PREFACE

With its grounding in the "guiding pillars of Access, Equity, Equality, Affordability and Accountability," the New Education Policy (NEP 2020) envisions flexible curricular structures and creative combinations for studies across disciplines. Accordingly, the UGC has revised the CBCS with a new Curriculum and Credit Framework for Undergraduate Programmes (CCFUP) to further empower the flexible choice based credit system with a multidisciplinary approach and multiple/ lateral entry-exit options. It is held that this entire exercise shall leverage the potential of higher education in three-fold ways – learner's personal enlightenment; her/his constructive public engagement; productive social contribution. Cumulatively therefore, all academic endeavours taken up under the NEP 2020 framework are aimed at synergising individual attainments towards the enhancement of our national goals.

In this epochal moment of a paradigmatic transformation in the higher education scenario, the role of an Open University is crucial, not just in terms of improving the Gross Enrolment Ratio (GER) but also in upholding the qualitative parameters. It is time to acknowledge that the implementation of the National Higher Education Qualifications Framework (NHEQF), National Credit Framework (NCrF) and its syncing with the National Skills Qualification Framework (NSQF) are best optimised in the arena of Open and Distance Learning that is truly seamless in its horizons. As one of the largest Open Universities in Eastern India that has been accredited with 'A' grade by NAAC in 2021, has ranked second among Open Universities in the NIRF in 2024, and attained the much required UGC 12B status, Netaji Subhas Open University is committed to both quantity and quality in its mission to spread higher education. It was therefore imperative upon us to embrace NEP 2020, bring in dynamic revisions to our Undergraduate syllabi, and formulate these Self Learning Materials anew. Our new offering is synchronised with the CCFUP in integrating domain specific knowledge with multidisciplinary fields, honing of skills that are relevant to each domain, enhancement of abilities, and of course deep-diving into Indian Knowledge Systems.

Self Learning Materials (SLM's) are the mainstay of Student Support Services (SSS) of an Open University. It is with a futuristic thought that we now offer our learners the choice of print or e-slm's. From our mandate of offering quality higher education in the mother tongue, and from the logistic viewpoint of balancing scholastic needs, we strive to bring out learning materials in Bengali and English. All our faculty members are constantly engaged in this academic exercise that combines subject specific academic research with educational pedagogy. We are privileged in that the expertise of academics across institutions on a national level also comes together to augment our own faculty strength in developing these learning materials. We look forward to proactive feedback from all stakeholders whose participatory zeal in the teaching-learning process based on these study materials will enable us to only get better. On the whole it has been a very challenging task, and I congratulate everyone in the preparation of these SLM's.

I wish the venture all success.

Professor Indrajit Lahiri
Authorised Vice-Chancellor
Netaji Subhas Open University
(NSOU)

Netaji Subhas Open University

Four Year Undergraduate Degree Programme
Under National Higher Education Qualifications Framework (NHEQF) &
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UG : Chemistry (HCH)

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Content

Basic Laboratory Knowledge

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Basic Laboratory Knowledge

LABORATORY SAFETY AND FIRST AID

Laboratory is a place for learning the experimental skills. You are strongly advised to be careful at all times. Without any apron and glasses students must not enter into the laboratory. It is recommended not to perform unauthorized experiments. This will ensure your safety as well as the safety of your fellow-students. Even a small accident involving minor injury must be reported to the counsellor. The following instructions should be observed during the laboratory work.

You must wear a laboratory coat or apron over your clothes while working in the chemistry laboratory. This will save you from injury and protect your clothes from damage.

ii) Handle the hot glass carefully; it cools very slowly and may be very hot without appearing so.

iii) Protect your eyes from any spurting of acid or a corrosive chemical. In case of such spurting into the eyes, immediately wash with lot of water and go to a doctor.

iv) You must not reach across lighted burners as it may result in an accident.

v) Wash your apparatus thoroughly with a washing powder.

vi) While heating substances, do not point the tube towards your neighbor or to yourself. A suddenly formed bubble may eject the contents violently and dangerously.

vii) When diluting sulphuric acid, pour the acid slowly and carefully into the water with constant stirring. Never add water to the acid as it may result in the liberation of a lot of heat.

viii) Read the label on the bottle carefully before using the required chemical. Never pour back the unused reagent into the bottle.

ix) Never touch or taste a chemical or solution as most of chemicals are either corrosive or poisonous.

x) Always bring your container to the reagent shelf and do not take the bottles to your desk. .

xi) Do not insert the pipette or dropper into the reagent bottles; this helps in avoiding any possible contamination.

xii) Graduated cylinders and bottles are not to be heated because these break very easily and their volume also changes.

xiii) At the end of the experiment, clean and dry the glass apparatus and wipe off the top of the working table. Ensure that the gas and water taps are closed before you leave the laboratory.

Laboratory First-Aid:

If a corrosive substance falls on your skin, immediately wash the spot with large quantities of water, followed by remedial action indicated below:

Acid spill : Treat with sodium bicarbonate or ammonium carbonate (2M) solution; then apply vaseline or a soothing cream.

Base spill : Treat with acetic acid (1 M) followed by vaseline or a soothing cream

Bromine : Treat with 2 M ammonia; keep the affected part dipped in dilute sodium bisulphite solution till bromine is washed off. Finally apply vaseline.

Phenol : Wash with ethanol and then take hospital treatment.

The most common accidents in the chemistry laboratory involve cuts, burns or fire. The first-aid to be given in each case is below:

Cuts : If you have a cut, wash the wound well with cold water immediately. If bleeding is severe, apply pressure directly on to the wound to stop the bleeding. Then an antiseptic cream can be applied to the wound; it should be followed by proper dressing of the wound.

Burns : Wash the burnt part with cold water for some time and then apply Burnol to it.

Fire : A small fire in a beaker, caused by the vapours of an inflammable liquid can be extinguished by covering it with a watch glass. If the clothes catch fire, one should lie on the flow and, fire can be put off by wrapping a thick blanket around the body

Module –I

Inorganic Chemistry

Unit 1 ❒ Method of preparation of standard solutions of titrants

1.0 Objectives

From this unit one can understand about the following regarding the method of preparation of standard solutions of titrants:

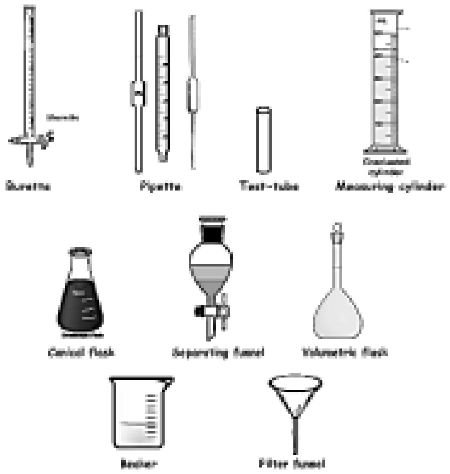
- Ensure the standard solutions are prepared accurately to a specified concentration, allowing precise titration results.
- Achieve consistent results by following precise measurement and preparation techniques for standard solutions.
- Implement safety protocols to handle chemicals and equipment properly during the preparation of standard solutions.
- Ensure compatibility of the standard solutions with the titration method and equipment being used.
- Maintain detailed records of the preparation process, including calculations, measurements, and any deviations from standard procedures.

- Validate the accuracy of the prepared standard solutions through calibration against primary standards or through inter-laboratory comparisons.
- Ensure proper storage conditions and determine the stability of standard solutions over time to maintain their reliability.
- Provide training and guidance to personnel involved in the preparation process to maintain consistency and adherence to procedures.

1.1 Introduction

Preparing standard solutions of titrants is essential in analytical chemistry to ensure precise and dependable titration outcomes. These solutions serve as exact reference materials with known concentrations of substances used in experiments. The preparation process involves meticulous procedures for accurately measuring and blending chemicals following standardized protocols and precise laboratory techniques. This careful preparation is crucial for achieving consistent and reliable analytical results in diverse fields such as pharmaceuticals and environmental monitoring.

A chemistry laboratory is a remarkable place where students witness the practical marvels of chemistry firsthand. It serves as a workshop for chemists and a learning environment where students grasp the fundamentals of applying chemistry. Here, students learn techniques for identifying, estimating, and preparing chemical substances. Due to the presence of various chemicals, it is vital for individuals in the laboratory to exercise caution to prevent harm from exposure, contact, or mishandling. Understanding equipment operation and adhering to safety precautions are crucial for safe laboratory practices. Typically, a chemistry laboratory houses a variety of glassware, examples of which are illustrated below.



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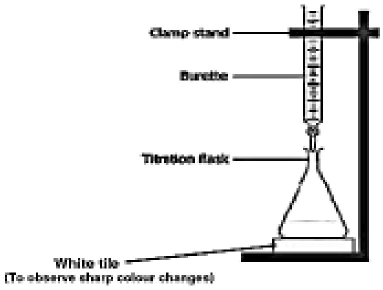
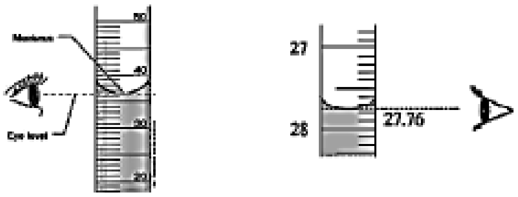
TITRATION ASSEMBLY



Correct method to note down the readings



Graduated Cylinder
The reading is 36.5 ml.

Burette
The reading is 27.8 ml

1.2 Preparation of Standard Solution

Solution whose strength is known is termed as standard solution. The substances are present in these solutions are classified into two classes i) Primary standard substances and ii) Secondary standard substances.

1.3. Primary Standard Solution

The substances are considered Primary standard should satisfy the following requirements–

a) The substance must be easily obtained in the highly pure state.

b) It is highly soluble in solvent (water).

c) It should neither hydroscopic nor be oxidised by air.

d) Its equivalent weight should be high so that weighing error is negligible.

e) It should not involve any chemical reaction with components (e.g. CO_2, H_2O, H_2S etc.) present in air during weighing.

Example: Oxalic acid ($H_2C_2O_4.2H_2O$); Anhydrous Na_2CO_3 ; Potassium bromate ($KBrO_3$) ; Zinc acetate [$Zn(CH_3COO)_2.2H_2O$] ; Potassium dichromate ($K_2Cr_2O_7$) ; Potassium iodate (KIO_3); etc.

1.4 Secondary Standard Solution

The strength of the solution can not be known by dissolving a definite weight of substance in a known volume of solution. Its strength can be determined by titrating against a primary standard solution. The strength of the solution is not constant it changes on day long standing.

Example: H_2SO_4; HCl; HNO_3; NaOH; KOH; $KMnO_4$; Sodium thiosulphate ($Na_2S_2O_3.5H_2O$); EDTA ; etc.

1.5 Strength of Solutions

The strength of a solution is defined by the amount of solute dissolved in a given amount of solvent. This is typically quantified using different concentration units:

Molarity (M): The number of moles of solute per liter of solution.

Molality (m): The number of moles of solute per kilogram of solvent.

Or99

Molarity (M): It is defined as the number of gram moles of the solute dissolved in one litre of the solution. [Gram mole = molecular weight when expressed in terms of gram]

Mass percent (% m/m): The mass of solute divided by the mass of the solution multiplied by 100.

Volume percent (% v/v): The volume of solute divided by the volume of the solution multiplied by 100.

Mole fraction (÷): The ratio of moles of solute to total moles of solute and solvent.

Normality (N): It is defined as the number of gram-equivalent weight of the solute dissolved in one litre of the solution.

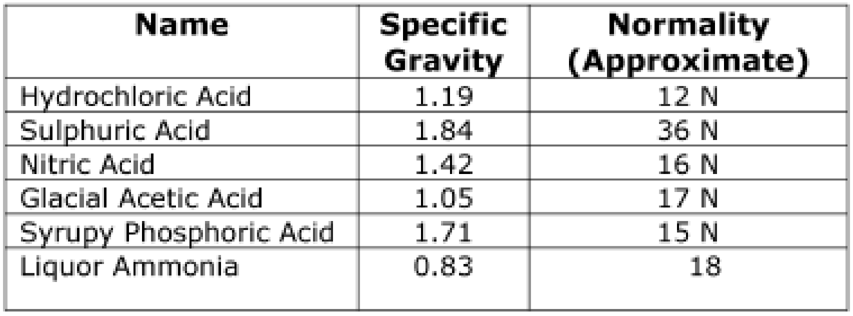
Equivalent weight of acid = Molecular weight / basicity

Equivalent weight of base = Molecular weight / acidity

Equivalent weight of salt = Molecular weight / No. of +charge(s)

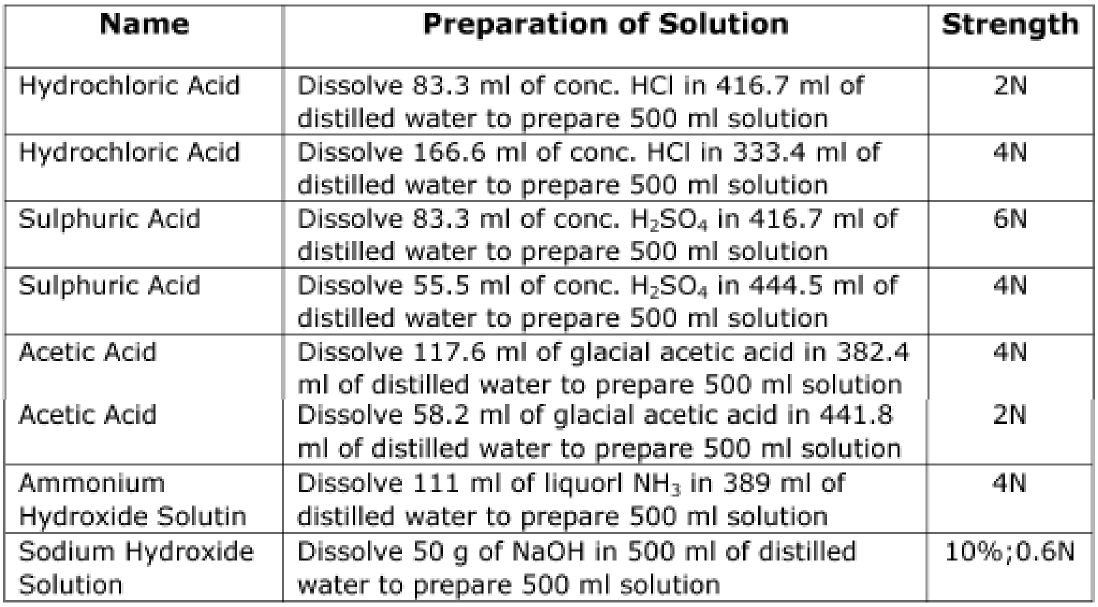
Equivalent weight of oxidant/reductant = Molecular weight / No. of electron transferred

1.6 Strength of Concentrated Acids and Bases



Name	Specific Gravity	Normality (Approximate)
Hydrochloric Acid	1.19	12 N
Sulphuric Acid	1.84	36 N
Nitric Acid	1.42	16 N
Glacial Acetic Acid	1.05	17 N
Syrupy Phosphoric Acid	1.71	15 N
Liquor Ammonia	0.83	18

1.7 Preparation of Dilute Acids and Bases Solutions

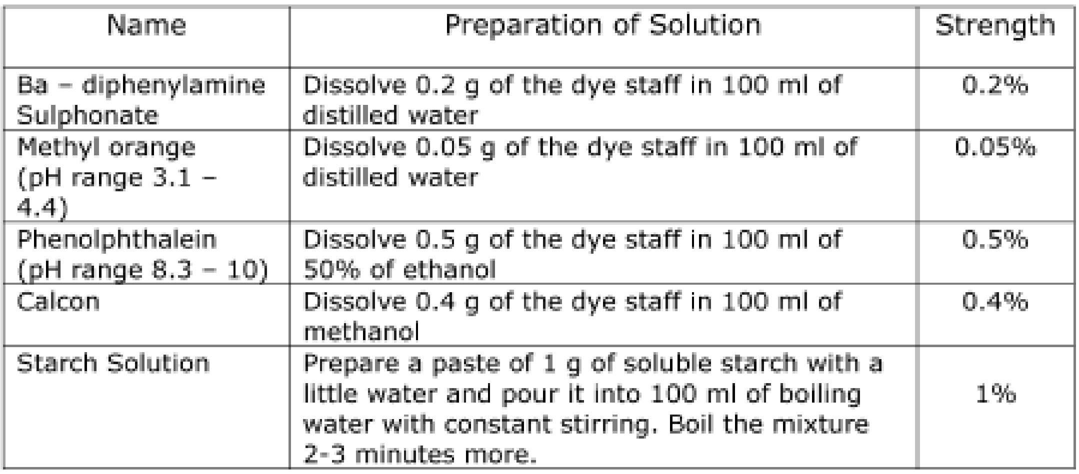


Name	Preparation of Solution	Strength
Hydrochloric Acid	Dissolve 83.3 ml of conc. HCl in 416.7 ml of distilled water to prepare 500 ml solution	2N
Hydrochloric Acid	Dissolve 166.6 ml of conc. HCl in 333.4 ml of distilled water to prepare 500 ml solution	4N
Sulphuric Acid	Dissolve 83.3 ml of conc. H_2SO_4 in 416.7 ml of distilled water to prepare 500 ml solution	6N
Sulphuric Acid	Dissolve 55.5 ml of conc. H_2SO_4 in 444.5 ml of distilled water to prepare 500 ml solution	4N
Acetic Acid	Dissolve 117.6 ml of glacial acetic acid in 382.4 ml of distilled water to prepare 500 ml solution	4N
Acetic Acid	Dissolve 58.2 ml of glacial acetic acid in 441.8 ml of distilled water to prepare 500 ml solution	2N
Ammonium Hydroxide Solutin	Dissolve 111 ml of liquorl NH_3 in 389 ml of distilled water to prepare 500 ml solution	4N
Sodium Hydroxide Solution	Dissolve 50 g of NaOH in 500 ml of distilled water to prepare 500 ml solution	10%;0.6N

1.8 Preparation of Aqua Regia

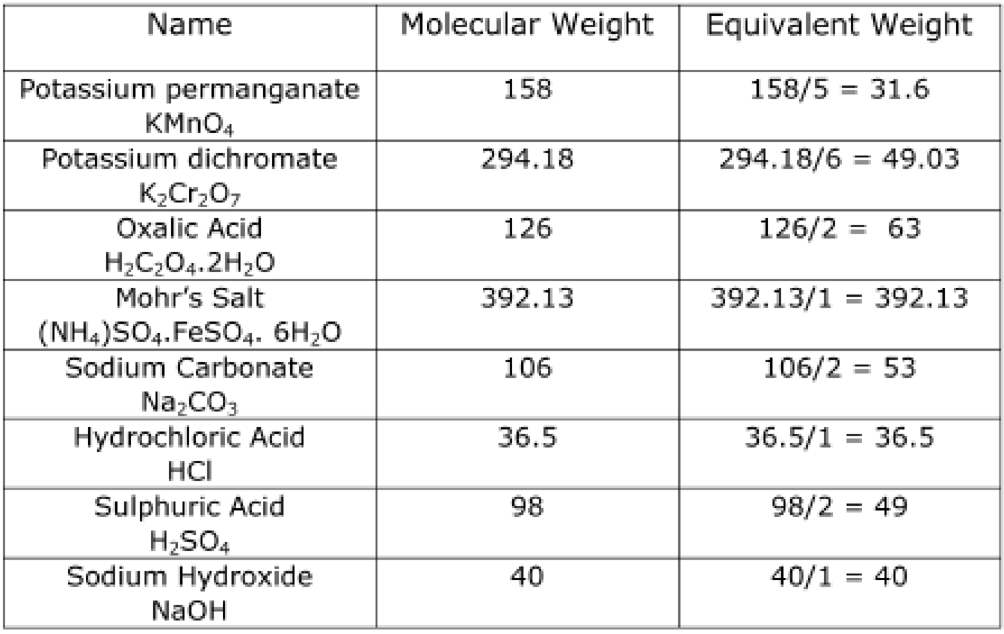
Prepared by mixing 1 volume of conc. HNO_3 and with 3 volume of conc. HCl.

1.9 Preparation of Some Common Indicators



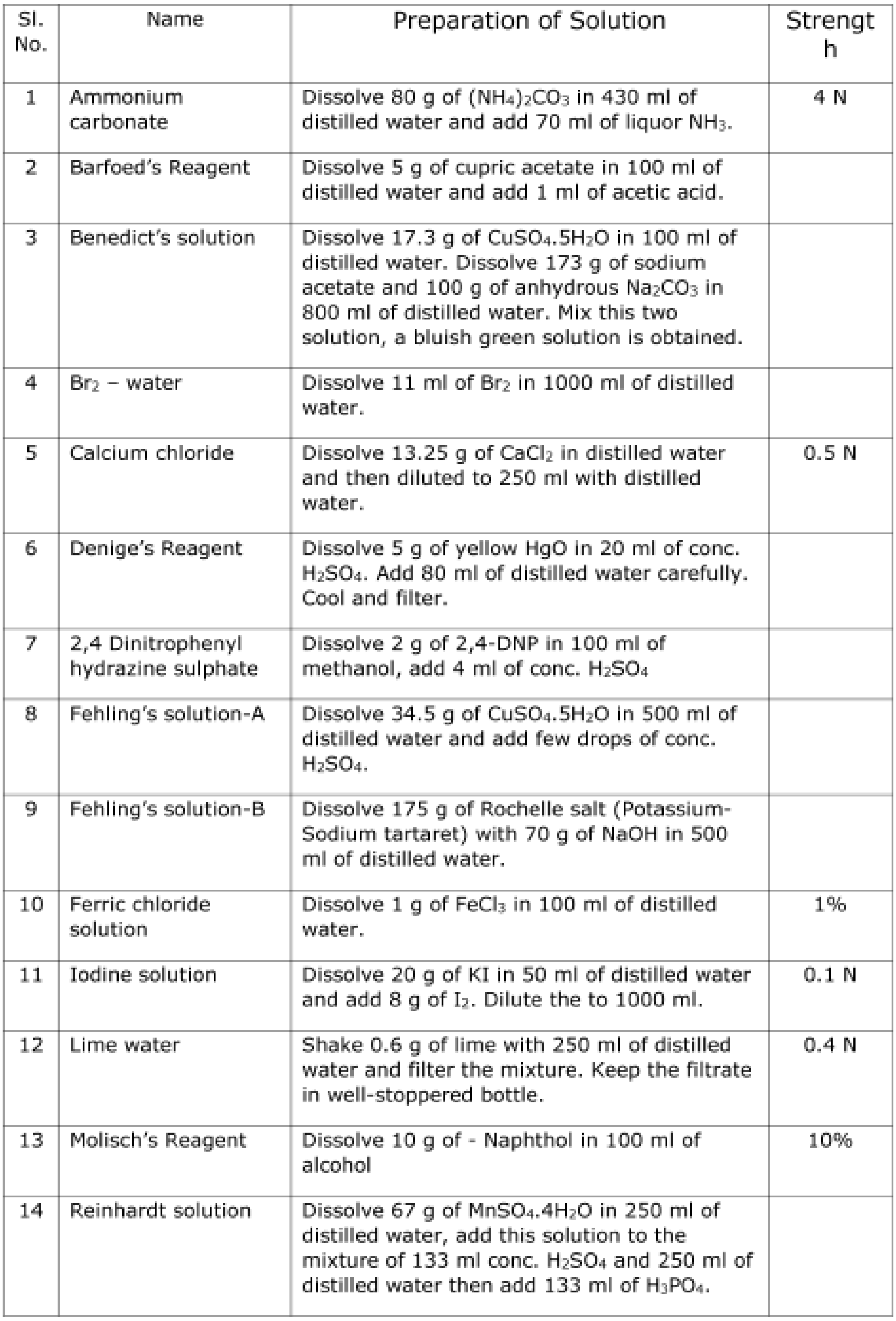
Name	Preparation of Solution	Strength
Ba – diphenylamine Sulphonate	Dissolve 0.2 g of the dye staff in 100 ml of distilled water	0.2%
Methyl orange (pH range 3.1 – 4.4)	Dissolve 0.05 g of the dye staff in 100 ml of distilled water	0.05%
Phenolphthalein (pH range 8.3 – 10)	Dissolve 0.5 g of the dye staff in 100 ml of 50% of ethanol	0.5%
Calcon	Dissolve 0.4 g of the dye staff in 100 ml of methanol	0.4%
Starch Solution	Prepare a paste of 1 g of soluble starch with a little water and pour it into 100 ml of boiling water with constant stirring. Boil the mixture 2-3 minutes more.	1%

1.10 Equivalent Weight of Some Common Reagents



Name	Molecular Weight	Equivalent Weight
Potassium permanganate $KMnO_4$	158	158/5 = 31.6
Potassium dichromate $K_2Cr_2O_7$	294.18	294.18/6 = 49.03
Oxalic Acid $H_2C_2O_4.2H_2O$	126	126/2 = 63
Mohr's Salt $(NH_4)SO_4.FeSO_4.\ 6H_2O$	392.13	392.13/1 = 392.13
Sodium Carbonate Na_2CO_3	106	106/2 = 53
Hydrochloric Acid HCl	36.5	36.5/1 = 36.5
Sulphuric Acid H_2SO_4	98	98/2 = 49
Sodium Hydroxide NaOH	40	40/1 = 40

1.11 Some Common Rack Reagents



Sl. No.	Name	Preparation of Solution	Strength
1	Ammonium carbonate	Dissolve 80 g of $(NH_4)_2CO_3$ in 430 ml of distilled water and add 70 ml of liquor NH_3.	4 N
2	Barfoed's Reagent	Dissolve 5 g of cupric acetate in 100 ml of distilled water and add 1 ml of acetic acid.	
3	Benedict's solution	Dissolve 17.3 g of $CuSO_4.5H_2O$ in 100 ml of distilled water. Dissolve 173 g of sodium acetate and 100 g of anhydrous Na_2CO_3 in 800 ml of distilled water. Mix this two solution, a bluish green solution is obtained.	
4	Br_2 – water	Dissolve 11 ml of Br_2 in 1000 ml of distilled water.	
5	Calcium chloride	Dissolve 13.25 g of $CaCl_2$ in distilled water and then diluted to 250 ml with distilled water.	0.5 N
6	Denige's Reagent	Dissolve 5 g of yellow HgO in 20 ml of conc. H_2SO_4. Add 80 ml of distilled water carefully. Cool and filter.	
7	2,4 Dinitrophenyl hydrazine sulphate	Dissolve 2 g of 2,4-DNP in 100 ml of methanol, add 4 ml of conc. H_2SO_4	
8	Fehling's solution-A	Dissolve 34.5 g of $CuSO_4.5H_2O$ in 500 ml of distilled water and add few drops of conc. H_2SO_4.	
9	Fehling's solution-B	Dissolve 175 g of Rochelle salt (Potassium-Sodium tartaret) with 70 g of NaOH in 500 ml of distilled water.	
10	Ferric chloride solution	Dissolve 1 g of $FeCl_3$ in 100 ml of distilled water.	1%
11	Iodine solution	Dissolve 20 g of KI in 50 ml of distilled water and add 8 g of I_2. Dilute the to 1000 ml.	0.1 N
12	Lime water	Shake 0.6 g of lime with 250 ml of distilled water and filter the mixture. Keep the filtrate in well-stoppered bottle.	0.4 N
13	Molisch's Reagent	Dissolve 10 g of - Naphthol in 100 ml of alcohol	10%
14	Reinhardt solution	Dissolve 67 g of $MnSO_4.4H_2O$ in 250 ml of distilled water, add this solution to the mixture of 133 ml conc. H_2SO_4 and 250 ml of distilled water then add 133 ml of H_3PO_4.	

1.12 Conclusion

In the realm of analytical chemistry, the accurate preparation and utilization of solutions is paramount for achieving reliable and reproducible results. This conclusion synthesizes the key points from various sections related to solution preparation and their applications.

Preparation of Standard Solutions:

The foundation of precise quantitative analysis lies in the preparation of standard solutions. Primary standard solutions (Section 3.1) are prepared using substances of high purity and known stoichiometry, ensuring accurate concentration without the need for calibration against another standard. Secondary standard solutions (Section 3.2), however, require standardization against a primary standard to determine their exact concentration, reflecting the importance of primary standards in establishing a hierarchy of accuracy.

Strength of Solutions:

Understanding the strength or concentration of solutions (Section 4.0) is essential for various analytical procedures. Accurate concentration measurements allow chemists to predict and control the reactions involving these solutions, ensuring consistency in experimental outcomes.

Strength of Concentrated Acids and Bases:

The strengths of concentrated acids and bases (Section 5.0) are crucial in many chemical processes. Knowledge of their concentrations and handling precautions is vital for ensuring safety and achieving the desired reactivity in chemical reactions.

Preparation of Dilute Acids and Bases Solutions:

The preparation of dilute acids and bases (Section 6.0) from their concentrated forms is a common laboratory practice. Proper techniques and safety measures are emphasized to ensure accurate dilutions and to prevent accidents due to the exothermic nature of dilution processes.

Preparation of Aqua Regia:

Aqua regia (Section 7.0), a highly corrosive mixture of nitric acid and hydrochloric acid, is prepared with precision due to its importance in dissolving noble metals like gold and platinum. Understanding its preparation and applications underscores the significance of handling strong acids with care and expertise.

Preparation of Some Common Indicators:

Indicators (Section 8.0) are prepared to detect the endpoint in titrations or to determine the pH of solutions. The selection and preparation of appropriate indicators are essential for achieving accurate and visually discernible results in various analytical procedures.

Equivalent Weight of Some Common Reagents:

Knowing the equivalent weight of reagents (Section 9.0) is fundamental for stoichiometric calculations in titrations and other quantitative analyses. It allows chemists to relate the mass of a reagent to the amount of substance involved in a reaction, facilitating precise measurements and consistency.

Some Common Rack Reagents:

Common rack reagents (Section 10.0), which are frequently used in various laboratory procedures, must be prepared and stored correctly to ensure their stability and effectiveness. Proper management of these reagents supports the smooth and efficient functioning of a laboratory.

1.13 Some Sample Questions

1. **What is a primary standard solution and why is it important in analytical chemistry?**

   Answer: A primary standard solution is a solution prepared from a substance of high purity and known stoichiometry, which can be weighed accurately to produce a solution of known concentration. It is important because it provides a reference with a precise concentration that can be used to calibrate other solutions and ensure accurate quantitative analysis.

2. **How do secondary standard solutions differ from primary standard solutions?**

   Answer: Secondary standard solutions are not prepared from highly pure substances. Instead, their exact concentrations are determined by titration against a primary standard solution. They are used in routine analysis where absolute precision is not as critical as in the case of primary standards.

3. **Why is it crucial to know the strength of solutions in chemical processes?**

   Answer: Knowing the strength (concentration) of solutions is crucial because it allows chemists to predict and control the outcome of chemical reactions. Accurate concentrations ensure that reactions proceed as expected and yield reliable, reproducible results.

4. **What precautions should be taken when diluting concentrated acids and bases?**

   Answer: When diluting concentrated acids and bases, it is important to add the acid or base to water slowly and with constant stirring to prevent exothermic reactions that can cause splattering and burns. Proper personal protective equipment (PPE) such as gloves, goggles, and lab coats should be worn, and the procedure should be carried out in a well-ventilated area, preferably in a fume hood.

5. **Describe the composition and use of aqua regia.**

   Answer: Aqua regia is a highly corrosive mixture of concentrated nitric acid and hydrochloric acid, usually in a molar ratio of 1:3. It is used to dissolve noble metals like gold and platinum, which are resistant to single acids. Due to its highly reactive nature, it must be prepared and handled with extreme caution.

6. **What is the role of indicators in titration, and how are they prepared?**

   Answer: Indicators are substances that change color at a specific pH range and are used to signal the endpoint of a titration. They are prepared by dissolving a small amount of the indicator compound in a suitable solvent, usually water or alcohol. The choice of indicator depends on the pH range over which the titration occurs and the expected endpoint.

7. **How is the equivalent weight of a reagent calculated, and why is it important?**

   Answer: The equivalent weight of a reagent is calculated by dividing the molecular weight of the reagent by the number of equivalents per mole. For acids, it is the number of moles of hydrogen ions (H+) the acid can donate, and for bases, it is the number of moles of hydroxide ions (OH-) the base can accept. Knowing the equivalent weight is important for stoichiometric calculations in titrations, allowing accurate determination of the concentration of unknown solutions.

8. **What are common rack reagents, and how should they be managed in a laboratory setting?**

   Answer: Common rack reagents are standard solutions and chemicals frequently used in various laboratory procedures. They should be clearly labeled, stored properly according to safety guidelines, and periodically checked for purity and concentration. Proper management ensures their stability, safety, and effectiveness in analytical procedures.

Unit 2 ❐ Estimation of carbonate and hydroxide present together in a mixture

2.0 Objectives

2.1 Introduction

2.2 Principle: for Estimation

2.3 Chemicals Required

4 Procedure:

2.4.1 Preparation of standard 250 ml (N/20) Na_2CO_3 solution

2.4.2 Standardization HCl solution against standard Na_2CO_3 solution using methyl orange as indicator.

2.4.3 Calculation

2.4.4 Titration of the supplied solution

2.4.5 Calculation

2.5 Conclusion

2.6 Some Sample Questions

2.0 Objectives

- To determine the concentration of sodium carbonate (NaCO) and sodium hydroxide (NaOH) present in the mixture
- To understand the titration procedure for a mixture of a weak base (NaCO) and a strong base (NaOH).
- Develop proficiency in distinguishing between the titration endpoints of NaCO and NaOH by observing the pH changes and using appropriate indicators

2.1 Introduction

The estimation of sodium carbonate (NaCO) and sodium hydroxide (NaOH) in a mixture using a standard hydrochloric acid (N/20) solution is a fundamental procedure in analytical chemistry. This titration method allows for the precise determination of both components by exploiting their different reactions with HCl. The process involves a two-step titration, distinguishing the endpoints for NaOH and NaCO. Accurate measurement of these substances is crucial in various industrial and laboratory applications, highlighting the importance of precise analytical techniques in chemical analysis. This experiment underscores the principles of acid-base titration and quantitative analysis.

2.2 Principle for Estimation

During the neutralisation of Na_2CO_3 solution by strong acid like HCl occurs in two steps as a result two equivalence points are observed on the titration curve.

$Na_2CO_3 + HCl = NaHCO_3 + NaCl$ [pH = 8.3 at this equivalence point]

$NaHCO_3 + HCl = NaCl + H_2O + CO_2$ [pH = 3 to 4 at this equivalence point]

So at the half neutralisation point phenolphthalein (pH range = 8.3 – 10) will show its colour change from pink to colourless.

If the mixture is titrated using methyl orange as indicator (pH range = 3.1 – 4.4) complete neutralisation will occur that means titre value corresponds to total amount of Na_2CO_3 and NaOH by changing the colour yellow to pink (or red).

½ mole Na_2CO_3 = 1 mole NaOH = 1 equivalent

∴ 1000 ml (N) HCl solution a” 53 g of Na_2CO_3 α 40 g of NaOH

2.3 Chemicals Required

i) Standard S (N/20) Na_2CO_3 solution [0.6625 g in 250 ml of water]

ii) S (N/20) HCl solution

iii) Phenolphthalein indicator [0.5% in alcohol]

iv) Methyl orange [0.05% in water]

v) Unknown Na_2CO_3 + NaOH mixture

[Mix 15 ml (N) NaOH solution and 30 ml (N) Na_2CO_3 solution and dilute to 1 litre.]

2.4 Procedure

2.4.1 Preparation of standard 250 ml (N/20) Na_2CO_3 solution

Dissolve near about 0.6625g Na_2CO_3(note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Table – 1:

Initial weight (g)	Final weight (g)	Amount of Na_2CO_3 taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	$S_1 = W/0.6625$ $= f$

2.4.2 Standardisation HCl solution against standard Na_2CO_3 solution using methyl orange as indicator.

Pipette out of 25 ml of standard Na_2CO_3 solution in a 250 ml conical flask and add 1-2 drops of methyl orange indicator. Solution turns to yellow colour. Titrate with the same HCl solution with constant shaking until the pink (or red) colour just appeared. Record the burette reading (V). Repeat process three times.

Table -2:

No. of obs.	Volm. of Na_2CO_3 (ml)	Burette reading		Volm. of HCl (ml)	Mean volm. of HCl (ml)	Strength of HCl soln. (N/20)
		Initial	Final			
1.	25	0	...	...	V	$S = (25 \times W/0.6625)/V$ $= (25 \times f)/V$
2.	25	...	...	...		
3.	25	...	...	...		

2.4.3 Calculation

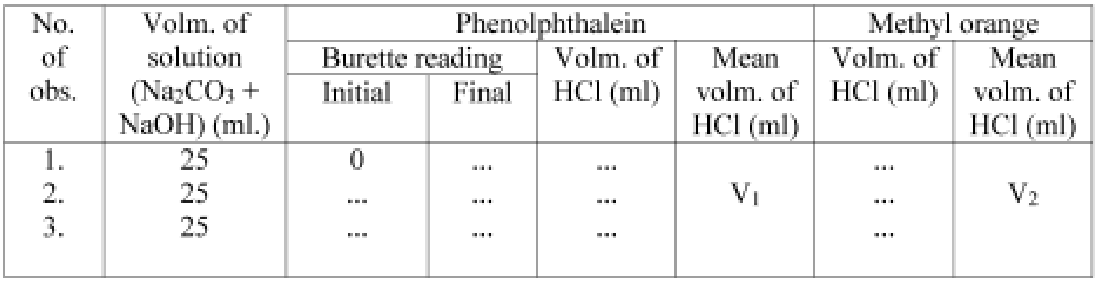
$$V \times S = V_1 \times S_1 \ ; \ V \times S = 25 \times f(N/20) \ ; \ S = 25 \times f/V \ (N/20)$$

2.5.4 Titration of the supplied solution

Pipette out of 25 ml of the supplied solution in a 250 ml conical flask and add 1-2 drops of phenolphthalein indicator. The solution turns to pink. Titrate the solution with the standard HCl solution with constant shaking until the pink colour just discharged. Burette reading (V_1) correspond to the half amount of Na_2CO_3 and full amount of NaOH.

To the above titrated solution add 2-3 drops of methyl orange indicator. Solution turns to yellow colour. Titrate with the same standard HCl solution with constant shaking until the pink (or red) colour just appeared. Burette reading (V_2) correspond to the half amount of Na_2CO_3. Repeat process three times.

Table -3:



No. of obs.	Volm. of solution (Na_2CO_3 + NaOH) (ml.)	Phenolphthalein				Methyl orange	
		Burette reading		Volm. of HCl (ml)	Mean volm. of HCl (ml)	Volm. of HCl (ml)	Mean volm. of HCl (ml)
		Initial	Final				
1.	25	0	...	...	V_1	...	V_2
2.	25	...	...	...		...	
3.	25	...	...	...		...	

2.4.5 Calculation:

(a) Strength of HCl solution = S (N/20)

(b) Using Phenolphthalein as indicator:

Half amount of Na_2CO_3 + full amount of NaOH in 25 ml of the supplied solution

a” V_1 ml S (N/20) HCl solution

a” V_1 x S/20 ml (N) HCl solution

(c) Using methyl orange as indicator:

Half amount of Na_2CO_3 a” V_2 ml S (N/20) HCl solution

a” V_2 x S/20 ml (N) HCl solution

Full amount of Na_2CO_3 in 25 ml mixture a” 2 V_2 x S/20 ml (N) HCl solution

We know that, 1000 ml (N) HCl solution a” 53 g of Na_2CO_3

2 V_2 x S/20 ml (N) HCl solution a” 0.053 x 2 V_2 x S/20 g of Na_2CO_3 in 25 ml

a” 0.0053 x V_2 x S x 40 g of Na_2CO_3 in 1 lit.

Again full amount of NaOH in 25 ml mixture a” (V_1 – V_2) ml S(N/20) HCl solution a” $(V_1 - V_2)$ x S/20 ml (N) HCl solution

We know that, 1000 ml (N) HCl solution a” 40 g of NaOH

$(V_1 - V_2)$ x S/20 ml (N) HCl solution a” 0.04 x $(V_1 - V_2)$ x S/20 g of NaOH in 25 ml

a” 0.002 x $(V_1 - V_2)$ x S g of NaOH in 25 ml

a” 0.002 x $(V_1 - V_2)$ x S x 40 g of NaOH in 1 lit.

The amount of Na_2CO_3 in the supplied mixture = 0.0053 x V_2 x S x 40 g of Na_2CO_3 / lit.

The amount of NaOH in the supplied mixture = 0.002 x $(V_1 - V_2)$ x S x 40 g of NaOH/ lit.

2.5 Conclusion

In this experiment, we aimed to determine the concentration of a supplied HCl solution using a titration method with NaCO as the primary standard. The detailed procedure involved several critical steps, starting with the preparation of a standard NaCO solution and proceeding through the standardization of the HCl solution with methyl orange as the indicator. Precise calculations were conducted at each stage to ensure accuracy in the results.

By standardizing the HCl solution against the NaCO standard, we established a reliable baseline for subsequent titrations. The titration of the supplied HCl solution allowed us to determine its concentration with high precision. Throughout the process, meticulous attention was given to the measurement and calculation steps, ensuring the reliability and accuracy of the experimental outcomes.

The principles of titration, including the use of indicators and the importance of standard solutions, were thoroughly applied in this experiment. The successful determination of the HCl concentration demonstrated the effectiveness of the titration method and reinforced the importance of standardization in quantitative chemical analysis. This experiment provided valuable hands-on experience in volumetric analysis and highlighted the critical role of precise measurement and calculation in achieving accurate and reproducible results in chemical estimations.

2.6 Some Sample Questions

Question 1: Why is standardization important in titration experiments?

Answer: Standardization is important in titration experiments to establish a reliable baseline for subsequent titrations, ensuring the accuracy and precision of the results.

Question 2: What was the primary objective of the experiment?

Answer: The primary objective of the experiment was to determine the concentration of a supplied HCl solution using a titration method with NaCO as the primary standard.

Question 3: What indicators were used in the titration processes and why?

Answer: Methyl orange and phenolphthalein were used as the indicator in the titration processes because these change color at the pH range corresponding to the neutralization point of the reaction.

Question 4: What are the final expressions for the amounts of Na, COƒ and NaOH in the supplied mixture?

Answer: The final expressions are:

The amount of Na, COƒ : 0.0053 x V2 x S x 40 g of Na, COƒ per liter.

The amount of NaOH: 0.002 x (V1 – V2) x S x 40 g of NaOH per liter.

Question 5: Given that 1000 ml (N) HCl solution is equivalent to 40 g of NaOH, how do you calculate the amount of NaOH in the supplied mixture?

Answer: The amount of NaOH in the supplied mixture is calculated as 0.002 x (V1 – V2) x S x 40 g of NaOH per liter.

Question 6: What is the endpoint of the titration with the standard HCl solution when using methyl orange as the indicator?

Answer: The endpoint is reached when the solution turns pink (or red).

Question 7: What color change occurs when methyl orange is added to the solution?

Answer: The solution turns yellow when methyl orange is added.

Unit 3 ❐ Estimation of carbonate and bicarbonate present together in a mixture

3.0 Objectives

From this practical unit one can get idea about the following:

- To comprehend the neutralization reactions of sodium carbonate (Na, COƒ) and sodium bicarbonate (NaHCOƒ) with hydrochloric acid (HCl).
- Recognize the two-step neutralization process of Na, COƒ with HCl and the corresponding pH changes.
- To identify and understand the significance of the two equivalence points in the titration curve during the neutralization of Na, COƒ by HCl.
- Determine the pH values at these equivalence points (pH 8.3 and pH 3-4).
- To understand the role of phenolphthalein and methyl orange as indicators in the titration process.
- Observe the color change of phenolphthalein from pink to colorless at pH 8.3 (first equivalence point).
- Observe the color change of methyl orange from yellow to pink (or red) at complete neutralization (second equivalence point).
- To perform the titration of a mixture of Na, COƒ and NaHCOƒ using a

standard N/20 HCl solution.

- Accurately measure the volume of HCl required to reach the first and second equivalence points.
- To calculate the amounts of Na, COƒ and NaHCOƒ present in the mixture based on the titration results.
- To enhance practical analytical skills in conducting titrations.
- Interpret titration curves and data to draw accurate conclusions about the composition of the mixture.

3.1 Introduction

This experiment aims to determine the quantities of sodium carbonate (NaCO) and sodium bicarbonate (NaHCO) in a mixture using standard N/20 hydrochloric acid (HCl) solution. The neutralization of NaCO by HCl occurs in two steps, each marked by distinct pH equivalence points. Phenolphthalein and methyl orange indicators facilitate the identification of these points through color changes. By performing titration and observing these changes, the individual amounts of NaCO and NaHCO in the mixture can be accurately calculated, enhancing practical analytical skills.

- **Principle for Estimation**

During the neutralization of Na_2CO_3 solution by strong acid like HCl occurs in two steps as a result two equivalence points are obsedved on the titration curve.

$Na_2CO_3 + HCl = NaHCO_3 + NaCl$ [pH = 8.3 at this equivalence point]

$NaHCO_3 + HCl = NaCl + H_2O + CO_2$ [pH = 3 to 4 at this equivalence point]

So at the half neutralization point phenolphthalein (pH range = 8.3 – 10) will show its colour change from pink to colourless.

If the mixture is titrated using methyl orange as indicator (pH range = 3.1 – 4.4) complete neutralization will occur that means titre value corresponds to total amount of Na_2CO_3 and$NaHCO_3$ by changing the colour yellow to pink (or red).

