane
Phenol		182	146	133
<i>o</i> -Cresol		191	138	142
<i>m</i> -Cresol		202	165	128
<i>p</i> -Cresol		201	189	146
Resorcinol		118*	201 [206]	206
Hydroquinon or Quinol		171*	317	247
Pyrogallol		132*	205	
1-Naphthol		95*	217	152
2-Naphthol		123*	210	157
<i>o</i> -Nitrophenol		45*	155	113

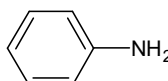
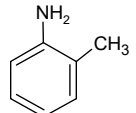
Carboxylic Acids and Their Derivatives

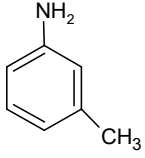
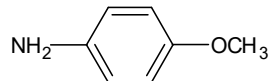
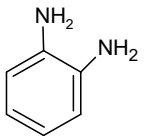
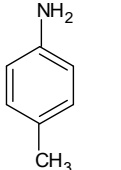
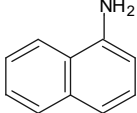
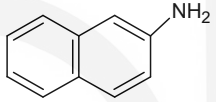
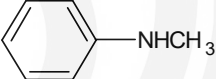
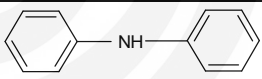
Compound	Formula	B.P./ M.P.* (°C)	M.P. of Derivatives (°C)		
			Amide	Anilide	<i>p</i> -toluidide
Formic acid	HCOOH	101	---	50	53
Acetic acid	CH ₃ COOH	118	82	114	147
Propenoic acid	CH ₃ CH ₂ COOH	140	85	105	141
Undecanoic acid	CH ₃ (CH ₂) ₉ COOH	26*	123	99	125
Oxalic acid (Dihydrate)	$\begin{array}{c} \text{COOH} \\ \\ \text{COOH} \end{array} \cdot 2\text{H}_2\text{O}$	101*	419d	254	268
Citric acid (Hydrated)	$\begin{array}{c} \text{CH}_2\text{COOH} \\ \\ \text{C}(\text{OH})\text{COOH} \\ \\ \text{CH}_2\text{COOH} \end{array}$	100*	210	192	189
Tartaric acid	$\begin{array}{c} \\ \text{CH}(\text{OH})\text{COOH} \\ \\ \text{CH}(\text{OH})\text{COOH} \end{array}$	169*	196d	246d	--
Succinic acid	$\begin{array}{c} \text{CH}_2\text{COOH} \\ \\ \text{CH}_2\text{COOH} \end{array}$	189*	260	230	255
Benzoic acid		121*	130	160	158
Salicylic acid		158*	139	135	
Phthalic acid		210*	200	253	201

Ester and Amides

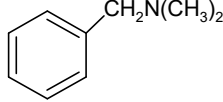
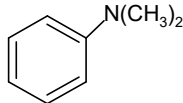
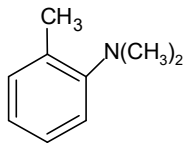
Compound	Formula	B.P./ M.P.* (°C)	Amide	Formula	M.P.
Methyl acetate	CH_3COOH_3	57	Acetamide Urea	CH_3CONH_2 NH_2CONH_2	82
Ethyl acetate	$\text{CH}_3\text{COOC}_2\text{H}_5$	77	N-Methylurea	$\text{CH}_3\text{NHCONH}_2$	132
Diethyl Oxalate	$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \\ \text{COOC}_2\text{H}_5 \end{array}$		N,N-Dimethyl urea	$\text{CH}_3\text{NHCONHCH}_3$	102
Methyl Oxalate	$\begin{array}{c} \text{COOCH}_3 \\ \\ \text{COOCH}_3 \end{array}$	186	Benzamide		182
Methyl benzoate		54*	Salicylamide		129
Methyl salicylate		199	Phthalimide		139
Phenyl salicylate		224			235

Primary and Secondary Amines and Their Derivatives

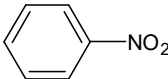
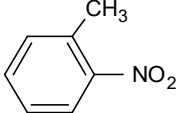
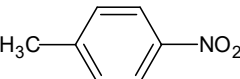
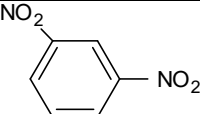
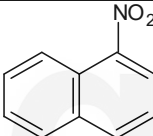
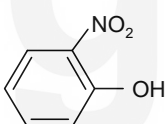
Compound	Formula	B.P./ M.P.* (°C)	M.P. of Derivatives (°C)			
			Benzoate	Picrate	Toluen e-4- sulpho nate	Acet- amide
Primary Amines						
1-Aminopropane	CH ₃ CH ₂ CH ₂ NH ₂	49	84	135	52	
Aniline		181	163	...	103	114
o-Toluidine		200	144	213	110	112

<i>m</i> -Toluidine		203	125	200	114	66
<i>o</i> -Anisidine		225	60	200	127	88
<i>o</i> -Phenetidine		229	104	...	164	79
<i>p</i> -Toluidine		45*	158	181	118	154
1-Aminonaphthalene		50*	161	163	157	160
2-Aminonaphthalene		113*	162	195	133	134
Secondary Amines						
Diethylamine	(C ₂ H ₅)NH	56	42	155	60	...
N-Methylaniline		193	63	145	95	
Diphenylamine		54*	180	182	142	

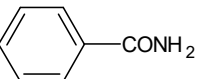
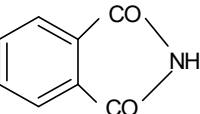
Tertiary Amines and Their Derivatives

Compound	Formula	B.P./ (°C)	B.P./ M.P. of Derivatives (°C)	
			Picrate	Methiodides
Trimethylamine	(CH ₃) ₃ N	33	216	230
Triethylamine	(C ₂ H ₅) ₃ N	89	173	...
N,N-Dimethylbenzylamine		184	93	179
N,N-Dimethylaniline		193	164	228
N,N-Dimethyl- <i>o</i> -toluidine		185	122	210

Nitro Compounds

Compound	Formula	B.P./M.P. (°C)
1-Nitropropane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	131
Nitrobenzene		211
o-Nitrotoluene		222
p-Nitrotoluene		54
m-Dinitrobenzene		90
Nitronaphthalene		61
o-Nitrophenol		45

Amides

Compound	Formula	B.P./M.P. (°C)
Acetamide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	82
Palmitamide	$\text{CH}_3(\text{CH}_2)_{14}\text{CONH}_2$	106
Benzamide		129
M-Methylurea	$\text{CH}_3\text{NHCONH}_2$	102
Urea	NH_2CONH_2	132
Phthalimide		238