½ mole Na_2CO_3 = 1 mole NaOH = 1 equivalent

1000 ml (N) HCl solution a” 53 g of Na_2CO_3 a” 84 g of $NaHCO_3$

3.3 Chemicals Required

- Standard S (N/20) Na_2CO_3 solution [0.6625 g in 250 ml of water]
- S (N/20) HCl solution
- Phenolphthalein indicator [0.5% in alcohol]

- Methyl orange [0.05% in water]
- Unknown Na_2CO_3 + NaOH mixture

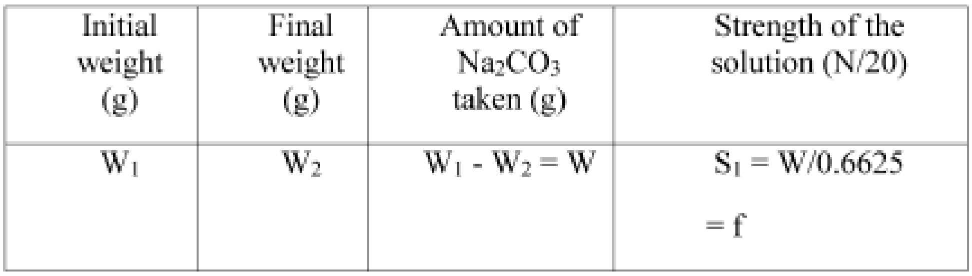
[Mix 15 ml (N) $NaHCO_3$ solution and 35 ml (N) Na_2CO_3 solution and dilute to 1 litre.]

3.4 Procedure

3.4.1 Preparation of standard 250 ml (N/20) Na_2CO_3 solution

Dissolve near about 0.6625g Na_2CO_3(note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Table – 1:



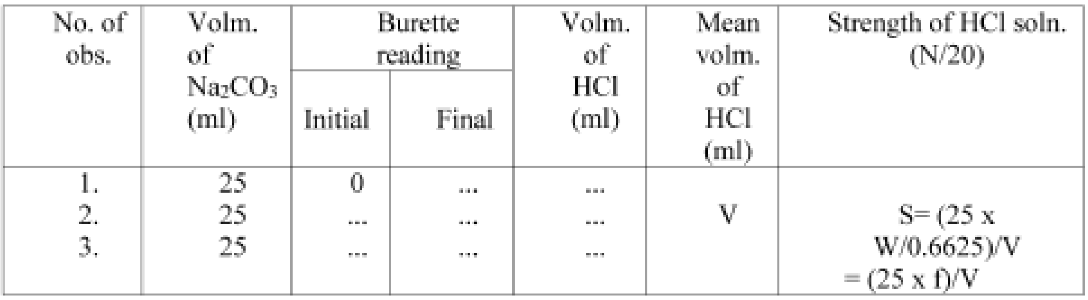
Initial weight (g)	Final weight (g)	Amount of Na_2CO_3 taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	$S_1 = W/0.6625$ $= f$

3.4.2 Standardization of HCl solution against standard Na_2CO_3 solution using methyl orange as indicator.

Pipette out of 25 ml of standard Na_2CO_3 solution in a 250 ml conical flask and add 1-2 drops of methyl orange indicator. Solution turns to yellow colour. Titrate with the same HCl solution with constant shaking until the pink (or red) colour just appeared. Record the burette reading (V). Repeat process three times.

Table -2:

- **Titration of the supplied solution:**



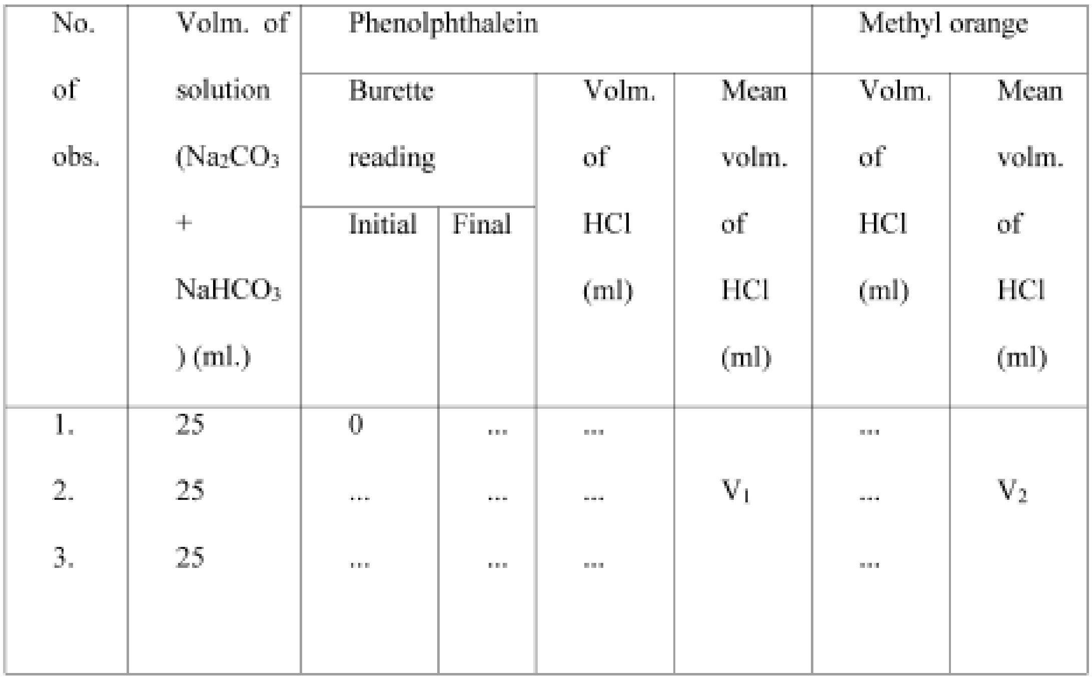
No. of obs.	Volm. of Na_2CO_3 (ml)	Burette reading		Volm. of HCl (ml)	Mean volm. of HCl (ml)	Strength of HCl soln. (N/20)
		Initial	Final			
1.	25	0	...	...		
2.	25	...	...	...	V	S= (25 x W/0.6625)/V = (25 x f)/V
3.	25	...	...	...		

Pipette out of 25 ml of the supplied solution in a 250 ml conical flask and add 1-2 drops of phenolphthalein indicator. The solution turns to pink. Titrate the solution with the standard HCl solution with constant shaking until the pink colour just discharged. Burette reading (V_1) correspond to the half amount of Na_2CO_3 and full amount of $NaHCO_3$.

To the above titrated solution add 2-3 drops of methyl orange indicator. Solution turns to yellow colour. Titrate with the same standard HCl solution with constant shaking until the pink (or red) colour just appeared. Burette reading (V_2) correspond to the half amount of Na_2CO_3. Repeat process three times.

Table -3:

3.4.4 Calculation



No. of obs.	Volm. of solution (Na_2CO_3 + $NaHCO_3$) (ml.)	Phenolphthalein				Methyl orange	
		Burette reading		Volm. of HCl (ml)	Mean volm. of HCl (ml)	Volm. of HCl (ml)	Mean volm. of HCl (ml)
		Initial	Final				
1.	25	0	...	...		...	
2.	25	...	...	...	V_1	...	V_2
3.	25	...	...	...		...	

Strength of HCl solution = S (N/20)

Using Phenolphthalein as indicator:

Half amount of Na_2CO_3 + full amount of $NaHCO_3$ in 25 ml of the supplied solution

a” V_1 ml S (N/20) HCl solution

a” V_1 x S/20 ml (N) HCl solution

Using methyl orange as indicator:

Half amount of Na_2CO_3 a” V_2 ml S (N/20) HCl solution

a” V_2 x S/20 ml (N) HCl solution

Full amount of Na_2CO_3 in 25 ml mixture a” 2 V_2 x S/20 ml (N) HCl solution

We know that, 1000 ml (N) HCl solution a” 53 g of Na_2CO_3

2 V_2 x S/20 ml (N) HCl solution a” 0.053 x 2 V_2 x S/20 g of Na_2CO_3 in 25 ml

a” 0.0053 x V_2 x S x 40 g of Na_2CO_3 in 1 lit.

Again full amount of $NaHCO_3$ in 25 ml mixture a” (V_1 – V_2) ml S(N/20) HCl solution

a” (V_1 – V_2) x S/20 ml (N) HCl solution

We know that, 1000 ml (N) HCl solution a” 84 g of $NaHCO_3$

(V_1 – V_2) x S/20 ml (N) HCl solution a” 0.084 x (V_1 – V_2) x S/20 g of $NaHCO_3$ in 25 ml

a” 0.0042 x (V_1 – V_2) x S g of $NaHCO_3$ in 25 ml

a” 0.0042 x (V_1 – V_2) x S x 40 g of $NaHCO_3$ in 1 lit.

The amount of Na_2CO_3 in the supplied mixture = 0.0053 x V_2 x S x 40 g of Na_2CO_3 / lit.

The amount of $NaHCO_3$ in the supplied mixture = 0.0042 x (V_1 – V_2) x S x 40 g of $NaHCO_3$/ lit.

3.5 Conclusion

This practical involves preparing a sodium carbonate (NaCO) solution with a normality of 1/20. This requires accurately weighing the appropriate amount of Na, CO*f* and dissolving it in distilled water to make up to a final volume of 250 ml. The preparation of this standard solution is crucial as it serves as the basis for the standardization process.

In this step, the prepared NaCO solution is used to determine the concentration of the hydrochloric acid (HCl) solution. Methyl orange is used as an indicator because it changes color at the pH corresponding to the end point of the titration between a strong acid and a weak base. The titration is performed by gradually adding HCl to the NaCO solution until the indicator signals the completion of the reaction, allowing the concentration of the HCl solution to be calculated.

Once the HCl solution is standardized, it can be used to titrate the supplied solution. The goal is to determine the concentration of a component in the supplied solution by using the now accurately known concentration of the HCl. The titration process involves adding the HCl to the supplied solution in the presence of an appropriate indicator until the reaction reaches its end point.

After completing the titrations, calculations are necessary to determine the unknown concentrations. Using the volume and concentration of the titrant (HCl) and the volume of the supplied solution, the concentration of the unknown component can be calculated through stoichiometric relationships.

The entire process—from preparing the NaCO solution, standardizing the HCl solution, performing the titration on the supplied solution, to calculating the final concentrations—ensures accurate and reliable analytical results. This multi-step approach allows for the precise determination of unknown concentrations in various solutions, which is fundamental in quantitative chemical analysis.

3.6 Some Sample Questions

1. **What is the primary aim of this experiment?**

   Answer: The primary aim of this experiment is to determine the quantities of sodium carbonate (NaCO) and sodium bicarbonate (NaHCO) in a mixture using standard N/20 hydrochloric acid (HCl) solution.

2. **What indicators are used to identify the equivalence points in the titration, and what color changes do they facilitate?**

   Answer: Phenolphthalein and methyl orange are the indicators used. Phenolphthalein changes color from pink to colorless at the first equivalence point (pH = 8.3). Methyl orange changes color from yellow to pink (or red) at the second equivalence point (pH = 3 to 4).

- **Describe the two-step neutralization reaction of sodium carbonate (NaCO) with hydrochloric acid (HCl).**

  Answer: The two-step neutralization reaction is as follows:

  - First step: Na, CO + HCl ’! NaHCO + NaCl (pH = 8.3)
  - Second step: NaHCO + HCl ’! NaCl + H, O + CO, (pH = 3 to 4)

- **How is the standard N/20 NaCO solution prepared?**

  Answer: To prepare the standard N/20 NaCO solution, dissolve approximately 0.6625 g of NaCO in a 250 mL volumetric flask, dilute up to the mark with distilled water, and shake to form a uniform solution.

- **What is the purpose of standardizing the HCl solution against the standard**

NaCO solution?

Answer: The purpose of standardizing the HCl solution against the standard NaCO solution is to accurately determine the concentration of the HCl solution. This is done by titrating a known volume of NaCO solution with HCl using methyl orange as an indicator and recording the volume of HCl required to reach the endpoint.

- **Explain the titration process of the supplied solution using phenolphthalein and methyl orange indicators.**

  Answer: The titration process involves two steps:

  First, pipette out 25 mL of the supplied solution into a conical flask, add 1-2 drops of phenolphthalein indicator, and titrate with standard HCl until the pink color disappears. Record the burette reading (V1).

  Next, add 2-3 drops of methyl orange to the same solution, which turns yellow. Continue titrating with the standard HCl until the solution turns pink (or red). Record the burette reading (V2).

- **How do you calculate the amounts of Na, COƒ and NaHCOƒ in the supplied mixture?**

  Answer: The amounts of Na, COƒ and NaHCOƒ are calculated using the recorded volumes (V1 and V2) from the titration:

  - Amount of NaCO = 0.0053 x V2 x S x 40 g/L
  - Amount of NaHCO = 0.0042 x (V1 - V2) x S x 40 g/L

- **What conclusion can be drawn from this experiment?**

  Answer: The experiment demonstrates the preparation of a standard Na, COƒ solution, the standardization of HCl solution, and the titration of a supplied mixture to accurately determine the concentrations of Na, COƒ and NaHCOƒ

  - This enhances practical analytical skills in quantitative chemical analysis.

Unit 4 ❐ Estimation of Fe(II) using $K_2Cr_2O_7$ solution

4.0 Objectives

- To accurately determine the concentration of Fe(II) in a given sample using a standardized $K_2Cr_2O_7$ solution through titration.
- To select and use an appropriate indicator that provides a clear and precise endpoint for the titration process.
- To ensure that the reaction between Fe(II) and $K_2Cr_2O_7$ goes to completion, preventing underestimation of Fe(II) concentration.
- By achieving these objectives, the estimation of Fe(II) using $K_2Cr_2O_7$solution can be performed with high accuracy, precision, and reliability.

4.1 Introduction

The estimation of Fe(II) ions using potassium dichromate ($K_2Cr_2O_7$) solution is a widely employed analytical technique in chemistry, particularly in the fields of environmental analysis, metallurgy, and pharmaceuticals. This method, known as redox titration, leverages the strong oxidizing properties of potassium dichromate to quantitatively oxidize Fe(II) to Fe(III).

In this titration process, the K_2Cr_2O acts as the titrant, and its reaction with Fe(II) is monitored until a stoichiometric equivalence point is reached. The endpoint of the titration can be detected using suitable indicators, such as diphenylamine sulfonate or ferroin, which undergo a distinct color change upon complete oxidation of Fe(II).

The method is valued for its accuracy, sensitivity, and ability to handle a wide range of Fe(II) concentrations. However, achieving reliable results requires careful standardization of the K_2Cr_2O solution, precise sample preparation, and stringent control of experimental conditions. By adhering to these protocols, the estimation of Fe(II) using K_2Cr_2O can provide vital data for quality control and assessment in various scientific and industrial applications.

4.2 Oxidation-Reduction Titrations or Redox titrations

4.2.1 Oxidation-reduction:

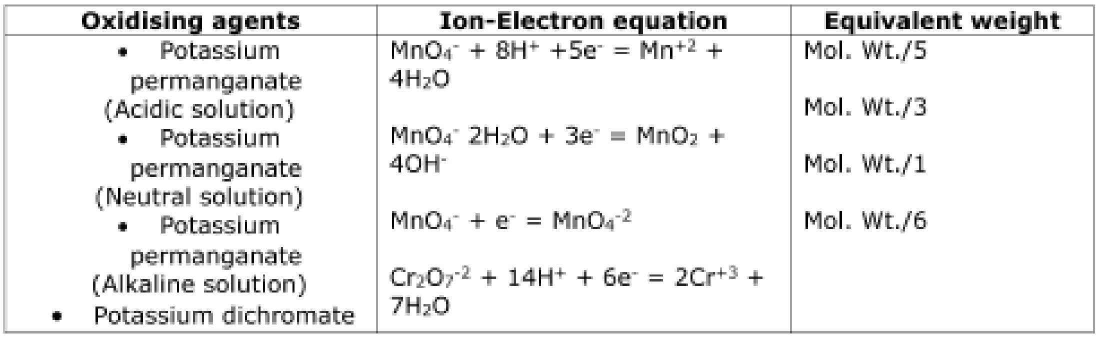
The terms oxidation and Reduction are defined as :

Oxidation is the process in which an atom or ion loses electron(s). For example ferrous ion (Fe^{+2}) is converted to ferric ion by loss of an electron as Fe^{+2} – e Fe^{+3}. Here Fe^{+2} loses electron, is the reducing agent and is oxidised to Fe^{+3} by losing an electron.

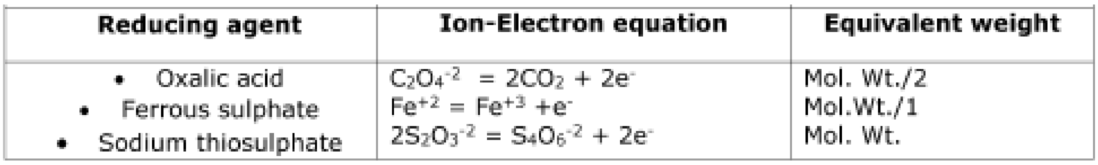
Reduction is the process in which there is a gain of electron(s). Chlorine atom is converted to chloride ion by gain of electron. i.e. Cl + e^- Cl^-. Here Cl atom is oxidising agent and is reduced to Cl^- by gaining an electron.

Oxidation and reduction simultaneously take place in any chemical reaction.

4.2.2 Equivalent weight of some oxidizing and reducing agents



Oxidising agents	Ion-Electron equation	Equivalent weight
• Potassium permanganate (Acidic solution)	$MnO_4^- + 8H^+ + 5e^- = Mn^{+2} + 4H_2O$	Mol. Wt./5
• Potassium permanganate (Neutral solution)	$MnO_4^-\ 2H_2O + 3e^- = MnO_2 + 4OH^-$	Mol. Wt./3
• Potassium permanganate (Alkaline solution)	$MnO_4^- + e^- = MnO_4^{-2}$	Mol. Wt./1
• Potassium dichromate	$Cr_2O_7^{-2} + 14H^+ + 6e^- = 2Cr^{+3} + 7H_2O$	Mol. Wt./6



Reducing agent	Ion-Electron equation	Equivalent weight
• Oxalic acid • Ferrous sulphate • Sodium thiosulphate	$C_2O_4^{-2} = 2CO_2 + 2e^-$ $Fe^{+2} = Fe^{+3} + e^-$ $2S_2O_3^{-2} = S_4O_6^{-2} + 2e^-$	Mol. Wt./2 Mol.Wt./1 Mol. Wt.

4.2.3 Comparison of the oxidizing and reducing property of a system:

The oxidizing and reducing property of a system is measured by its reducing potential. Hence the standard reduction potentials of the various systems indicating their oxidizing or reducing power. For example, standard reduction potential of acidified $KMnO_4$ is +1.52V and that of acidified $K_2Cr_2O_7$ is +1.30V in the redox reactions. Hence acidified $KMnO_4$ is stronger oxidizing agent than acidified $K_2Cr_2O_7$ in redox reactions.

4.3 Principal

Because of the higher standard reduction potential than that of Fe^{+3} Potassium dichromate quantitatively oxidised Fe^{+2} to Fe^{+3} in acid medium.

4.3.1 Reaction:

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

Ionically:

$$Cr_2O_7^{-2} + 6Fe^{+2} + 14H^+ = 2Cr^{+3} + 6Fe^{+3} + 7H_2O$$

4.3.2 Indicator

Sodium or Barium diphenylamine sulphonate (BaDS) is usually used as indicator. Freshly prepared Diphenylamine may also be used as indicator. But BaDS works better as its solution can resist aerial oxidation and can be stored for a long time. BaDS gives a very sharp colour change from colourless through green to red-violet. To use BaDS or diphenylamine as indicator H_3PO_4 or F^- (NH_4HF_2) should be added prior to the start of the titration to lower the reduction potential of Fe^{+2}/Fe^{+3} system. N-phenyl anthranilic acid (E^0= +1.08V) or 5,6 dimethyl ferroin (E^0=+1.06V) may also be used as indicator and in these case addition of H_3PO_4 or F^- is not necessary.

End point: Bluish-violet or purple colour.

4.4 Procedure

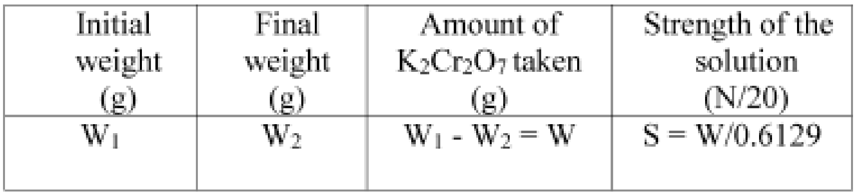
4.4.1 Preparation of standard 250 ml S (N/20) $K_2Cr_2O_7$ solution.

Dissolve near about 0.6129 g $K_2Cr_2O_7$(note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Equivalent weight of $K_2Cr_2O_7$ = Mol. Wt./6 = 294.18/6 = 49.03

250 ml (N/20) $K_2Cr_2O_7$ solution a” a” 0.6129 g of $K_2Cr_2O_7$

Table- 1:

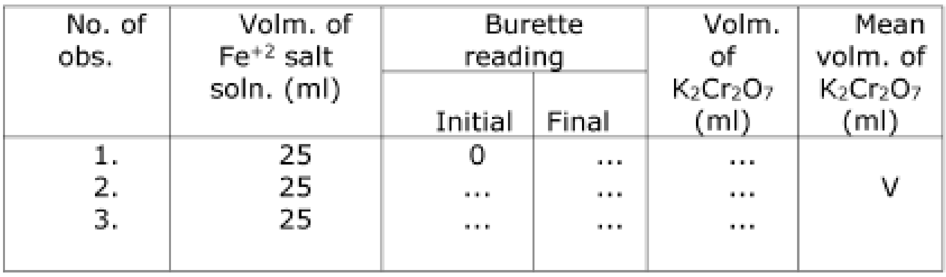


Initial weight (g)	Final weight (g)	Amount of $K_2Cr_2O_7$ taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	S = W/0.6129

4.4.2 Titration with standard $K_2Cr_2O_7$ solution

Take standard $K_2Cr_2O_7$ solution in burette. Pipette out 25 ml of Mohr’s salt (ferrous salt) solution in a 250 ml conical flask. Add 150 ml of distilled water. Now pour 5 ml conc. H_2SO_4 and 5 ml of syrupy H_3PO_4. Add 2-3 drops of BaDS indicator. Titrate with $K_2Cr_2O_7$ solution with constant shaking till red-violet or purple colour appeared. Note the burette reading. Repeat the experiment three times.

Table-2:



No. of obs.	Volm. of Fe^{+2} salt soln. (ml)	Burette reading		Volm. of $K_2Cr_2O_7$ (ml)	Mean volm. of $K_2Cr_2O_7$ (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V
3.	25	...	...	...	

4.4.3 Calculation

25 ml of Morh’s salt or (Fe^{+2})solution a” V ml W/0.6129 (N/20) $K_2Cr_2O_7$ solution

a” V x W/0.6129 ml (N/20) $K_2Cr_2O_7$ solution

We know, 1000 ml (N/20) $K_2Cr_2O_7$ solution a” 1000 ml (N/20) mohr’s solution

a” 1000 ml (N/20) Fe^{+2}

a” 55.85/20 g of Fe

a” 2.779 g of Fe

1 ml (N/20) $K_2Cr_2O_7$ solution a” 0.002779 g of Fe

V x W/0.6129 ml (N/20) $K_2Cr_2O_7$solution a” 0.002779 x V x W/0.6129 g of Fe

25 ml Mohr's salt solution contain 0.002779 x V x W/0.6129 g of Fe
250 ml ... ... 0.002779 x V x W/0.6129 x 10 g of Fe
Or 1 lit or 1000 ml ... ... 0.002779 x V x W/0.6129 x 10 x 4 g of Fe

4.5 Conclusion

The titrimetric method using $K_2Cr_2O_7$ for the estimation of Fe(II) is accurate and reliable. The process leverages the strong oxidizing nature of $K_2Cr_2O_7$ in an acidic medium to quantitatively oxidize Fe(II) to Fe(III). By measuring the volume of $K_2Cr_2O_7$ solution required to reach the endpoint, the concentration of Fe(II) in the sample can be precisely determined. This method is widely used in various analytical chemistry applications due to its robustness and reproducibility.

4.6 Some Sample Questions

Question: What is the primary oxidizing agent in this titration?
Answer: Potassium dichromate ($K_2Cr_2O_7$).
Question: What ion is being oxidized in this titration?
Answer: Fe(II) or ferrous ion.
Question: In which medium is the titration carried out?
Answer: Acidic medium, typically using sulfuric acid.
Question: What is the color change indicator commonly used?
Answer: Diphenylamine sulfate or N-phenylanthranilic acid.
Question: What is the stoichiometric ratio of Fe(II) to $Cr_2O_7^{2-}$ in the reaction?
Answer: 6 Fe(II) ions react with 1 $Cr_2O_7^{2-}$ ion.
Question: What is the final oxidation state of iron after the reaction?
Answer: Fe(III) or ferric ion.
Question: What is formed alongside Fe(III) in the reaction?
Answer: Cr(III) or chromium(III) ions and water.
Question: Why is sulfuric acid used in the titration?
Answer: To provide an acidic medium which is necessary for the reaction to proceed.
Question: What is the main purpose of using an indicator in this titration?
Answer: To signal the endpoint of the titration by a color change.

Question: How is the concentration of Fe(II) determined from the titration?

Answer: By measuring the volume of $K_2Cr_2O_7$ solution used and using the stoichiometric relationship.

Unit 5 ❐ Standardization of given $KMnO_4$ solution with standard Oxalic acid solution & Estimation of Fe(III) using standard S (N/20) $K_2Cr_2O_7$ / $KMnO_4$ Solution

5.0 Objectives

From this unit one can understand about the following:

- About Oxidation-Reduction titration
- Knowledge about oxidation and reduction reactions
- Concept about redox indicator
- To confirm the purity and strength of the potassium permanganate solution.
- To accurately determine the molarity of the given potassium permanganate solution by titrating it against a known concentration of standard oxalic acid solution, ensuring precise stoichiometric calculations and reliable experimental results.

5.1 Introduction

In analytical chemistry, the standardization of solutions is a critical procedure to ensure accurate and reliable results in various quantitative analyses. Potassium permanganate (KMnO4) is a widely used oxidizing agent in redox titrations due to its strong oxidizing properties and distinctive color change at the endpoint. However, the exact concentration of KMnO4 solutions can vary over time due to decomposition and other factors, necessitating regular standardization. This process involves titrating the KMnO4 solution against a primary standard solution of known concentration, such as oxalic acid, to determine its precise molarity. This introduction aims to outline the objectives and importance of standardizing a KMnO4 solution using a standard oxalic acid solution, ensuring accurate and consistent analytical results.

5.2 Standardisation of given $KMnO_4$ solution with standard Oxalic acid solution

5.2.1 Principle : As a reductant oxalic acid acts as follows:

$C_2O_4^{-2}$ $-2e^- = 2CO_2$

Equivalent weight of oxalic acid = Mol.Wt./2 = 126.066/2 = 63.033

250 ml. (N/20) oxalic acid solution a” 63.033/80 = 0.7879 g of oxalic acid.

5.2.2 Reaction:

$2MnO_4^- + 5C_2O_4^{-2} + 16H^+ = 2Mn^{+2} + 10CO_2 + 8H_2O$

5.2.3 Chemicals required:

- Oxalic acid
- S (N/20) $KMnO_4$ solution

  [Dissolve S 1.6 g of $KmnO_4$ in 500 ml distilled water, boil the mixture for about 20-30 mins., cool, diluted to 1lit., then filter off through glass wool and store in an amber coloured bottle.]
- 4(N) H_2SO_4
- Indicator : $KMnO_4$ solution act as a self-indicator

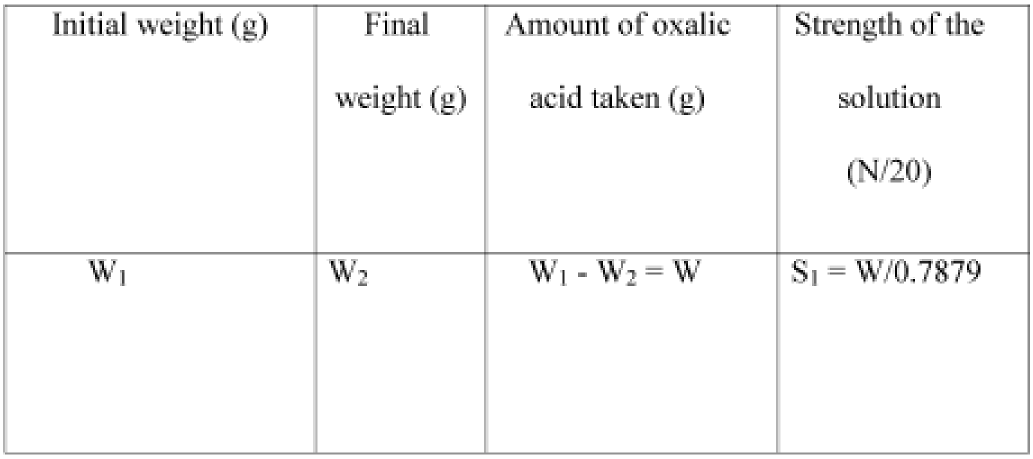
5.3 Procedure

5.3.1 Preparation of standard 250 ml. (N/20) oxalic acid solution

Dissolve near about 0.7879g oxalic acid (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Strength of prepared oxalic acid solution = S_1 (N)

Table-1:

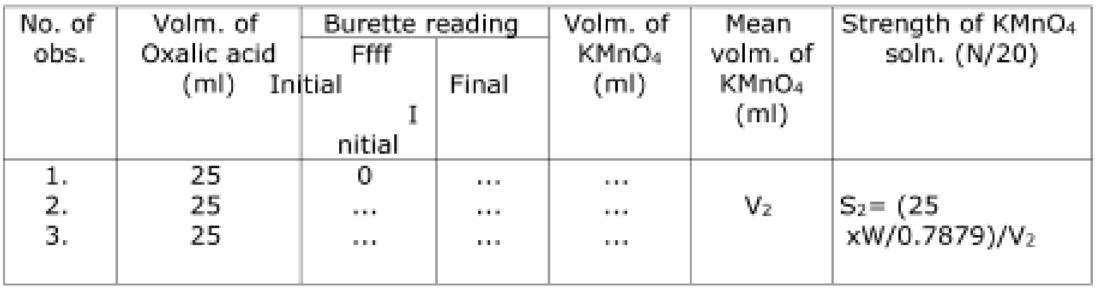


Initial weight (g)	Final weight (g)	Amount of oxalic acid taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	$S_1 = W/0.7879$

5.3.2 Standardisation of given KMnO4 solution with standard Oxalic acid solution

Take $KMnO_4$ solution in a burette. Pipette out 25 ml of the standard oxalic acid solution in a 250 ml conical flask. Add 25 ml of 4(N) H_2SO_4 in it and warm the mixture up to 60-70^{0}C. Titrate the solution by S (N/20) $KMnO_4$ solution in hot condition until a faint pink colour stable for 30 sec. Note the volume (V_1).

Table-2:



No. of obs.	Volm. of Oxalic acid (ml)	Burette reading		Volm. of $KMnO_4$ (ml)	Mean volm. of $KMnO_4$ (ml)	Strength of $KMnO_4$ soln. (N/20)
		Ffff Initial I nitial	Final			
1.	25	0	...	...	V_2	S_2= (25 xW/0.7879)/V_2
2.	25	...	...	...		
3.	25	...	...	...		

5.3.3 Calculation:

V_1 x S_1 = V_2 x S_2

i.e., 25 x W/0.7879(N/20) = V_2 x S_2

Strength of $KMnO_4$ solution(S_2)=(25x W/0.7879)/V_2 (N/20)

5.4 Estimation of Fe(III) using standard S (N/20) $K_2Cr_2O_7$ / $KMnO_4$ Solution

5.4.1 Principle :

Fe^{+3} in the given solution first reduced to Fe^{+2} with $SnCl_2$ in hot 6(N) HCl medium. After cooling the solution to the room temperature excess $SnCl_2$ is removed by adding $HgCl_2$ solution, a silky white precipitate appears. This ensure the complete removable of excess $SnCl_2$.

$2Fe^{+3} + Sn^{+2} = 2Fe^{+2} + Sn^{+4}$

$Sn^{+2} + HgCl_2 = Hg_2Cl_2 + Sn^{+4} + 2Cl^-$

The reduction may be carried out by using A.R. Al – foil in 5-6(N) HCl acid medium.

$3Fe^{+3} + Al = 3Fe^{+2} + Al^{+3}$

Titration of the solution with a standard S (N/20) $KMnO_4$ in 2(N) H_2SO_4 medium in presence of Zimmermann-Reinhardt reagent will correspond to the amount of Fe. Here $KMnO_4$ oxidised Fe^{+2} to Fe^{+3} and itself gets reduced to Mn^{+2}.

$MnO_4^- + 8\ H^+ + 5\ Fe^{+2} = Mn^{+2} + 4\ H_2O + 5\ Fe^{+3}$

MnO_4^-a” 5 Fe^{+2}

Or, 1/5 MnO_4^-a” Fe^{+2} a” 1 equivalent

1000 ml (N) $KMnO_4$ solution a” 55.847 g of Fe.

Or;

Titration of the solution with a standard S (N/20) $K_2Cr_2O_7$ in 2(N) H_2SO_4 medium in presence of syrupy ortho phosphoric acid and BaDS as indicator will correspond to the amount of Fe. Here $K_2Cr_2O_7$ oxidised Fe^{+2} to Fe^{+3} and itself gets reduced to Cr^{+3}.

$Cr_2O_7^{-2} + 14\ H^+ + 6\ Fe^{+2} = 2Cr^{+3} + 6\ Fe^{+3} + 7\ H_2O$

Or, 1/6 $Cr_2O_7^{-2}$a” Fe^{+2} a” 1 equivalent

1000 ml (N) $K_2Cr_2O_7$ solution a” 55.847 g of Fe.

5.4.2 Chemicals Required:

- For $KMnO_4$method
- 5% $HgCl_2$ solution
- 15% $SnCl_2$ solution
- Zimmermann-Reinhardt reagent
- Fe^{+3} solution
- Standard S (N/20) oxalic acid solution
- S (N/20) $KMnO_4$
- For$K_2Cr_2O_7$method
- Standard S (N/20) $K_2Cr_2O_7$ solution
- Fe^{+3} solution
- Al foil
- Syrupy ortho phosphoric acid
- BaDS indicator

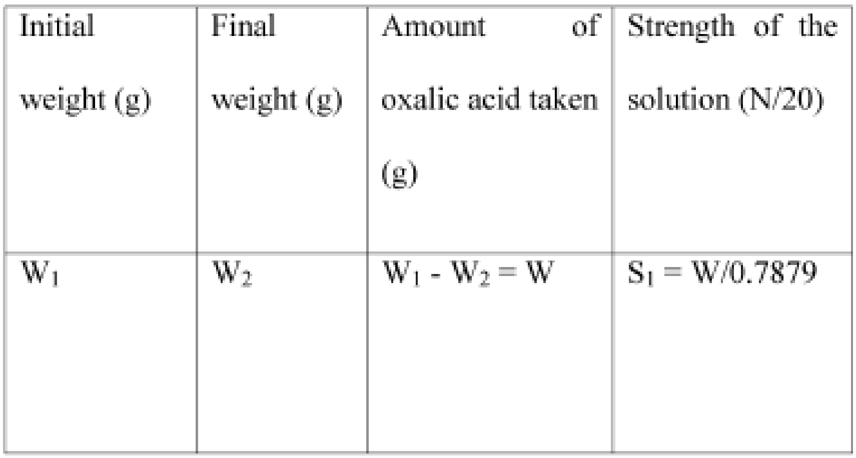
5.5 Procedure-I ($KMnO_4$ method):

5.5.1 Preparation of 250ml (N/20) oxalic acid solution:

Dissolve near about 0.7879g oxalic acid (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

+.Strength of prepared oxalic acid solution = S_1 (N)

Table -1

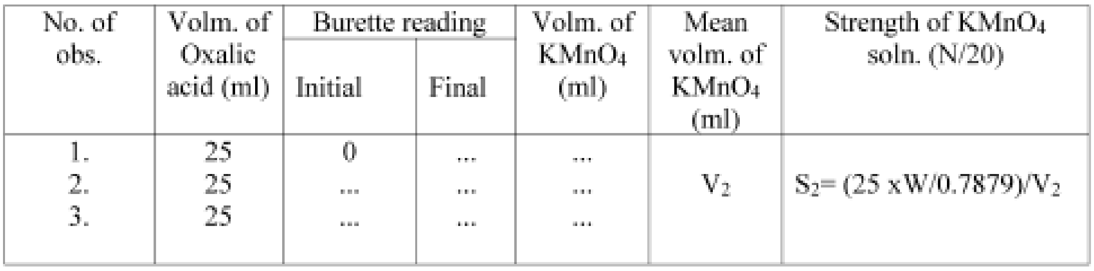


Initial weight (g)	Final weight (g)	Amount of oxalic acid taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	$S_1 = W/0.7879$

5.5.2 Standardisation of $KMnO_4$ solution against standard oxalic acid solution

Take $KMnO_4$ solution in a burette. Pipette out 25 ml of the standard oxalic acid solution in a 250 ml conical flask. Add 25 ml of 4(N) H_2SO_4 in it and warm the mixture up to 60-70^{0}C. Titrate the solution by S (N/20) $KMnO_4$ solution in hot condition until a faint pink colour stable for 30 sec. Note the volume (V_2).

Table – 2



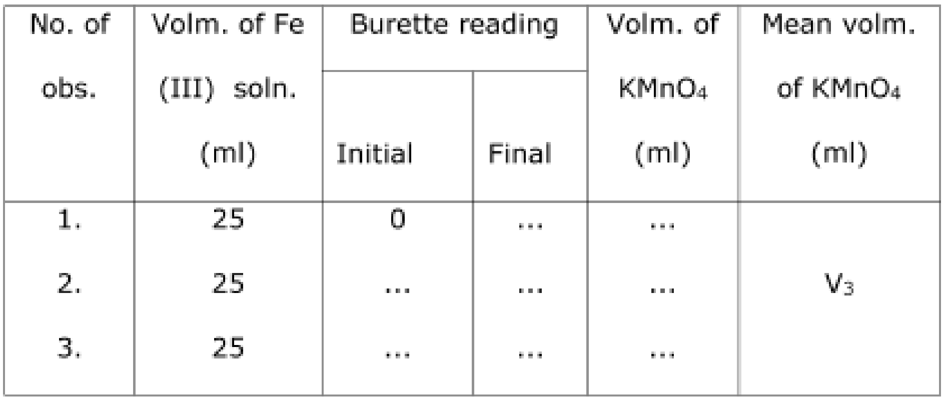
No. of obs.	Volm. of Oxalic acid (ml)	Burette reading		Volm. of $KMnO_4$ (ml)	Mean volm. of $KMnO_4$ (ml)	Strength of $KMnO_4$ soln. (N/20)
		Initial	Final			
1.	25	0	...	...	V_2	$S_2 = (25 \times W/0.7879)/V_2$
2.	25	...	...	...		
3.	25	...	...	...		

5.5.3 Reduction with $SnCl_2$ and Estimation of Fe(III):

Pipette out 25 ml of the supplied Fe (III) solution in a 500 ml conical flask.Add 20 ml conc. HCl and heat nearly to boiling (approx. 90^{0}C) then reduce with 15% $SnCl_2$ solution adding drop wise with constant shaking until the yellow colour of the mother solution is just disappeared. Add 1-2 drops of excess $SnCl_2$ solution. Add 10 ml of 5% $HgCl_2$ solution at a time and shake the mixture gently. Allow to stand for 5 minutes a silky white precipitate of Hg_2Cl_2 appears.

Dilute the above reduced solution with 250 ml distilled water to maintain the acidity of the solution below the 0.8(N), add 25 ml of Zimmermann-Reinhardt reagent and titrate with standard S (N/20) $KMnO_4$ solution till pink colour stands for 15 sec. Note the consumed volume (V_3 ml).

Table – 3 Estimation of Fe(III)



No. of obs.	Volm. of Fe (III) soln. (ml)	Burette reading		Volm. of $KMnO_4$ (ml)	Mean volm. of $KMnO_4$ (ml)
		Initial	Final		
1.	25	0	...	...	V_3
2.	25	...	...	...	
3.	25	...	...	...	

5.5.4 Calculation:

- Strength of $KMnO_4$ solution:

  V_1 x S_1 = V_2 x S_2

  i.e., 25 x W/0.7879(N/20) = V_2 x S_2

  S_2=(25x W/0.7879)/V_2 (N/20)

- **Estimation of Fe (III):**

  25 ml given Fe(III) solution a” V_3 ml S_2 (N/20) $KMnO_4$ solution

  a” V_3 x S_2 /20 ml (N) $KMnO_4$ solution

  We have, 1000 ml (N) $KMnO_4$ solution a” 55.847 g of Fe

  V_3 x S_2 /20 ml (N) $KMnO_4$ solution a” 0.055847 x V_3 x S_2 /20 g of Fe in 25 ml.

  a” 0.002792 x V_3 x S_2 g of Fe in 25 ml.

25 ml of the supplied solution contain 0.002792 x V_3 x S_2 g of Fe

1000 ml ... ... 0.002792 x V_3 x S_2x 40 g of Fe

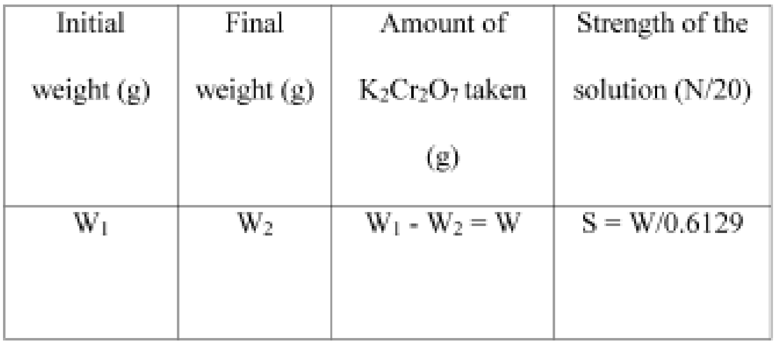
The amount of iron in the supplied solution = 0.002792 x V_3 x S_2x 40 g / lit.

5.6 Procedure-II ($K_2Cr_2O_7$ method)

5.6.1 Preparation of standard S (N/20) $K_2Cr_2O_7$ solution.

Dissolve near about 0.6129 g $K_2Cr_2O_7$(note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Table – 1:



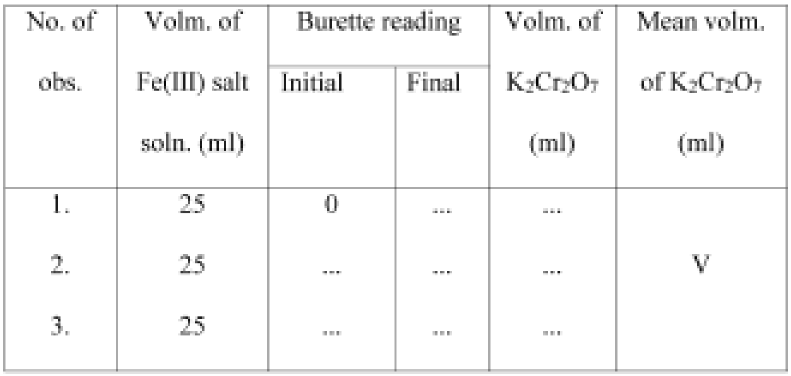
Initial weight (g)	Final weight (g)	Amount of $K_2Cr_2O_7$ taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	$S = W/0.6129$

5.6.2 Reduction with Aluminium foil and Estimation of Fe(III):

Pipette out 25 ml of the supplied Fe (III) solution in a 500 ml conical flask. Add 20 ml conc. HCl and heat nearly to boiling (approx. 90^0C) with few pieces of Al foil. Add more pieces of Al foil , if required, until the yellow colour of the mother solution is just disappeared.

Dilute the above reduced solution with 200 ml distilled water then add 5 ml of conc. H_2SO_4 and 5 ml of syrupy H_3PO_4 followed by 3-5 drops of Barium diphenylamine sulphonate indicator. Titrate with standard S (N/20) $K_2Cr_2O_7$ solution till the solution gets red-violet colouration. Note the consumed volume (Vml).

Table – 2:



No. of obs.	Volm. of Fe(III) salt soln. (ml)	Burette reading		Volm. of $K_2Cr_2O_7$ (ml)	Mean volm. of $K_2Cr_2O_7$ (ml)
		Initial	Final		
1.	25	0	...	...	V
2.	25	...	...	...	
3.	25	...	...	...	

5.6.3 Calculation

25 ml given fe(III) solution a” V ml S (N/20) $K_2Cr_2O_7$ solution

a” V x S /20 ml (N) $K_2Cr_2O_7$ solution

We have, 1000 ml (N) $K_2Cr_2O_7$ solution a” 55.847 g of Fe

V x S /20 ml (N) $K_2Cr_2O_7$ solution a” 0.055847 x V x S /20 g of Fe in 25 ml.

a” 0.002792 x V x S g of Fe in 25 ml.

25 ml of the supplied solution contain 0.002792 x V x S g of Fe

1000 ml ... ... 0.002792 x V x S x 40 g of Fe

The amount of iron in the supplied solution = 0.002792 x V x Sx 40 g / lit.

5.7 Conclusion

The estimation of Fe(III) using standard (N/20)(N/20)(N/20) K, Cr, O‡ and KMnO„ solutions involves precise and methodical procedures to ensure accurate results. This study demonstrates the application of two distinct titration methods—KMnO„ and K, Cr, O‡ —to determine the concentration of Fe(III) in a sample.

In Procedure-I, the KMnO„ method is employed, starting with the preparation of a 250 ml (N/20)(N/20)(N/20) oxalic acid solution. This standard solution is then used to standardize the KMnO„ solution. The Fe(III) is reduced using SnCl, , and the subsequent titration with the standardized KMnO„ solution allows for the estimation of Fe(III). Accurate calculation of the Fe(III) concentration is derived from the titration data, ensuring reliability in the results.

Procedure-II utilizes the K, Cr, O‡ method. A standard (N/20)(N/20)(N/20) K, Cr, O‡ solution is prepared, and Fe(III) is reduced using aluminium foil. The titration with the standardized K, Cr, O‡ solution follows, providing an alternative method to estimate Fe(III). This method offers a comparative approach to the KMnO„ titration, showcasing the versatility and applicability of different oxidizing agents in redox titrations.

5.8 Some sample Questions

Question: What is the principle behind the estimation of Fe(III) using $K_2Cr_2O_7$ or $KMnO_4$? **Answer:** The principle involves the oxidation of Fe(II) to Fe(III) by $K_2Cr_2O_7$or $KMnO_4$ in acidic medium, followed by titration to determine the amount of Fe(III) present.

Question: What are the chemicals required for the estimation of Fe(III)?

Answer: The chemicals required include standard ~ (N/20) $K_2Cr_2O_7$ or $KMnO_4$ solution, oxalic acid, $SnCl_2$, H_2SO_4, and aluminium foil.

Question: How do you prepare a 250 ml (N/20) oxalic acid solution?

Answer: To prepare a 250 ml (N/20) oxalic acid solution, dissolve the required amount of oxalic acid in distilled water and make up the volume to 250 ml.

Question: Why is it necessary to standardize the $KMnO_4$ solution?

Answer: Standardization is necessary to determine the exact concentration of the $KMnO_4$ solution to ensure accurate titration results.

Question: What role does $SnCl_2$ play in the estimation of Fe(III)?

Answer: $SnCl_2$ acts as a reducing agent to convert Fe(III) to Fe(II), which can then be titrated with $KMnO_4$.

Question: How do you calculate the amount of Fe(III) in the sample?

Answer: The amount of Fe(III) is calculated using the volume of $KMnO_4$ solution used in the titration and its standardized concentration.

Question: How do you prepare a standard ~ (N/20) $K_2Cr_2O_7$ solution?

Answer: To prepare a standard ~ (N/20) $K_2Cr_2O_7$ solution, dissolve the required amount of $K_2Cr_2O_7$ in distilled water and make up the volume to the desired level.

Question: What is the purpose of using aluminium foil in the $K_2Cr_2O_7$ method?

Answer: Aluminium foil is used to reduce Fe(III) to Fe(II), which can then be titrated with the standard $K_2Cr_2O_7$ solution to estimate Fe(III) concentration.

Unit 6 ❐ Estimation of Ca^{2+} using $KMnO_4$ solution

6.0 Objectives

- To accurately determine the concentration of calcium ions (Ca²z) in a given sample using potassium permanganate (KMnO„) solution as a titrant.
- To develop proficiency in performing redox titration, specifically focusing on the interaction between calcium ions and potassium permanganate.
- To understand the chemical principles and reactions involved in the redox titration process, particularly the oxidation-reduction mechanism between Ca²z and KMnO„ .
- To identify and use appropriate indicators that signal the end point of the titration process effectively.
- To enhance skills in achieving accurate and precise measurements of Ca²z concentrations, minimizing experimental errors.
- To compare the efficiency and reliability of KMnO„ solution in estimating Ca²z with other standard methods.

6.1 Introduction

The estimation of calcium ions (Ca^2z) is a crucial analytical process in various fields, including environmental science, biochemistry, and industrial chemistry. One effective method for determining the concentration of Ca^2z is through redox titration using potassium permanganate (KMnO„) solution. This titration technique exploits the strong oxidizing properties of KMnO„ to react with calcium ions, facilitating precise and accurate quantification. Understanding the principles behind this redox reaction and mastering the titration process are essential for achieving reliable results. This method not only aids in academic and research settings but also has significant practical applications in assessing water quality, monitoring biological samples, and ensuring the purity of industrial products.

6.2 Estimation of Ca^{2+} using $KMnO_4$ solution

6.2.1 Principle:

Calcium is precipitated as calcium oxalate by treating a hot hydrochloric acid solution with ammonium oxalate or oxalic acid neutralizing with NH_4OH solution (1:1).

$$Ca^{++} + C_2O_4^{=} + H_2O = CaC_2O_4.H_2O.$$

This precipitation of Ca^{+2} as oxalate is quantitative at a pH of 4.The precipitate is then dissolved in hot dil. H_2SO_4 to liberate equivalent amount of oxalic acid. Since $KMnO_4$ is powerful oxidising agent, oxidises quantitatively oxalic acid to CO_2.

$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4$$

$$KMnO_4 + 3\ H_2SO_4 + 5\ H_2C_2O_4 = K_2SO_4 + 2\ MnSO_4 + 10\ CO_2 + 8\ H_2O$$

6.2.2 Chemicals required:

- Standard (N/10) oxalic acid solution
- Standard S (N/10) $KMnO_4$ solution
- 6% ammmonium oxalate solution
- 4(N) H_2SO_4 solution
- 2(N) HCl solution
- NH_4OH (1:1) solution
- Methyl orange indicator
- Supplied solution

  [Dissolve 13.875 g of anhydrous $CaCl_2$ in 250 ml of distilled water and supply 7-8 ml as stock solution.]

- Conc. HCl

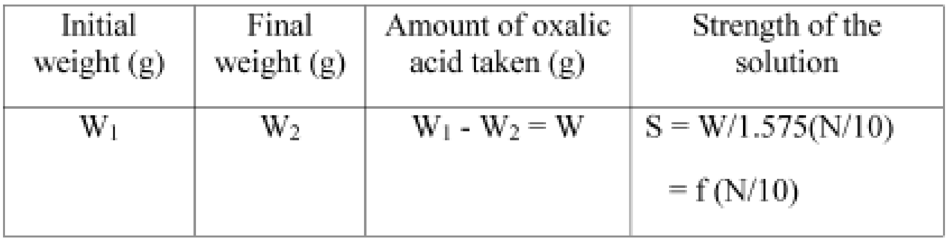
6.3 Procedure:

6.3.1 Preparation of 250 ml N/10 oxalic acid solution

Dissolve near about 1.575g oxalic acid (note accurate weight of taken amount) in 250mL volumetric flask, dilute up to the mark with distilled water and then shake to form a uniform solution.

Table -1:

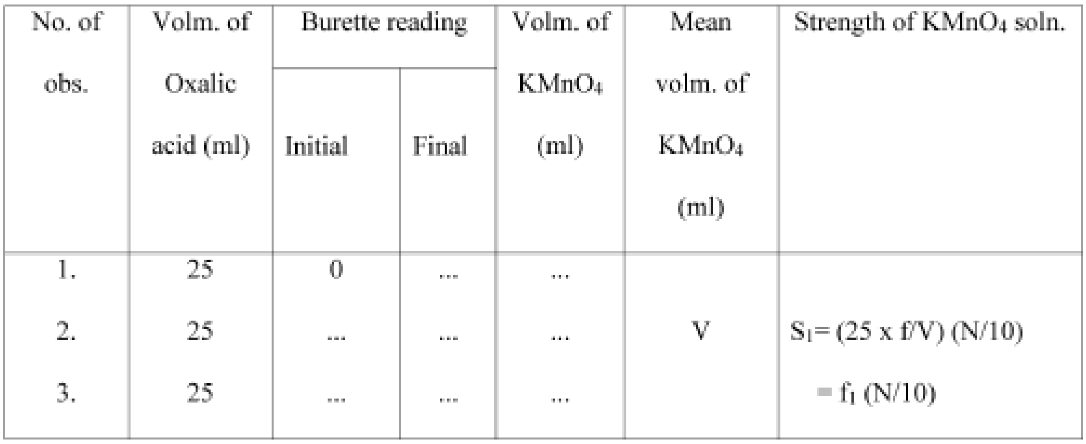
6.3.2 Standardisation of $KMnO_4$ solution against standard oxalic acid solution



Initial weight (g)	Final weight (g)	Amount of oxalic acid taken (g)	Strength of the solution
W_1	W_2	$W_1 - W_2 = W$	$S = W/1.575(N/10)$ $= f\,(N/10)$

Take $KMnO_4$ solution in a burette. Pipette out 25 ml of the standard oxalic acid solution in a 250 ml conical flask. Add 25 ml of 4(N) H_2SO_4 in it and warm the mixture up to 60-70^{0}C. Titrate the solution by S (N/10) $KMnO_4$ solution in hot condition until a faint pink colour stable for 30 sec. Note the volume (V).

Table -2



No. of obs.	Volm. of Oxalic acid (ml)	Burette reading		Volm. of $KMnO_4$ (ml)	Mean volm. of $KMnO_4$ (ml)	Strength of $KMnO_4$ soln.
		Initial	Final			
1.	25	0	...	...	V	$S_1 = (25 \times f/V)\,(N/10)$ $= f_1\,(N/10)$
2.	25	...	...	...		
3.	25	...	...	...		

6.4 Estimation of Ca^{+2}

- Transfer the supplied solution in a 100 ml volumetric flask. Wash the container 4-5 times with distilled water and transfer to the volumetric flask carefully. Make up the volume with distilled water.

- Pipette out 25 ml of the Ca-salt solution in a 250 ml beaker. Diluted to 100 ml with distilled water (i.e., by adding 75 ml of distilled water). Add 1 drop of methyl orange indicator. Add small quantities of NH_4OH solution until the solution smells faintly of NH_3. Then add 2(N) HCl solution dropwise with stirring until a faint pink colour appears, then add 5 ml of conc. HCl. Heat the solution to boiling. To this hot solution add slowly 15-20 ml of 6% ammonium oxalate solution with constant stirring with a glass- rod. Now add NH_4OH (1:1) drop wise until the smell of NH_3 persists. A white precipitation of Ca-oxalate comes down. The beaker is than allowed to stand on low flame on an asbestos board (or on water bath) for 20-30 minutes. The precipitate will settle down leaving a clear solution at the top. Complete precipitation is tested by a few more drops of the ammonium oxalate solution down the inclined side of the beaker.

  The precipitate is carefully filtered off by Whatman 42. Rinse the beaker 4-5 times with hot water. Now wash the filter paper and precipitate by hot water until it is free from oxalate & Cl^-.

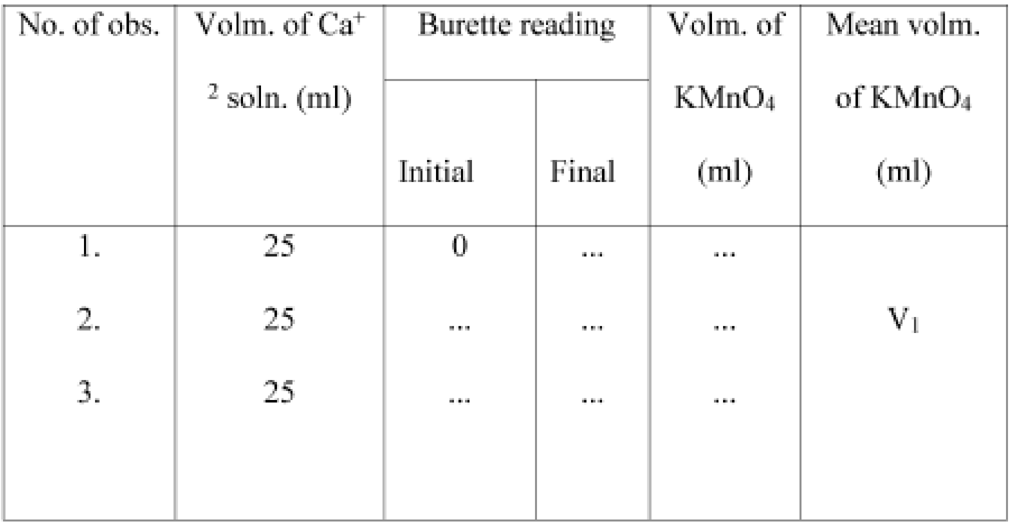
  [To test for oxalate ion : Take about 1 ml of the filtrate in a clean test tube and add few drops of CH_3COOH and few drops of clear $CaCl_2$ solution. Formation of white ppt. indicate the presence of $C_2O_4^=$ in filtrate.

  To test for Cl^- ion: Take about 1 ml of the filtrate in a clean test tube, acidify with HNO_3 then add 1-2 drops of $AgNO_3$ solution. Curdy white ppt. indicates the presence of Cl^- in the filtrate.]

  Place the funnel containing precipitate on a 250 ml conical flask. Pierce the filter paper with a glass rod and wash down the precipitate with a jet of hot water completely in to the conical flask. Boil the mixture. Now add 4(N) H_2SO_4 (i.e., 1:8) into the filter paper to dissolve any adhering oxalate precipitate and wash it down again with hot water. Add excess amount of 4(N) H_2SO_4 to dissolve the precipitate of oxalate if require.

- The solution is diluted to 150 ml with distilled water, head on a asbestos board to about 60-70^{0}C and then titrate with standard $KMnO_4$ solution, until pink colour appears.

Table-3



No. of obs.	Volm. of Ca^{+2} soln. (ml)	Burette reading		Volm. of $KMnO_4$ (ml)	Mean volm. of $KMnO_4$ (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

6.5 Calculation

25 ml of Ca^{+2} solution a” V_1 ml of f_1 (N/10) $KMnO_4$ solution

a” V_1 x f_1 ml of (N/10) $KMnO_4$ solution

1000 ml of (N) $KMnO_4$a” 20 g of Ca^{+2}

1 ml of N/10 $KMnO_4$a” 0.002 g of Ca^{+2}

V_1 x f_1 ml of (N/10) $KMnO_4$ solution a” 0.002 x V_1 x f_1 g of Ca^{+2}

25 ml solution contain 0.002 x V_1 x f_1 g of Ca^{+2}

1000 ml ... . 0.002 x V_1 x f_1 x 40 g of Ca^{+2}

Ca^{+2} present in the solution = 0.002 x V_1 x f_1 x 40 g of Ca^{+2} / lit.

6.6 Conclusion

The estimation of calcium ions (Ca^{2+}) using potassium permanganate ($KMnO_4$) solution is a valuable analytical technique. The method is based on the principles of redox titration, where $KMnO_4$ acts as an oxidizing agent.

A precise quantity of oxalic acid is dissolved in distilled water to prepare 250 ml of N/10 oxalic acid solution. This standard solution serves as a primary standard for the titration.

The prepared $KMnO_4$ solution is standardized using the N/10 oxalic acid solution. The volume of $KMnO_4$ required to reach the endpoint, where a faint pink color persists, is recorded. The standardized $KMnO_4$ solution is then used to titrate the sample containing Ca^{2+}. The calcium in the sample reacts with the oxalic acid to form calcium oxalate, which is subsequently titrated with the $KMnO_4$ solution. The volume of $KMnO_4$ used in this titration is directly proportional to the amount of Ca^{2+} in the sample.

6.7 Some sample Questions

1. What role does $KMnO_4$ play in the redox titration for estimating calcium ions (Ca^{2+})?
2. What solution is used as the primary standard in the titration process?
3. How is the endpoint of the titration with $KMnO_4$ identified?
4. What compound is formed when calcium in the sample reacts with oxalic acid?
5. How the amount of Ca^{2+} in the sample is determined using the $KMnO^4$ solution?
6. What is the underlying principle behind using KMnO„ for the estimation of $Ca^{2}z$ ions?
7. How does the redox reaction between KMnO„ and the analyte help in the estimation process?
8. What are the roles of oxalic acid and KMnO„ in this titration method?
9. Why is it necessary to perform the titration in an acidic medium?
10. Why is oxalic acid used as a standard solution in this method?
11. What is the role of sulfuric acid in the titration process?
12. Why is distilled water used in the preparation of solutions?
13. What is the procedure for standardizing KMnO„ solution using a standard oxalic acid solution?
14. How does the endpoint of the titration appear when using KMnO„ as a titrant?
16. Why is it necessary to standardize KMnO„ solution before using it for estimation?
17. What could cause discrepancies in the standardization process?
18. Describe the complete procedure for the estimation of $Ca^{2}z$ ions using standardized KMnO„ solution.

19. What is the stoichiometric relationship between $KMnO_4$ and Ca^{2+} ions in the titration?
20. How would you calculate the concentration of Ca^{2+} in the sample after titration?
21. What are some potential sources of error in the estimation of Ca^{2+} using this method, and how can they be minimized?

Unit 7 ❒ Estimation of Cu^{2+}iodometrically

7.0 Objectives

- To get the detail practical idea about Iodometric titration.
- Determine the Concentration of Cu^{2+} Ions
- Optimize Iodometric Titration Conditions
- Compare Iodometric Method with Other Analytical Techniques
- Evaluate Sensitivity and Detection Limits
- Identify potential interfering substances and develop strategies to enhance the selectivity of the method.

7.1 Introduction

The estimation of copper ions (Cu^{2}z) in various samples is a critical task in analytical chemistry, with significant applications in environmental monitoring, industrial quality control, and biochemical research. One of the most reliable and widely used methods for determining the concentration of Cu^{2}z ions is iodometric titration. This method is favored due to its high accuracy, sensitivity, and relatively straightforward procedure.

Iodometric titration involves the indirect determination of Cu^{2}z ions through a redox reaction with iodide ions (I{). In an acidic medium, Cu^{2}z ions oxidize iodide ions to iodine (I,), which can be quantitatively analyzed by titration with a standard sodium thiosulfate (Na, S, Of) solution. The end point of the titration is detected by the disappearance of the blue starch-iodine complex, providing a clear and easily observable indication.

This technique is particularly advantageous for its specificity and precision in the presence of various interfering substances. Moreover, iodometric titration of Cu^2z ions is adaptable to a wide range of sample matrices, including water, soil, and biological materials. The methodology can be performed with standard laboratory equipment, making it accessible for routine analytical procedures.

In this study, we will outline the step-by-step procedure for the iodometric estimation of Cu^2z ions, discuss the underlying chemical principles, and evaluate the method's accuracy and reproducibility. The results obtained will underscore the method's efficacy in accurately determining copper concentrations in diverse sample types.

7.2 Estimation of Cu^{2+} iodometrically

7.2.1 Principle

Copper is estimated iodometrically based upon the reaction

$Cu^{+2} + 4\,I^- = 2CuI + I_2$

The precipitation of CuI causes the rise of formal potential of the Cu^{+2}/Cu^+ to about 0.858 Volt from $E^0_{Cu^{+2}/Cu^{+}}$ = 0.15 volt). As a result, Cu^{+2} oxidises I^- to I_2 ($E^0_{I_2/2I^-}$ = 0.54 volt) quantitavely and the liberated iodine is then titrated with standard $Na_2S_2O_3$ solution using starch as indicator. The precipitate of CuI adsorbs some iodine. Ammonium thiocyanate is thus added. The SCN^- ions liberates the adsorbed iodine due to the preferential adsorption over CuI.

7.2.2 Chemicals Required:

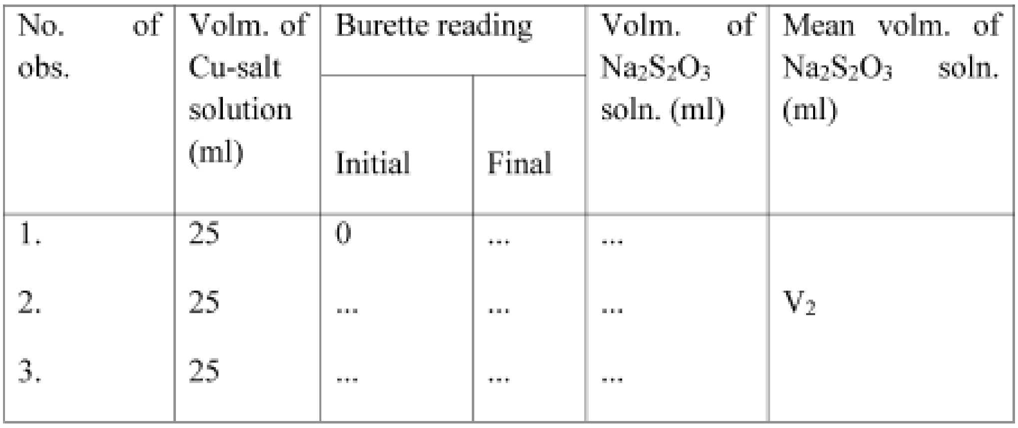
- Standard (N/20) $K_2Cr_2O_7$ solution
- Standard (N/20) $Na_2S_2O_3$ solution
- 4(N) H_2SO_4
- KI solution
- 1% starch solution
- NH_4SCN
- $CuSO_4$ solution

[Dissolve 12.434 g $CuSO_4.5H_2O$ in 100 ml of distilled water and add 1-2 drops of conc. H_2SO_4 to prepare (N) solution. 4-6 ml may be supplied for determination of Cu^{+2}].

7.2.3 Procedure for the estimation of Cu^{+2} using standard thiosulphate solution:

- Transfer the supplied solution in a 100 ml volumetric flask. Wash the container 4-5 times with distilled water and transfer to the volumetric flask carefully. Make up the volume with distilled water.
- Pipette out 25 ml of the copper sulphate solution into 250 ml conical flask. Add dilute solution of NH_4OH (1:1) until a slight permanent precipitate of cupric hydroxide is just formed (with excess of NH_4OH the precipitate dissolves forming a blue colouration). Add 2 ml of glacial acetic acid; the solution will be slightly acidic and will dissolve any precipitate formed. Cool the solution (pH – 3). Add about 1 g of KI, mix it well and cover the flask with a watch glass and allow to stand for 1 minute in dark place. A precipitate appears and the solution becomes brown. Rinse down the sides of the wall of the flask and dilute to about 100 ml. Titrate with standard thiosulphate solution from the burette until the brown colour due to iodine changes to very light yellow. Add 2 ml of starch solution; colour of the solution becomes blue. Continue adding thiosulphate solution from burette slowly with stirring until blue colour begins to fade. Now add about 1-2 g of ammonium thiocyanate. Continue the titration with thiosulphate adding it dropwise with stirring until with one drop, the blue colour is discharged and the colour changes to white. Note the volume of thiosulphate consumed. Repeat the experiment three times.

Table – 3:



No. of obs.	Volm. of Cu-salt solution (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	25	0	...	...	V_2
2.	25	...	...	...	
3.	25	...	...	...	

7.2.4 Calculation:

25 ml Cu^{+2} salt solution a” V_2 ml of f_1 (N/20) $Na_2S_2O_3$ solution

a” V_2 x f_1/20 ml of (N) $Na_2S_2O_3$ solution

We know that, 1000 ml of (N) $Na_2S_2O_3$ a” 63.357 g of copper

[since g. Eq. Wt of Cu = g. Atomic wt./1]

1 ml ... ... a” 0. 063357 g of copper

V_2 x f_1/20 ml of (N) $Na_2S_2O_3$ solution a” 0. 063357 x V_2 x f_1/20 g of copper

25 ml of the cupric salt solution contain 0. 063357 x V_2 x f_1/20 g of copper

1000 ml ... ... 0. 063357 x V_2 x f_1/20 x 40 g of copper

Amount of Cu = 0. 063357 x V_2 x f_1/20 x 40 g/lit.

7.4 Conclusion

The iodometric estimation of Cu^{2}z ions are an essential and reliable technique in analytical chemistry, utilized extensively for its accuracy and sensitivity. This method leverages the redox reaction between Cu^{2}z and iodide ions in an acidic medium to generate iodine, which is then titrated with a standard sodium thiosulfate solution. The clear and observable end point, indicated by the disappearance of the blue starch-iodine complex, underscores the method’s precision.

Our study has detailed the step-by-step procedure, from the preparation of the solutions to the titration process, ensuring a thorough understanding of the methodology. The experiment’s reproducibility was confirmed through multiple trials, demonstrating consistent results.

This titration method’s adaptability to various sample matrices, including water, soil, and biological materials, highlights its versatility and practical application in diverse fields such as environmental monitoring, industrial quality control, and biochemical research. The use of standard laboratory equipment further makes this method accessible for routine analytical procedures.

In conclusion, the iodometric method for Cu^{2}z estimation is both effective and efficient, providing reliable data essential for monitoring and controlling copper concentrations in a wide array of samples.

7.5 Some Sample Questions

Question 1: What is the principle behind the iodometric estimation of Cu^{2+} ions?

Answer: The principle behind the iodometric estimation of Cu^{2+} ions is based on a redox reaction where Cu^{2+} ions oxidize iodide ions (I^-) to iodine (I_2) in an acidic medium. The liberated iodine is then titrated with a standard sodium thiosulfate ($Na_2S_2O_3$) solution. The end point is indicated by the disappearance of the blue starch-iodine complex, which provides a clear visual cue for the completion of the reaction.

Question 2: Why is ammonium thiocyanate added during the titration process?

Answer: Ammonium thiocyanate is added to the reaction mixture to liberate any iodine that is adsorbed onto the precipitate of copper(I) iodide (CuI). This ensures that all the iodine is available for reaction with the sodium thiosulfate solution, thereby improving the accuracy of the titration.

Question 3: What are the key chemicals required for the iodometric estimation of Cu^{2+} ions?

Answer: The key chemicals required for the iodometric estimation of Cu^{2+} ions include:

- Standard (N/20) potassium dichromate ($K_2Cr_2O_7$) solution
- Standard (N/20) sodium thiosulfate ($Na_2S_2O_3$) solution
- 4(N) sulfuric acid (H_2SO_4)
- Potassium iodide (KI) solution
- 1% starch solution
- Ammonium thiocyanate (NH_4SCN)
- Copper sulfate ($CuSO_4$) solution

Question 4: How is the end point of the iodometric titration of Cu^{2+} detected?

Answer: The end point of the iodometric titration is detected by the disappearance of the blue color of the starch-iodine complex. Initially, the solution turns brown due to the formation of iodine. Upon titration with sodium thiosulfate, the brown colour fades to a light yellow. Adding starch solution turns the solution blue. Continued titration until the blue color just disappears, indicating the end point.

Question 5: Why is it important to perform the titration in an acidic medium?

Answer: It is important to perform the titration in an acidic medium because the reaction between Cu^{2}z ions and iodide ions to form iodine (I) occurs efficiently in such conditions. The acidic medium ensures that the iodide ions are oxidized to iodine, which is necessary for the subsequent titration with sodium thiosulfate.

Question 6: What is the role of starch in the iodometric titration?

Answer: Starch acts as an indicator in the iodometric titration. It forms a blue complex with iodine, which makes it easier to observe the end point of the titration. When the blue color disappears, it indicates that all the iodine has reacted with the sodium thiosulfate, signifying the end point.

Question 7: How is the concentration of copper ions calculated from the titration data?

Answer: The concentration of copper ions is calculated using the volume of sodium thiosulfate solution required to reach the end point. The calculation involves the following steps:

- Determine the mean volume of sodium thiosulfate solution used (V,).
- Use the relationship between the volumes of copper sulfate solution and sodium thiosulfate solution to find the concentration of copper.
- Apply the formula: Amount of Cu=0.063357×V2×f120×40 g/L\text{Amount of Cu} = 0.063357 \times V, \times \frac{f• }{20} \times 40 \, \text{g/L}Amount of Cu=0.063357×V2 ×20f1 ×40g/L where f1f• f1 is the factor of the thiosulfate solution.

Question 8: What are some advantages of the iodometric method for estimating Cu^{2}z ions?

Answer: Some advantages of the iodometric method for estimating Cu^{2}z ions include:

- High accuracy and sensitivity
- Clear and easily observable end point
- Specificity and precision, even in the presence of interfering substances

- Adaptability to various sample matrices (water, soil, biological materials)
- Utilization of standard laboratory equipment, making it accessible for routine use.

Unit 8 ❒ Estimation of Cr^{3+} using $K_2Cr_2O_7$ solution

8.0 Objectives

- Determine the concentration of Cr^3z ions in a given sample accurately and precisely using potassium dichromate (K, Cr, O‡) as the titrant.
- Understand the redox reaction mechanism between Cr^3z ions and K, Cr, O‡ in an acidic medium.
- Standardize the potassium dichromate solution to ensure accurate and reproducible titration results.
- Perform titration to the endpoint, ensuring the complete reaction of Cr^3z with K, Cr, O‡ , indicated by a distinct color change or with the use of a suitable indicator.
- Calculate the concentration of Cr^3z ions in the sample based on the volume of K, Cr, O‡ solution consumed during the titration.
- Evaluate the accuracy and reproducibility of the method through multiple trials and comparison with known standards.
- Interpret the results in the context of environmental monitoring, industrial quality control, and other relevant applications.
- Assess the potential interferences from other ions or substances present in the sample and determine the method's selectivity for Cr^3z ions.
- Develop proficiency in the practical skills and techniques associated with

redox titration and analytical chemistry procedures.

8.1 Introduction

The estimation of trivalent chromium ions (Cr^{3}z) in various samples is a critical task in analytical chemistry, particularly due to chromium's significant industrial applications and environmental impact. Accurate determination of Cr^{3}z concentration is essential for monitoring pollution levels, ensuring compliance with environmental regulations, and maintaining quality control in industrial processes.

One of the most reliable and widely used methods for determining the concentration of Cr^{3}z ions is through redox titration with potassium dichromate (K, Cr, O‡). This method is favored for its high precision, sensitivity, and straightforward procedure. Potassium dichromate acts as a strong oxidizing agent, and in an acidic medium, it effectively oxidizes Cr^{3}z to CrO„ ^{2}{ . The endpoint of the titration can be observed by a distinct color change or with the help of a suitable indicator, making it easy to detect.

This technique is particularly advantageous due to its specificity and precision, even in the presence of various interfering substances. The methodology is adaptable to a wide range of sample matrices, including water, industrial effluents, and biological materials. Moreover, the use of standard laboratory equipment makes this method accessible for routine analytical procedures.

In this study, we will outline the step-by-step procedure for the estimation of Cr^{3}z ions using K, Cr, O‡ solution, discuss the underlying chemical principles, and evaluate the method's accuracy and reproducibility. The results obtained will highlight the method's efficacy in accurately determining chromium concentrations in diverse sample types**.**

8.2 Estimation of Cr3+ using K2Cr2O7 solution

8.2.1 Principle:

Ammonium persulphate quantitatively oxidised Cr^{+3} to $Cr_2O_7^{=}$ in sulphuric acid medium in presence of $AgNO_3$ as catalyst. $Cr_2O_7^{=}$ so formed is then estimated by adding measured excess of standard Mohr's salt solution. the excess Mohr's salt being back titrated with the standard $K_2Cr_2O_7$ solution using Barium diphenylsulphonate (BaDS) as indicator.

$$2Cr^{+3} + 3S_2O_8^{-3} + 7H_2O = Cr_2O_7^{=} + 6SO_4^{-2} + 14H^{+}$$

$$Cr_2O_7^{=} \ + \ 6Fe^{+2} \ + \ 14H^+ \ = \ 2Cr^{+3} \ + \ 6Fe^{+3} \ + \ 7H_2O$$

2 moles Cr^{+3} a” 1 mole of $Cr_2O_7^{-2}$ a” 6 moles of Fe^{+2}

Or, 1 mole Fe^{+2} a” 1/6 mole of $K_2Cr_2O_7$ a” 1/3 mole mole of Cr a” 1 equivalent

1000 ml (N) Mohr’s salt solution a” 49.03 g of $K_2Cr_2O_7$ a” 51.996/3 or 17.332 g of Cr

8.2.2 Chemicals Required:

- Standard 250 ml (N/20) $K_2Cr_2O_7$ solution
- Standard 250 ml (N/20) Mohr’s salt solution
- Conc. H_2SO_4
- 10% ammonium persuphate solution
- 1.5% $AgNO_3$ solution
- Syrupy H_3PO_4
- Barium diphenylsulphonate indicator (BaDS)

8.2.3 Procedure:

- Prepare standard 250 ml S (N/20) $K_2Cr_2O_7$ solution [0.6129 g $K_2Cr_2O_7$ in 250 ml water]
- Prepare S (N/20) $Na_2S_2O_3$ solution [Dissolve 12.5 – 13 g of $Na_2S_2O_3$.$5H_2O$ in 500 ml of boiled distilled water and diluted to 1 litre. Add 3-4 drops of $CHCl_3$ to improve the stability of the solution and store in a amber colour bottle].
- Transfer the supplied solution in 100 ml of volumetric flask. Wash the container carefully. Dilute the solution with distilled water up to the mark.
- Standardize the Mohr’s salt solution by standard $K_2Cr_2O_7$ solution using usual procedure

Take standard $K_2Cr_2O_7$ solution in burette. Pipette out 25 ml of Mohr’s salt (ferrous salt) solution in a 250 ml conical flask. Add 150 ml of distilled water. Now pour 5 ml conc. H_2SO_4 and 5 ml of syrupy H_3PO_4. Add 2-3 drops of BaDS indicator. Titrate with $K_2Cr_2O_7$ solution with constant shaking till red-violet or purple colour appeared. Note the burette reading. Repeat the experiment three times. Repeat the experiment thrice.

- **Estimation of Cr^{+3}**

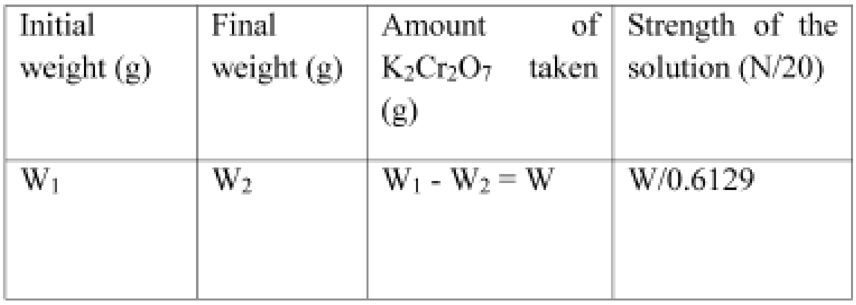
- Oxidation: Pipette out 25 ml of prepared stock solution in 500 ml conical flask. Add 10 ml 1.5% $AgNO_3$ solution and 30 ml of 10% ammonium persuphate solution. Now carefully pour 8 ml of conc. H_2SO_4. Stir the mixture gently. Cover the mouth of the conical flask with watch glass. Heat the mixture slowly and then boil it for about 20 minutes.

- Back titration of the excess Mohr's salt solution: Cool the solution. Add 100 ml of distilled water. Add 50 ml of the standard Mohr's salt solution with a pipette. Add 3 ml of syrupy H_3PO_4 and 3-4 drops of Barium diphenylsulphonate indicator (BaDS). Titrate the excess Mohr's salt with standard S (N/20) $K_2Cr_2O_7$ solution. [mentioned above].

- **Experimental Results:**

Table-1: Preparation of standard 250 ml S (N/20) $K_2Cr_2O_7$ solution

Strength of the $K_2Cr_2O_7$ solution = W/0.6129 x N/20 = W/0.6129 x 20 (N) = S (N)

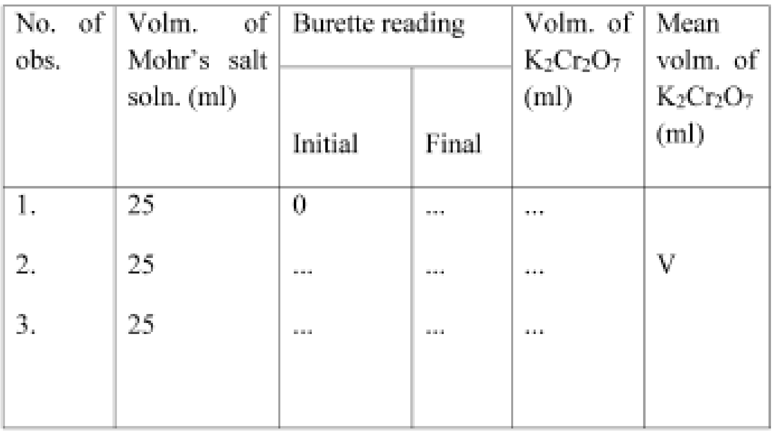


Initial weight (g)	Final weight (g)	Amount of $K_2Cr_2O_7$ taken (g)	Strength of the solution (N/20)
W_1	W_2	$W_1 - W_2 = W$	W/0.6129

Table -2: Standardization of S (N/20) Mohr's salt solution:

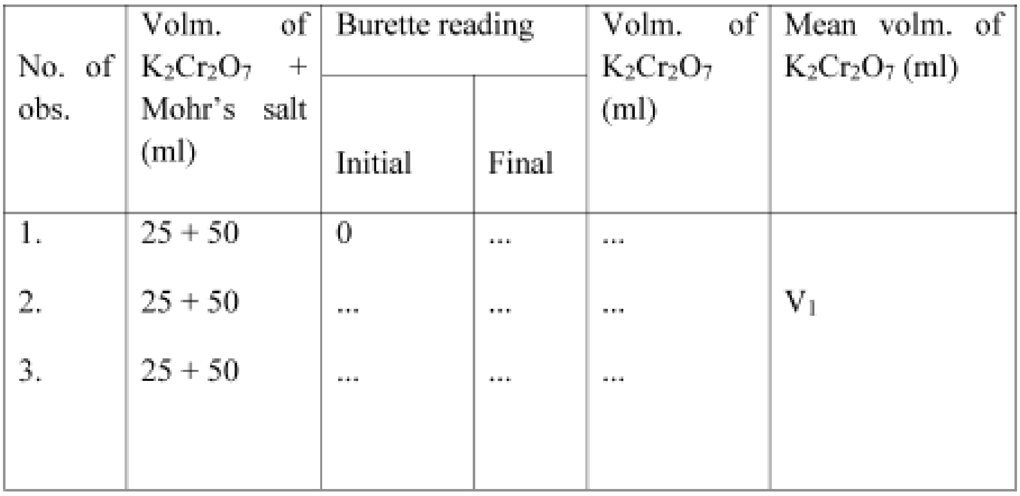
Strength of Mohr's salt solution = V x S / 25 (N) = S_1 (N)

Table-3:Estimation of Cr^{+3} :



No. of obs.	Volm. of Mohr's salt soln. (ml)	Burette reading		Volm. of $K_2Cr_2O_7$ (ml)	Mean volm. of $K_2Cr_2O_7$ (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V
3.	25	...	...	...	

- **Calculation:**
  - Strength of $K_2Cr_2O_7$ solution = S (N)



No. of obs.	Volm. of $K_2Cr_2O_7$ + Mohr's salt (ml)	Burette reading		Volm. of $K_2Cr_2O_7$ (ml)	Mean volm. of $K_2Cr_2O_7$ (ml)
		Initial	Final		
1.	25 + 50	0	...	...	V_1
2.	25 + 50	...	...	...	
3.	25 + 50	...	...	...	

  - Strength of Mohr's salt solution = S_1 (N)
- Estimation of Cr:

25 ml Mohr's salt solution a” V ml S (N) $K_2Cr_2O_7$ solution

25 ml Mohr's salt solution + 50 ml Mohr's salt solution a” V_1 ml S (N) $K_2Cr_2O_7$ solution

Mohr's salt consumed by $K_2Cr_2O_7$ in 25 ml diluted stock solution a” (2V – V_1) ml S(N) $K_2Cr_2O_7$ solution

a” (2V – V_1) x S ml (N) $K_2Cr_2O_7$ solution
a” (2V – V_1) x S ml (N) Mohr's salt solution

We have, 1000 ml (N) Mohr's salt solution a” 17.332 g of Cr
(2V – V_1) x S ml (N) Mohr's salt solution a” 0.017332 x (2V – V_1) x S g of Cr
25 ml of the stock solution contain 0.017332 x (2V – V_1) x S g of Cr
1000 ml ... ... 0.017332 x (2V – V_1) x S x 40 g of Cr
Amount of Cr present = 0.017332 x (2V – V_1) x S x 40 g/ lit.

- **Conclusion**

The estimation of Cr3+ using $K_2Cr_2O_7$ solution is a reliable and precise analytical method. The process involves the reduction of dichromate ions to chromium ions in acidic conditions, which can be quantitatively measured. This method provides high sensitivity and specificity for Cr^{3+} ions, making it suitable for various applications in environmental and industrial chemistry. The results obtained from this method are reproducible and accurate, ensuring its utility in both research and practical applications for the determination of chromium concentration in diverse samples.

8.5 Some Sample Questions

Q-1: In permanganometry no external indicator is used- why?

Ans: $KMnO_4$ act as self indicator for its pink colour.

Q-2: What is the formula of Mohr's salt?

Ans: $(NH_4)_2SO_4.FeSO_4.6H_2O$

Q-3: What type of salt it is?

Ans: It is double salt.

Q-4: Why $KMnO_4$ is not use as Primary standard?

Ans: a) It is not available in pure sate.

b) Trace of organic matters present in distilled water helps to decomposition of $KMnO_4$ in solution.

$4MnO_4^- + 2H_2O = 4MnO_2 + 4OH^- + 3O_2$

c) $KMnO_4$ solution decomposes in bright sun light.

d) Solid MnO_2 obtained in reaction also catalyse the decomposition of $KMnO_{4.}$

Q-5: Why $KMnO_4$ is behaves more powerful oxidising agent in acid medium compare to other medium?

Ans: $KMnO_4$ act as a powerful oxidant in acid medium due to its higher standard reduction potential value. But the potential value falls and thus oxidising power decreases with decrease of concentration of H^+ ie., increase of pH value of the medium.

In acid medium : $MnO_4^- + 8H^+ + 5e \quad Mn^{+2} + 4H_2O$ $E^0 = 1.51V$

In neutral medium: $MnO_4^- + 2H_2O + 3e \quad MnO_2 + 4OH^-$ $E^0 = 0.59V$

In alkaline medium: $MnO_4^- + e \quad MnO_4^{-2}$ $E^0 = 0.56V$

Q-6: What is the basic criteria of choosing indicator in redox titration?

Ans: The standard reduction potential of the indicator should be higher than reductant and lower that of the oxidant.

Q-7: Why removal of mineral acid is essential for precipitation of Ca- oxalate?

Ans: Because Ca-oxalate is soluble in mineral acid.

Q-8: Why in the titration of oxalic acid with $KMnO_4$ pink colour disappears slowly at the beginning but rapidly afterwards?

Ans: The reaction between oxalic acid and $KMnO_4$ is slow; so the pink colour disappears slowly at the beginning, but once the reaction starts, Mn^{+2} formed and accelerate the rate of reaction.

Q-9: Why this reaction is carried out at hot condition?

Ans: To make the reaction rate fast.

Q-10: What is Zimmernmann – Reinhardt (Z.R) solution?

Ans: The solution consists of $MnSO_4$, H_3PO_4 and H_2SO_4.

Module –II

Organic Chemistry

Unit-9 ❒ Separation of Organic Compounds

9.0 Objectives

- To separate components of a binary solid mixture based on their solubility using common laboratory reagents such as cold and hot water, dilute HCl, dilute NaOH, and dilute NaHCOƒ .
- To identify and utilize the solubility differences of the mixture components in the selected reagents for effective separation.

- To purify one of the separated components through crystallization.
- To determine the melting point of the purified component to confirm its identity and purity.
- To apply the separation techniques to mixtures like:
- Benzoic acid/p-Toluidine
- p-Nitrobenzoic acid/p-Aminobenzoic acid
- p-Nitrotoluene/p-Anisidine

9.1 Introduction

The separation of organic compounds is a fundamental process in chemistry, often required to isolate and purify individual components from a mixture. One of the most effective methods for achieving this involves exploiting the differences in solubility of the compounds in various solvents. By using common laboratory reagents such as cold and hot water, dilute hydrochloric acid (HCl), dilute sodium hydroxide (NaOH), and dilute sodium bicarbonate (NaHCOƒ), it is possible to selectively dissolve and separate the components of a binary solid mixture.

This method leverages the unique solubility properties of each compound in different solvents. For instance, acidic compounds are more soluble in basic solutions, while basic compounds are more soluble in acidic solutions. By carefully choosing the appropriate solvent, one can achieve effective separation of the components. Once separated, the compounds can be further purified through crystallization, a technique that allows for the removal of impurities and enhances the purity of the isolated compound. The determination of the melting point of the purified component serves as a confirmation of its identity and purity.

This approach is particularly useful for separating mixtures such as benzoic acid and p-toluidine, p-nitrobenzoic acid and p-aminobenzoic acid, and p-nitrotoluene and p-anisidine. Each of these mixtures contains components with distinct solubility profiles, making them ideal candidates for separation based on solubility differences. Through careful application of these techniques, chemists can achieve high-purity separations essential for further analysis and application.

9.2 Separation of organic compounds based on solubility

The separation of organic compounds can be efficiently achieved by leveraging their solubility differences in various solvents. Common laboratory reagents such as cold and hot water, dilute hydrochloric acid (HCl), dilute sodium hydroxide (NaOH), and dilute sodium bicarbonate (NaHCOƒ) are used to selectively dissolve and separate components of a binary solid mixture. Once separated, the components can be purified through crystallization, and their identity and purity can be confirmed by determining their melting points. This method is applicable to various mixtures, including benzoic acid/p-toluidine, p-nitrobenzoic acid/p-aminobenzoic acid, and p-nitrotoluene/p-anisidine.

9.3 Separation by using common laboratory reagents like water (cold, hot), dil. HCl, dil. NaOH, dil. $NaHCO_3$

Based on solubility, you can identify and differentiate between various classes of compounds using common laboratory reagents such as water (cold and hot), dilute hydrochloric acid (HCl), dilute sodium hydroxide (NaOH), and dilute sodium bicarbonate (NaHCO3). Here’s a detailed approach to how these reagents can be used:

Water (Cold and Hot)

- **Cold Water**: Polar compounds such as many ionic salts (e.g., NaCl, KNO_3) and some low molecular weight organic compounds (e.g., ethanol, acetone) are generally soluble in cold water. Non-polar compounds (e.g., hydrocarbons) are usually insoluble.

- **Hot Water**: Heating can increase the solubility of many compounds. For instance, compounds like benzoic acid and certain organic crystals dissolve in hot water due to increased molecular motion and interaction with water molecules.

Dilute Hydrochloric Acid (HCl)

- **Acid-Soluble Compounds**: Compounds that react with HCl include many carbonates, bicarbonates, and metal oxides, forming soluble chlorides. For instance, calcium carbonate reacts with HCl to produce calcium chloride, water, and carbon dioxide gas. $CaCO_3$+2HCl’!$CaCl_2$+H_2O+CO_2‘!\

- **Acid-Resistant Compounds**: Many organic compounds, especially hydrocarbons and high molecular weight esters, do not react with or dissolve in dilute HCl.

Dilute Sodium Hydroxide (NaOH)

- **Base-Soluble Compounds**: Compounds that are acidic in nature often dissolve in dilute NaOH. For example, phenols and carboxylic acids react with NaOH to form water-soluble salts. $C_6H_5OH+NaOH$’!$C_6H_5ONa+H_2O$

- **Base-Resistant Compounds**: Non-acidic compounds like most hydrocarbons and alcohols typically do not react with or dissolve in dilute NaOH.

Dilute Sodium Bicarbonate ($NaHCO_3$)

- **Weak Base Soluble Compounds**: Sodium bicarbonate is a weaker base compared to NaOH. It reacts with stronger acids like carboxylic acids to form carbon dioxide gas, water, and a salt. $RCOOH+NaHCO_3$’!$RCOONa+H_2O+CO_2$‘!
- **Base-Resistant Compounds**: Compounds that do not have strong acidic properties (e.g., alcohols, phenols) generally do not react with $NaHCO_3$.

9.4 Separation

9.4.1 Crystallization Techniques

Solid organic compounds when obtained from any chemical reaction or mixture, are usually contaminated with small amount of other compounds, known as impurities, which are produced or mixed along with the desired product. The purification of impure crystalline compounds is usually effected by crystallization from a suitable solvent or mixture of solvents.

The purification of solids by crystallization is based upon differences in their solubility in a given solvent or mixture of solvents. The crystallization process consists of the following sequential process:

- Dissolve the impure substance in some suitable solvent at or near the boiling point.
- Filter the hot solution to remove insoluble materials or dust if any present.
- Evaporate the solution to concentrate the mixture and then cool thus causing the dissolved substance to crystallize out.
- Separate the crystals from the supernatant solution (i.e, mother-liquor).
- The resulting solid, after drying, is tested purity by determining melting. point.

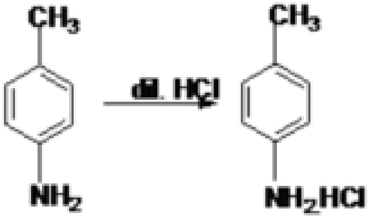
List of common solvents for crystallization:

Solvent	Boiling .Point (^0C)
Water	100
Methanol	64.5
Ethanol	78
Acetone	56
Chloroform	61
Benzene	80

9.5 Separation of p-Toluidine /Benzoic acid

9.5.1 Principle:

It is a mixture of two compounds of different nature. One is acidic and other basic in nature. P- Toludine is basic in nature so it is soluble in dil. HCl solution on other hand benzoic acid is acidic and thus soluble in alkaline solution.



P-Toluidine and benzoic acid in ether

Extraction with aqueous HCl solution

Aqueous layer containing
p- toluidine hydrochloride

Ether layer contain
Benzoic acid

Hydrolysis with dil.NaOH

Drying and evaporation

Bezoic acid

Discard the
Aqueous layer

Ether layer drying and
evaporation

p- Toluidine

9.5.2 Procedure

The procedural instructions are given below in sequential order. You are expected to go through the complete procedure and prepare a broad mental outline of the same.

1. Clean the separating funnel first with soap water and then with plenty of distilled water. Grease the stopcock to ensure its smooth movement.
2. Close the stopcock and mount the separatory funnel in the ring support, on an iron stand. If the ring support is not available, you may use a tripod stand for the purpose.
3. Weigh 2 g of the mixture on a rough weighing balance and dissolve it in about 30 ml of solvent ether in a conical flask.
4. Transfer the solution to the separatory funnel after ensuring that the stopcock is closed. Wash the conical flask with a little (5 mL) of ether and pour this also into the separatory funnel. This ensures complete transfer of the mixture.
5. Add about 20 ml of 2 (N) hydrochloric acid solution to the solution.
6. Gently swirl the contents of the funnel to mix them. Release the pressure build up inside the flask. This pressure is due to the evaporation of highly volatile ether. To release the pressure, carefully turn the funnel upside down then the stopper may be cautiously open and then closed. You will hear the sound of escaping vapours.
7. Allow the mixture to stand in the funnel (on the ring support) until the two immiscible layers are separated. .
8. Remove the stopper and draw off the lower layer into a 100 ml conical flask labelled ‘A’
9. Put additional 5 ml of H_20 in the funnel, shake the contents, allow the layers to separate and draw off the lower layer (water layer) again in flask ‘A’.
10. Pour about 15 ml of saturated aqueous solution of sodium chloride in the separatory funnel shake vigorously for about a minute and allow the layers to separate. Draw out the lower layer and discard it.
11. Place little amount of anhydrous Na_2SO_4 to dehydrate the ether layer.
12. Pour the ether layer into a conical flask labeled ‘B’.

9.5.3 Recovery Of Separated Compounds

By following the above procedure, you will obtain two flasks containing the separated compounds.

Flask 'A': p-toluidine as p-toluidine hydrochloride in water.

Flask 'B' : Benzoic acid in ether.

The desired compounds can be obtained as follow:

Recovery of p-toluidine from Part A (water layer): As said above p-toluidine can be recovered by hydrolysing the solution with aqueous alkali. Take flask 'A' containing the solution of p-toluidine hydrochloride and add dilute NaOH solution dropwise into it with constant shaking. Continue addition till the solution becomes alkaline. This can be checked with the help of a pH paper. When pH of the solution approaches 10, you may see the separation of p-toluidine as a solid. It may so happen that you may get the solid even after adding little more of NaOH solution. This can be because of a low melting point of toluidine (43°C).

If you get the solid, filter it and dry the crystals in the folds of filter paper. Report the amount of p-toluidine obtained and determine the m.p.

If you get oily mass or emulsion instead of solid then proceed with the process given below.

Transfer the above solution from flask 'A' to a separatory funnel mounted on a ring stand. Put about 20 ml of ether into it and gently swirl it so as to dissolve any p-toluidine droplets sticking on the walls. Transfer this ether also to the separatory funnel. Gently swirl the separatory funnel to extract p-toluidine into ether. Keep the funnel for some time so as to allow the layers to separate. Collect the aqueous layer again in the flask 'A' and pour the ethereal layer to flask labelled 'C'. Repeat the process with another 20 ml of solvent ether.

Dry the ethereal fraction in flask 'C' by putting in some anhydrous sodium sulphate crystals. Decant the ether solution from flask 'C' into another flask. Put about 5 ml of ether into flask 'C' and thoroughly rinse the flask along with drying agent. Wait for a minute or two and mix this ether with the previous lot by completely decanting it. Take care not to transfer the drying agent. Evaporate the ether on a steam bath, or preferably distil it.

Recovery of Benzoic acid from Part B (ether layer): Evaporate the ether solution from flask 'B' by placing it over a steam bath. Scratch the solid with a neat spatula and weigh it. Report the amount of Benzoic aci obtained and save the sample and determine m.p.

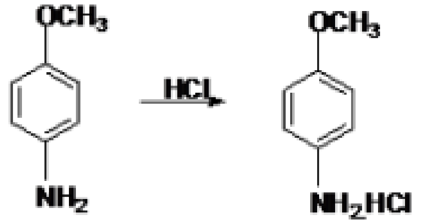
Crystallisation: Take the benzoic acid in a beaker. Dissolve it in minimum volume of distilled water by heating. Now add drop by drop distilled water to make the solution turbid. Boil the mixture till it becomes transparent. Filter the solution in hot condition. Cool the filtrate.

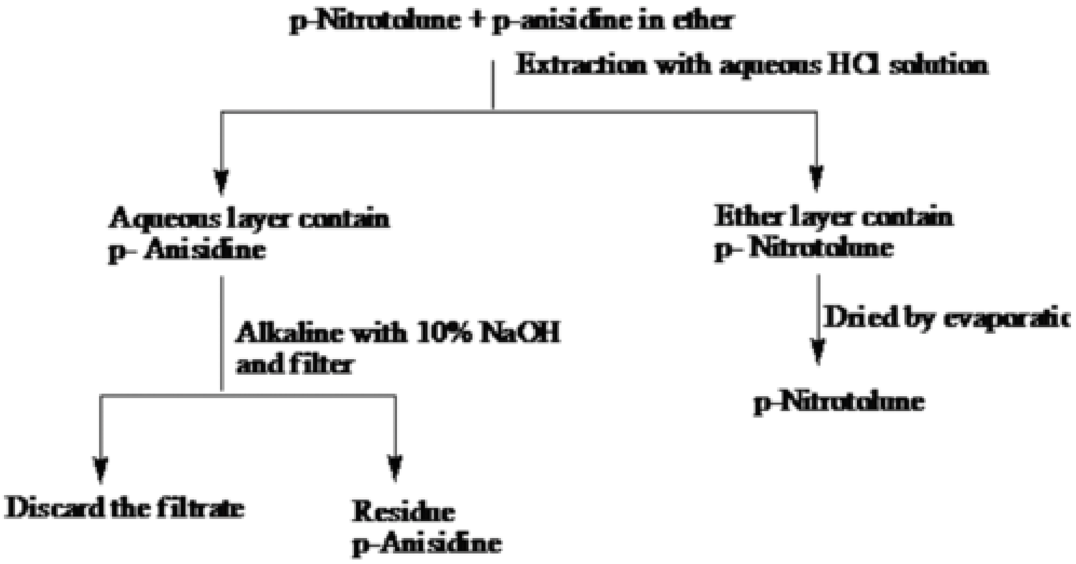
Needle shape crystals of benzoic acid are separated out. Filter, dry and collect the product and note the m.p. (121.5^0C)

9.6 Separation of p-Nitrotolune / p- Anisidine

9.6.1 Principle

It is a mixture of two compounds of different nature. One is neutral and other basic in nature. P- Anisidine is basic in nature so it is soluble in dil. HCl solution on other hand p- Nitrotolune is neutral and thus insoluble in acid.





9.6.2 Procedure:

The procedural instructions are given below in sequential order. You are expected to go through the complete procedure and prepare a broad mental outline of the same.

1. Clean the separating funnel first with soap water and then with plenty of distilled water. Grease the stopcock to ensure its smooth movement.

2 Close the stopcock and mount the separatory funnel in the ring support, on an iron stand. If the ring support is not available, you may use a tripod stand for the purpose.

3. Weigh 2 g of the mixture on a rough weighing balance and dissolve it in about 30 ml of solvent ether in a conical flask.

4. Transfer the solution to the separatory funnel after ensuring that the stopcock is closed. Wash the conical flask with a little (5 ml) of ether and pour this also into the separatory funnel. This ensures complete transfer of the mixture.

5 Add about 20 ml of 2 (N) hydrochloric acid solution to the solution.

6. Gently swirl the contents of the funnel to mix them. Release the pressure build up inside the flask. This pressure is due to the evaporation of highly volatile ether. To release the pressure, carefully turn the funnel upside down then the stopper may be cautiously open and then closed. You will hear the sound of escaping vapours.

7. Allow the mixture to stand in the funnel (on the ring support) until1 the two immiscible layers are separated. .

8. Remove the stopper and draw off the lower layer (water layer) into a 100 ml conical flask labelled 'A'

9. Put additional 5 ml of H_20 in the funnel, shake the contents, allow the layers to separate and draw off the lower layer again in flask 'A'.

10. Pour about 15 ml of saturated aqueous solution of sodium chloride in the separatory funnel shake vigorously for about a minute and allow the layers to separate. Draw out the lower layer and discard it.

11. Place little amount of anhydrous Na_2SO_4 to dehydrate the ether layer.

12. Pour the ether layer into a conical flask labelled 'B'.

9.6.3 Recovery of Separated Compounds:

By following the above procedure, you will obtain two flasks containing the separated compounds.

Flask 'A': p-Anisidine as p-Anisidine hydrochloride in water.

Flask 'B': p-Nitrotolune in ether.

The desired compounds can be obtained as follow:

Recovery of p-Anisidine from part A: As said above p-Anisidine can be recovered by hydrolyzing the solution with aqueous alkali. Take flask 'A' containing the solution of p-Anisidine hydrochloride and add dilute NaOH solution dropwise into it with constant shaking. Continue addition till the solution becomes alkaline. This can be checked with the help of a pH paper. When pH of the solution approaches 10, you may see the separation of p-Anisidine as a solid. It may so happen that you may get the solid even after adding little more of NaOH solution. This can be because of a low melting point of p-Anisidine.

If you get the solid, filter it and dry the crystals in the folds of filter paper. Report the amount of p-Anisidine obtained and determine the m.p.

If you get oily mass or emulsion instead of solid, then proceed with the process given below.

Transfer the above solution from flask 'A' to a separatory funnel mounted on a ring stand. Put about 20 ml of ether into it and gently swirl it so as to dissolve any p-Anisidine droplets sticking on the walls. Transfer this ether also to the separatory funnel. Gently swirl the separatory funnel to extract p-Anisidine into ether. Keep the funnel for some time so as to allow the layers to separate. Collect the aqueous layer again in the flask 'A' and pour the ethereal layer to flask labeled 'C'. Repeat the process with another 20 ml of solvent ether.

Dry the ethereal fraction in flask 'C' by putting in some anhydrous sodium sulphate crystals. Decant the ether solution from flask 'C' into another flask. Put about 5 ml of ether into flask 'C' and thoroughly rinse the flask along with drying agent. Wait for a minute or two and mix this ether with the previous lot by completely decanting it. Take care not to transfer the drying agent. Evaporate the ether on a steam bath, or preferably distil it.

Recovery of p- Nitrotolune from part B: Evaporate the ether solution from flask 'B' by placing it over a steam bath. Scratch the solid with a neat spatula and weigh it. Report the amount of p- Nitrotolune obtained and save the sample and determine m.p.

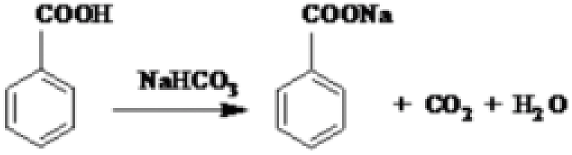
Crystallization: Take the p- Nitrotolune and p- Anisidine in two separate beakers. Dissolve it in minimum volume of alcohol by heating. Now add drop by drop distilled water to make the solution turbid. Cool, filter, dry and collect the product and note the m.p.

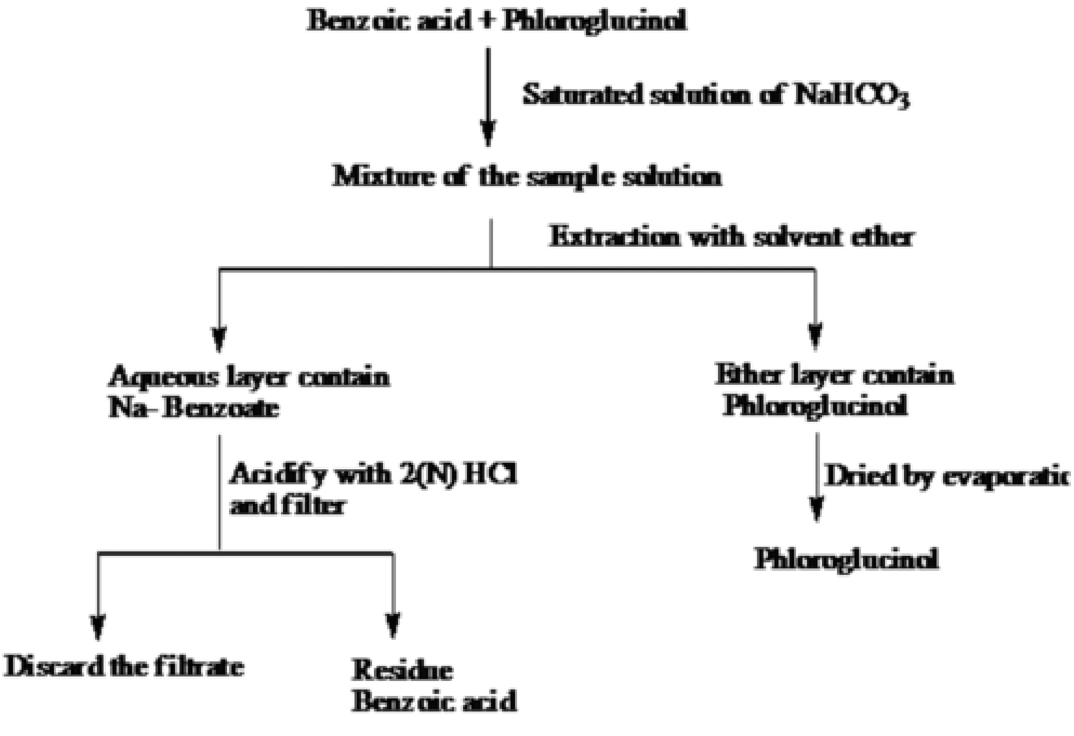
[Melting Point of p- Anisidine is 57^0C and p- Nitrotolune is 52^0C]

9.7 Separation of Benzoic acid / Phloroglucinol (3,5-dihydroxy phenol)

9.7.1 Principle

It is a mixture of two compounds of different nature. One is strong acid compare to other. Benzoic acid is stronger than phloroglucinol for this reason benzoic acid reacts with $NaHCO_3$ to produce sodium benzoate but phloroglucinol remain unreacted.





9.7.2 Procedure:

The procedural instructions are given below in sequential order. You are expected to go through the complete procedure and prepare a broad mental outline of the same.

1. Clean the separating funnel first with soap water and then with plenty of distilled water. Grease the stopcock to ensure its smooth movement.

2 Close the stopcock and mount the separatory funnel in the ring support, on an iron stand. If the ring support is not available, you may use a tripod stand for the purpose.

3. Weigh 2 g of the mixture on a rough weighing balance and take the whole mixture in a 250 ml beaker.

4. Now add saturated solution of sodium bicarbonate slowly by stirring till all the CO_2 is liberated.

4. Transfer the solution to the separatory funnel after ensuring that the stopcock is closed. Wash the conical flask with a little (5 ml) of ether and pour this also into the separatory funnel. This ensures complete transfer of the mixture.

5 Add about 30 – 40 ml ether to the solution.

6. Gently swirl the contents of the funnel to mix them. Release the pressure build up inside the flask. This pressure is due to the evaporation of highly volatile ether. To release the pressure, carefully turn the funnel upside down then the stopper may be cautiously open and then closed. You will hear the sound of escaping vapours.

7. Allow the mixture to stand in the funnel (on the ring support) until the two immiscible layers are separated.

8. Remove the stopper and draw off the lower layer (water layer) into a 100 ml conical flask labelled ‘A’

9. Put additional 5 ml of H_20 in the funnel, shake the contents, allow the layers to separate and draw off the lower layer again in flask ‘A’.

10. Pour about 15 ml of saturated aqueous solution of sodium chloride in the separatory funnel shake vigorously for about a minute and allow the layers to separate. Draw out the lower layer and discard it.

11. Place little amount of anhydrous Na_2SO_4 to dehydrate the ether layer.

12. Pour the ether layer into a conical flask labelled ‘B’.

9.7.3 Recovery of Separated Compounds:

By following the above procedure, you will obtain two flasks containing the separated compounds.

Flask ‘A’: Benzoic acid as sodium benzoate in water.

Flask ‘B’: Phloroglucinol in ether.

The desired compounds can be obtained as follow:

Recovery of Benzoic acid from part A: The aqueous layer in flask ‘A’, which contains the sodium salt of benzoic acid, is now worked up on by adding dil. HCl to neutralize sodium salt. When neutralization is complete filtered and dried.

Crystallisation: Take the benzoic acid in a beaker. Dissolve it in minimum volume of distilled water by heating. Now add drop by drop distilled water to make the solution turbid. Boil the mixture till it becomes transparent. Filter the solution in hot condition. Cool the filtrate.

Needle shape crystals of benzoic acid are separated out. Filter, dry and collect the product and note the m.p.

Recovery of Phloroglucinol from part B: Evaporate the ether solution from flask ‘B’ by placing it over a steam bath. Take the liquid from electrical water bath after a minute. Now, take the precipitate obtained after adding the ether is pressed with filter paper until the moisture is dried up and determine m.p.

[Melting point of benzoic acid = 121.5^0C and Phloroglucinol = 218^0C]

9.8 Conclusion

Separation Based on Solubility:

- This method exploits the differences in solubility of organic compounds in various solvents. By choosing appropriate solvents, compounds can be selectively dissolved and separated.

Separation Using Common Laboratory Reagents:

- Water (cold and hot), dilute hydrochloric acid (HCl), dilute sodium hydroxide (NaOH), and dilute sodium bicarbonate (NaHCOƒ) are used to selectively dissolve or react with specific compounds, aiding in their separation from mixtures.

Crystallization Techniques:

- Crystallization is an effective method for purifying solid compounds. By dissolving the mixture in a suitable solvent and allowing it to crystallize, pure crystals of the desired compound can be obtained.

Separation of Specific Compound Mixtures:

- Detailed procedures and principles were provided for the separation of:
- p-Toluidine and Benzoic Acid: Utilizing differences in solubility and acid-base reactions to separate these compounds.
- p-Nitrotoluene and p-Anisidine: Employing selective solubility and chemical reactivity.
- Benzoic Acid and Phloroglucinol: Using their differing solubility and reactivity for effective separation.

9.9 Some Sample Questions

Q1: Describe a method to separate a mixture of naphthalene and benzoic acid using their solubility differences.

Solution:

- **Dissolution:** Dissolve the mixture in a solvent like ethanol. Both naphthalene and benzoic acid are soluble in ethanol.
- **Selective Precipitation:** Slowly add water to the ethanol solution. Naphthalene is less soluble in water and will precipitate out first.
- **Filtration:** Filter the mixture to separate the solid naphthalene.
- **Crystallization:** Evaporate the ethanol-water mixture to crystallize benzoic acid.

Q2: How can you separate a mixture of benzoic acid and p-toluidine using dilute hydrochloric acid (HCl)?

Solution:

- **Dissolution:** Dissolve the mixture in an organic solvent like ether.
- **Extraction with HCl:** Add dilute HCl to the solution. Benzoic acid remains in the organic layer, while p-toluidine reacts with HCl to form water-soluble p-toluidine hydrochloride.
- **Separation:** Separate the aqueous layer containing p-toluidine hydrochloride from the organic layer containing benzoic acid.
- **Recovery:**
  - **Benzoic Acid:** Evaporate the solvent from the organic layer to obtain benzoic acid.

- **p-Toluidine:** Neutralize the aqueous layer with a base like NaOH to precipitate p-toluidine, which can then be filtered and dried.

Q3: Expain the crystallization process used to purify an impure sample of phloroglucinol.

Solution:

- **Dissolution:** Dissolve the impure phloroglucinol in a minimal amount of hot solvent (e.g., water or ethanol).
- **Hot Filtration:** Filter the hot solution to remove insoluble impurities.
- **Crystallization:** Allow the hot solution to cool slowly to room temperature and then in an ice bath. Pure phloroglucinol will crystallize out.
- **Filtration:** Filter the crystals from the solution.
- **Drying:** Dry the crystals under vacuum or in a desiccator.

Q4: What is the principle behind the separation of p-toluidine and benzoic acid?

Solution:

- **Principle:** The separation is based on the acid-base properties of the compounds. Benzoic acid is an acidic compound, whereas p-toluidine is a basic compound.
- **Procedure:**
  - Dissolve the mixture in an organic solvent like ether.
  - Extract the solution with dilute HCl. p-Toluidine will form water-soluble p-toluidine hydrochloride, moving into the aqueous phase, while benzoic acid remains in the organic phase.
  - Separate the layers.
  - Recover benzoic acid by evaporating the organic solvent.
  - Recover p-toluidine by neutralizing the aqueous layer with a base like NaOH to precipitate p-toluidine, then filter and dry the precipitate.

Q5: Outline a method to separate a mixture of benzoic acid and phloroglucinol based on their chemical properties.

Solution:

- **Dissolution:** Dissolve the mixture in an organic solvent like ether.
- **Extraction:** Add dilute NaHCO to the solution. Benzoic acid will react with NaHCOƒ to form water-soluble sodium benzoate, moving into the aqueous phase, while phloroglucinol remains in the organic phase.

  - **Separation:** Separate the aqueous layer containing sodium benzoate from the organic layer containing phloroglucinol.
- **Recovery:**
  - **Benzoic Acid:** Acidify the aqueous layer with HCl to precipitate benzoic acid, then filter and dry the precipitate.
  - **Phloroglucinol:** Evaporate the organic solvent to obtain phloroglucinol

Unit 10 ❒ Determination of boiling point

Determination of boiling point of common organic liquid compounds e.g., ethanol, cyclohexane, chloroform, ethyl methyl ketone, cyclohexanone, acetyl acetone, anisole, crotonaldehyde, mesityl oxide, etc. [Boiling point of the chosen organic compounds should preferably be less than 160 °C]

10.1 Objectives

- To accurately determine the boiling points of selected organic liquid compounds, including ethanol, cyclohexane, chloroform, ethyl methyl ketone, cyclohexanone, acetyl acetone, anisole, crotonaldehyde, and mesityl oxide.
- To gain a deeper understanding of the physical properties of organic compounds by analyzing their boiling points and how these properties relate to molecular structure and intermolecular forces.
- To compare the boiling points of various organic compounds and analyze trends based on molecular weight, functional groups, and structural differences.
- To develop proficiency in using laboratory techniques for determining boiling points, such as simple distillation, and ensuring accurate temperature measurement.
- To understand and implement appropriate safety measures for handling and heating volatile organic liquids, minimizing risks associated with flammable and toxic substances.

10.1 Introduction

The determination of boiling points is a fundamental aspect of physical chemistry, providing essential insights into the properties and behaviors of organic compounds. Boiling points serve as crucial identifiers for substances, influencing their applications across various industries, including pharmaceuticals, chemical manufacturing, and environmental science. This study focuses on determining the boiling points of a selection of common organic liquids, namely ethanol, cyclohexane, chloroform, ethyl methyl ketone, cyclohexanone, acetyl acetone, anisole, crotonaldehyde, and mesityl oxide. These compounds, characterized by boiling points below 160°C, present a diverse range of molecular structures and functional groups, offering a rich landscape for analysis.

By examining the boiling points of these substances, we aim to understand the relationship between molecular structure and physical properties, enhance laboratory technique proficiency, and ensure accurate and reproducible data collection. This exploration not only deepens our knowledge of organic chemistry but also underscores the practical significance of boiling point data in real-world applications.

10.3 Methods for Boiling Point Determination of Organic Compounds

- **Simple Distillation:**
  - Description: This method involves heating a liquid to its boiling point and condensing the vapor back into a liquid. The temperature at which the vaporization occurs is recorded as the boiling point.
  - Application: Suitable for separating liquids with significantly different boiling points and for determining the boiling point of a single volatile liquid.
- **Reflux Method:**
  - Description: Involves heating a liquid in a closed system where the vapor is condensed and returned to the boiling flask. The temperature remains constant at the boiling point of the liquid.
  - Application: Commonly used in organic synthesis to maintain a reaction at a constant temperature.
- Thermocouple or Digital Thermometer:
  - Description: A precise and modern method that uses a thermocouple or digital thermometer to measure the temperature of the boiling liquid or vapor.
  - Application: Offers high accuracy and is suitable for both laboratory and industrial settings.

- **Capillary Tube Method (Micro-Boiling Point Method):**
    - Description: A small capillary tube is placed in a liquid, which is then heated. The boiling point is observed as the temperature at which a continuous stream of bubbles emerges from the capillary.
    - Application: Ideal for determining the boiling points of small quantities of liquid and for high-precision measurements.
- Differential Scanning Calorimetry (DSC):
    - Description: A thermal analysis method that measures the amount of heat required to increase the temperature of a sample. The boiling point is indicated by an endothermic peak corresponding to vaporization.
    - Application: Useful for detailed thermal analysis and for studying the boiling points of mixtures and complex substances.
- Ebulliometry:
    - Description: A technique that involves measuring the boiling point elevation caused by the addition of a solute to a solvent. The boiling point of the pure solvent can be deduced from the boiling point of the solution.
    - Application: Often used in the study of solutions and for determining the boiling points of solvents.
- Boiling Point Apparatus (Boiling Point Tube):
    - Description: A specialized piece of laboratory equipment designed to measure the boiling point of a liquid by heating it in a controlled environment and observing the temperature at which boiling occurs.
    - Application: Provides a straightforward and accurate determination of boiling points, particularly useful in educational and research laboratories.

10.3 Details Procedure of Boiling Point Determination

Boiling point can be taken as a test for the purity of a liquid. A pure liquid will have a certain definite boiling point only at a particular pressure, as the boiling point is affected both by impurities and by the ambient or external pressure. Impurities generally raise the boiling point. Since boiling point is the temperature at which the vapour pressure of a Liquid becomes equal to the ambient pressure, the boiling point of a liquid will be higher at higher pressures, and the liquid will boil at a lower temperature if the pressure is reduced.

Unless only minute quantities of the liquid are available the boiling-point is usually determined by simple distillation. For this purpose, the apparatus shown in Fig. 2 is assembled. A pear-shaped flask, A (between 10 – 25 ml) is chosen for determination of boiling point of liquid. The flask when charged with liquid should be one-half to two-third full. Now place few pieces of porous bead into the liquid. The flask is then fitted with a thermometer E (range 200^0C or 360^0C) attached cork so that the bulb of the thermometer is just at the centre of the neck and placed just below the vapour exit tube of the distilling flask. The flask is carefully connected with a water condenser B and then heat with a semi-luminous Bunsen flame with care.

Initially the temperature will rise rapidly until it near the boiling point of the liquid, then slowly, and finally will remain practically constant. Note the temperature. This is the boiling point of the liquid.

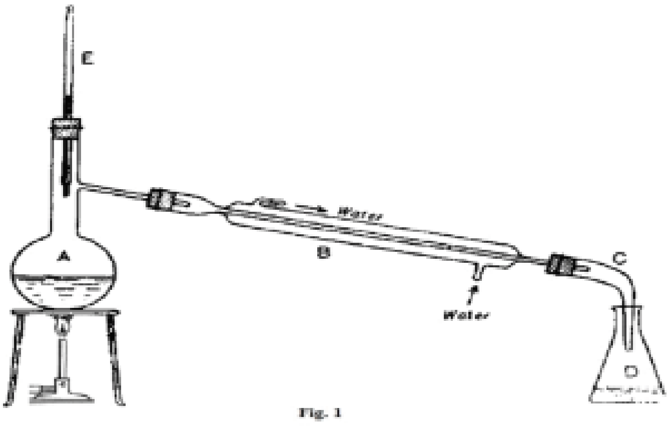


Fig. 1

Boiling point of the organic compounds which will be given to the students for practice, should preferably be less than 160 ^{o}C. Boiling Point of some organic compound are given below.

Name of the compound	**Boiling Point (^{0}C)**
Ethanol	78.37
Cyclohexane	81
Chloroform	61.2
Ethyl methyl ketone	79.64
Cyclohexanone	155.6
Acetylacetone	140
Anisole	153.8
Crotonaldehyde	104
Mesityl oxide	130

10.4 Conclusion

The determination of the boiling point of organic compounds is a fundamental technique in organic chemistry that provides crucial information about the physical properties of a substance. Accurate boiling point measurement can help identify and characterize organic compounds, assess their purity, and understand their intermolecular interactions. Techniques such as simple distillation, fractional distillation, and the use of boiling point apparatus enable precise determination. The boiling point is influenced by molecular weight, structure, and intermolecular forces, making it a valuable parameter in the study and application of organic chemistry.

10.5 Some Sample Questions

Q1: Why is boiling point determination important in organic chemistry?

A1: Boiling point determination is important in organic chemistry because it helps in identifying and characterizing organic compounds, assessing their purity, and understanding their intermolecular interactions. It provides essential information about the physical properties of the substance.

Q2: What factors influence the boiling point of an organic compound?

A2: The boiling point of an organic compound is influenced by several factors, including molecular weight, molecular structure, and the type and strength of intermolecular forces (such as hydrogen bonding, dipole-dipole interactions, and Van der Waals forces).

Q3: What are the common techniques used to determine the boiling point of an organic compound?

A3: Common techniques for determining the boiling point of an organic compound include simple distillation, fractional distillation, and the use of a boiling point apparatus. Each technique varies in precision and is chosen based on the specific requirements of the experiment.

Q4: How does the presence of impurities affect the boiling point of a substance?

A4: The presence of impurities can affect the boiling point of a substance. Typically, impurities can cause the boiling point to increase or decrease depending on the nature of the impurity and its interactions with the pure substance. This effect is often used to assess the purity of a compound.

Q5: What is the principle behind fractional distillation, and why is it used?

A5: Fractional distillation is based on the principle of repeated condensation and vaporization within a fractionating column. It is used to separate mixtures of liquids with close boiling points by providing a more efficient separation than simple distillation, allowing for the isolation of individual components with higher purity.

Q6: How can boiling point determination help in identifying an unknown organic compound?

A6: Boiling point determination can help identify an unknown organic compound by comparing the measured boiling point with known values in literature. If the measured boiling point matches a known compound, it provides a strong indication of the compound's identity.

Q7: What is a boiling point apparatus, and how is it used?

A7: A boiling point apparatus is a device used to accurately measure the boiling point of a liquid. It typically consists of a thermometer, a heating source, and a sample container. The sample is heated, and the temperature at which the liquid transitions to gas is recorded as the boiling point.

Q8: Why might a chemist choose simple distillation over fractional distillation for boiling point determination?

A8: A chemist might choose simple distillation over fractional distillation when the compounds in the mixture have significantly different boiling points or when the goal is to obtain a quick and rough estimation of the boiling point. Simple distillation is less complex and quicker but less precise than fractional distillation.

Q9: Can boiling point determination be used for both organic and inorganic compounds? A9: Yes, boiling point determination can be used for both organic and inorganic compounds. However, it is more commonly applied to organic compounds due to their diverse structures and the wide range of boiling points they exhibit.

Q10: What safety precautions should be taken during boiling point determination?

A10: During boiling point determination, safety precautions include wearing appropriate personal protective equipment (PPE) such as lab coats, gloves, and safety goggles, ensuring proper ventilation, using heat-resistant glassware, and carefully monitoring the heating process to avoid overheating and potential hazards.

Unit-11❒ Identification of a Pure Solid Organic Compound by chemical test(s)

Oxalic acid, tartaric acid, citric acid, succinic acid, resorcinol, urea, glucose, cane sugar, benzoic acid and salicylic acid.

11.0 Objectives

11.1 Introduction

11.2 Identification of Organic Compounds

11.3 Preliminary Studies of Pure Sample

11.4 Preparation of Neutral Solution Of Acid

11.5 Identification of Oxalic Acid By Chemical Tests

11.6 Identification of Tartaric Acid By Chemical Tests

11.7 Identification of Citric Acid By Chemical Tests

11.8 Identification of Resorcinol By Chemical Tests

11.9 Identification of Urea By Chemical Tests

11.10 Identification of Glucose By Chemical Tests

11.11 Identification of Can Sugar By Chemical Tests

11.12 Identification of Benzoic Acid By Chemical Tests

11.13 Identification of Salicylic Acid By Chemical Tests

11.14 Conclusion

11.15 Some Sample Questions

11.1 Introduction:

The organic compound supplied as sample, solid or liquid, is to be detected as a whole by systematic quantative analytical methods.

The following samples will be provided for analysis in the pure form.

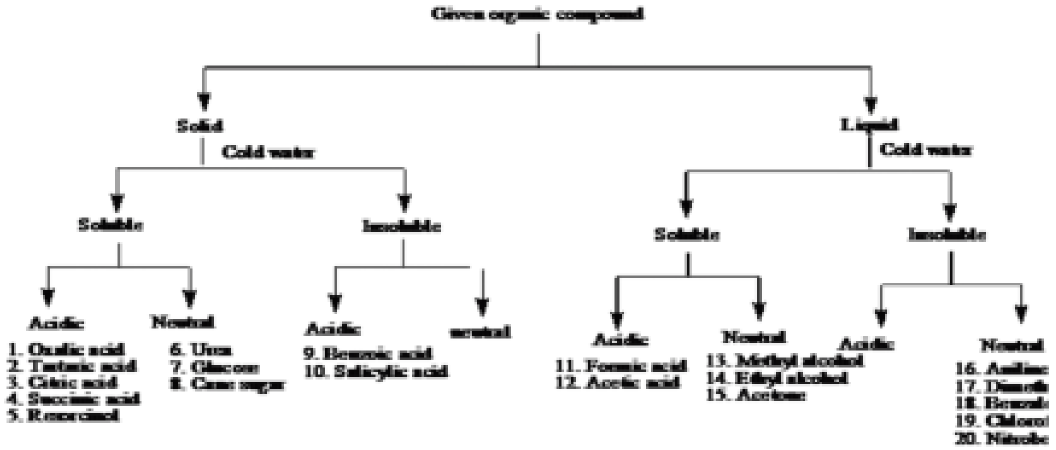
Solid	**Liquid**
S-1. Oxalic acid	L-11. Formic acid
S-2. Tartaric acid	L-12. Acetic acid

Solid	Liquid
S-3. Citric acid	L-13. Methyl alcohol
S-4. Succinic acid	L-14. Ethyl alcohol
S-5. Resorcinol	L-15. Acetone
S-6. Urea	L-16. Aniline
S-7. Glucose	L-17. Dimethyl aniline
S-8. Cane sugar (Sucrose)	L-18. Benzaldehyde
S-9. Benzoic acid	L-19. Chloroform
S-10. Salicylic acid	L-20. Nitrobenzene

11.2 Identification of Organic Compounds

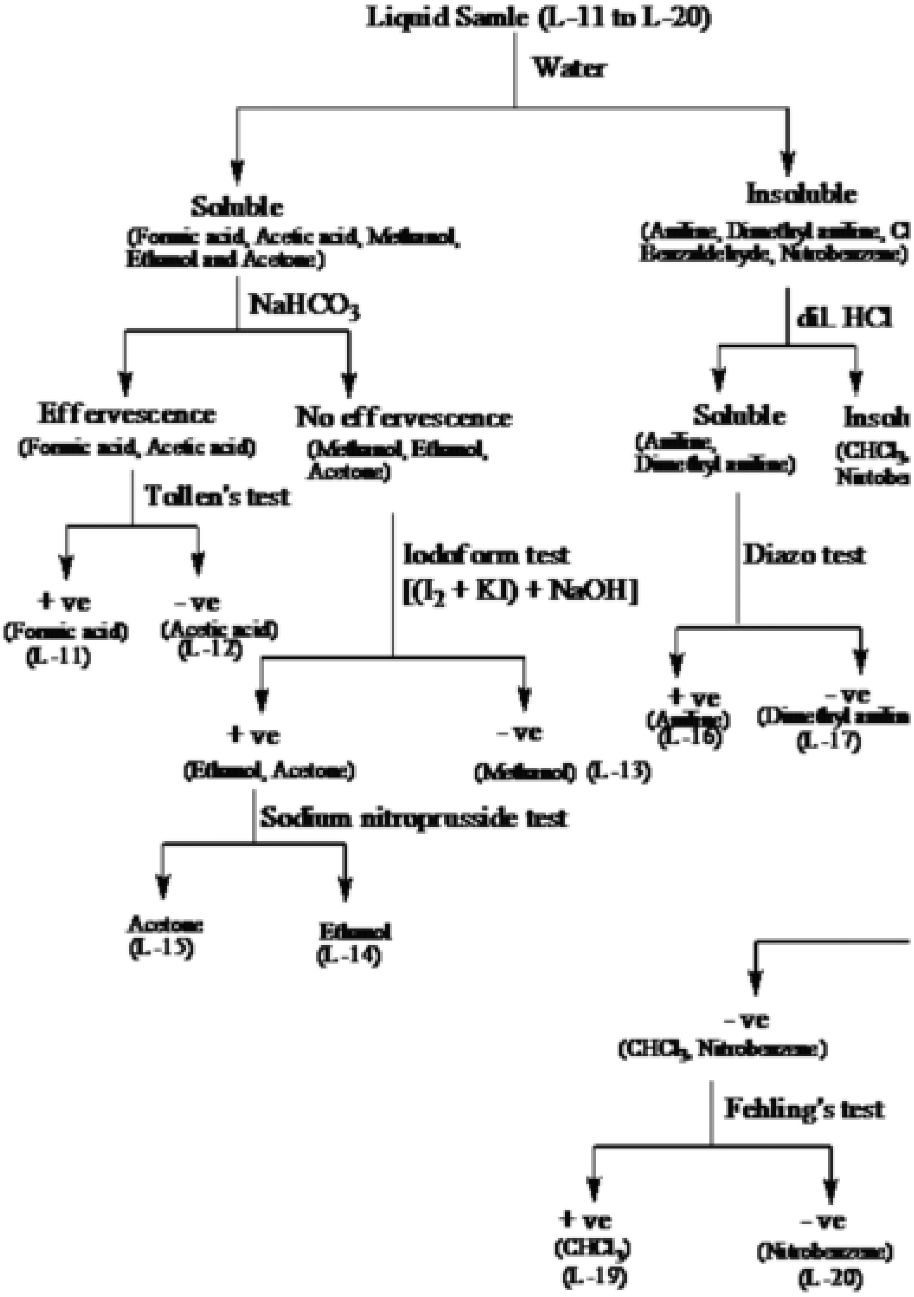
An organic compound supplied to the student may be solid or liquid, soluble or insoluble in cold water, acidic or neutral. So it is great important to the student for preliminary identification of the supplied sample belongs to the listed above. In each case small amount of sample (0.1 – 0.2 g) and reagent (2 ml) are to be taken for testing.

For liquid sample particularly, specific gravity and odour are the vital characteristic to identify them. As for example, among water soluble liquids specific gravity is less, should belong to CH_3OH, C_2H_5OH and $CH_3.CO.CH_3$. Liquids with pungent smell are HCOOH and CH_3COOH. $CHCl_3$ is sweet smelling water insoluble with specific gravity greater than water. Aniline and dimethyl anilne is insoluble in water but soluble in dil. HCl. Benzaldehyde and Nitrobenzene both are insoluble in acid and alkali. Based on above, the given compound under investigation can be classified as follows:



11.3 Preliminary studies of Pure Sample

The given sample should be treated with some solvents, acidic/basic, reaction condition as follows and classified depending upon their nature and reactivity.



11.4 Preparation of neutral solution of acid

It is necessary to prepare neutral solution if the sample is acidic in nature. Dissolve half of the original sample (supplied) in water in a beaker. Add solid Na_2CO_3 pinch by pinch to the solution with continuous stirring with the help of a glass rod till the effervescence ceases. Dissolve little excess Na_2CO_3 to make the solution alkaline (test with red litmus paper). Now add drop wise dil. HNO_3 till the solution becomes distinctly acidic (test with blue litmus paper). Now add dil. NH_4OH solution till the smell of ammonia persists after through mixing. Boil the solution to remove excess ammonia and concentrate if require.

11.5 Identification of Oxalic Acid by Chemical Tests

S-1. OXALIC ACID

COOH

COOH ,$2H_2O$

Physical characteristics:

- State : Solid
- Colour : White/ Colourless
- Odour : Odourless
- Texture : Crystalline
- Solubility : Soluble in cold water
- Litmus : Blue litmus turns to red

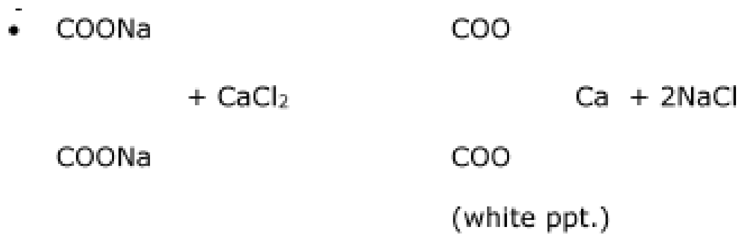
Preliminary Test:

- Ignition Test: Burns with non-sooty blue flame

Special Tests:

Experiment	Observation
• **Calcium Chloride Test**: Few drops of $CaCl_2$ solution is added to the neutral solution of the sample. The precipitate is devided into two parts. • In first part dilute acetic acid is added • In second part dil. HCl is added	• A white precipitate is formed • The ppt. does not dissolve • The ppt. dissolve and clear solution obtained
• **Denige's Test:** Denige's reagent is added to the neutral solution of the sample	• White precipitate is obtained which is insoluble on heating
• **Silver Nitrate Test:** Add few drops of $AgNO_3$ to the neutral or slightly alkaline sample solution. The white precipitate is divided into three parts • Add NH_4OH solution in one part of the ppt. • Add dil. HNO_3 in second part of the ppt. • Heat the third part gently to dryness and then heat strongly	• White ppt. is formed • The ppt. dissolves • The ppt. dissolves • Black metallic silver is formed
• **Potassium permanganate Test:** The sample solution is warmed after adding few drops of dil. H_2SO_4 . Now add few drops of dil. $KMnO_4$ solution.	• The pink colour of $KMnO_4$ solution disappears.
• **Manganous sulphate Test:** Take 1 ml of $MnSO_4$ solution in a test tube and alkaline with dil. NaOH solution. A white ppt. of $Mn(OH)_2$ is formed. Heat the mixture gently till the white ppt. turns to brown due to formation of MnO(OH). Then add sample solution drop wise to the mixture.	• The brown ppt. dissolves and red/ pinkish red colour appears.
• **Conc. H_2SO_4 Test:** Heat little amount of the sample with conc. H_2SO_4.	• A colourless gas evolves which clear lime solution to milky.

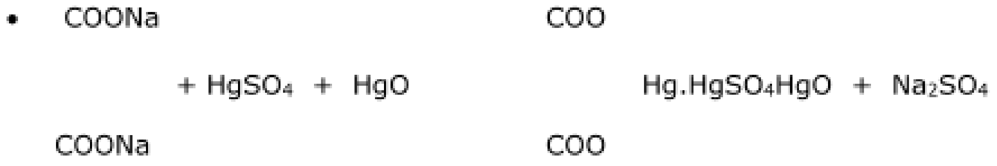
Explanations and Reactions:



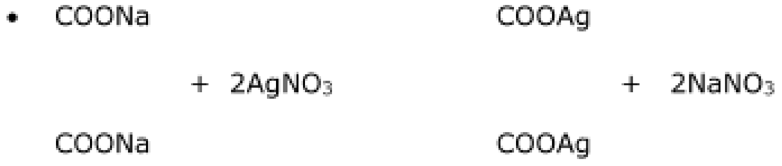
$$\begin{matrix}\text{COONa}\\ \\ \text{COONa}\end{matrix} + \text{CaCl}_2 \qquad \begin{matrix}\text{COO}\\ \\ \text{COO}\end{matrix}\text{Ca} + 2\text{NaCl}$$

(white ppt.)

$$\begin{matrix}\text{COO}\\ \\ \text{COO}\end{matrix}\text{Ca} + 2\text{HCl} \qquad \begin{matrix}\text{COOH}\\ \\ \text{COOH}\end{matrix} + \text{CaCl}_2$$



- $$\begin{matrix}\text{COONa}\\ \\ \text{COONa}\end{matrix} + HgSO_4 + HgO \qquad \begin{matrix}\text{COO}\\ \\ \text{COO}\end{matrix} Hg.HgSO_4HgO + Na_2SO_4$$



- $$\begin{matrix}\text{COONa}\\ \\ \text{COONa}\end{matrix} + 2AgNO_3 \qquad \begin{matrix}\text{COOAg}\\ \\ \text{COOAg}\end{matrix} + 2NaNO_3$$

(white ppt.)

Δ

$2Ag + CO_2$

- $H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \quad K_2SO_4 + MnSO_4 + 2H_2O + 10CO_2$

- $MnSO_4 + 2NaOH \quad Mn(OH)_2 + Na_2SO_4$

(white)

[O] Aerial oxidation

MnO(OH) (brown)

$Na_2C_2O_4 + MnO(OH) \quad Na_3[Mn(C_2O_4)_3] + H_2O$

- $H_2C_2O_4.\ 2H_2O + H_2SO_4 \quad CO_2 + CO + [H_2SO_4 + 3H_2O]$

$CO_2 + Ca(OH)_2 \quad CaCO_3$

11.6 Identification of Tartaric Acid By Chemical Tests:

S-2. TARTARIC ACID

$HO_2C.CH(OH) - CH(OH)CO_2H$

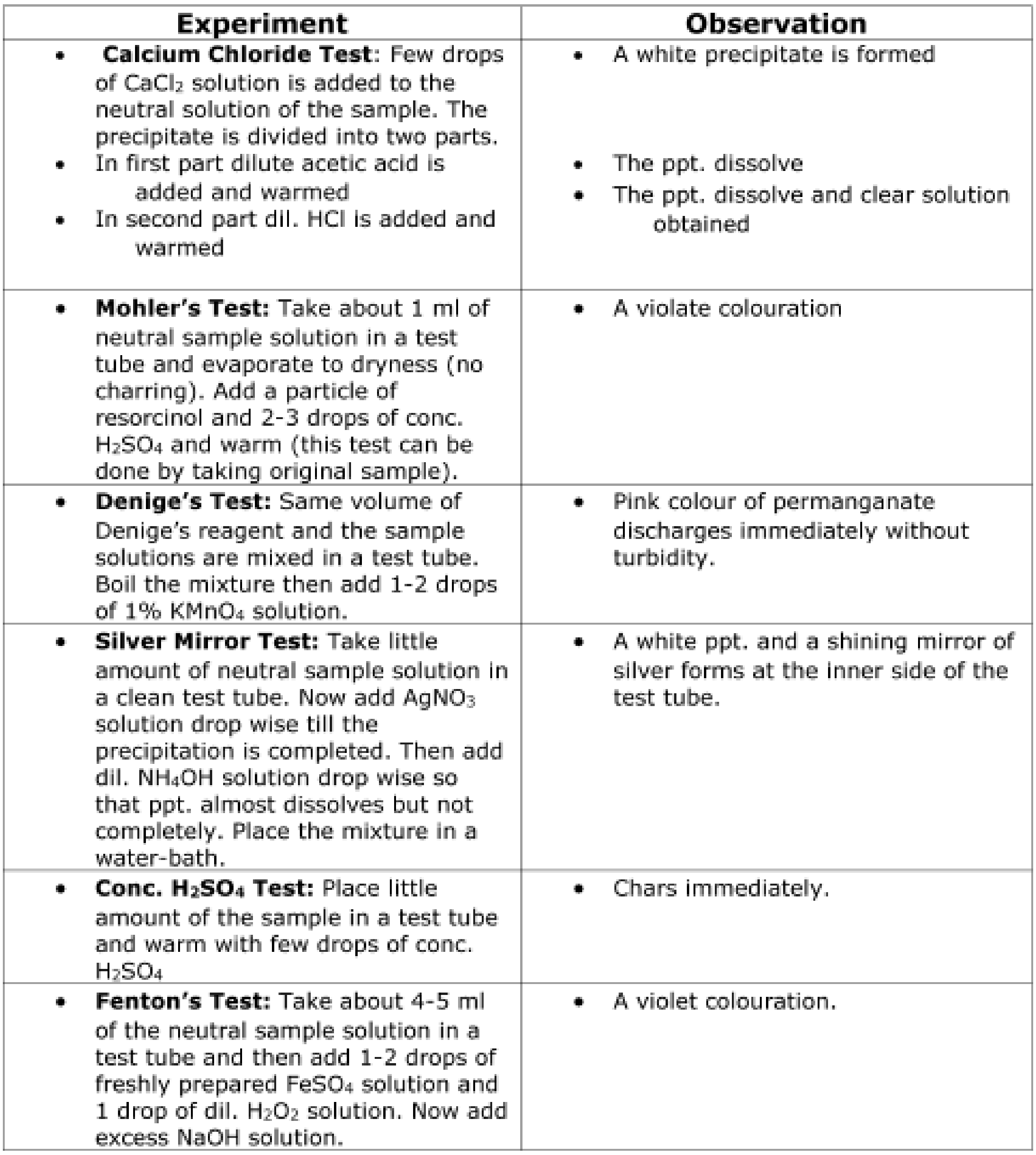
Physical characteristics:

State	: Solid
Colour	: White/ Colourless
Odour	: Odourless
Texture	: Crystalline
Solubility	: Soluble in cold water
Litmus	: Blue litmus turns to red

Preliminary Test:

- Ignition Test : Burns with non-sooty blue flame

Special Tests:



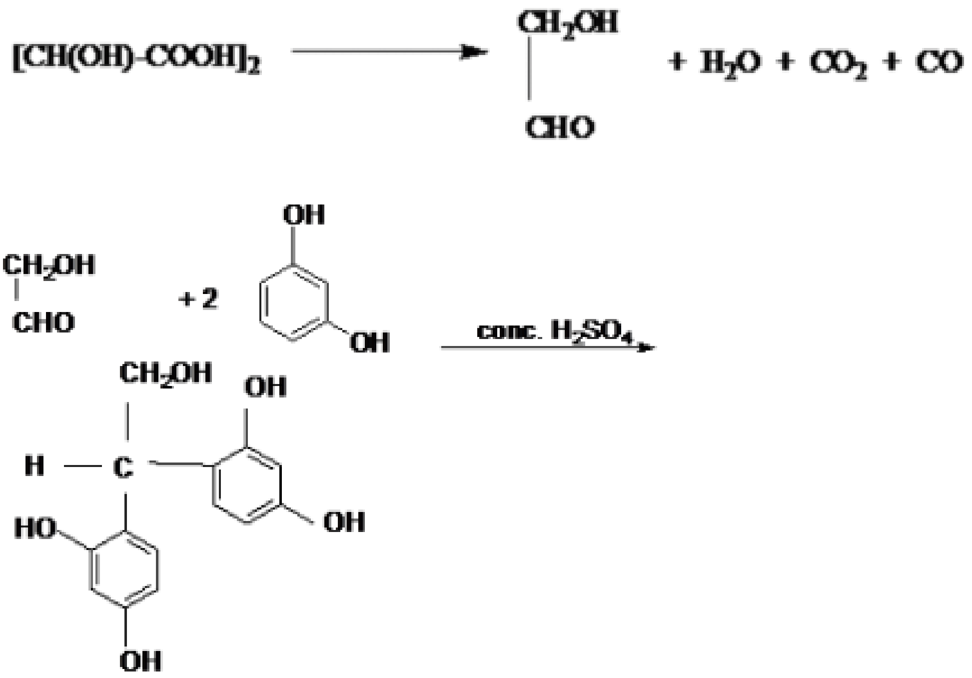
Experiment	Observation
• **Calcium Chloride Test**: Few drops of $CaCl_2$ solution is added to the neutral solution of the sample. The precipitate is divided into two parts. • In first part dilute acetic acid is added and warmed • In second part dil. HCl is added and warmed	• A white precipitate is formed • The ppt. dissolve • The ppt. dissolve and clear solution obtained
• **Mohler's Test:** Take about 1 ml of neutral sample solution in a test tube and evaporate to dryness (no charring). Add a particle of resorcinol and 2-3 drops of conc. H_2SO_4 and warm (this test can be done by taking original sample).	• A violate colouration
• **Denige's Test:** Same volume of Denige's reagent and the sample solutions are mixed in a test tube. Boil the mixture then add 1-2 drops of 1% $KMnO_4$ solution.	• Pink colour of permanganate discharges immediately without turbidity.
• **Silver Mirror Test:** Take little amount of neutral sample solution in a clean test tube. Now add $AgNO_3$ solution drop wise till the precipitation is completed. Then add dil. NH_4OH solution drop wise so that ppt. almost dissolves but not completely. Place the mixture in a water-bath.	• A white ppt. and a shining mirror of silver forms at the inner side of the test tube.
• **Conc. H_2SO_4 Test:** Place little amount of the sample in a test tube and warm with few drops of conc. H_2SO_4	• Chars immediately.
• **Fenton's Test:** Take about 4-5 ml of the neutral sample solution in a test tube and then add 1-2 drops of freshly prepared $FeSO_4$ solution and 1 drop of dil. H_2O_2 solution. Now add excess NaOH solution.	• A violet colouration.

Explanations and Reactions:

- $CaCl_2$ test:

  $[CH(OH)COONa]_2$ + $CaCl_2$ $[CH(OH)COO]_2$ Ca + 2NaCl

- Mohler's test:



(Violet colour)

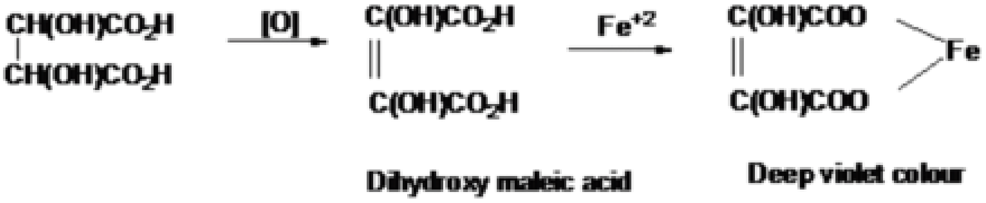
- Mirror Test:

  [$CH(OH)COONa]_2$ 2 $AgNO_3$ $[CH(OH)COOAg]_2$ + 2 $NaNO_3$

  Ä

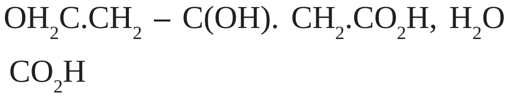
  Ag

- Fenton's Test:



11.6 Identification of Citric Acid By Chemical Tests:

S-3. CITRIC ACID



$$OH_2C.CH_2 - \underset{CO_2H}{C(OH)}.\ CH_2.CO_2H,\ H_2O$$

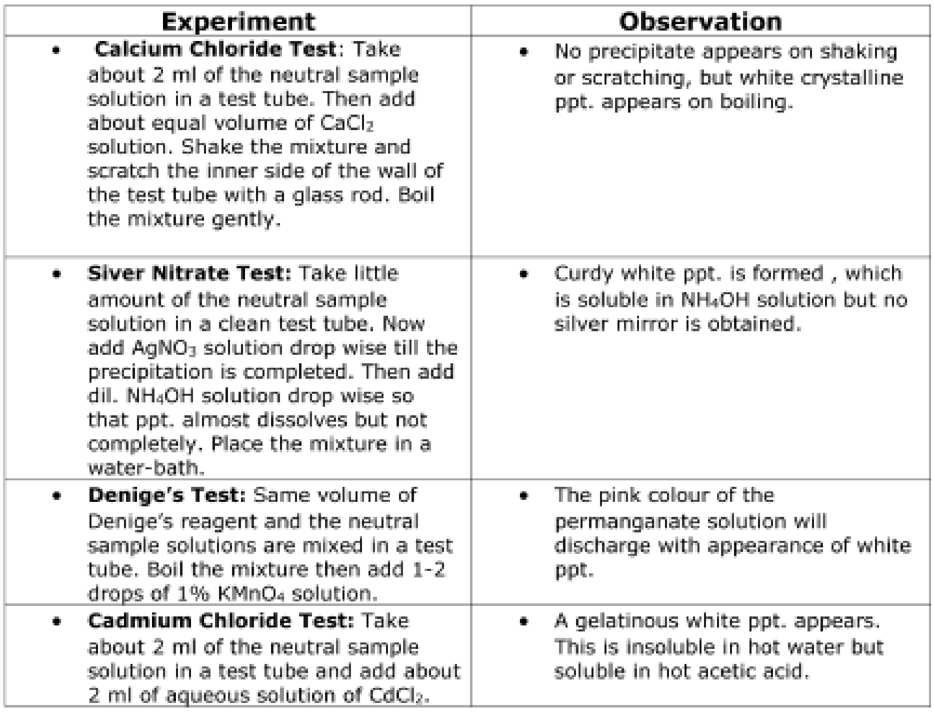
Physical characteristics:

- State : Solid
- Colour : White/ Colourless
- Odour : Odourless
- Texture : Crystalline
- Solubility : Soluble in cold water
- Litmus : Blue litmus turns to red

Preliminary Test:

- Ignition Test : Burns with non-sooty blue flame

Special Tests:



Experiment	Observation
• **Calcium Chloride Test**: Take about 2 ml of the neutral sample solution in a test tube. Then add about equal volume of $CaCl_2$ solution. Shake the mixture and scratch the inner side of the wall of the test tube with a glass rod. Boil the mixture gently.	• No precipitate appears on shaking or scratching, but white crystalline ppt. appears on boiling.
• **Siver Nitrate Test:** Take little amount of the neutral sample solution in a clean test tube. Now add $AgNO_3$ solution drop wise till the precipitation is completed. Then add dil. NH_4OH solution drop wise so that ppt. almost dissolves but not completely. Place the mixture in a water-bath.	• Curdy white ppt. is formed , which is soluble in NH_4OH solution but no silver mirror is obtained.
• **Denige's Test:** Same volume of Denige's reagent and the neutral sample solutions are mixed in a test tube. Boil the mixture then add 1-2 drops of 1% $KMnO_4$ solution.	• The pink colour of the permanganate solution will discharge with appearance of white ppt.
• **Cadmium Chloride Test:** Take about 2 ml of the neutral sample solution in a test tube and add about 2 ml of aqueous solution of $CdCl_2$.	• A gelatinous white ppt. appears. This is insoluble in hot water but soluble in hot acetic acid.

Explanations and Reactions:

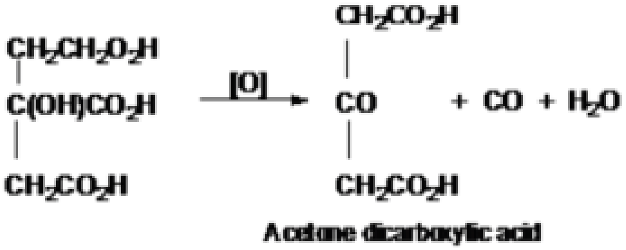
- $CaCl_2$ test:

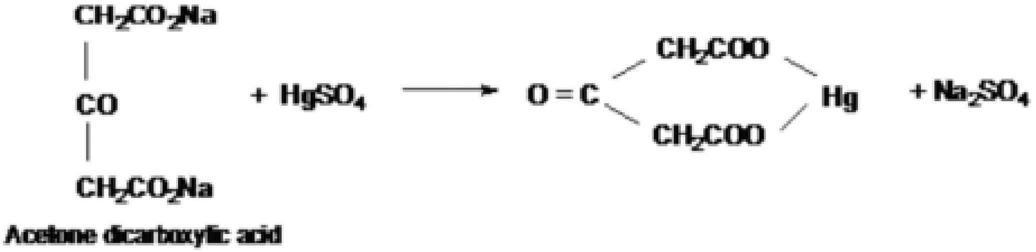
  $2C_6H_5O_7Na_3 + 3CaCl_2 \qquad Ca_3(C_6H_5O_7)_2 + 6NaCl$

- $AgNO_3$ test:

  $C_3H_4(OH).(COONa)_3 + 3AgNO_3 \qquad C_3H_4(OH).(COOAg)_3 + 3NaNO_3$

- Denige's test:





11.7 Identification of Citric Acid By Chemical Tests:

S-4. SUCCINIC ACID

$HOOC.CH_2.CH_2.COOH$

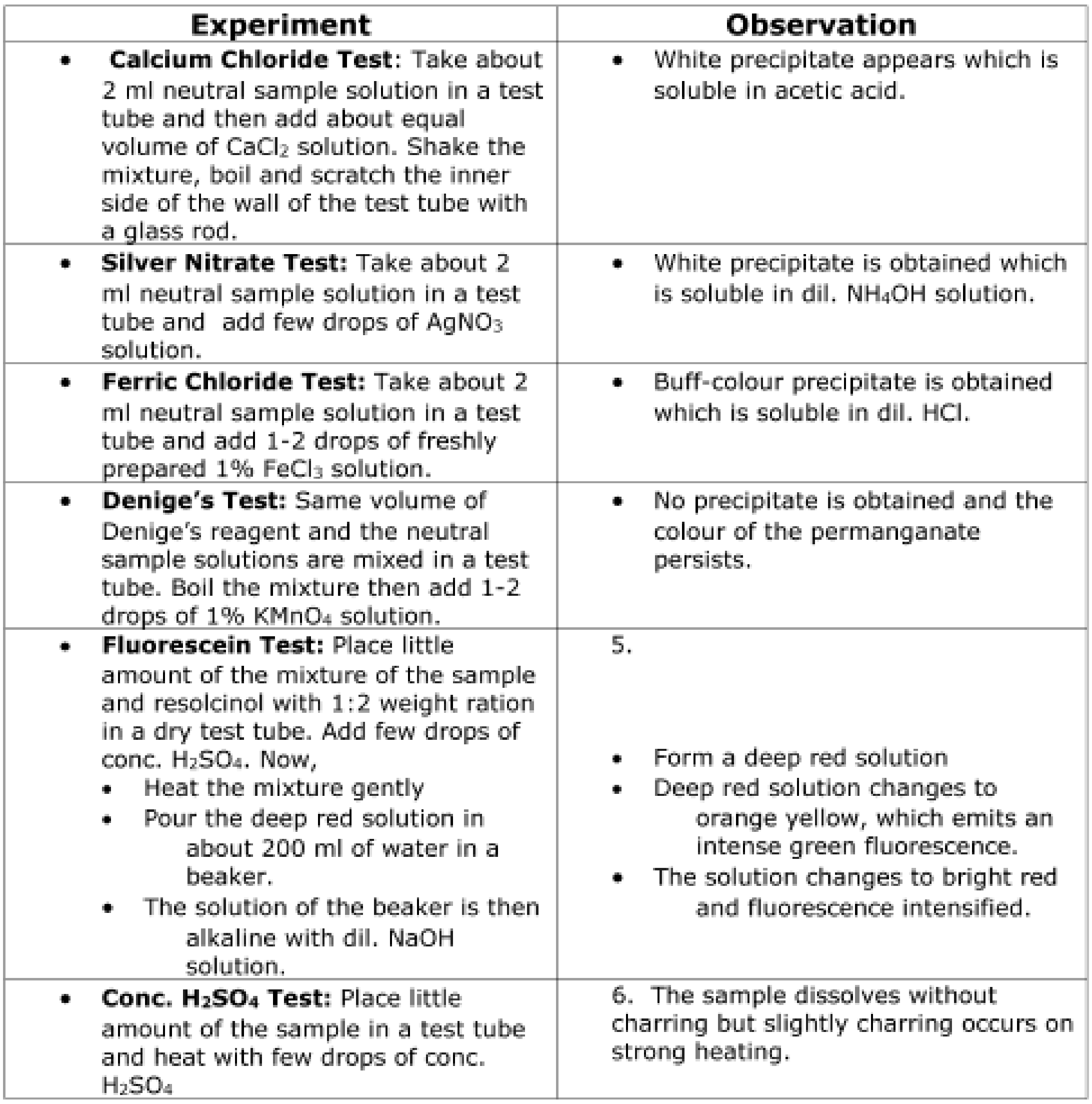
Physical characteristics:

• State	: Solid
• Colour	: White/ Colourless
• Odour	: Odourless
• Texture	: Crystalline
• Solubility	: Soluble in cold water
• Litmus	: Blue litmus turns to red

Preliminary Test:

- Ignition Test : Burns with non-sooty blue flame

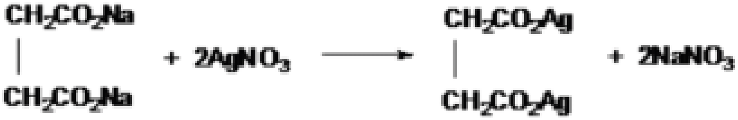
Special Tests:



Experiment	Observation
• **Calcium Chloride Test:** Take about 2 ml neutral sample solution in a test tube and then add about equal volume of $CaCl_2$ solution. Shake the mixture, boil and scratch the inner side of the wall of the test tube with a glass rod.	• White precipitate appears which is soluble in acetic acid.
• **Silver Nitrate Test:** Take about 2 ml neutral sample solution in a test tube and add few drops of $AgNO_3$ solution.	• White precipitate is obtained which is soluble in dil. NH_4OH solution.
• **Ferric Chloride Test:** Take about 2 ml neutral sample solution in a test tube and add 1-2 drops of freshly prepared 1% $FeCl_3$ solution.	• Buff-colour precipitate is obtained which is soluble in dil. HCl.
• **Denige's Test:** Same volume of Denige's reagent and the neutral sample solutions are mixed in a test tube. Boil the mixture then add 1-2 drops of 1% $KMnO_4$ solution.	• No precipitate is obtained and the colour of the permanganate persists.
• **Fluorescein Test:** Place little amount of the mixture of the sample and resolcinol with 1:2 weight ration in a dry test tube. Add few drops of conc. H_2SO_4. Now, • Heat the mixture gently • Pour the deep red solution in about 200 ml of water in a beaker. • The solution of the beaker is then alkaline with dil. NaOH solution.	5. • Form a deep red solution • Deep red solution changes to orange yellow, which emits an intense green fluorescence. • The solution changes to bright red and fluorescence intensified.
• **Conc. H_2SO_4 Test:** Place little amount of the sample in a test tube and heat with few drops of conc. H_2SO_4	6. The sample dissolves without charring but slightly charring occurs on strong heating.

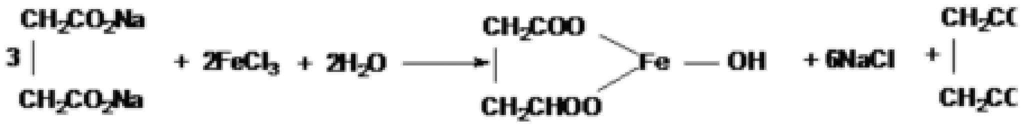
Explanations and Reactions:

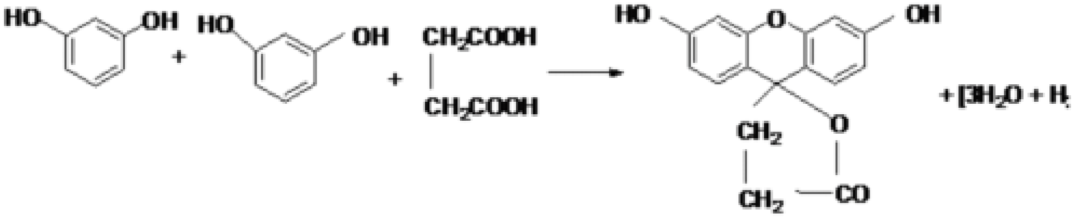
- Silver nitrate test:



$$\begin{array}{l} CH_2CO_2Na \\ | \\ CH_2CO_2Na \end{array} + 2AgNO_3 \longrightarrow \begin{array}{l} CH_2CO_2Ag \\ | \\ CH_2CO_2Ag \end{array} + 2NaNO_3$$

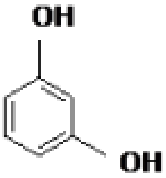
- Ferric chloride test:





11.8 Identification of Resorcinol By Chemical Tests:

S-5. RESORCINOL



- Fluorescein test:

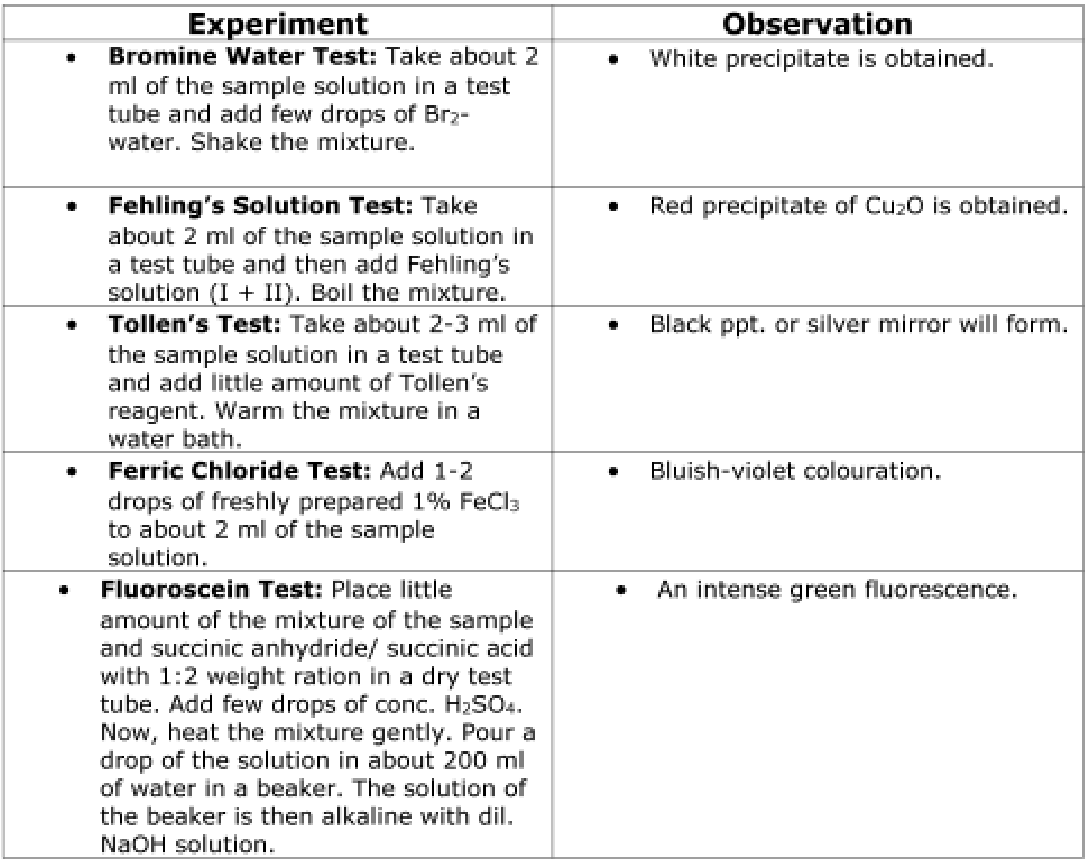
Physical characteristics:

- State : Solid
- Colour : White/ Pink (Actual colour is white but becomes pink on exposure to light)
- Odour : Odourless
- Texture : Crystalline
- Solubility : Soluble in cold water
- Ph paper : Slightly acidic

Preliminary Test:

- Ignition Test : Burns with yellow-sooty flame

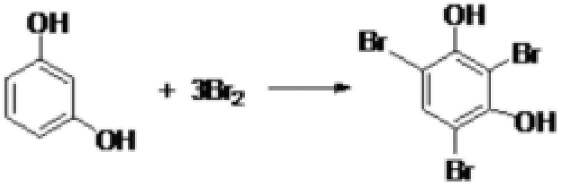
Special Tests:



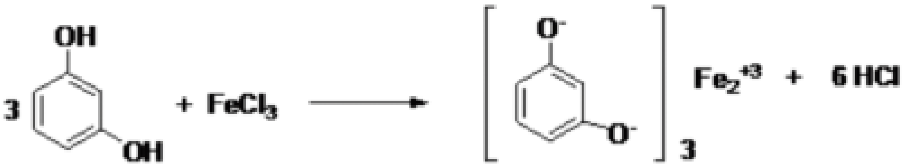
Experiment	Observation
• **Bromine Water Test:** Take about 2 ml of the sample solution in a test tube and add few drops of Br_2-water. Shake the mixture.	• White precipitate is obtained.
• **Fehling's Solution Test:** Take about 2 ml of the sample solution in a test tube and then add Fehling's solution (I + II). Boil the mixture.	• Red precipitate of Cu_2O is obtained.
• **Tollen's Test:** Take about 2-3 ml of the sample solution in a test tube and add little amount of Tollen's reagent. Warm the mixture in a water bath.	• Black ppt. or silver mirror will form.
• **Ferric Chloride Test:** Add 1-2 drops of freshly prepared 1% $FeCl_3$ to about 2 ml of the sample solution.	• Bluish-violet colouration.
• **Fluoroscein Test:** Place little amount of the mixture of the sample and succinic anhydride/ succinic acid with 1:2 weight ration in a dry test tube. Add few drops of conc. H_2SO_4. Now, heat the mixture gently. Pour a drop of the solution in about 200 ml of water in a beaker. The solution of the beaker is then alkaline with dil. NaOH solution.	• An intense green fluorescence.

Explanations and Reactions:

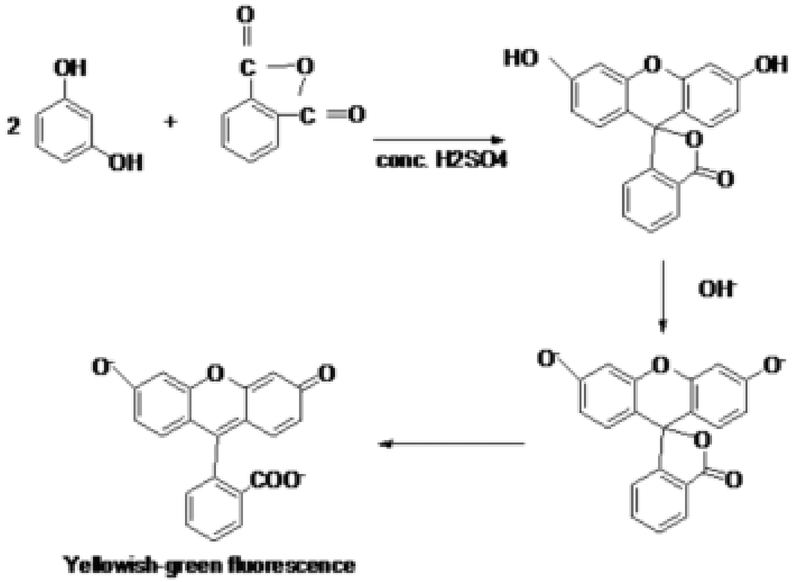
- Bromine water test:



- $FeCl_3$ test:

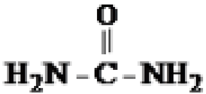


- Fluorescein test:



11.9 Identification of Urea By Chemical Tests

S-6. UREA



$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2$$

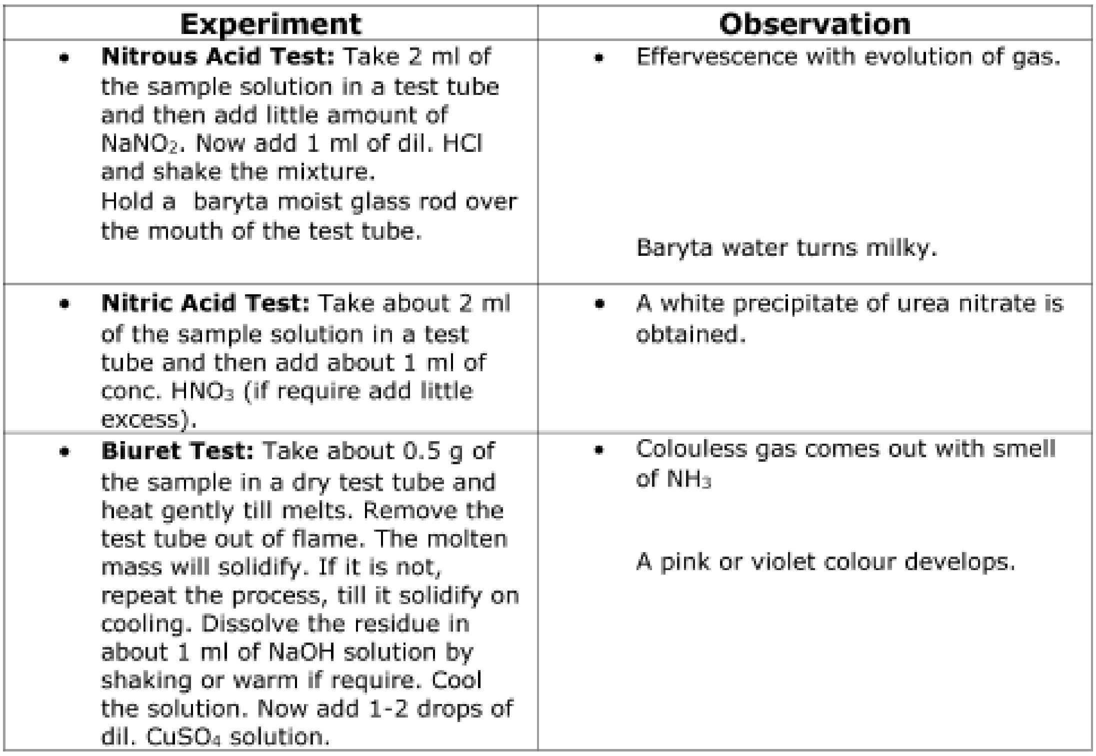
Physical characteristics:

- State : Solid
- Colour : Colourless
- Odour : Odourless
- Texture : Crystalline
- Solubility : Soluble in cold water
- Litmus : Neutral

Preliminary Test:

- Ignition Test : Burns with non-sooty blue flame

Special Tests:



Experiment	Observation
• **Nitrous Acid Test:** Take 2 ml of the sample solution in a test tube and then add little amount of $NaNO_2$. Now add 1 ml of dil. HCl and shake the mixture. Hold a baryta moist glass rod over the mouth of the test tube.	• Effervescence with evolution of gas. Baryta water turns milky.
• **Nitric Acid Test:** Take about 2 ml of the sample solution in a test tube and then add about 1 ml of conc. HNO_3 (if require add little excess).	• A white precipitate of urea nitrate is obtained.
• **Biuret Test:** Take about 0.5 g of the sample in a dry test tube and heat gently till melts. Remove the test tube out of flame. The molten mass will solidify. If it is not, repeat the process, till it solidify on cooling. Dissolve the residue in about 1 ml of NaOH solution by shaking or warm if require. Cool the solution. Now add 1-2 drops of dil. $CuSO_4$ solution.	• Colouless gas comes out with smell of NH_3 A pink or violet colour develops.

Explanations and Reactions:

- Nitrous acid test:

$$H_2N-CO-OH_2 + 2HNO_2 \longrightarrow CO_2 + N_2 + 3H_2O$$

- Nitric acid test:

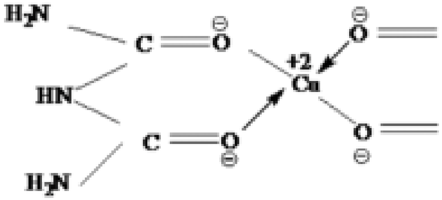
$$CO(NH_2)_2 + HNO_3 \longrightarrow \underset{\text{Urea nitrate}}{CO(NH_2)_2HNO_3}$$

- Biuret test:

$$H_2N-CO-NH-\boxed{H + H_2N}-CO-NH_2 \quad \Delta$$

$$\underset{\text{Biuret}}{H_2N-CO-NH-CO-NH_2} + NH_3$$

$CuSO_4$



Copper biurate sulphate
(Violet colour)

11.10 Identification of Glucose By Chemical Tests:

S-7. GLUCOSE

$C_6H_{12}O_6$ or $HOCH_2(CHOH)_4CHO$

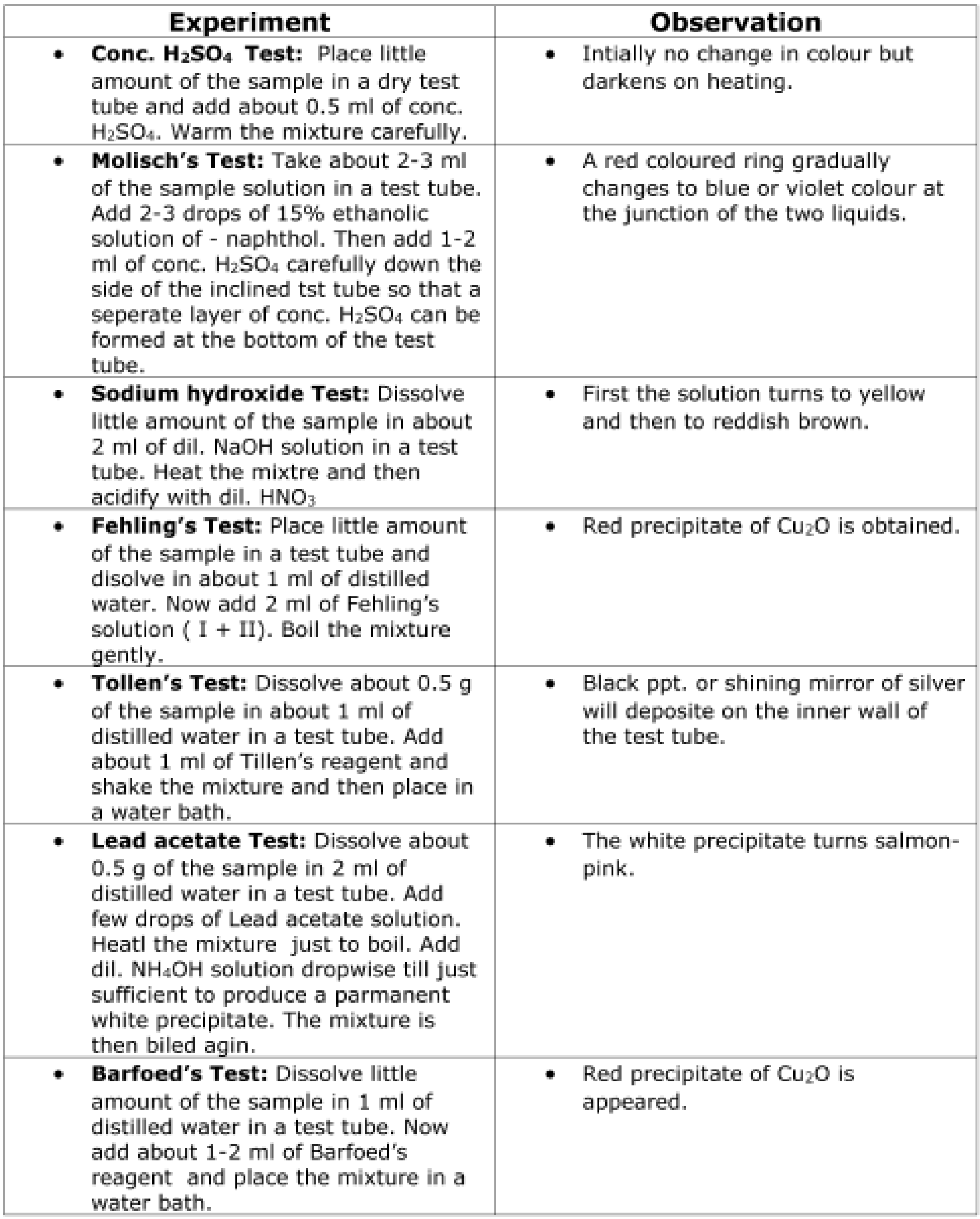
Physical characteristics:

- State : Solid
- Colour : Colourless
- Odour : Odourless
- Texture : Crystalline
- Solubility : Soluble in cold water
- Litmus : Neutral

Preliminary Test:

- Ignition Test : Burns with non-sooty blue flame
- Action of heat : Melts, turns to black on futher heating due to charring.

Special Tests:



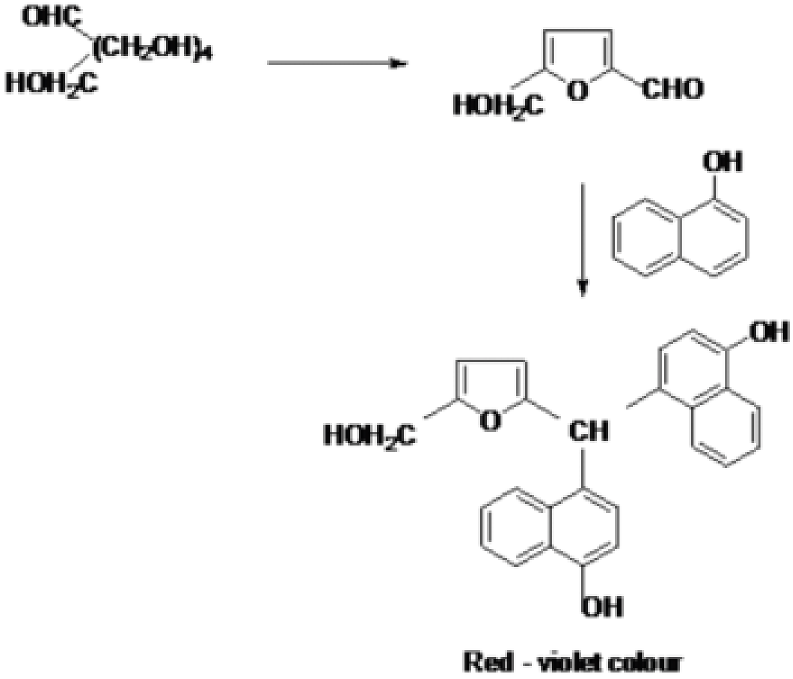
Experiment	Observation
- **Conc. H_2SO_4 Test:** Place little amount of the sample in a dry test tube and add about 0.5 ml of conc. H_2SO_4. Warm the mixture carefully.	- Intially no change in colour but darkens on heating.
- **Molisch's Test:** Take about 2-3 ml of the sample solution in a test tube. Add 2-3 drops of 15% ethanolic solution of - naphthol. Then add 1-2 ml of conc. H_2SO_4 carefully down the side of the inclined tst tube so that a seperate layer of conc. H_2SO_4 can be formed at the bottom of the test tube.	- A red coloured ring gradually changes to blue or violet colour at the junction of the two liquids.
- **Sodium hydroxide Test:** Dissolve little amount of the sample in about 2 ml of dil. NaOH solution in a test tube. Heat the mixtre and then acidify with dil. HNO_3	- First the solution turns to yellow and then to reddish brown.
- **Fehling's Test:** Place little amount of the sample in a test tube and disolve in about 1 ml of distilled water. Now add 2 ml of Fehling's solution (I + II). Boil the mixture gently.	- Red precipitate of Cu_2O is obtained.
- **Tollen's Test:** Dissolve about 0.5 g of the sample in about 1 ml of distilled water in a test tube. Add about 1 ml of Tillen's reagent and shake the mixture and then place in a water bath.	- Black ppt. or shining mirror of silver will deposite on the inner wall of the test tube.
- **Lead acetate Test:** Dissolve about 0.5 g of the sample in 2 ml of distilled water in a test tube. Add few drops of Lead acetate solution. Heatl the mixture just to boil. Add dil. NH_4OH solution dropwise till just sufficient to produce a parmanent white precipitate. The mixture is then biled agin.	- The white precipitate turns salmon-pink.
- **Barfoed's Test:** Dissolve little amount of the sample in 1 ml of distilled water in a test tube. Now add about 1-2 ml of Barfoed's reagent and place the mixture in a water bath.	- Red precipitate of Cu_2O is appeared.

Explanations and Reactions:

- Conc. H_2SO_4 test:

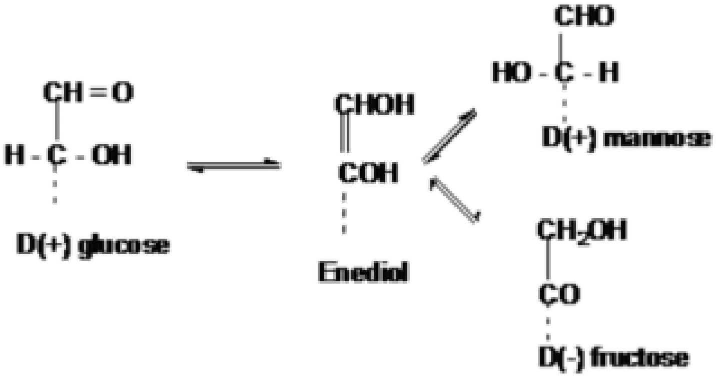
  $C_6H_{12}O_6 + H_2SO_4 \qquad\qquad 6C + [\ 6H_2O + H_2SO_4]$

- Molisch's test:



- Sodium hydroxide test:

  Lobry-de-Van Ekenstein rearrangement occurs when D(+)- glucose is warmed with NaOH to give a mixture of D(+)- glucose, D(+)- mannose and D(-)- fructose.



11.11 Identification of Can Sugar By Chemical Tests

S-8. CANE SUGAR or SUCROSE

$C_{12}H_{22}O_{11}$

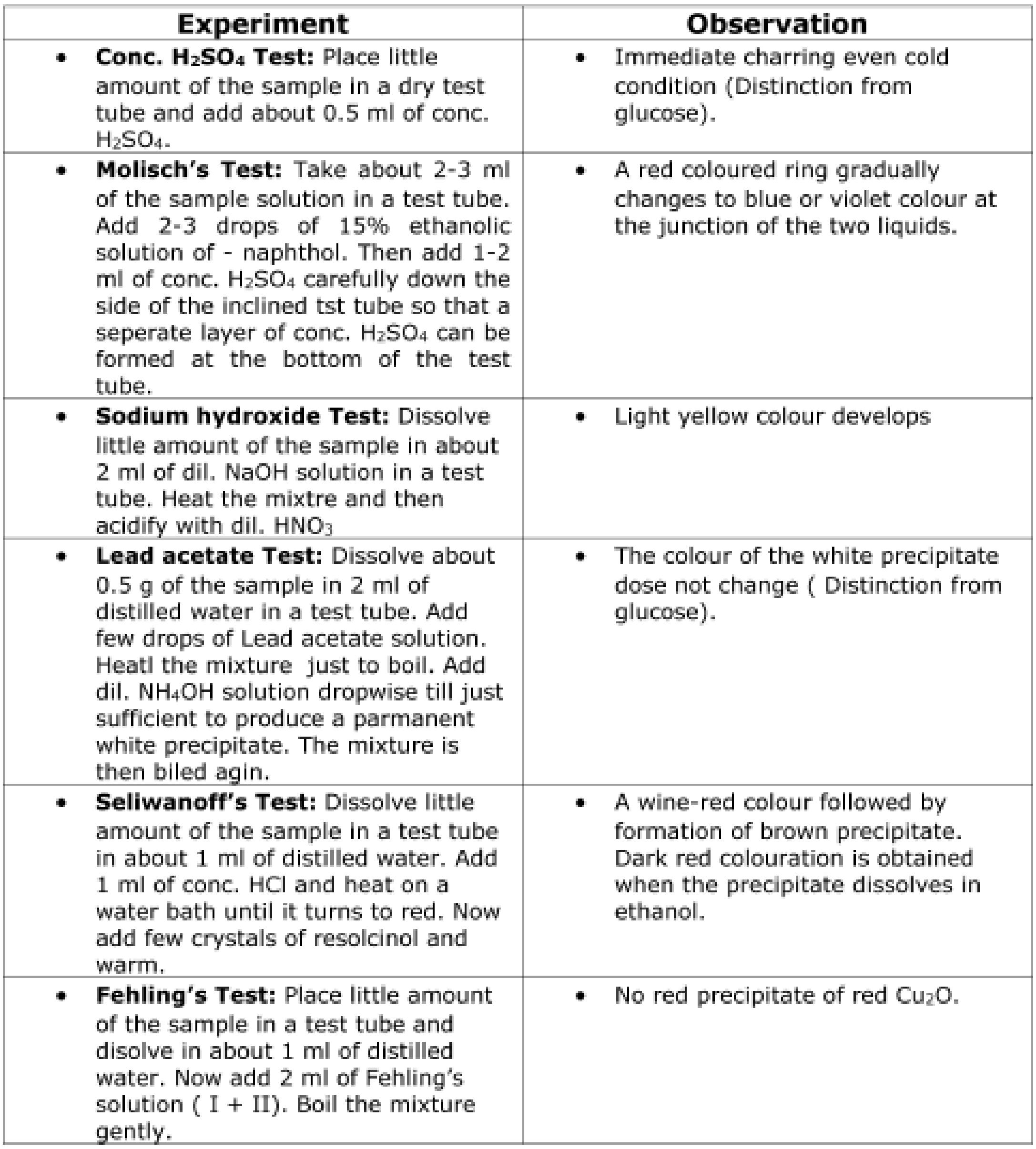
Physical characteristics:

- State : Solid
- Colour : Colourless
- Odour : Odourless
- Texture : Crystalline
- Solubility : Soluble in cold water
- Litmus : Neutral

Preliminary Test:

- Ignition Test : Burns with non-sooty blue flame
- Action of heat : Melts, turns to black on futher heating due to charring.

Special Tests:

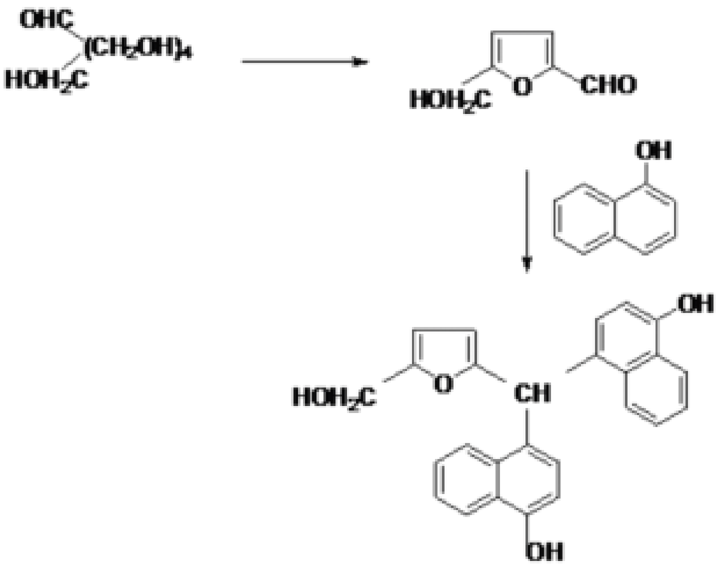


Experiment	Observation
• **Conc. H_2SO_4 Test:** Place little amount of the sample in a dry test tube and add about 0.5 ml of conc. H_2SO_4.	• Immediate charring even cold condition (Distinction from glucose).
• **Molisch's Test:** Take about 2-3 ml of the sample solution in a test tube. Add 2-3 drops of 15% ethanolic solution of - naphthol. Then add 1-2 ml of conc. H_2SO_4 carefully down the side of the inclined tst tube so that a seperate layer of conc. H_2SO_4 can be formed at the bottom of the test tube.	• A red coloured ring gradually changes to blue or violet colour at the junction of the two liquids.
• **Sodium hydroxide Test:** Dissolve little amount of the sample in about 2 ml of dil. NaOH solution in a test tube. Heat the mixtre and then acidify with dil. HNO_3	• Light yellow colour develops
• **Lead acetate Test:** Dissolve about 0.5 g of the sample in 2 ml of distilled water in a test tube. Add few drops of Lead acetate solution. Heatl the mixture just to boil. Add dil. NH_4OH solution dropwise till just sufficient to produce a parmanent white precipitate. The mixture is then biled agin.	• The colour of the white precipitate dose not change (Distinction from glucose).
• **Seliwanoff's Test:** Dissolve little amount of the sample in a test tube in about 1 ml of distilled water. Add 1 ml of conc. HCl and heat on a water bath until it turns to red. Now add few crystals of resolcinol and warm.	• A wine-red colour followed by formation of brown precipitate. Dark red colouration is obtained when the precipitate dissolves in ethanol.
• **Fehling's Test:** Place little amount of the sample in a test tube and disolve in about 1 ml of distilled water. Now add 2 ml of Fehling's solution (I + II). Boil the mixture gently.	• No red precipitate of red Cu_2O.

Explanations and Reactions:

- Molisch's test:

  Cane sugar first breacks into glucose and fructose.

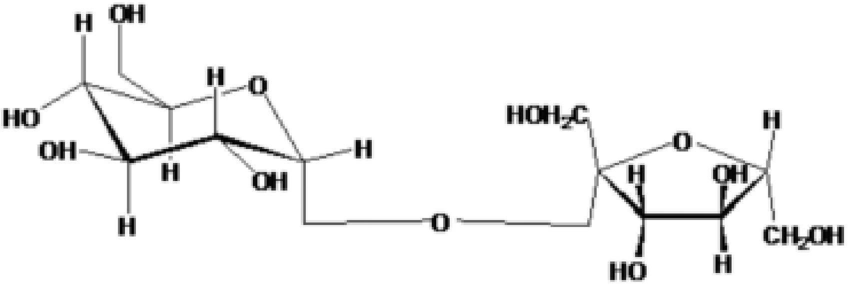


Red - violet colour

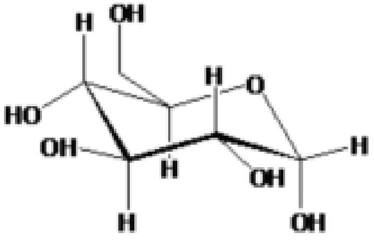
- Fehling's test:

  Sucrose dose not respond in fehling's test, as it is non-reducing sugar. This is due to the fact that one glucose and one fructose molecules are joint togather through –CHO and C=O group respectively in sucrose.

  Hydrolysis of cane sugar (sucrose):

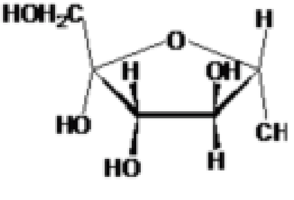


Cane sugar (Sucrose)



Glucose

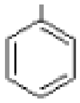
+



Fructose

11.12 Identification of Benzoic Acid By Chemical Tests:

S-9. BENZOIC ACID



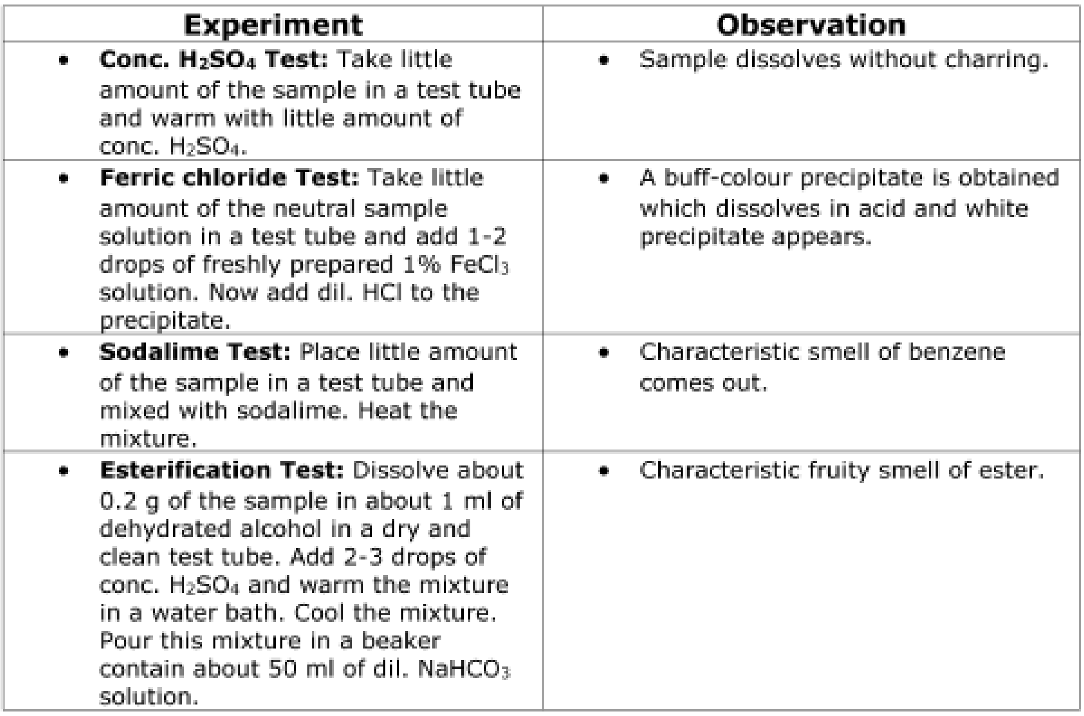
Physical characteristics:

- State : Solid
- Colour : Colourless
- Odour : Odourless
- Texture : Crystalline
- Solubility : Soluble in hot water
- Litmus : Blue litmus turns red

Preliminary Test:

- Ignition Test : Burns with yellow sooty flame
- Action of heat : Melts and sublimes with copious white fume.

Special Tests:



Experiment	Observation
• **Conc. H_2SO_4 Test:** Take little amount of the sample in a test tube and warm with little amount of conc. H_2SO_4.	• Sample dissolves without charring.
• **Ferric chloride Test:** Take little amount of the neutral sample solution in a test tube and add 1-2 drops of freshly prepared 1% $FeCl_3$ solution. Now add dil. HCl to the precipitate.	• A buff-colour precipitate is obtained which dissolves in acid and white precipitate appears.
• **Sodalime Test:** Place little amount of the sample in a test tube and mixed with sodalime. Heat the mixture.	• Characteristic smell of benzene comes out.
• **Esterification Test:** Dissolve about 0.2 g of the sample in about 1 ml of dehydrated alcohol in a dry and clean test tube. Add 2-3 drops of conc. H_2SO_4 and warm the mixture in a water bath. Cool the mixture. Pour this mixture in a beaker contain about 50 ml of dil. $NaHCO_3$ solution.	• Characteristic fruity smell of ester.

Explanations and Reactions:

- Ferric chloride test:

  $3C_6H_5COONa + 2FeCl_3 + 3H_2O \quad (C_6H_5COO)_3 Fe.Fe(OH)_3 + 3HCl + 3NaCl$

  $(C_6H_5COO)_3 Fe.Fe(OH)_3 + 6HCl \quad 3 C_6H_5COOH + 2FeCl_3 + 3H_2O$

- Sodalime test:

  $C_6H_5COOH + 2NaOH \quad C_6H_6 + Na_2CO_3 + H_2O$

- Estarification test:

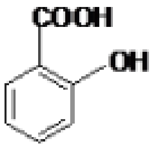
  $C_6H_5COOH + C_2H_5OH \quad C_6H_5COOC_2H_5 + H_2O$

  Ethyl benzoate

  (ester)

11.13 Identification of Salicylic Acid By Chemical Tests:

S-10. SALICYLIC ACID



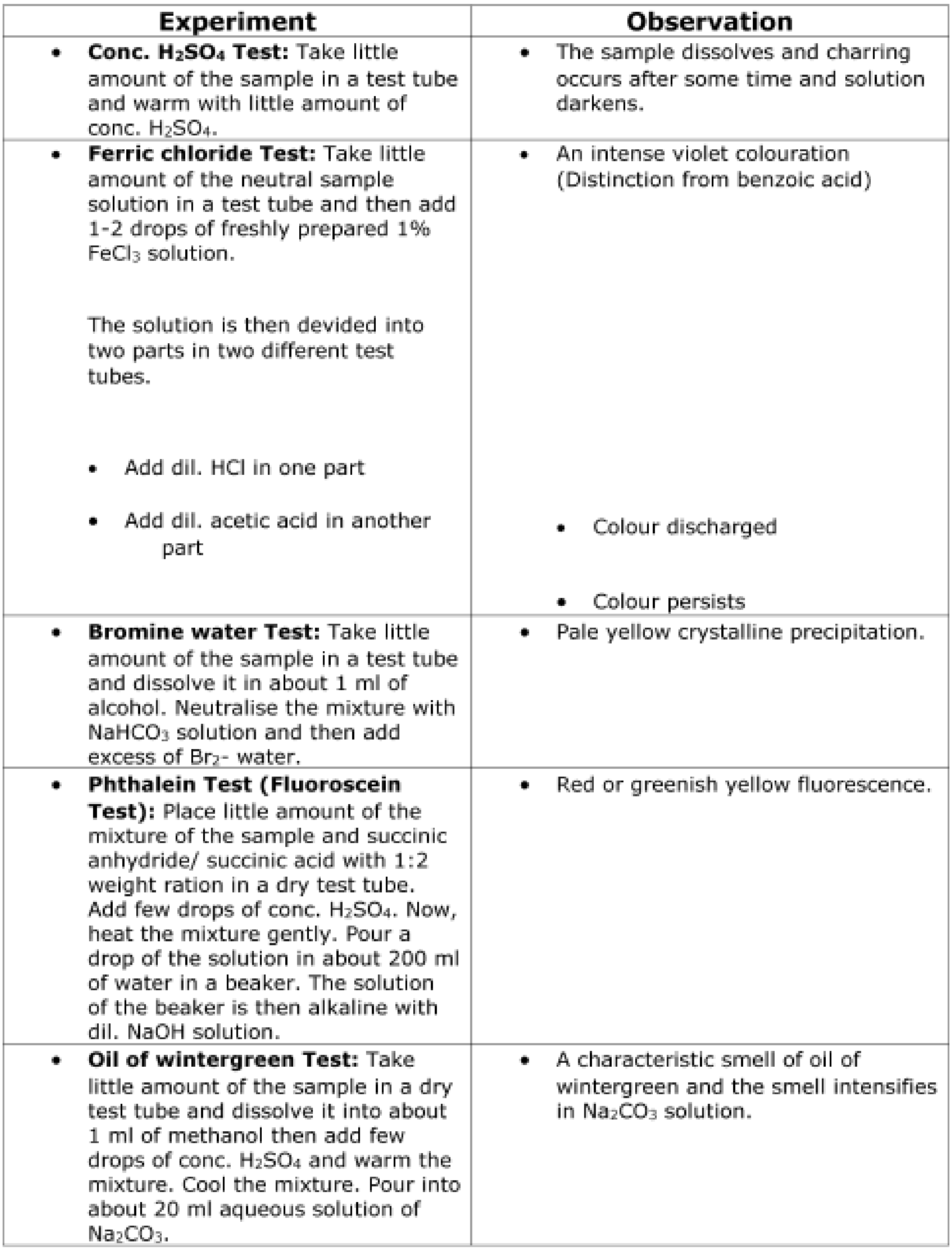
Physical characteristics:

- State : Solid
- Colour : White
- Odour : Odourless
- Texture : Needle shaped crystals
- Solubility : Soluble in hot water
- Litmus : Blue litmus turns red

Preliminary Test:

- ● Ignition Test : Burns with yellow sooty flame
- Action of heat : Melts and sublimes on gentle heating.

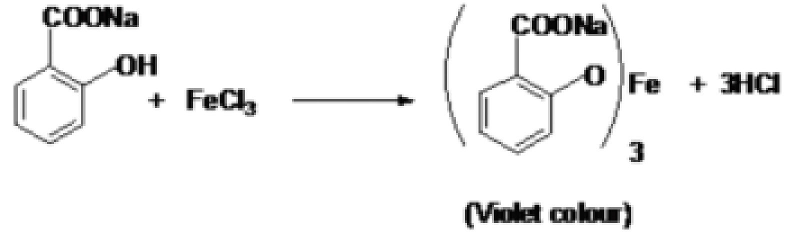
Special Tests:



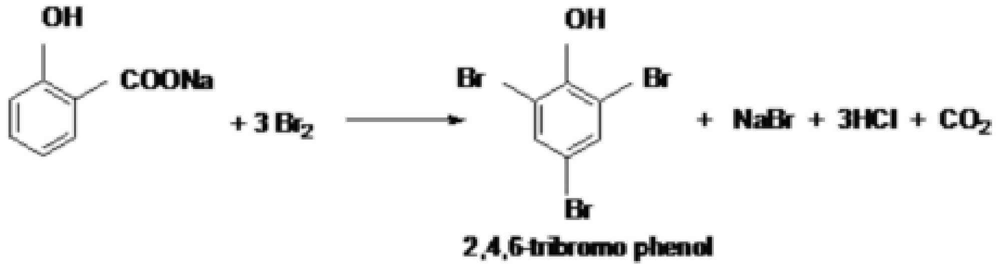
Experiment	Observation
• **Conc. H_2SO_4 Test:** Take little amount of the sample in a test tube and warm with little amount of conc. H_2SO_4.	• The sample dissolves and charring occurs after some time and solution darkens.
• **Ferric chloride Test:** Take little amount of the neutral sample solution in a test tube and then add 1-2 drops of freshly prepared 1% $FeCl_3$ solution. The solution is then devided into two parts in two different test tubes. • Add dil. HCl in one part • Add dil. acetic acid in another part	• An intense violet colouration (Distinction from benzoic acid) • Colour discharged • Colour persists
• **Bromine water Test:** Take little amount of the sample in a test tube and dissolve it in about 1 ml of alcohol. Neutralise the mixture with $NaHCO_3$ solution and then add excess of Br_2- water.	• Pale yellow crystalline precipitation.
• **Phthalein Test (Fluoroscein Test):** Place little amount of the mixture of the sample and succinic anhydride/ succinic acid with 1:2 weight ration in a dry test tube. Add few drops of conc. H_2SO_4. Now, heat the mixture gently. Pour a drop of the solution in about 200 ml of water in a beaker. The solution of the beaker is then alkaline with dil. NaOH solution.	• Red or greenish yellow fluorescence.
• **Oil of wintergreen Test:** Take little amount of the sample in a dry test tube and dissolve it into about 1 ml of methanol then add few drops of conc. H_2SO_4 and warm the mixture. Cool the mixture. Pour into about 20 ml aqueous solution of Na_2CO_3.	• A characteristic smell of oil of wintergreen and the smell intensifies in Na_2CO_3 solution.

Explanations and Reactions:

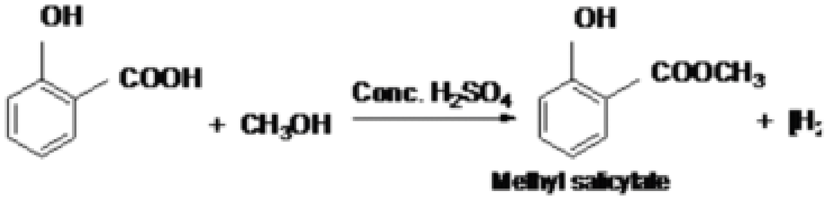
- Ferric chloride test:



- Bromine water test:



- Oil of wintergreen test:



11.14 Conclusion

The identification of organic compounds involves a systematic approach that begins with preliminary studies and extends to specific chemical tests for individual compounds. Preliminary studies, including observations of physical properties such as melting point, boiling point, and solubility, provide an initial understanding of the sample's nature and purity. These properties help in the tentative classification of the compound.

Preparation of neutral solutions of acids is a crucial step, especially for acidic compounds, to ensure accurate results in subsequent chemical tests. This process often involves dissolving the acid in water and neutralizing it to create a solution suitable for further analysis.

The identification of specific organic compounds is achieved through distinctive chemical tests that exploit unique chemical reactions and properties. For instance, oxalic acid is confirmed through precipitation reactions with calcium chloride and decolorization of potassium permanganate, while tartaric acid and citric acid can be distinguished through specific reactions such as the formation of Rochelle salt and calcium citrate, respectively.

Resorcinol is identified by its characteristic reactions, including a violet color with ferric chloride and formation of a white precipitate with bromine water. Urea is confirmed by its reaction in the Biuret test, indicating the presence of peptide bonds.

Glucose and cane sugar (sucrose) are differentiated through their reactions with Benedict's and Fehling's solutions, where glucose gives a positive result while sucrose requires hydrolysis for similar detection. Benzoic acid and salicylic acid are identified by specific reactions, such as sublimation and the formation of coloured complexes with ferric chloride, respectively.

11.15 Some Sample Questions

Question: What is the importance of preliminary studies in identifying pure samples of organic compounds?

Answer: Preliminary studies help determine the physical properties of a sample, such as melting point, boiling point, solubility, and appearance. These properties provide initial clues about the compound's identity and purity, assisting in narrowing down the possible functional groups and compound classes.

Question: How can a neutral solution of an acid be prepared for analysis?

Answer: To prepare a neutral solution of an acid, dissolve the acid in distilled water and then carefully neutralize it with a dilute solution of a strong base, such as sodium hydroxide (NaOH), while constantly checking the pH. The solution is considered neutral when the pH is close to 7.

Question: What chemical tests can be used to identify oxalic acid?

Answer: Oxalic acid can be identified by the following tests:

- **Calcium Chloride Test:** When oxalic acid solution is added to calcium chloride, a white precipitate of calcium oxalate forms.
- **KMnO„ Test:** Oxalic acid decolorizes a pink solution of potassium permanganate due to its reducing properties.

Question: What are the characteristic reactions of tartaric acid in chemical tests?

Answer: Tartaric acid can be identified by:

- **Rochelle Salt Formation:** Mixing tartaric acid with sodium carbonate forms sodium potassium tartrate, known as Rochelle salt.
- **Silver Mirror Test:** Tartaric acid reduces silver nitrate to metallic silver, forming a mirror-like deposit on the inner surface of a test tube.

Question: How can citric acid be distinguished from other acids using chemical tests? **Answer:** Citric acid can be identified by:

- **Calcium Citrate Test:** Adding calcium chloride to citric acid results in the formation of a white precipitate of calcium citrate.
- **Ferric Chloride Test:** Citric acid gives a yellowish color with ferric chloride due to complex formation.

Question: What are the specific tests for identifying resorcinol?

Answer: Resorcinol can be identified by:

- **Ferric Chloride Test:** It forms a violet color with ferric chloride solution.
- **Bromine Water Test:** Resorcinol reacts with bromine water to give a white precipitate.

Question: Describe a test that can confirm the presence of urea.

Answer: Urea can be identified by the **Biuret Test**, where heating urea results in the formation of biuret. The addition of copper sulfate and sodium hydroxide gives a violet color, indicating the presence of peptide bonds.

Question: What chemical tests can be used to identify glucose?

Answer: Glucose can be identified by:

- **Benedict's Test:** Glucose reduces Benedict's reagent to form a red precipitate of copper(I) oxide.
- **Fehling's Test:** Glucose also reduces Fehling's solution, resulting in a red precipitate.

Question: How can cane sugar be distinguished from other sugars in chemical tests?

Answer: Cane sugar (sucrose) can be identified by:

- **Hydrolysis Test:** When heated with dilute acid, sucrose hydrolyzes into glucose and fructose, which can be tested with Benedict's or Fehling's solutions.
- **Barfoed's Test:** Sucrose does not react with Barfoed's reagent, distinguishing it from reducing sugars.

Question: What are the characteristic reactions for identifying benzoic acid?

Answer: Benzoic acid can be identified by:

- **Sublimation Test:** Benzoic acid sublimes when gently heated, leaving a white residue.
- **Ferric Chloride Test:** It gives a buff-coloured precipitate with ferric chloride solution.

Question: Describe the chemical tests used to identify salicylic acid.

Answer: Salicylic acid can be identified by:

- **Ferric Chloride Test:** It gives a violet color when mixed with ferric chloride due to phenolic OH groups.
- **Melting Point Test:** Salicylic acid has a distinct melting point that can be measured for confirmation.

Question: Describe the observation and its significance when a sample is subjected to the Phthalein Test.

Answer: The appearance of a red or greenish-yellow fluorescence in an alkaline solution after heating the sample with succinic anhydride and concentrated H, SO„ indicates the formation of fluorescein derivatives. This fluorescence is a characteristic test for compounds containing a phenolic structure, specifically resorcinol.

Question: What does a characteristic smell of oil of wintergreen indicate when a sample is treated with methanol and concentrated H, SO„ , followed by Na, COƒ ?

Answer: The characteristic smell of oil of wintergreen indicates the formation of methyl salicylate, suggesting the presence of salicylic acid or its derivatives in the sample. The intensification of the smell in Na, COƒ solution confirms the formation of this ester.

Question: What does the production of a characteristic fruity smell after performing the esterification test suggest?

Answer: The production of a fruity smell indicates the formation of an ester, suggesting the presence of an alcohol and a carboxylic acid group in the sample. The esterification reaction, facilitated by concentrated H, SO,, and an alcohol, confirms the presence of these functional groups when a distinctive ester odor is produced.

Unit 12 ❐ Identification of a Pure Liquid Organic Compound by chemical test(s)

Formic acid, acetic acid, methyl alcohol, ethyl alcohol, acetone, aniline, dimethylaniline, benzaldehyde, chloroform and nitrobenzene.

12.0 Objectives

- Detection of Carboxylic Acids (Formic Acid, Acetic Acid)
- Distinguishing Alcohols (Methyl Alcohol, Ethyl Alcohol)
- Identification of Ketones (Acetone)
- Identification of Aromatic Amines (Aniline, Dimethylaniline)
- Detection of Aldehydes (Benzaldehyde)
- Identification of Halogenated Compounds (Chloroform)
- Detection of Nitro Compounds (Nitrobenzene)

12.1 Introduction

In the field of analytical chemistry, the identification and characterization of organic compounds are crucial for a wide range of applications, from industrial quality control to environmental monitoring and forensic analysis. This study focuses on the detection and differentiation of specific functional groups and compounds, including carboxylic acids, alcohols, ketones, aromatic amines, aldehydes, halogenated compounds, and nitro compounds.

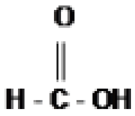
Carboxylic acids, such as formic acid and acetic acid, are commonly encountered in various chemical processes and biological systems. Their detection is often necessary for assessing purity and understanding reaction mechanisms. Alcohols, including methyl alcohol and ethyl alcohol, are ubiquitous solvents and reagents in chemical synthesis. Distinguishing between these alcohols is essential due to their differing physical and chemical properties.

Ketones, represented by acetone, are widely used as solvents and precursors in organic synthesis. Their identification is important in industries ranging from pharmaceuticals to coatings. Aromatic amines, like aniline and dimethylaniline, are key intermediates in dye and polymer manufacturing. The detection of these compounds is vital due to their potential health hazards and environmental impact.

Aldehydes, such as benzaldehyde, are valuable in the fragrance and flavour industries, and their identification is crucial for quality control. Halogenated compounds, exemplified by chloroform, are significant in various industrial applications and are often scrutinized for their environmental and health effects. Lastly, nitro compounds like nitrobenzene are used in the production of dyes, explosives, and pharmaceuticals. Accurate detection of these compounds is necessary due to their toxic and hazardous nature.

12.2 Identification of Formic Acid by Chemical Tests

L-11. FORMIC ACID



$$H-\overset{\overset{O}{\|}}{C}-OH$$

Physical characteristics:

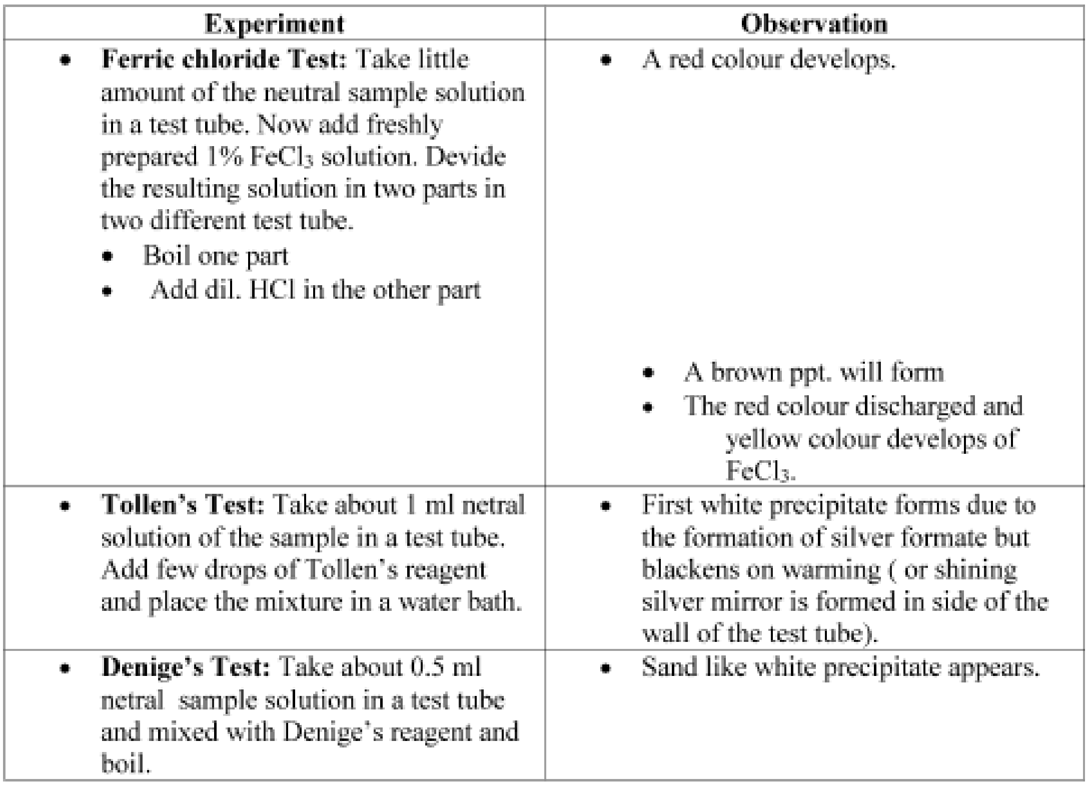
- State : Liquid
- Colour : Colourless

- Odour : Pungent odour
- Miscibility : Miscible in water
- Litmus : Blue litmus turns red

Preliminary Test:

- Ignition Test : Burns with non- sooty blue flame

Chemical Tests:



Experiment	Observation
• **Ferric chloride Test:** Take little amount of the neutral sample solution in a test tube. Now add freshly prepared 1% $FeCl_3$ solution. Devide the resulting solution in two parts in two different test tube. • Boil one part • Add dil. HCl in the other part	• A red colour develops. • A brown ppt. will form • The red colour discharged and yellow colour develops of $FeCl_3$.
• **Tollen's Test:** Take about 1 ml netral solution of the sample in a test tube. Add few drops of Tollen's reagent and place the mixture in a water bath.	• First white precipitate forms due to the formation of silver formate but blackens on warming (or shining silver mirror is formed in side of the wall of the test tube).
• **Denige's Test:** Take about 0.5 ml netral sample solution in a test tube and mixed with Denige's reagent and boil.	• Sand like white precipitate appears.

Explanations and Reactions:

- **Ferric chloride test:**

$$3HCOONa + FeCl_3 = (HCOO)_3Fe + 3NaCl$$

(Red colour)

$$(HCOO)_3Fe + 2H_2O = (HCOO)Fe(OH)_2 + 2HCOOH$$

(Basic ferric formate)

Brown ppt.

- Silver nitrate test:

$$HCOOH + 2[Ag(NH_3)_2]^+ + 2OH^- = 2Ag + CO_2 + 2H_2O + 4NH_3$$

12.3 Identification of Acetic Acid by Chemical Tests:

L-12. ACETIC ACID

$CH_3 - COOH$

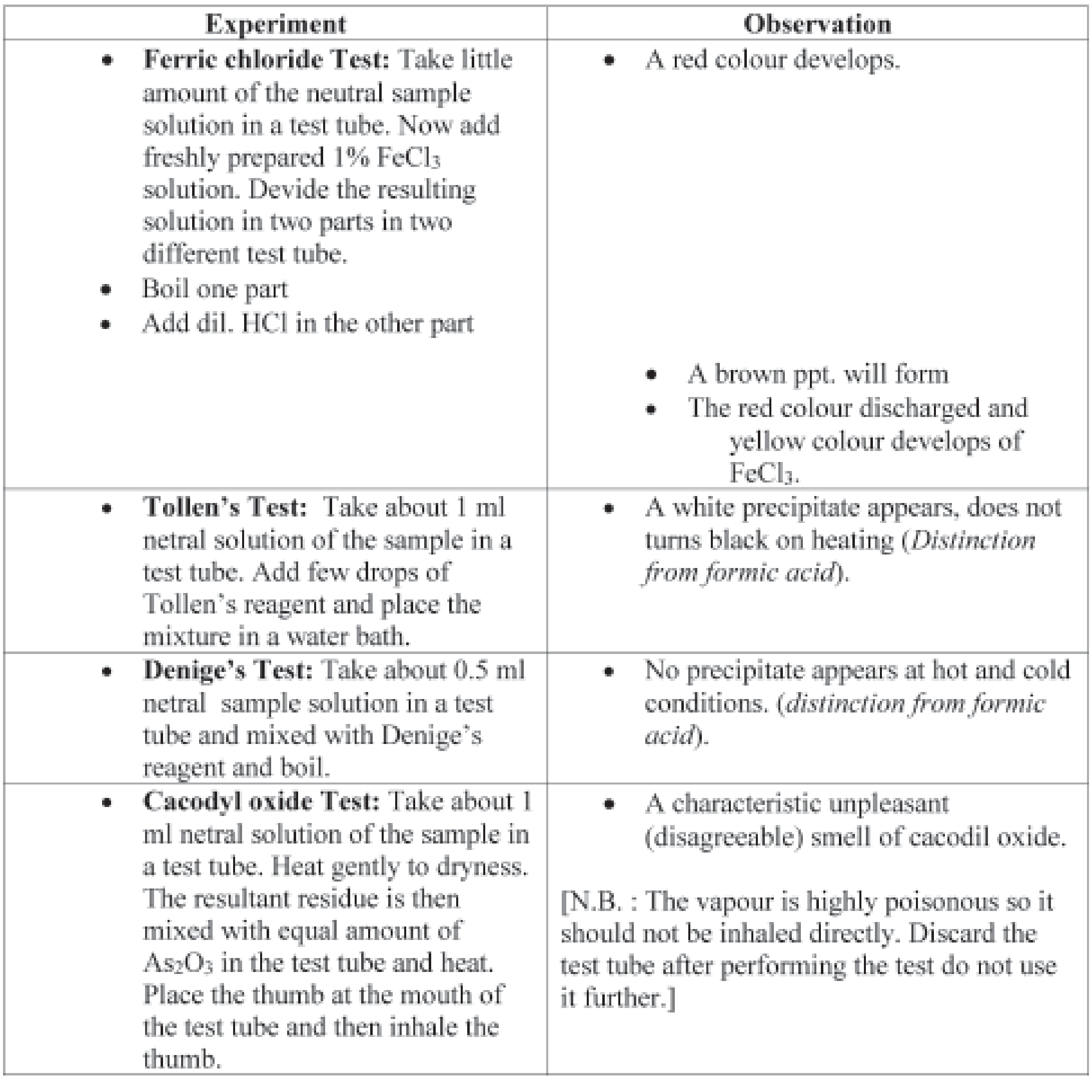
Physical characteristics:

- State : Liquid
- Colour : Colourless
- Odour : Characteristic smell of vinegar
- Miscibility : Miscible in water
- Litmus : Blue litmus turns red

Preliminary Test:

- Ignition Test : Burns with non- sooty blue flame

Chemical Tests:



Experiment	Observation
• **Ferric chloride Test:** Take little amount of the neutral sample solution in a test tube. Now add freshly prepared 1% $FeCl_3$ solution. Devide the resulting solution in two parts in two different test tube. • Boil one part • Add dil. HCl in the other part	• A red colour develops. • A brown ppt. will form • The red colour discharged and yellow colour develops of $FeCl_3$.
• **Tollen's Test:** Take about 1 ml netral solution of the sample in a test tube. Add few drops of Tollen's reagent and place the mixture in a water bath.	• A white precipitate appears, does not turns black on heating (*Distinction from formic acid*).
• **Denige's Test:** Take about 0.5 ml netral sample solution in a test tube and mixed with Denige's reagent and boil.	• No precipitate appears at hot and cold conditions. (*distinction from formic acid*).
• **Cacodyl oxide Test:** Take about 1 ml netral solution of the sample in a test tube. Heat gently to dryness. The resultant residue is then mixed with equal amount of As_2O_3 in the test tube and heat. Place the thumb at the mouth of the test tube and then inhale the thumb.	• A characteristic unpleasant (disagreeable) smell of cacodil oxide. [N.B. : The vapour is highly poisonous so it should not be inhaled directly. Discard the test tube after performing the test do not use it further.]

Explanations and Reactions:

- Ferric chloride test:

$$3CH_3COONa + FeCl_3 = (CH_3COO)_3Fe + 3NaCl$$

(Red colour)

$$(CH_3COO)_3Fe + 2H_2O = (CH_3COO)Fe(OH)_2 + 2CH_3COOH$$

(Basic ferric acetate)

Brown ppt.

- Tollen's test:

  $CH_3COONa + AgNO_3 = CH_3COOAg + NaNO_3$
- Cacodyl oxide test:

$$4CH_3COONa + As_2O_3 \longrightarrow \underset{\text{(Cacodyl oxide)}}{(CH_3)_2As-O-As(CH_3)_2} + CO_2 + 2Na_2C$$

12.4 Identification of Methyl Alcohol by Chemical Tests

L-13. METHYL ALCOHOL

$CH_3 - OH$

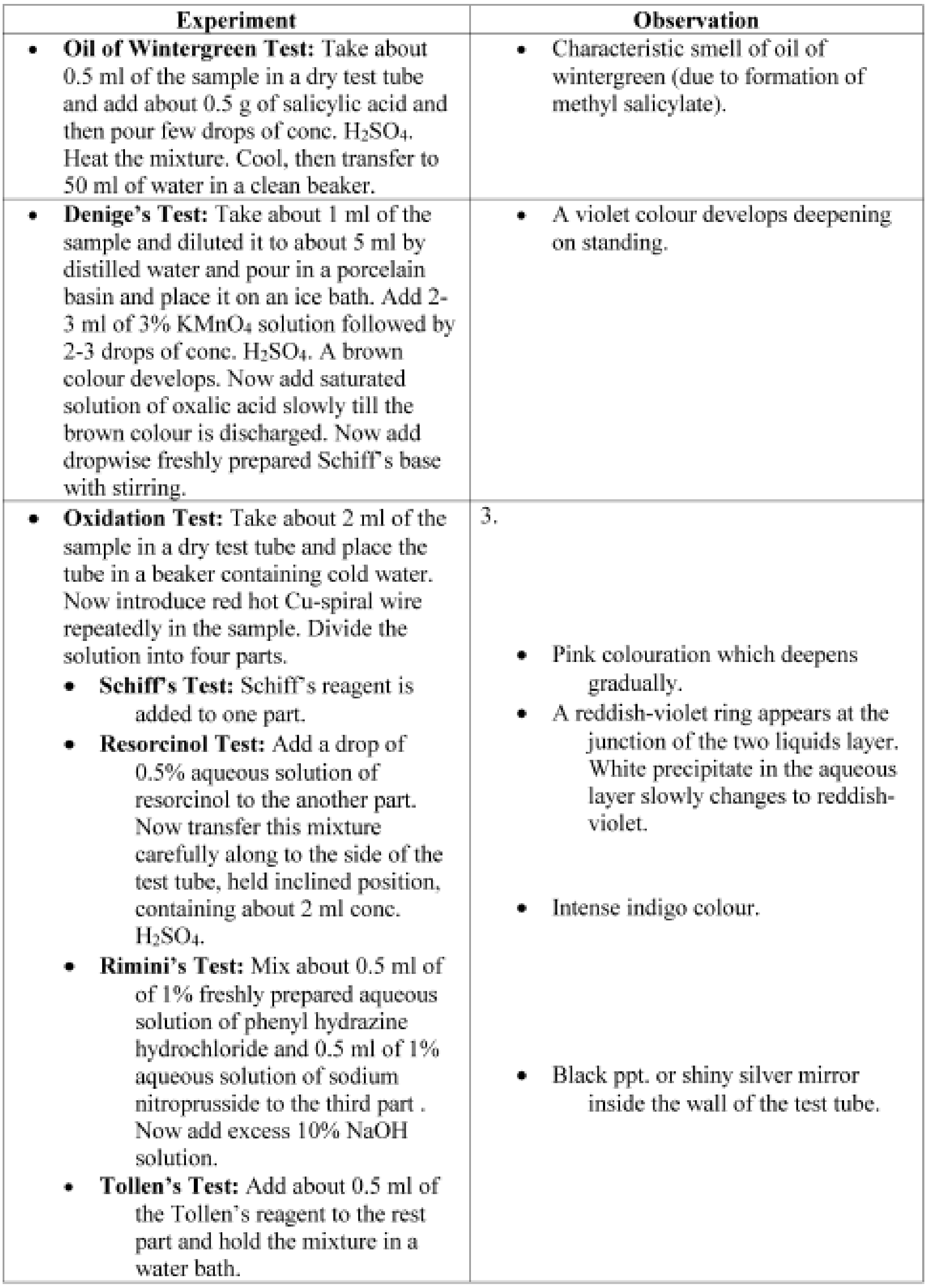
Physical characteristics:

- State : Liquid
- Colour : Colourless
- Odour : Characteristic smell of alcohol
- Miscibility : Miscible in water
- Litmus : Neutral

Preliminary Test:

- Ignition Test : Burns with non- sooty blue flame

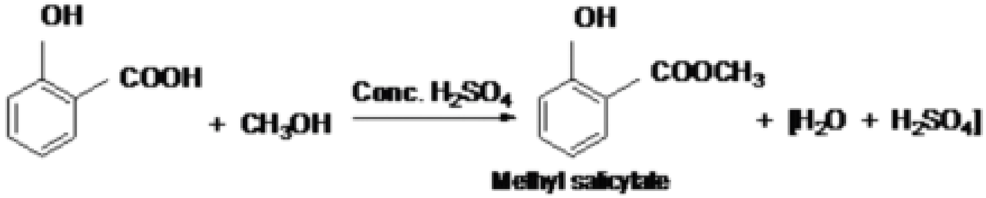
Chemical Tests:



Experiment	**Observation**
- **Oil of Wintergreen Test:** Take about 0.5 ml of the sample in a dry test tube and add about 0.5 g of salicylic acid and then pour few drops of conc. H_2SO_4. Heat the mixture. Cool, then transfer to 50 ml of water in a clean beaker.	- Characteristic smell of oil of wintergreen (due to formation of methyl salicylate).
- **Denige's Test:** Take about 1 ml of the sample and diluted it to about 5 ml by distilled water and pour in a porcelain basin and place it on an ice bath. Add 2-3 ml of 3% $KMnO_4$ solution followed by 2-3 drops of conc. H_2SO_4. A brown colour develops. Now add saturated solution of oxalic acid slowly till the brown colour is discharged. Now add dropwise freshly prepared Schiff's base with stirring.	- A violet colour develops deepening on standing.
- **Oxidation Test:** Take about 2 ml of the sample in a dry test tube and place the tube in a beaker containing cold water. Now introduce red hot Cu-spiral wire repeatedly in the sample. Divide the solution into four parts. - **Schiff's Test:** Schiff's reagent is added to one part. - **Resorcinol Test:** Add a drop of 0.5% aqueous solution of resorcinol to the another part. Now transfer this mixture carefully along to the side of the test tube, held inclined position, containing about 2 ml conc. H_2SO_4. - **Rimini's Test:** Mix about 0.5 ml of of 1% freshly prepared aqueous solution of phenyl hydrazine hydrochloride and 0.5 ml of 1% aqueous solution of sodium nitroprusside to the third part . Now add excess 10% NaOH solution. - **Tollen's Test:** Add about 0.5 ml of the Tollen's reagent to the rest part and hold the mixture in a water bath.	3. - Pink colouration which deepens gradually. - A reddish-violet ring appears at the junction of the two liquids layer. White precipitate in the aqueous layer slowly changes to reddish-violet. - Intense indigo colour. - Black ppt. or shiny silver mirror inside the wall of the test tube.

Explanations and Reactions:

- Oil of Wintergreen test:



12.5 Identification of Ethyl Alcohol by Chemical Tests

L-14. ETHYL ALCOHOL

$CH_3.CH_2 - OH$

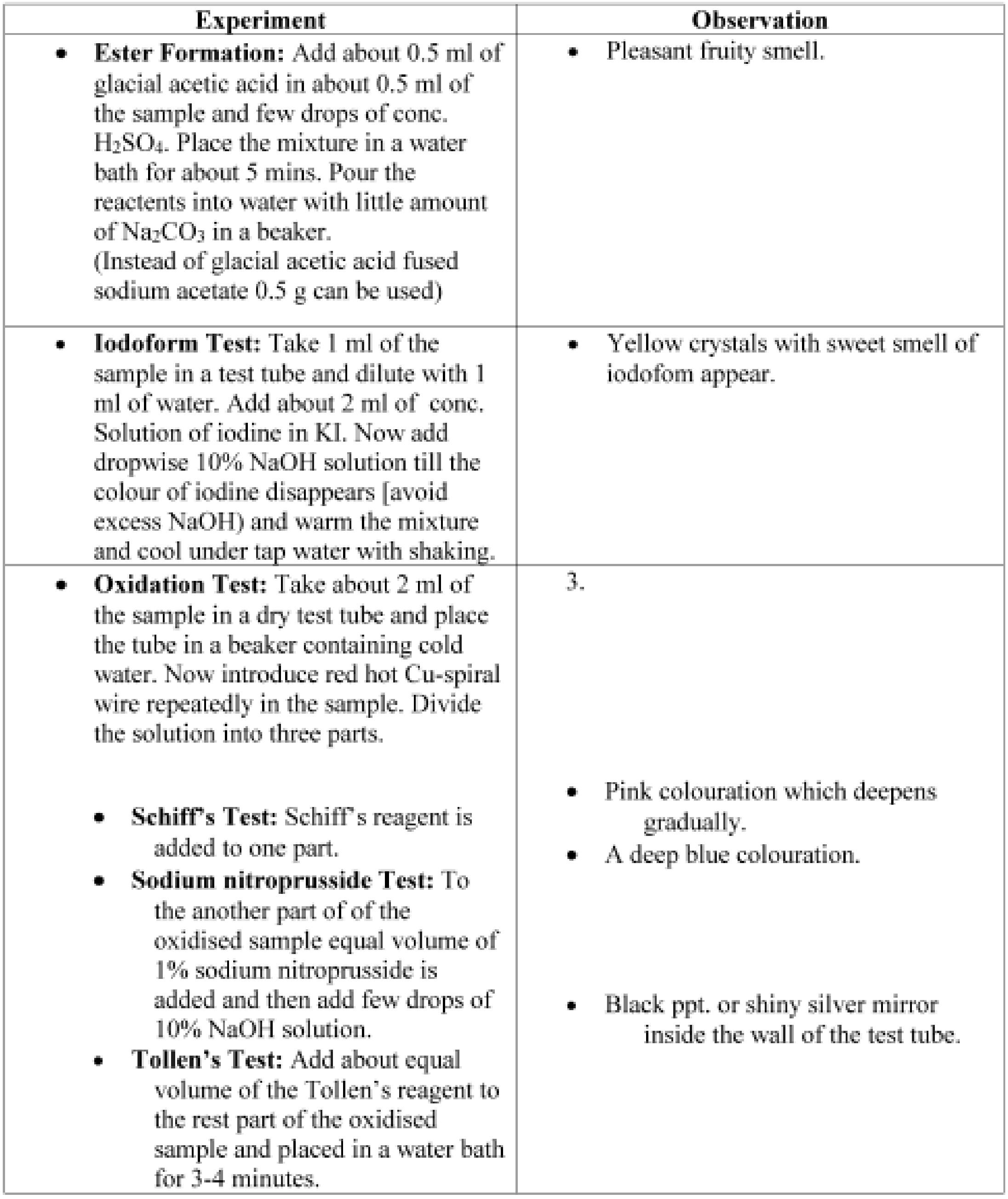
Physical characteristics:

State	: Liquid
Colour	: Colourless
Odour	: Characteristic smell of alcohol
Miscibility	: Miscible in water
Litmus	: Neutral

Preliminary Test:

- Ignition Test : Burns with non- sooty blue flame

Chemical Tests:



Experiment	Observation
• **Ester Formation:** Add about 0.5 ml of glacial acetic acid in about 0.5 ml of the sample and few drops of conc. H_2SO_4. Place the mixture in a water bath for about 5 mins. Pour the reactents into water with little amount of Na_2CO_3 in a beaker. (Instead of glacial acetic acid fused sodium acetate 0.5 g can be used)	• Pleasant fruity smell.
• **Iodoform Test:** Take 1 ml of the sample in a test tube and dilute with 1 ml of water. Add about 2 ml of conc. Solution of iodine in KI. Now add dropwise 10% NaOH solution till the colour of iodine disappears [avoid excess NaOH) and warm the mixture and cool under tap water with shaking.	• Yellow crystals with sweet smell of iodofom appear.
• **Oxidation Test:** Take about 2 ml of the sample in a dry test tube and place the tube in a beaker containing cold water. Now introduce red hot Cu-spiral wire repeatedly in the sample. Divide the solution into three parts.	3.
• **Schiff's Test:** Schiff's reagent is added to one part.	• Pink colouration which deepens gradually.
• **Sodium nitroprusside Test:** To the another part of of the oxidised sample equal volume of 1% sodium nitroprusside is added and then add few drops of 10% NaOH solution.	• A deep blue colouration.
• **Tollen's Test:** Add about equal volume of the Tollen's reagent to the rest part of the oxidised sample and placed in a water bath for 3-4 minutes.	• Black ppt. or shiny silver mirror inside the wall of the test tube.

Explanations and Reactions:

- Ester Formation:

  $CH_3CH_2 - OH + CH_3COOH \quad = CH_3COOC_2H_5 + H_2O$

- Iodoform test:

  $CH_3CH_2 - OH + 4I_2 + 6NaOH = CHI_3 + HCOONa + 5NaI + 5H_2O$

- Sodium nitroprusside test:

  $CH_3CH_2 - OH + CuO = CH_3CHO + H_2O + Cu$

  $CH_3CHO + Na_2[Fe(CN)_5NO] + OH^- \qquad Na_2[Fe(CN)_5NO - CH_2CHO]$
  (Blue colour)

12.6 Identification of Acetone by Chemical Tests

L-15. ACETONE

$CH_3 - CO - CH_3$

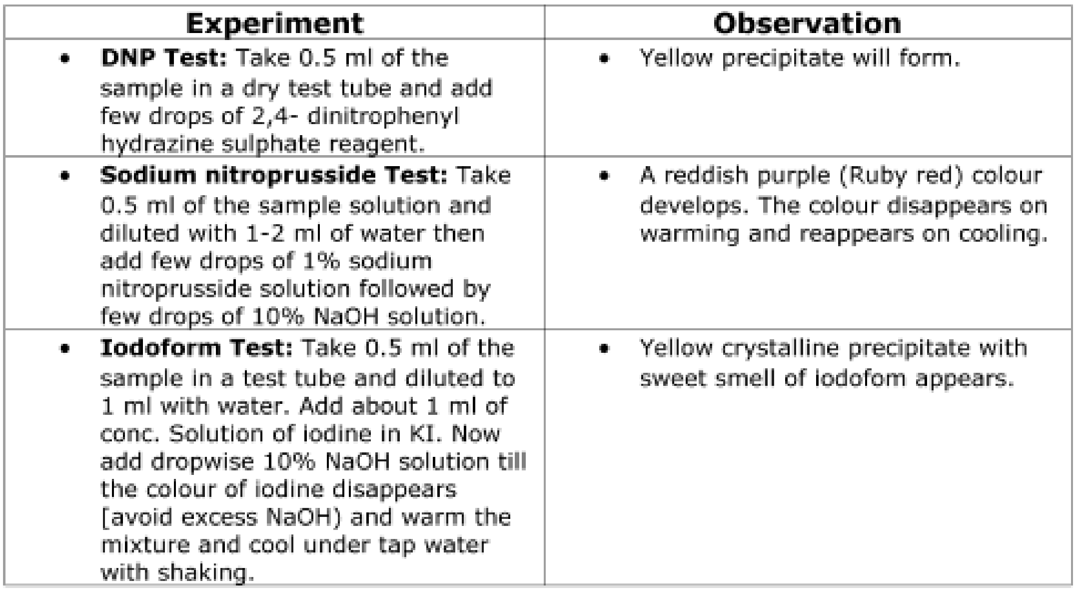
Physical characteristics:

- State : Liquid
- Colour : Colourless
- Odour : Characteristic pleasant smell
- Miscibility : Miscible in water
- Litmus : Neutral

Preliminary Test:

- Ignition Test : Burns with non- sooty blue flame

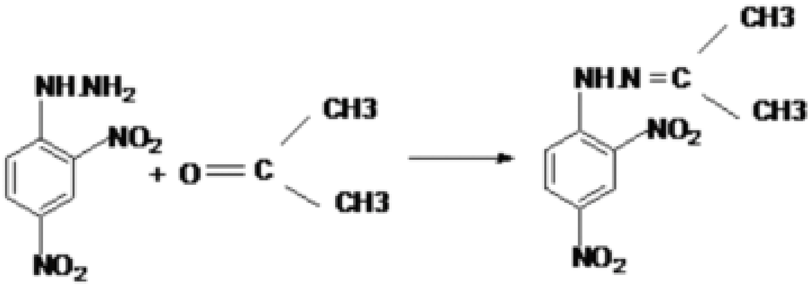
Chemical Tests:



Experiment	Observation
• **DNP Test:** Take 0.5 ml of the sample in a dry test tube and add few drops of 2,4- dinitrophenyl hydrazine sulphate reagent.	• Yellow precipitate will form.
• **Sodium nitroprusside Test:** Take 0.5 ml of the sample solution and diluted with 1-2 ml of water then add few drops of 1% sodium nitroprusside solution followed by few drops of 10% NaOH solution.	• A reddish purple (Ruby red) colour develops. The colour disappears on warming and reappears on cooling.
• **Iodoform Test:** Take 0.5 ml of the sample in a test tube and diluted to 1 ml with water. Add about 1 ml of conc. Solution of iodine in KI. Now add dropwise 10% NaOH solution till the colour of iodine disappears [avoid excess NaOH) and warm the mixture and cool under tap water with shaking.	• Yellow crystalline precipitate with sweet smell of iodofom appears.

Explanations and Reactions:

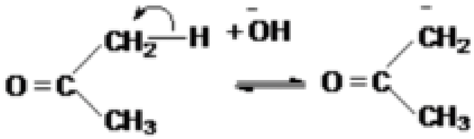
- DNP Test:



- Sodium nitroprusside test:

$CH_3COCH_3 + Na_2[Fe(CN)_5NO] + OH^-$ $Na_2[Fe(CN)_5\ NO–CH_2COCH_3]$ (Ruby red colour)

In presence of alkali acetone converted to first $CH_3COCH_2^-$, which reacts with $[Fe(CN)_5NO]^{-2}$ to give highly coloured $[Fe(CN)_5\ NO–CH_2COCH_3]^{-2}$

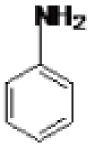


- Iodoform test:

  $CH_3COCH_3 + 3I_2 + 4NaOH = CHI_3 + CH_3COONa + 3NaI + 3H_2O$

12.7 Identification of Aniline by Chemical Tests:

L-16. ANILINE



Physical characteristics:

- State : Liquid
- Colour : Reddish brown *
- Odour : Characteristic smell
- Miscibility : Immiscible in water but soluble in dil. HCl
- Litmus : Neutral

Preliminary Test:

- Ignition Test : Burns with yellow sooty flame

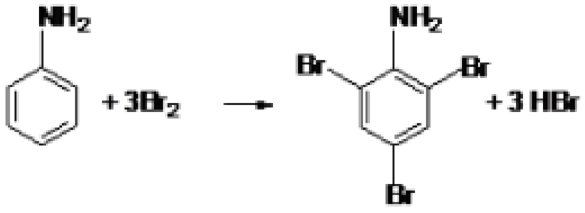
* [Colour of the freshly distilled liquid is colourless but turns brown on exposure in air and light.]

Chemical Tests:

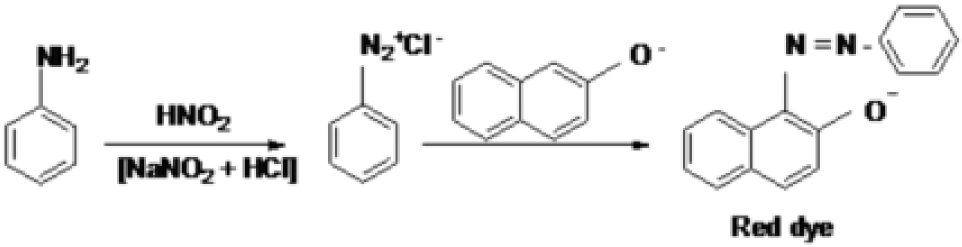
Experiment	**Observation**
• **Bromine water Test:** Take about 0.5 ml of the sample and dissolve in 1 ml of dil. HCl and then add about 0.5 ml of bromine water.	• White precipitate.
• **Diazo-coupling Test:** Take three test tubes. a) In first tube take 0.5 ml of the sample and dissolve it into 1 ml of dil. HCl. b) In second test tube prepare 1ml 10% $NaNO_2$ solution. c) In third test tube dissolve about 10 mg – naphthol in 5 ml 10% NaOH. Place the three mixtures in an ice bath. When the solutions are throughly chilled, tranfer $NaNO_2$ solution (b) into acidified sample solution (a). Now pour a drop of this diazotised mixture to alkaline sodium - naphthoxide solution.	2. Brilliant red dye will form.
• **Bleaching Powder Test:** Take 1-2 drops of the sample in a test tube and dissolve it into about 1 ml of dil. HCl. Now add few drops of bleaching powder solution.	3. Purple or violet colouration.
• **Carbylamine Test:** Take 2-3 drops of the sample in a test tube and add 2-3 drops of chloroform and 1-2 ml of alcohol and a bead of KOH or NaOH. Warm the mixture.	4. A colourless gas comes out with a irritating smell of iso-cyanide.
• **Potassium dichromate Test:** Place a drop of the sample in spot plate and add 3-4 drops of conc. H_2SO_4. Stir the mixture well with a glass rod. Now pour a drop of $K_2Cr_2O_7$ solution.	5. Intense blue colouration.

Explanations and Reactions:

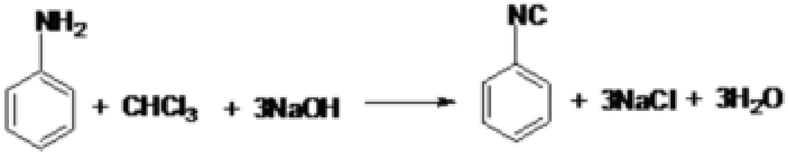
- Bromine water test:



- Diazo- coupling reaction:

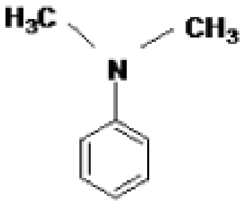


- Carbylamine test:



12.8 Identification of Dimethyl Aniline by Chemical Tests:

L-17. DIMETHYL ANILINE



Physical characteristics:

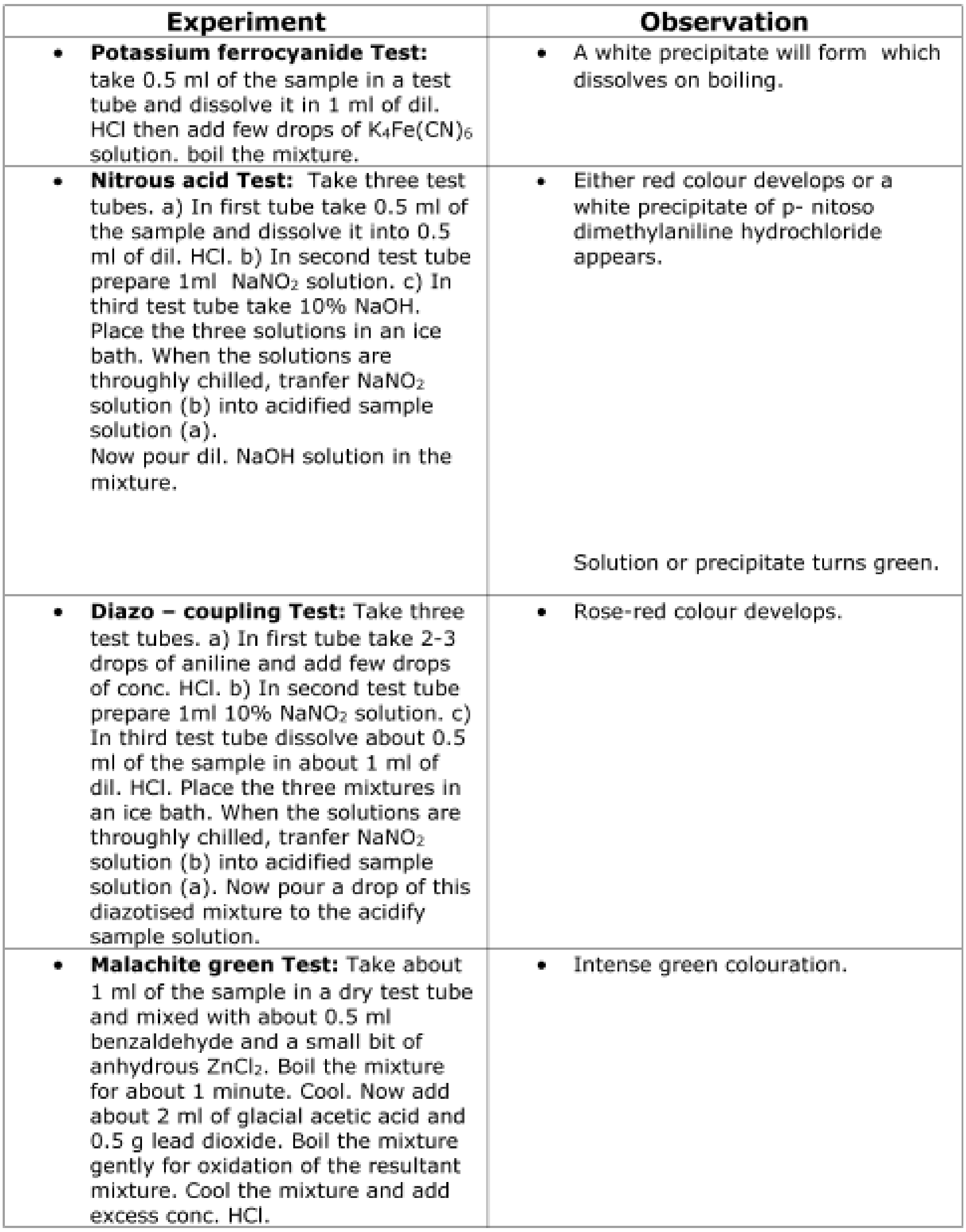
- State : Liquid
- Colour : Brown *
- Odour : Characteristic bad smell
- Miscibility : Immiscible in water but soluble in dil. HCl
- Litmus : Neutral

* [Colour of the freshly distilled liquid is colourless but turns brown on exposure in air and light.]

Preliminary Test:

- Ignition Test : Burns with yellow sooty flame

Chemical Tests:



Experiment	Observation
• **Potassium ferrocyanide Test:** take 0.5 ml of the sample in a test tube and dissolve it in 1 ml of dil. HCl then add few drops of $K_4Fe(CN)_6$ solution. boil the mixture.	• A white precipitate will form which dissolves on boiling.
• **Nitrous acid Test:** Take three test tubes. a) In first tube take 0.5 ml of the sample and dissolve it into 0.5 ml of dil. HCl. b) In second test tube prepare 1ml $NaNO_2$ solution. c) In third test tube take 10% NaOH. Place the three solutions in an ice bath. When the solutions are throughly chilled, tranfer $NaNO_2$ solution (b) into acidified sample solution (a). Now pour dil. NaOH solution in the mixture.	• Either red colour develops or a white precipitate of p- nitoso dimethylaniline hydrochloride appears. Solution or precipitate turns green.
• **Diazo – coupling Test:** Take three test tubes. a) In first tube take 2-3 drops of aniline and add few drops of conc. HCl. b) In second test tube prepare 1ml 10% $NaNO_2$ solution. c) In third test tube dissolve about 0.5 ml of the sample in about 1 ml of dil. HCl. Place the three mixtures in an ice bath. When the solutions are throughly chilled, tranfer $NaNO_2$ solution (b) into acidified sample solution (a). Now pour a drop of this diazotised mixture to the acidify sample solution.	• Rose-red colour develops.
• **Malachite green Test:** Take about 1 ml of the sample in a dry test tube and mixed with about 0.5 ml benzaldehyde and a small bit of anhydrous $ZnCl_2$. Boil the mixture for about 1 minute. Cool. Now add about 2 ml of glacial acetic acid and 0.5 g lead dioxide. Boil the mixture gently for oxidation of the resultant mixture. Cool the mixture and add excess conc. HCl.	• Intense green colouration.

Explanations and Reactions:

- Potassium ferrocyanide test:

$$C_6H_5N(CH_3)_2 + HCl \longrightarrow C_6H_5N(CH_3)_2HCl$$

$$2C_6H_5N(CH_3)_2.HCl + 2HCl + K_4[Fe(CN)_6] \longrightarrow \underset{\text{(White ppt.)}}{[C_6H_5N(CH_3)_2]_2.H_4Fe}$$

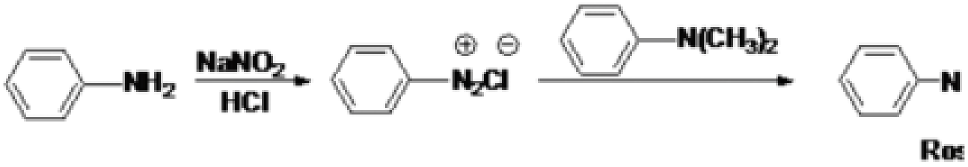
- Nitrous acid test:

$$C_6H_5N(CH_3)_2HCl + NaNO_2 \longrightarrow \underset{\text{(Red colour or white ppt).}}{ON-C_6H_5-N(CH_3)_2HCl} + Na$$

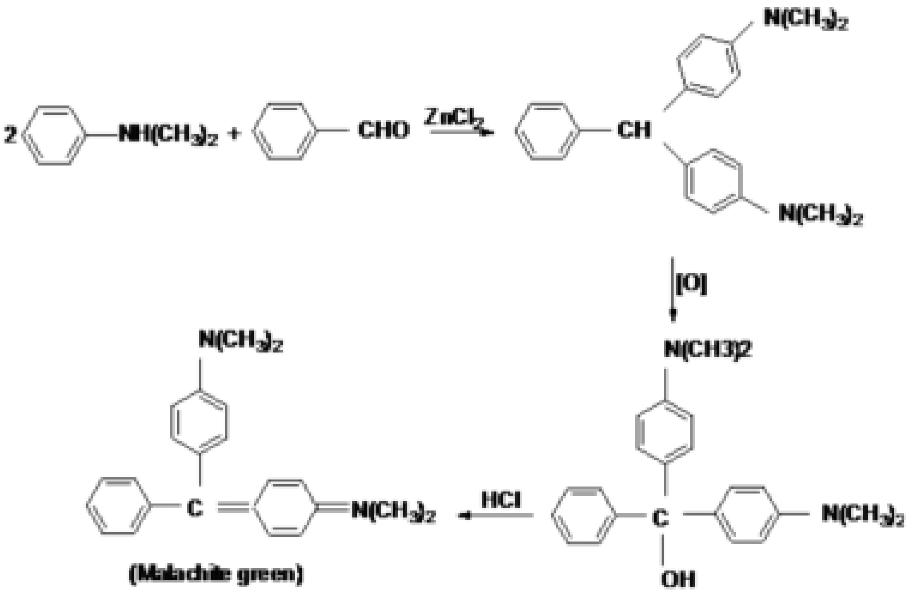
$$\Big\downarrow$$

$$\underset{\text{(Green)}}{ON-C_6H_5-N(CH_3)_2} + NaCl +$$

- Diazo-coupling test:

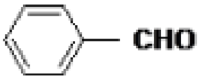


- Malachite green test:



12.9 Identification of Benzaldehyde by Chemical Tests:

L-18. BENZALDEHYDE



Physical characteristics:

• State	: Liquid
• Colour	: Colourless
• Odour	: Characteristic odour of bitter almonds
• Miscibility	: Immiscible with water
• Litmus	: Neutral (for freshly distilled)

* [Colour of the freshly distilled liquid is colourless but turns brown on exposure in air and light.]

Preliminary Test:

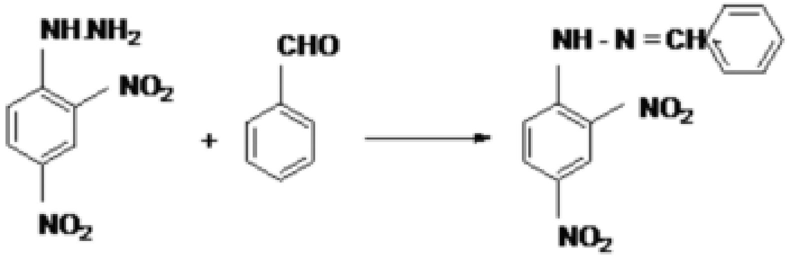
- Ignition Test : Burns with yellow sooty flame

Chemical Tests:

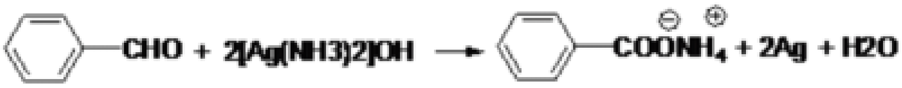
Experiment	Observation
• **Schiff's Test:** Take about 2 ml of Schiff's reagent in a test tube and add a drop of the sample and the mixture is then shaken.	• Pink or purple colour develops immediately.
• **Fehling's Test:** Take about 2 ml of Fehling's solution (I & II) in a test tube and add 2-3 drops of the sample and warm.	• No red precipitate of Cu_2O.
• **Tollen's Test:** Take about 1 ml of Tollen's reagent in a test tube and pour few drops of the sample. Shake the mixture and place in a water bath.	• Black ppt. or silver mirror form on the sides of the test tube.
• **2,4- DNP Test:** Add 2,4- Dinitro phenyl hydrazine sulphate reagent to 0.5 ml of the sample in a dry test tube.	• Red or reddish yellow ppt. forms immediately.
• **Malachite green Test:** Take about 0.5 ml of the sample in a dry test tube and mixed with about 1 ml of benzaldehyde and a small bit of anhydrous $ZnCl_2$. Boil the mixture for about 1 minute. Cool. Now add about 2 ml of glacial acetic acid and 0.5 g lead dioxide. Boil the mixture gently for oxidation of the resultant mixture. Cool the mixture and add excess conc. HCl.	• Intense green colouration.

Explanations and Reactions:

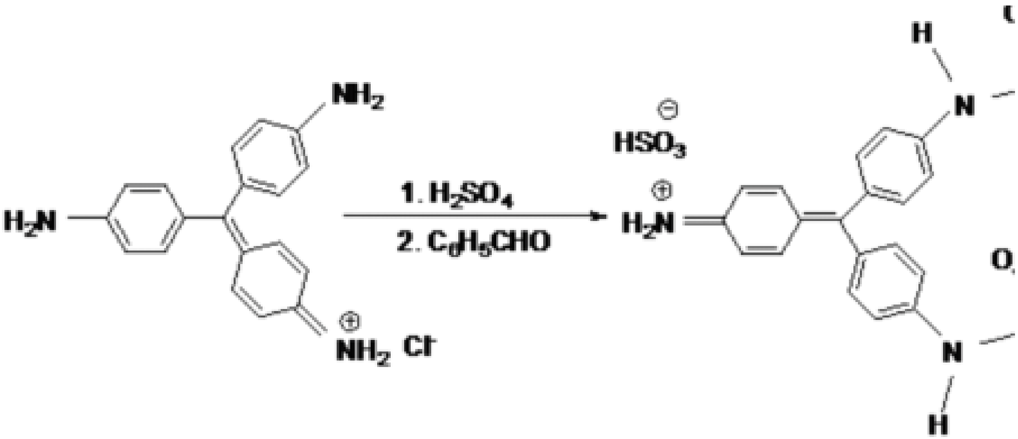
- 2,4- DNP test:



- Tollen's test:



- Schiff's test:



- Malachite green test: See N,N-dimethyl aniline

12.10 Identification of Chloroform by Chemical Tests:

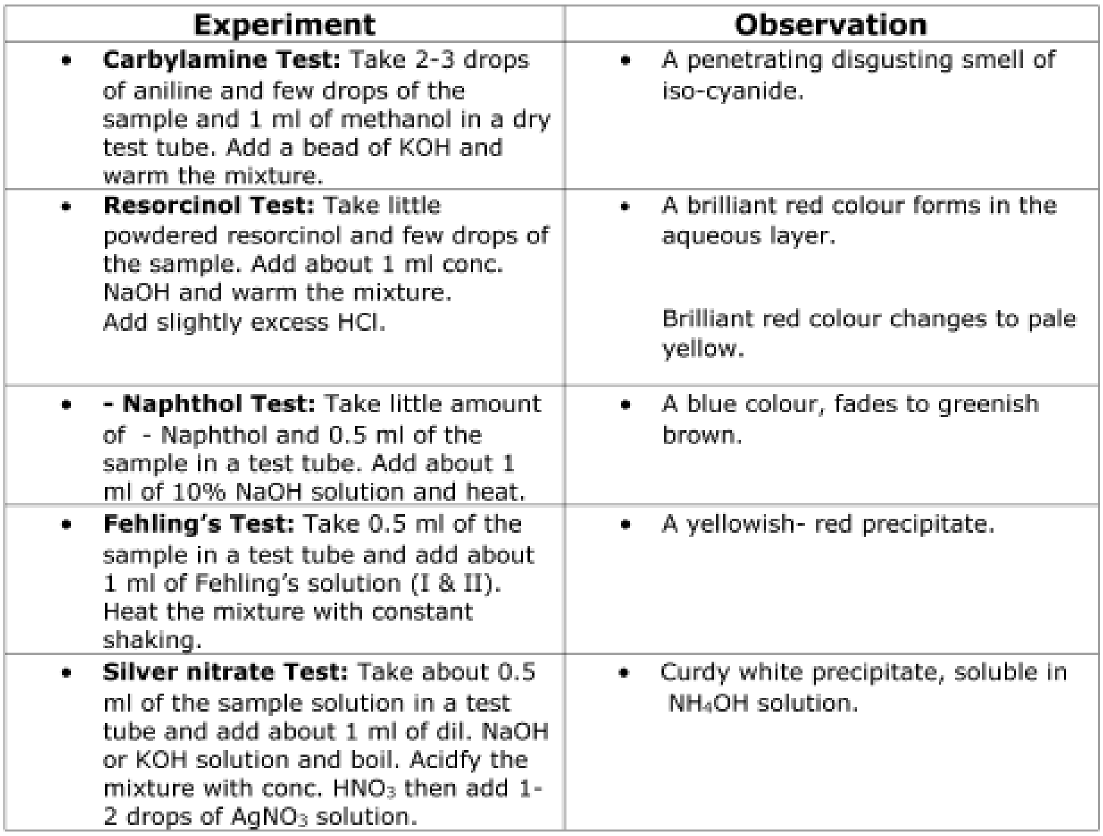
L-19. CHLOROFORM

$CHCl_3$

Physical characteristics:

- State : Liquid
- Colour : Colourless
- Odour : Sweet smell
- Miscibility : Immiscible with water
- Litmus : Neutral (for freshly distilled)
- Preliminary Test:
- Ignition Test : Burns with yellow sooty flame (c.f. aromatic compounds C;H = 1:1)

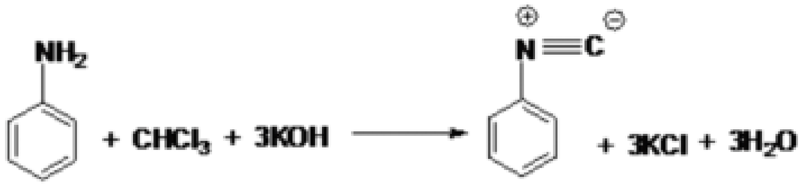
Chemical Tests:



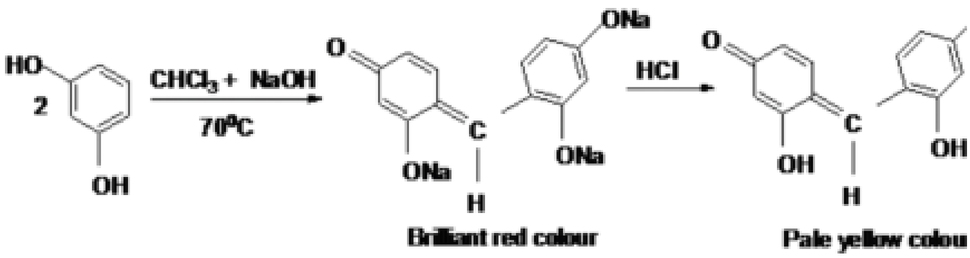
Experiment	Observation
• **Carbylamine Test:** Take 2-3 drops of aniline and few drops of the sample and 1 ml of methanol in a dry test tube. Add a bead of KOH and warm the mixture.	• A penetrating disgusting smell of iso-cyanide.
• **Resorcinol Test:** Take little powdered resorcinol and few drops of the sample. Add about 1 ml conc. NaOH and warm the mixture. Add slightly excess HCl.	• A brilliant red colour forms in the aqueous layer. Brilliant red colour changes to pale yellow.
• **- Naphthol Test:** Take little amount of - Naphthol and 0.5 ml of the sample in a test tube. Add about 1 ml of 10% NaOH solution and heat.	• A blue colour, fades to greenish brown.
• **Fehling's Test:** Take 0.5 ml of the sample in a test tube and add about 1 ml of Fehling's solution (I & II). Heat the mixture with constant shaking.	• A yellowish- red precipitate.
• **Silver nitrate Test:** Take about 0.5 ml of the sample solution in a test tube and add about 1 ml of dil. NaOH or KOH solution and boil. Acidify the mixture with conc. HNO_3 then add 1-2 drops of $AgNO_3$ solution.	• Curdy white precipitate, soluble in NH_4OH solution.

Explanations and Reactions:

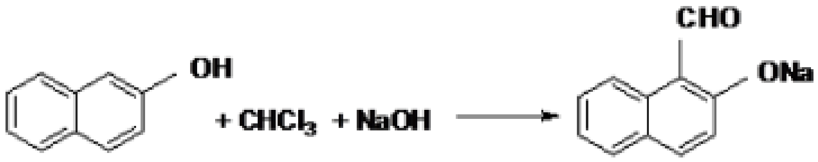
- Carbylamine test:



- Resorcinol test:



- Naphthol Test:



- Fehling's test:

  $CHCl_3 + 2Cu(OH)_2 + 3KOH = Cu_2O + K_2CO_3 + 3KCl \quad 5H_2O$

- Silver nitrate test:

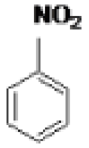
  $CHCl_3 + 4NaOH = HCOONa + 3NaCl + 2H_2O$

  $AgNO_3$

  $3AgCl + 3NaNO_3$

12.11 Identification of Nitrobenzene by Chemical Tests:

L-20. NITRO BENZENE



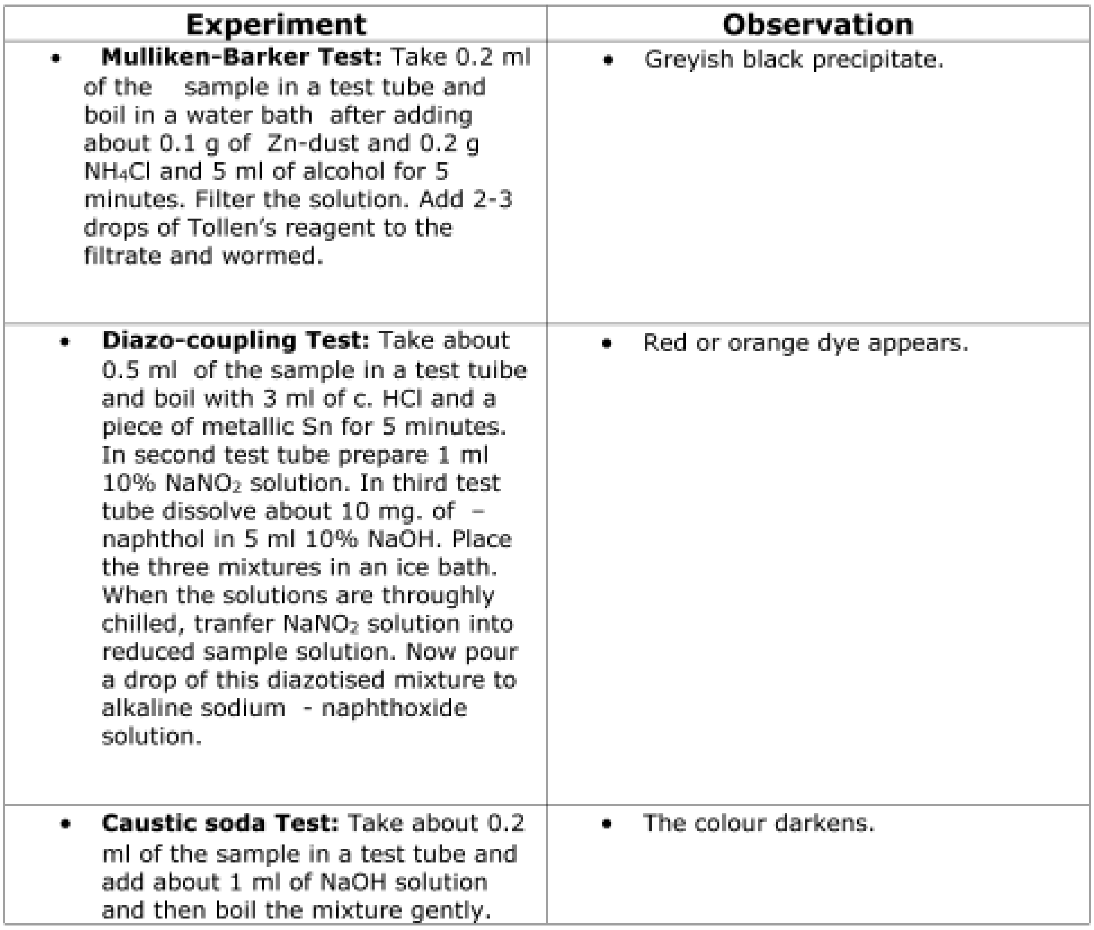
Physical characteristics:

- State : Liquid
- Colour : pale yellow
- Odour : Characteristic odour of bitter almonds
- Miscibility : Immiscible with water
- Litmus : Neutral

Preliminary Test:

- Ignition Test : Burns with yellow sooty flame

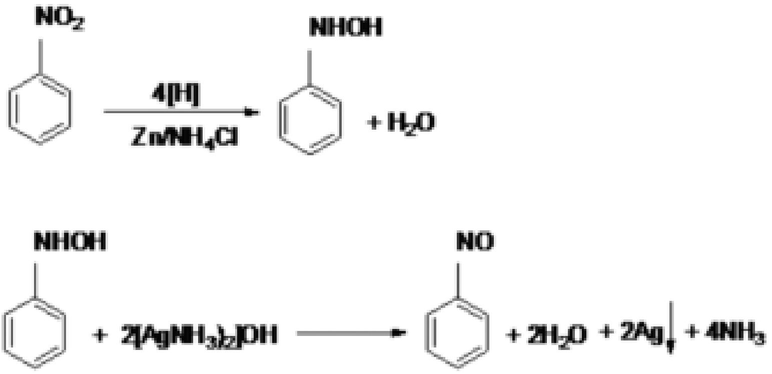
Chemical Tests:



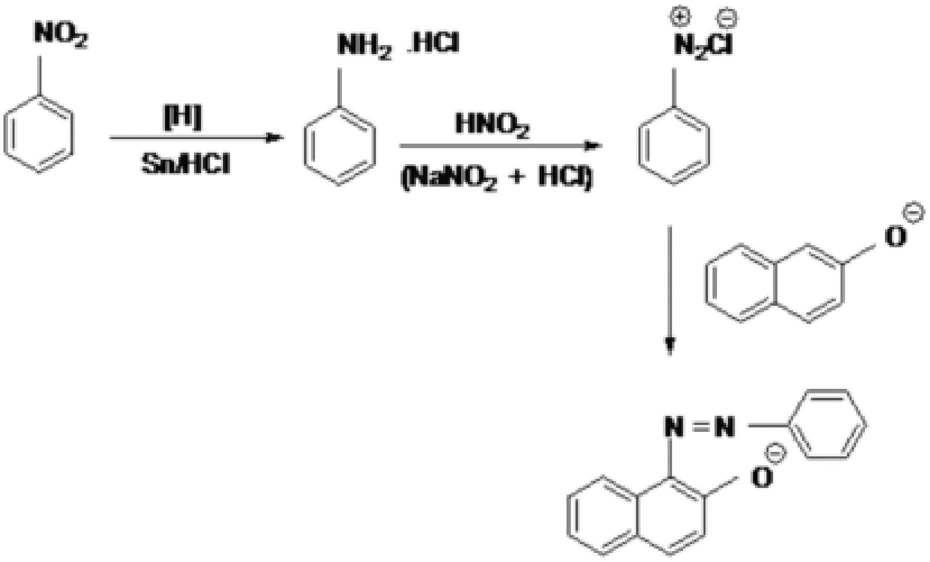
Experiment	Observation
• **Mulliken-Barker Test:** Take 0.2 ml of the sample in a test tube and boil in a water bath after adding about 0.1 g of Zn-dust and 0.2 g NH_4Cl and 5 ml of alcohol for 5 minutes. Filter the solution. Add 2-3 drops of Tollen's reagent to the filtrate and wormed.	• Greyish black precipitate.
• **Diazo-coupling Test:** Take about 0.5 ml of the sample in a test tuibe and boil with 3 ml of c. HCl and a piece of metallic Sn for 5 minutes. In second test tube prepare 1 ml 10% $NaNO_2$ solution. In third test tube dissolve about 10 mg. of – naphthol in 5 ml 10% NaOH. Place the three mixtures in an ice bath. When the solutions are throughly chilled, tranfer $NaNO_2$ solution into reduced sample solution. Now pour a drop of this diazotised mixture to alkaline sodium - naphthoxide solution.	• Red or orange dye appears.
• **Caustic soda Test:** Take about 0.2 ml of the sample in a test tube and add about 1 ml of NaOH solution and then boil the mixture gently.	• The colour darkens.

Explanations and Reactions:

- Mulliken-Barker test:



- Diazo-coupling test:



12.12 Conclusions

The identification of various organic compounds such as formic acid, acetic acid, methyl alcohol, ethyl alcohol, acetone, aniline, dimethyl aniline, benzaldehyde, chloroform, and nitrobenzene can be effectively achieved through specific chemical tests. Each compound exhibits distinct reactions when subjected to particular reagents, allowing for their differentiation based on observable changes such as color, precipitation, or the evolution of gases. These tests are valuable tools in both qualitative analysis and the practical applications of organic chemistry, facilitating the accurate identification of substances in research and industrial settings.

12.13 Some Sample Questions

Q-1: Why chloroform burns with sooty flame?

Ans: Its aromatic behaviour due to C:H=1:1.

Q-2: Will back-dye test be responded by all phenolic compounds?

Ans: Ortho and para substituted phenols do not response to this test.

Q-3: Glucose is a reducing sugar but sucrose is not – explain with a test.

Ans: Glucose responses on Fehling’s or Tollen’s test but sucrose is not.

Q-4: Name a test which is given by both glucose and sucrose.

Ans: Molisch's test.

Q-5: Name at least two compounds responding to fluorescence test.

Ans: Resorcinol and succinc acid

Q-6: What type of compounds responding haloform test?

Ans: Compounds containing $CH_3 – CO –$ group or a group can be converted to keto-methyl, eg., $CH_3 – CHOH$ - , during chemical reaction will response to haloform test.

Q-7: Both the ethyl alcohol and acetone response on Iodoform test. How can you distinguish between them?

Ans: Acetone gives Iodoform in presence of both NaOH and NH_4OH but ethyl alcohol gives in presence of NaOH only.

Q-8: How can you distinguish between aliphatic and aromatic aldehyde?

Ans: By Fehling's test.

Q-9: What is the characteristic property by which aldehyde and ketone cab be distinguished?

Ans: Reducing property of aldehyde.

Unit 13 ❐ Organic Preparations

13.0 Objectives

- **Understanding Crystallization Techniques**: To explore and comprehend various purification methods of crystallization, highlighting their importance and application in organic synthesis.
- **Selection of Solvents**: To discuss the criteria for selecting appropriate solvents for crystallization, considering factors like solubility, purity, and environmental impact.
- **Percentage Yield Calculation**: To learn and apply methods for calculating the percentage yield of purified compounds, ensuring accurate evaluation of the synthesis process.
- **Comprehensive Analysis of Organic Synthesis**: To provide a general discussion on the preparation, purification, melting point determination, and percentage yield calculation of organic compounds.
- **Experimental Applications**: To conduct and analyse specific experiments that illustrate various organic synthesis reactions, such as nitration, condensation, hydrolysis, acetylation, benzoylation, oxidation, diazo coupling, bromination, selective reduction, and multi-component-coupling reactions.
- **Green Chemistry Approaches**: To emphasize the importance of green chemistry in organic synthesis, focusing on sustainable methods and environmentally friendly reagents and solvents.

13.1 Introduction

In the previous units of Block-2 you have learned about the experimental techniques used in the organic laboratory. In this unit we will discuss about the Preparation, purification, Melting point check and percentage yield calculation of organic compounds. After practicing the following organic synthesis, you will acquire expertise in this field and will be able to perform new reaction if procedure is supplied.

The topic in this course will provide hands-on opportunities to develop and apply the knowledge of an experiment in organic synthesis. The student will be able to:

- learn and apply basic techniques used in the organic laboratory for preparation, purification and identification of organic compounds.

- employ the major techniques used in organic chemistry laboratory for analyses such as crystallization, melting point determination.
- will correctly calculate reaction yield for relevant lab experiments.
- analyse the given procedure of an experiment and suggest or recommend improvements.

13.2 Purification methods of Crystallisation:

The compounds directly obtained by means of chemical reactions are, only in rare cases, pure; they must therefore be subjected to a process of purification before they can be further utilized. For this purpose, the operations most frequently employed is crystallisation.

The crude solid product obtained directly as the result of a reaction is generally amorphous or not well crystallised. In order to obtain the compound in uniform, well-defined crystals, as well as to separate it from impurities like filter-fibres, inorganic substances, by-products, etc., it is dissolved, usually with the aid of heat, in a proper solvent, filtered from the impurities remaining undissolved, and allowed to cool gradually. For the crystallization process the quantity of solvent taken at first should be insufficient to dissolve the substance completely even on heating; then; more of the solvent is gradually added, until all of the substance is just dissolved. The dissolved compound then separates out in a crystallised form, while the dissolved impurities are retained by the mother-liquor (Crystallisation by Cooling). Many compounds are so easily soluble in all solvents, even at the ordinary temperature, that they do not separate from their solutions on mere cooling. In this case, in order to obtain crystals, a portion of the solvent must be allowed to evaporate (Crystallisation by Evaporation).

13.3 Solvents for crystallization:As solvents for organic compounds, the following substances are principally used

CLASS I. Water,
Alcohol,
Ether,
Petroleum Ether
Glacial Acetic Acid,
Benzene.

Also mixtures of these:

CLASS II. Water + Alcohol,
Water + Glacial Acetic Acid,
Ether + Petroleum Ether,
Benzene + Petroleum Ether

Less frequently used than these are: carbon disulphide, acetone, chloroform, ethyl acetate, methyl alcohol, amyl alcohol, toluene, xylene etc. But rarely used solvents are: pyridine, phenol, nitrobenzene, aniline, and others. If a compound is very difficultly soluble, solvents with high boiling points are used, as toluene, xylene, nitrobenzene, aniline, phenol, and others.

13.4 Calculation of percentage yield:

Let us consider that, Molecular weight of starting material taken = M_1
Molecular weight of final product obtained = M_2
Weight of starting material taken = X
Weight of the final product obtained (Practical yield) = Y

Then, theoretically M_1 g starting material will give M_2 g of final product.

Therefore, Theoretical Yield of product =

□2×□□1 g

Percentage yield of the product

Practical yield Theoretical yield ×100=□×□1×100□2×□

13.5 General discussion for the preparation, purification, Melting point check and percentage yield calculation of organic compounds

There is a need to proper plan for the preparation of organic compounds in the laboratory. For this following points to be keep in minds-

- Read the procedure in details before preforming the reaction
- Check the availability of the reagents and instruments required for the reaction in your laboratory
- Check if there is any possibility of accident, poisonous gas evolution during the reaction or during the handling of chemicals.

- After completing the reaction, crude product should be collected after workup process as described the procedure. Note the amount of the crude product.
- Crude product should be purified and dried before recording the melting point.

13.5.1 Experiment-1:

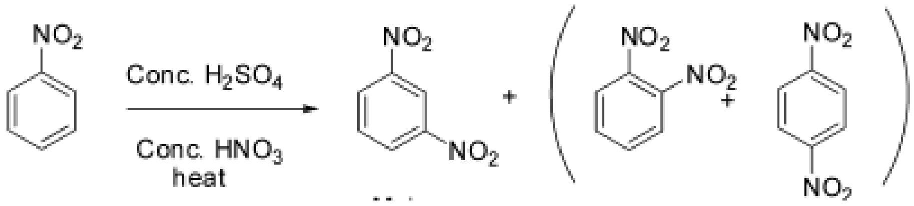
Application of Nitration of aromatic compounds in Organic synthesis; Preparation of m-Dinitrobenzene

Introduction: Benzene rings are components of many important natural products and other useful organic compounds. Therefore, the ability to put substituents on a benzene ring, at specific positions relative to each other, is a very important factor in synthesizing many organic compounds. The two main reaction types used for this are both substitutions: Electrophilic Aromatic Substitution and Nucleophilic Aromatic Substitution. The benzene ring itself is electron-rich, which makes Nucleophilic Aromatic Substitution difficult, unless there are a number of strongly electron withdrawing substituents on the ring. Electrophilic Aromatic Substitution, on the other hand, is a very useful method for putting many different substituents on a benzene ring, even if there are other substituents already present. Electrophilic Aromatic Substitution chapter describes the factors involved in the regioselectivity for Electrophilic Aromatic Substitution reactions using benzene rings, which already have substituents on them. In this experiment you will put a nitro (-NO_2) group on a benzene ring. The actual electrophile in the reaction is the nitronium ion (NO_2^+), which is generated in situ.

Reaction: Aromatic compounds may be nitrated, i.e., the hydrogen atoms replaced by nitro (-NO_2) groups, with concentrated nitric acid in the presence of concentrated sulphuric acid. The function of the sulphuric acid is to furnish a strongly acid medium and to convert the nitric acid into the highly reactive nitronium ion NO_2^+ which is the real nitrating agent:

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

For an example nitration of nitrobenzene on treatment with mixed acid (conc. H_2SO_4 and fuming HNO_3) produces m-Dinitrobenzene.



Instruments required:

- Round-bottomed flask (100ml)
- Reflux condenser
- Steam bath
- Glass beads
- Stand and clamp
- Filter with suction pump

Chemicals required:

- Concentrated sulphuric acid (10 ml)
- Fuming nitric acid (8 ml)
- Nitrobenzene (6 ml)
- Rectified spirit

Experimental Procedure: Place 10 ml. of concentrated sulphuric acid and 8 ml of fuming nitric acid, in a 100 ml. round-bottomed flask; add a few fragments of porcelain or of glass beads. Attach a reflux condenser and place the apparatus in a fume chamber. Add slowly dropwise6 ml. of nitrobenzene with shaking the flask to ensure thorough mixing. After complete addition, heat the mixture on water bath for 30 min with occasional shaking. Then allow the mixture to cool and pour it cautiously with vigorous stirring into about 200 ml. of ice cold water; the dinitrobenzene soon solidifies. Filter with suction, wash thoroughly with cold water to make it acid free, and allow to drain water as completely as possible. Place the crude m-dinitrobenzene on a blotting paper, dry on air and note the weight of crude m-dinitrobenzene.

Purification by recrystallization: Transfer the crude dinitrobenzene to a conical flask fitted, add minimum amount of methanol or rectified spirit and heat on a water bath until all the crystalline solid dissolves. If the resulting solution is not quite clear, filter it through a filter paper on a funnel in hot condition. Colourless crystals of m-dinitrobenzene are deposited on cooling. Note the weight of recrystallized product, calculate its percentage yield and check its melting point

Calculation of percentage yield:

Molecular weight of starting material i.e. nitrobenzene ($C_6H_5NO_2$) = 123

Molecular weight of product i.e. m-dinitrobenzene ($C_6H_4N_2O_4$) = 168

Theoretical Yield: 123g nitrobenzene gives 168g of m-dinitrobenzene

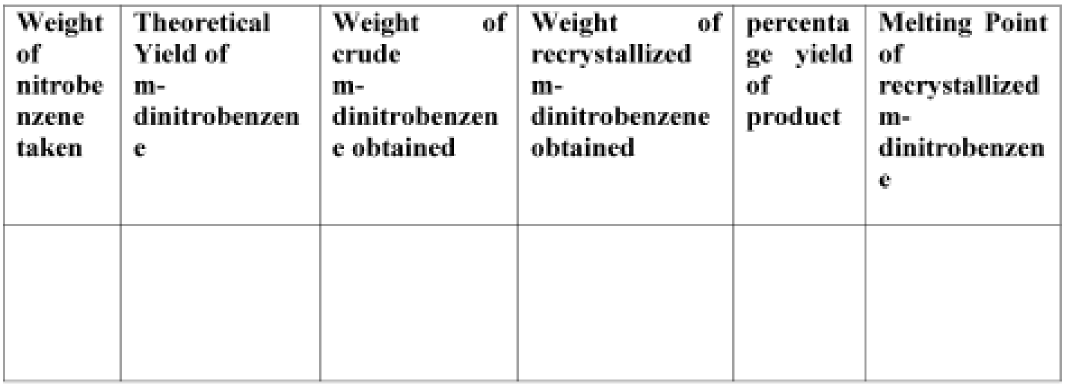
Therefore, Xg of nitrobenzene should giveg of m-dinitrobenzene

If practical yield of product is Y g, then the percentage yield of the product

Where, X = Weight of nitrobenzene taken

Y = Weight of the m-dinitrobenzene obtained

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.



Weight of nitrobenzene taken	Theoretical Yield of m-dinitrobenzene	Weight of crude m-dinitrobenzene obtained	Weight of recrystallized m-dinitrobenzene obtained	percentage yield of product	Melting Point of recrystallized m-dinitrobenzene

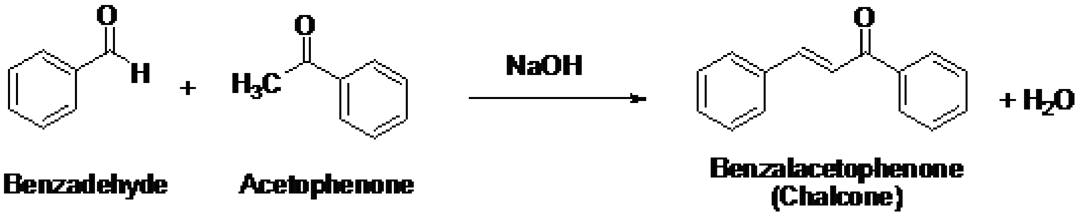
13.5.2 Experiment-2:

Application of Condensation reactions in Organic synthesis; Preparation of Chalcone and Phthalimide

Introduction: In a condensation reaction, two molecules or parts thereof combine, releasing a small molecule. When this small molecule is water, it is known as a dehydration reaction. Other possible lost molecules include hydrogen chloride, methanol, and acetic acid. It is a versatile class of reactions that can occur in acidic or basic conditions or in the presence of a catalyst. In this experiment you will prepare i) Benzalacetophenoneor Chalcone and ii) Pthalimide by the use of condensation reaction.

13.5.2.1 Benzalacetophenone (Chalcone) preparation

Reaction: Chalcones can be prepared by the aldol condensation reaction between benzaldehyde and acetophenone in the presence of sodium hydroxide as a catalyst.



Instruments required:

- Round-bottomed flask (100ml)
- mechanical stirrer
- Ice chest
- Stand and clamp
- Buchner funnel with suction pump

Chemicals required:

- Sodium hydroxide (2.2 g)
- Acetophenone (5.2 g)
- Benzaldehyde (4.6 g)
- Rectified spirit

Experimental Procedure: Place a solution of 2.2 g. of sodium hydroxide in 20 ml. of water and13 ml. of rectified spirit in a 100 ml. r.b. flask provided with a mechanical stirrer. Immerse the flask in a bath of crushed ice, pour in 5.2 g. of freshly-distilled acetophenone, start the stirrer, and then slowly add 4.6 g. of pure benzaldehyde. Keep the temperature of the mixture at about 25° (the limits are 15-30°) and stir vigorously for 2-3 hours. Remove the stirrer and cool the reaction mixture in an ice chest. Filter the solid product with suction on a Buchner funnel, wash with cold water until the washings are neutral to litmus. Place the crude chalcone on a blotting paper, dry on air and note the weight of crude chalcone. This substance should be handled with great care since it acts as a skin irritant.

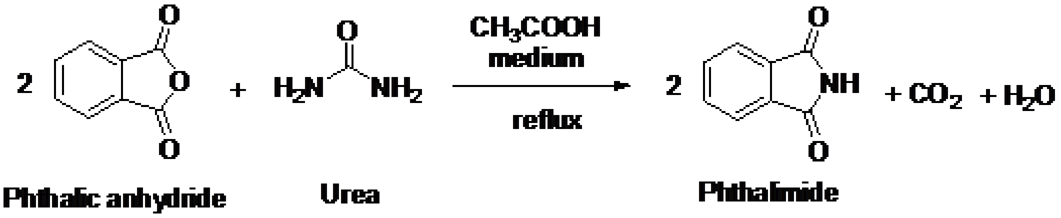
Purification by recrystallization: Transfer your weighed crude chalcone into a conical flask. Then add the minimum amount of hot 95% ethanol required to just dissolve your crude product. After dissolving your product, cork the flask and allow the mixture to cool slowly. When it appears that crystallization is complete, place the mixture in an ice water bath for 5 minutes. Filter it through a filter paper crystal of chalcone and dry on air. Note the weight of recrystallized product, calculate its percentage yield and check its melting point.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of acetophenone taken	Theoretical Yield of chalcone	Weight of crude Chalcone obtained	Weight of recrystallized Chalcone obtained	percentage yield of product	Melting Point of recrystallized chalcone

13.5.2.2 Phthalimide preparation:

Reaction: Phthalimide can be prepared by refluxing Phthalic anhydride and Urea in acetic acid medium using the Condensation reaction.



Instruments required:

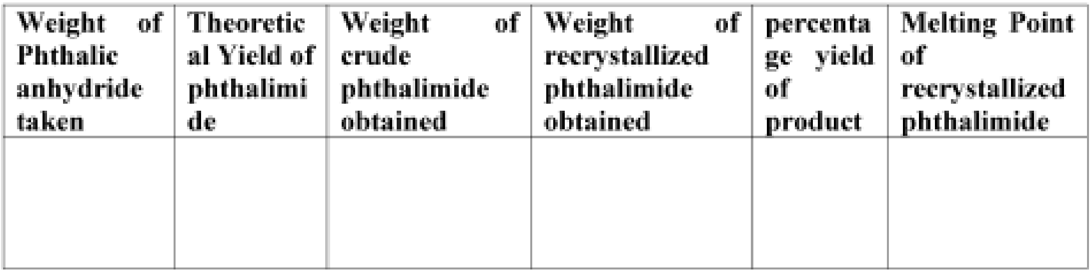
- Round-bottomed flask (100ml)
- Condenser
- Stand and clamp
- Bunsen burner
- Buchner funnel with suction pump

Chemicals required:

- Phthalic anhydride (5 g)
- Urea (2.5 g)
- Glacial acetic acid (10 ml)

Experimental Procedure: Take 5 g. of Phthalic anhydride, 2.5 g urea and 10 ml glacial acetic acid in a 100 ml r.b. flask fitted with a condenser. Heat the mixture to reflux on a Bunsen burner for 1 hour. Then cool the reaction mixture at room temperature and the mixture get solidifies on cooling. Pour 20-30 ml water in the mixture with shaking. Filter the solid phthalimide on a Buchner funnel and wash it with cold water to make it acid free. Recrystallize the crude phthalimide from hot water and note the weight of obtained product, calculate its percentage yield and check its melting point.

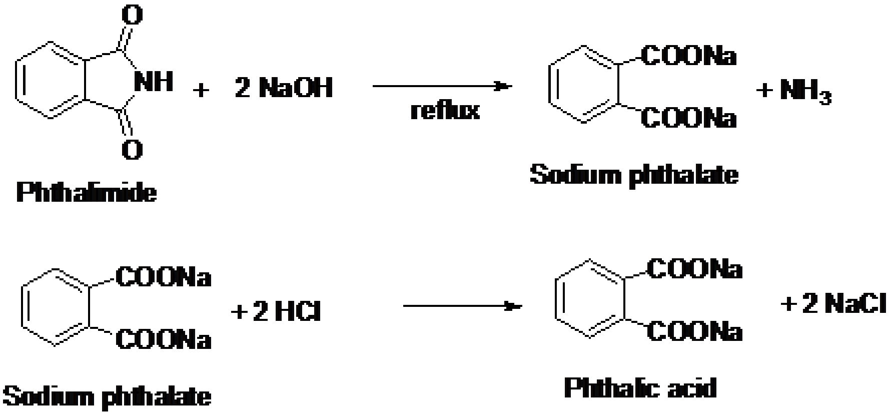
Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.



Weight of Phthalic anhydride taken	Theoretical Yield of phthalimide	Weight of crude phthalimide obtained	Weight of recrystallized phthalimide obtained	percentage yield of product	Melting Point of recrystallized phthalimide

13.5.3 Experiment-3: Application of Hydrolysis reaction in Organic synthesis; Preparation of Phthalic acid

Reaction: Phthalimide on hydrolysis with 10% aqueous NaOH solution produces Sodium phthalate. Aqueous solution of sodium phthalate on treatment with conc. HCl produces Phthalic acid.



Instruments required:

- Round-bottomed flask (100ml)
- Beaker
- Condenser
- Stand and clamp
- Bunsen burner
- Buchner funnel with suction pump

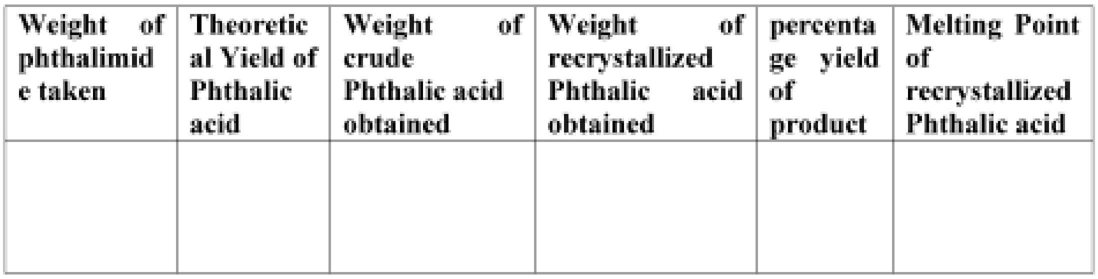
Chemicals required:

- Phthalimide (5 g)

- NaOH (5 g)
- conc. HCl

Experimental Procedure: Take 5 g. of Phthalimide in a 100 ml r.b. flask fitted with a condenser. Pour 50 ml 10% NaOH (5 gm NaOH in 50 ml water) in it and put some glass beads into the solution. Heat the mixture to reflux on a Bunsen burner for 30 minutes. Then cool the reaction mixture at room temperature and transfer the mixture in a 250 ml beaker. Cool the beaker in ice. After cooling acidify the mixture strongly by adding conc HCL with stirring. Filter the white solid Phthalic acid on a Buchner funnel and wash it with water to make it acid free. Recrystallize the crude phthalimide from hot water and note the weight of obtained product, calculate its percentage yield and check its melting point.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.



Weight of phthalimide taken	Theoretical Yield of Phthalic acid	Weight of crude Phthalic acid obtained	Weight of recrystallized Phthalic acid obtained	percentage yield of product	Melting Point of recrystallized Phthalic acid

13.5.4 Experiment-4: Application of Acetylation reaction in Organic synthesis; Preparation of acetanilide

Acetyl derivatives of aromatic amines may be prepared either with acetic anhydride or acetic acid or with a mixture of both reagents. Acetylation reaction using acetic anhydride is simple and provides good yield of product. But acetic anhydride is a banned item and hence we will perform acetylation using acetic acid.

Reaction: Acetanilide is produced when aniline is refluxed with excess glacial acetic acid in presence of catalytic amount of Zn dust. The zinc reduces the coloured impurities in the aniline and also helps to prevent oxidation of the amine during the reaction.

Instruments required:

- Round-bottomed flask (100ml)
- Beaker
- Refluxing condenser
- Stand and clamp
- Bunsen burner
- Buchner funnel with suction pump

Chemicals required:

- Aniline (10 ml)
- Glacial acetic acid (20 ml)
- Zinc dust
- Charcoal

Experimental Procedure: Take 10 ml aniline and 20 ml glacial acetic acid in a dry 100 ml r.b. flask fitted with a condenser. Put pinch of zinc dust and some glass beads into the solution. Reflux the mixture on a Bunsen burner for 2-3 hour. Pour the hot liquid cautiously in a thin stream into a 500 ml beaker containing 200 ml of ice-water with continuous stirring. Solid acetinalide will precipitate. Filter the solid acetinalide on a Buchner funnel and wash it with water to make it acid free. Dry the solid over air and note the weight of obtained crude product, calculate its percentage yield and check its melting point.

Purification of acetinalide (if gummy texture appears)

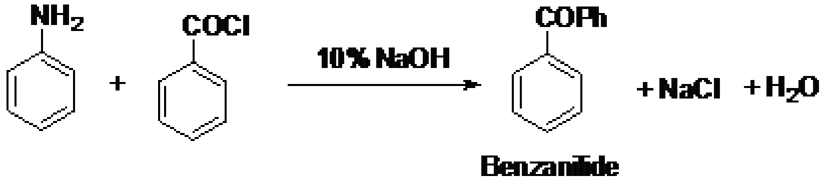
Place the moist acetanilide in a beaker and add gradually about 300 ml. of boiling water. It must be remembered that the crude acetanilide melts slightly below 114°; the substance may therefore melt when heated with water. All the material, liquid or solid, must be dissolved: the addition of a little alcohol will assist the process of solution. Filter, if necessary, through a Buchner funnel. If the solution is coloured, add 1 g. of decolourising charcoal before filtration. Solid acetinalide precipitates on cooling. Filter and dry upon filter paper in the air. The acetanilide may also be recrystallized using toluene as solvent.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of Phthalic anhydride taken	Theoretical Yield of acetinalide	Weight of crude acetinalide obtained	Weight of pure acetinalide obtained	percentage yield of product	Melting Point of pure acetinalide

13.5.5 Experiment-5: Application of Benzoylation reaction in Organic synthesis; Preparation of Benzanilide

Reaction: Aniline on treatment with benzoyl chloride in presence of NaOH produces Benzanilide in good yield. This reaction is also called *Schotten-Baumann* reaction.



Instruments required:

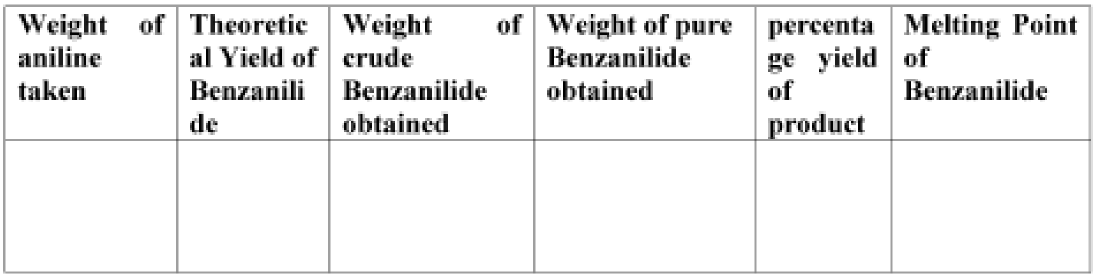
- Stoppered conical flask
- Buchner funnel with suction pump

Chemicals required:

- Aniline (5 ml)
- 10 % aqueous NaOH solution
- benzoyl chloride (7 ml)

Experimental Procedure: Place 5 ml of aniline and 45 ml. of 10 % aqueous NaOH solution in a stoppered conical flask, and then add 7 ml of benzoyl chloride, stopper, and shake vigorously for 10-15 minutes. Heat is evolved in the reaction. The crude benzoyl derivative separates as white solid mass. Complete the reaction. If the odour of benzoyl chloride is detected (smell cautiously) add few ml of NaOH and make sure that the reaction mixture is alkaline. Dilute with water. Filter off the product with suction on a Buchner funnel, break up the mass on the filter (if necessary), wash well with water, and drain. Collect the Benzanilide and dry in the air and note the weight of obtained crude product, calculate its percentage yield and check its melting point. Recrystallize from hot alcohol (or methylated spirit); filter the hot solution through a Buchner funnel.

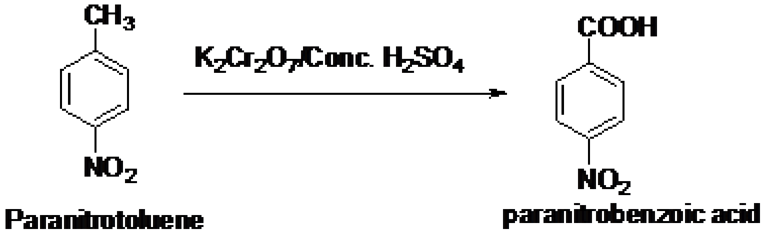
Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.



Weight of aniline taken	Theoretical Yield of Benzanilide	Weight of crude Benzanilide obtained	Weight of pure Benzanilide obtained	percentage yield of product	Melting Point of Benzanilide

13.5.6 Experiment-6: Application of Side chain oxidation of aromatic compounds in Organic synthesis; Preparation of paranitrobenzoic acid

Reaction: Paranitrotoluene on oxidation with potassium dichromate/conc H_2SO_4 produces paranitrobenzoic acid.



Instruments required:

- 100 ml r.b. flask
- refluxing condenser
- Bunsen burner
- 250 ml beaker
- Buchner funnel with suction pump

Chemicals required:

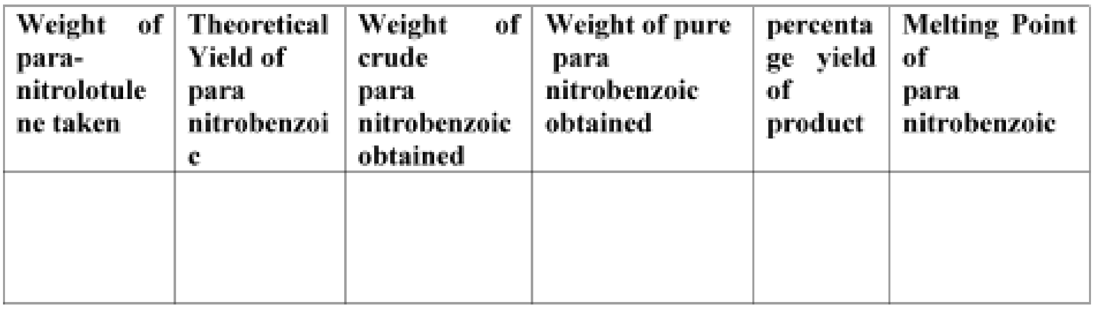
- para-nitrolotulene (5 gm)
- Conc H_2SO_4 (20 ml)
- saturated NaHCO3 solution
- charcoal
- potassium dichromate (15 gm)

Experimental Procedure: Add slowly 20 ml of conc H_2SO_4 into a 100 ml r.b. flask containing 30 ml water and then add 15 gm potassium dichromate into the solution. It will form a warm solution mixture. Heat is evolved during mixing. 5 gm para-nitrolotulene is then added to the warm solution for 5-10 minutes with shaking the flask. Fit a refluxing condenser and put some glass beads into the solution. Reflux the mixture on a Bunsen burner for 30 minutes. Bring the reaction mixture at room temperature and pour the mixture slowly into a 250 ml beaker containing 100 ml ice water. Stir the mixture during this addition. The crude para-nitrobenzoic acid separates as solid mass. Filter off the product with suction on a Buchner funnel, wash with 5 % H_2SO_4, and drain. Collect the para-nitrobenzoic acid and dry in the air and note the weight of obtained crude product, calculate its percentage yield.

Purification of para-nitrobenzoic acid

Dissolve the crude para nitrobenzoic acid in minimum amount of saturated NaHCO3 solution. Add little amount of decolourising charcoal and heat the mixture (don't boil). Filter through a Buchner funnel after cooling. Acidify the filtrate by 15% H2SO4. Solid para-nitrobenzoic acid will be precipitated. Filter the solid through a Buchner funnel and wash with little amount of cold water and dry. Check the melting point of pure para-nitrobenzoic acid.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

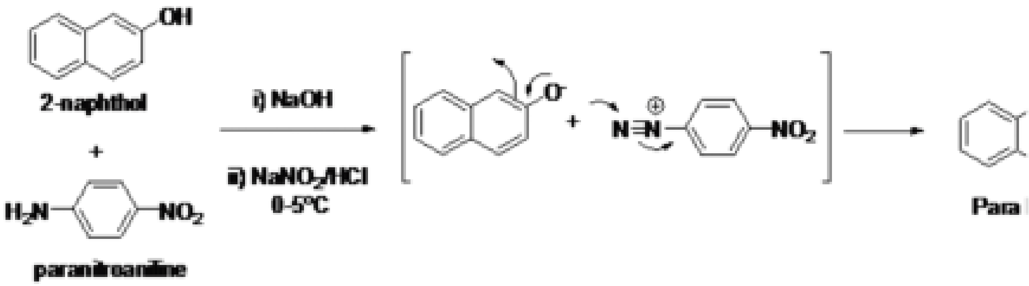


Weight of para-nitrolotulene taken	Theoretical Yield of para nitrobenzoic	Weight of crude para nitrobenzoic obtained	Weight of pure para nitrobenzoic obtained	percentage yield of product	Melting Point of para nitrobenzoic

13.5.7 Experiment-7: Application of Diazo coupling reactions of aromatic amines in Organic synthesis; Preparation of phenylazo-ß-naphthol (para red)

Diazonium ions are weak electrophiles, however, they undergo coupling with activated aromatic nuclei such as aryl amines, phenols and aromatic heterocyclic compounds. However, the careful control of the pH of the reaction medium is necessary for the success of the process. Aromatic azo-compounds are coloured. Several of those compounds synthesized by the diazo-coupling are employed as dye-stuffs. In this experiment you will prepare phenylazo-ß-naphthol (i.e. called para red, a dyestuff) by the use of diazo coupling reactions of aromatic amines

Reaction: Para red is prepared by diazo coupling reactions of 2-napthol with p-nitrobenzenediazonium salt.



Instruments required:

- 250 ml. conical flask
- 250 ml beaker
- Thermometer
- Glass rod
- Ice bath
- Buchner funnel with suction pump

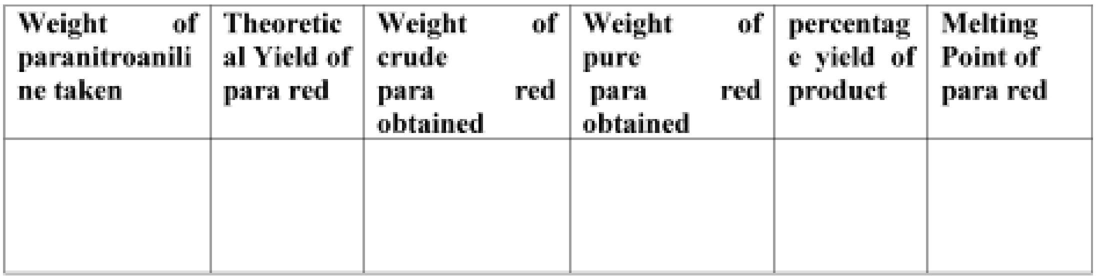
Chemicals required:

- paranitroaniline (5 gm)
- Conc HCl (16 ml)
- NaNO2 (4 gm)
- ß-naphthol
- glacial acetic acid (30-35 ml.)
- 10% sodium hydroxide solution

Experimental Procedure:

Dissolve 5 g. of paranitroaniline in a mixture of 16 ml. of concentrated hydrochloric acid and 16 ml. of water contained in a 250 ml. conical flask. Place a thermometer in the solution and immerse the flask in a bath of crushed ice; cool until the temperature of the stirred solution falls below 5°. Dissolve 4 g. of sodium nitrite in 20 ml. of water and chill the solution by immersion in the ice bath; add the sodium nitrite solution in small volumes (1-2 ml. at a time) to the cold paranitroaniline hydrochloride solution, and keep the latter well stirred. Heat is evolved by the reaction. The temperature should not be allowed to rise above 10° (add a few grams of ice to the reaction mixture if necessary) otherwise appreciable decomposition of the diazonium compound and of nitrous acid will occur. Prepare a solution of 7.8 g. of ß-naphthol in 45 ml. of 10 % sodium hydroxide solution in a 250 ml. beaker; cool the solution to 5° C by immersion in an ice bath, assisted by the direct addition of about 25 g. of crushed ice. Stir the naphthol solution vigorously and add the cold diazonium salt solution very slowly: a red colour develops and red crystals of phenylazo-ß-naphthol (para red) soon separate. When all the diazonium salt solution has been added, allow the mixture to stand in an ice bath for 30 minutes with occasional stirring. Filter the crystals through a Buchner funnel with gentle suction, wash well with water, and drain thoroughly. Recrystallize the product from glacial acetic acid (30-35 ml.). Filter the recrystallized product with suction, wash with a little alcohol (or methylated spirit) to eliminate acetic acid, and dry upon filter paper. The yield of deep red crystals is about 3 g. Pure phenylazo-ß-naphthol has m.p. 131° ; if the m.p. is low, recrystallize the dry product from alcohol.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.



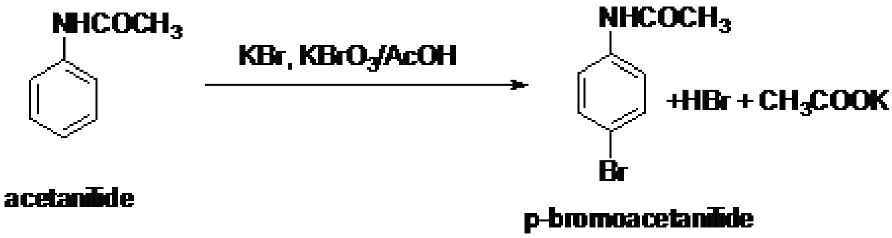
Weight of paranitroaniline taken	Theoretical Yield of para red	Weight of crude para red obtained	Weight of pure para red obtained	percentage yield of product	Melting Point of para red

13.5.8 Experiment-8: Application of Bromination of acetanilide using green approach (Bromate-Bromide method) in Organic synthesis; Preparation of p-bromoacetanilide

The traditional experiment involves the use of Br_2-AcOH and is described in several laboratory textbooks. However, liquid bromine is extremely corrosive and is hazardous to handle. To avoid risks in using liquid bromine, methods to generate bromine in situ have been developed now a day. In acidic medium, KBrO3-KBr is known to release bromine according to equation

5 KBr + KBrO3 + 6 CH3COOH = 3 Br2 + 3 H2O + 6 CH_3 COOK

Reaction: p-bromoacetanilide is prepared by Bromination of acetanilide on treatment with KBr and KBrO3 in acetic acid medium using green approach.



Instruments required:

- 100 ml. conical flask fitted with a cork
- 250 ml beaker
- Glass rod
- Buchner funnel with suction pump

Chemicals required:

- acetanilide - 5 g
- Glacial Acetic acid - 20 ml
- Potassium bromide – 7.5 g
- Potassium bromate – 2.5 g

Experimental Procedure:

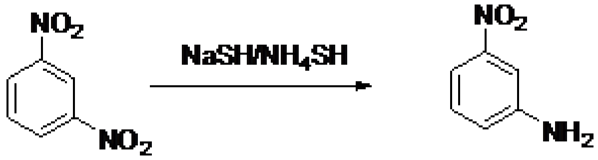
5 gm acetanilide is dissolved in glacial acetic acid (20 ml) in a 100 ml conical flask fitted with a cork (warming if necessary). The flask is cooled under water to room temperature. In another conical flask dissolve 7.5 gm potassium bromide and 2.5 gm potassium bromate in 20 ml water. Add the bromate-bromide mixture to the acetinalide solution slowly at room temperature keeping the cork closed and with shaking. The reaction mixture was then stirred occasionally with for additional 1 hour. Then add the reaction mixture to a beaker containing 100 ml of ice-cold water stirring all the while with a glass rod. The developed light brown colour disappeared. The precipitate of p-bromoacetanilide separated out (If no precipitate is formed then neutralize the acid by sodium hydroxide solution). The white crystals were filtered through Buchner funnel and the solid was dried. Recrystallize the crude product from ethanol. M.P. of p-bromoacetanilide = 165 ^{o}C

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of p-nitro aniline taken	Theoretical Yield of p-bromo acetanilide	Weight of crude p-bromo acetanilide obtained	Weight of pure p-bromo acetanilide obtained	percentage yield of product	Melting Point of p-bromo acetanilide

13.5.9 Experiment-9: Selective reduction of m-dinitrobenzene to m-nitroaniline in Organic synthesis; Preparation of m-Nitroaniline

Reaction: m-Nitroaniline is prepared by partial reduction of m-dinitrobenzene on treatment with NaSH or NH_4SH.



Instruments required:

- 250 ml beaker
- Refluxing condenser
- Glass rod
- Buchner funnel with suction pump

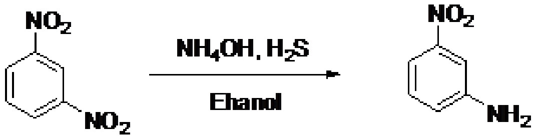
Chemicals required:

- m-dinitrobenzene
- sodium sulfide
- hydrogen sulfide
- ammonium chloride
- ammonium hydroxide
- ethanol

Experimental Procedure:

A solution of 11 grams of crystalline sodium sulfide ($Na_2S.9H_2O$) in 20 cc. water is treated with hydrogen sulfide until the solution is completely saturated. In this way a clear solution of sodium hydrosulfide (NaSH) is obtained. In a beaker, another solution is prepared containing 1 grams of ammonium chloride in 40 cc. hot water, and to this solution is added, at 90°C, 8 grams of pure m-dinitrobenzene, stirring the mixture vigorously enough to produce a fine emulsion. The temperature is allowed to fall to 85° and then, with continued vigorous stirring, the previously prepared hydrosulfide solution is added slowly from a dropping funnel during the course of 15 minutes, maintaining the temperature between 80 and 85°. When the addition has been completed, stirring is continued for 5 minutes without further heating and then the mixture is cooled to 20° by the addition of 50 gm ice. The end-point of the reaction may be recognized by the fact that a drop of the reaction solution on a filter paper gives a black streak of metallic sulfide with an iron or copper sulfate solution. Stirring is continued for about 1 hour more at room temperature, and then the m-nitroaniline, which has separated in yellow crystals, is filtered with suction and washed with cold water. The crude product can be recrystallized from boiling water. The mp of pure recrystallized m-nitraniline is 114° C.

Alternative Experimental Procedure:



10 g of m-dinitrobenzene is dissolved in 40 g of ethanol and the solution is cooled down, upon which a portion of the m-dinitrobenzene separates out. This solution is further treated with 8 g of concentrated ammonium hydroxide solution (each 1 g of m-dinitrobenzene requires 0.8 g of concentrated ammonium hydroxide solution). The reaction flask with its content is tared, the mixture is saturated with hydrogen sulfide at room temperature and after saturation is complete the flask is heated under reflux for 30 minutes. Then the reaction flask content is cooled to room temperature and hydrogen sulfide again passed into it to solution until there is an increase of 6 g in weight (or 0.6 g for every gram of m-dinitrobenzene used). If correct weight is not reached hydrogen sulfide is again passed into the mixture. The solution is diluted with water, the precipitated crude 3-nitroaniline is filtered, washed with water, and extracted by warming with dilute hydrochloric acid. 3-Nitroaniline hydrochloride is converted to 3-nitroaniline base by neutralizing with ammonium hydroxide. Finally, 3-nitroaniline is recrystallized from water yielding 70-80% of product which melts at 114° C.

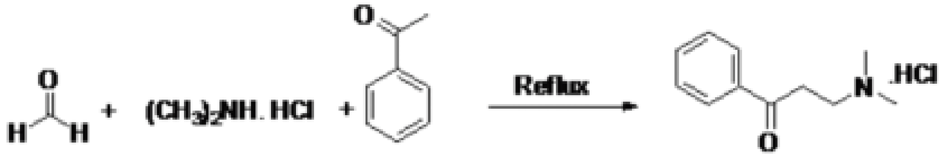
Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.

Weight of m-dinitro benzene taken	Theoretical Yield of m-Nitroaniline	Weight of crude m-Nitroaniline obtained	Weight of pure m-Nitroaniline obtained	percentage yield of product	Melting Point of m-Nitroaniline

13.5.10 Experiment-10: Green 'multi-component-coupling' reaction in Organic synthesis; Preparation of ß-Dimethylaminopropiophenone hydrochloride by Mannich Reaction

This multi-component condensation of a non-enolizable aldehyde, a primary or secondary amine and an enolizable carbonyl compound affords aminomethylated products. The iminium derivative of the aldehyde is the acceptor in the reaction. The involvement of the Mannich Reaction has been proposed in many biosynthetic pathways, especially for alkaloids.

Reaction: The Mannich reaction consists in the condensation of formaldehyde with ammonia or a primary or a secondary amine and a compound containing at least one hydrogen atom of pronounced reactivity; the active hydrogen atom may be derived from a methylene group activated by a neighbouring keto group, or from a nitroparaffin, or it may be the o- or p-hydrogen atoms in phenols. Thus when acetophenone is boiled in alcoholic solution with formaldehyde and dimethylamine hydrochloride, the Mannich base ß-dimethylaminopropiophenone hydrochloride is readily formed.



β-dimethylaminopropiophenone hydrochloride

Instruments required:

- 100 ml. conical flask fitted with a cork
- 250 ml beaker
- Glass rod

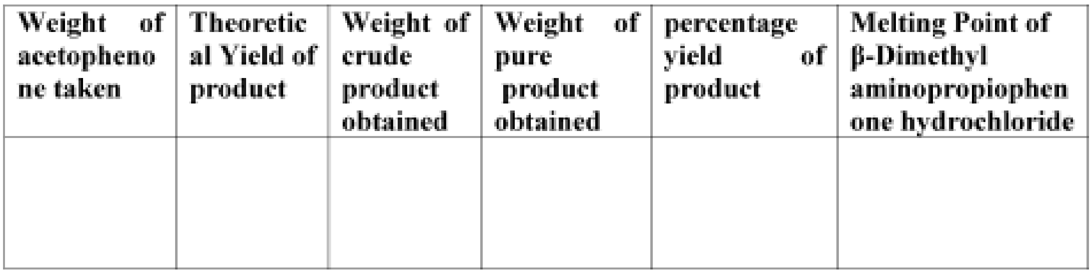
?Buchner funnel with suction pump

- Chemicals required:

- dimethylamine hydrochloride – 5.3 g
- paraformaldehyde – 2 g
- acetophenone – 6 g
- ethanol – 10 ml
- concentrated hydrochloric acid
- acetone

ß-Dimethylaminopropiophenone hydrochloride. Place 5.3 g of dry dimethylamine hydrochloride, 2.0 g. of powdered paraformaldehyde and 6.0g. (6 ml.) of acetophenone in a 50 ml. round bottomed flask attached to a reflux condenser. Introduce 10 ml. of 95 percent, ethanol to which 0.1 ml. of concentrated hydrochloric acid has been added, and reflux the mixture on a water bath for 2 hours; the reaction mixture should ultimately be almost clear and homogeneous. Filter the yellowish solution (if necessary) through a hot water funnel transfer the filtrate to a 100 ml. wide-mouthed conical flask and, while still warm, add 40 ml. of acetone. Allow to cool to room temperature and leave in a refrigerator overnight. Filter the crystals at the pump, wash with 15 ml. of acetone, and dry for 6 hours at 40-50°: Recrystallize the crude product by dissolving in 8 ml. of hot rectified spirit and slowly adding 40 ml. of acetone to the solution; collect the solid which separates by suction filtration and dry at 70°. The m.p. of purified material is 155-156°C.

Submit the product to your instructor in a paper wrapped and labelled including your name(s). Note down the experimental results following the chart given below.



Weight of acetophenone taken	Theoretical Yield of product	Weight of crude product obtained	Weight of pure product obtained	percentage yield of product	Melting Point of β-Dimethyl aminopropiophenone hydrochloride

13.6 Conclusion

The exploration of crystallization methods, solvent selection, and percentage yield calculation is crucial for the efficient purification of organic compounds. By conducting various experiments involving different reactions, such as nitration, condensation, hydrolysis, and green synthesis approaches, we gain practical insights into the preparation and purification processes. These studies not only enhance our understanding of organic synthesis but also emphasize the importance of sustainable practices in the laboratory. Overall, this comprehensive examination equips us with essential skills and knowledge for advancing in the field of organic chemistry.

13. 7 Some Sample Questions

1. Question: **What is the principle behind crystallization as a purification method?**

Answer: Crystallization is based on the principle that the solubility of a compound generally increases with temperature. By dissolving the impure compound in a hot solvent and then cooling the solution, pure crystals of the desired compound can be obtained as they precipitate out of the solution, leaving impurities behind.

2. Question: How do you choose an appropriate solvent for crystallization?

Answer: An appropriate solvent for crystallization should:

- Dissolve the compound well at high temperatures but poorly at low temperatures.
- Not dissolve impurities at low temperatures, so they can be filtered off.
- Be chemically inert with respect to the compound being purified.
- Be safe, non-toxic, and cost-effective, if possible.

3. Question: How is the percentage yield of a purified compound calculated?

Answer: The percentage yield is calculated using the formula:

Percentage Yield=(Actual YieldTheoretical Yield)×100%\text{Percentage Yield} = \left(\frac{\text{Actual Yield}}{\text{Theoretical Yield}}\right) \times 100\%Percentage Yield=(Theoretical YieldActual Yield†)×100%

Where the actual yield is the amount of purified compound obtained, and the theoretical yield is the maximum amount expected based on the starting materials.

4. Question: Why is it important to check the melting point of a purified compound?

Answer: Checking the melting point is important because it helps verify the purity of the compound. A pure substance typically has a sharp and specific melting point range, whereas impurities tend to lower and broaden the melting point range.

5. Question: What is the significance of green chemistry in organic synthesis?

Answer: Green chemistry aims to design chemical processes that reduce or eliminate the use and generation of hazardous substances. In organic synthesis, this can include using safer solvents, renewable materials, energy-efficient processes, and catalysts to minimize environmental impact and improve safety.

6. Question: Describe the role of recrystallization in the purification of organic compounds.

Answer: Recrystallization is a technique used to purify solid organic compounds. It involves dissolving the impure solid in a suitable solvent at high temperature and then slowly cooling the solution. As the solution cools, the pure compound crystallizes out, while impurities remain in the solution or form separate crystals. The pure crystals can then be collected by filtration.

7. Question: What are the potential challenges in using crystallization as a purification technique?

Answer: Challenges in crystallization include:

- Difficulty in finding an appropriate solvent or solvent mixture.
- Loss of product due to incomplete crystallization or adherence to the filter.
- Co-crystallization of impurities with the desired compound.
- The formation of polymorphs, which are different crystalline forms of the same compound that can have different properties.

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