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
Vice Chancellor

Netaji Subhas Open University

Under Graduate Degree Programme

Four Year Degree Programme Under NEP 2020

Subject : Chemistry

Corse Credit–4

Course Title : Practical Paper–II

Course Code : 6CC-CH-03

First Print : March, 2025

বিশ্ববিদ্যালয় মঞ্জুরি কমিশনের দূরশিক্ষা ব্যুরোর বিধি ও জাতীয় শিক্ষানীতি (2020) অনুযায়ী মুদ্রিত।
Printed in accordance with the regulations of the Distance Education Bureau of the University Grants Commission & NEP-2020.

Netaji Subhas Open University

Under Graduate Degree Programme

Four Year Degree Programme Under NEP 2020

Subject : Chemistry

Corse Credit–4

Course Title : Practical Paper–II

Course Code : 6CC-CH-03

: Course Writer :

Unit–1 to 6 : Sanjay Roy
Associate Professor of Chemistry, NSOU

Unit–7 to 14 : Dr. Sintu Ganai
Assistant Professor of Chemistry, NSOU

: Course Editor :

Unit–1 to 6 : Dr. Sintu Ganai
Assistant Professor of Chemistry, NSOU

Unit–7 to 14 : Dr. Puspal Mukherjee
Assistant Professor of Chemistry, NSOU

: Format Editor :

Dr. Sintu Ganai
Assistant Professor, Department of Chemistry
School of Sciences, NSOU

Netaji Subhas Open University

UG : Chemistry (HCH)

Practical Paper–II (Practical)

Course Title : Practical Paper–II

Course Code : 6CC-CH-03

Module-I : Estimation of Ions

Unit–1 : Estimation of Fe(II) and Fe(III) in a given mixture using $K_2Cr_2O_7$ solution 13

Unit–2 : Estimation of Fe(III) and Cu(II) in a given mixture using $K_2Cr_2O_7$ solution 22

Unit–3 : Estimation of Cr(VI) and Mn(II) in a given mixture using $K_2Cr_2O_7$ solution 29

Unit–4 : Estimation of Fe(III) and Cr(VI) in a given mixture using $K_2Cr_2O_7$ solution 37

Unit–5 : Estimation of Fe(II) and Mn(II) in a given mixture using $KMnO_4$ solution 44

Unit–6 : Estimation of Fe(III) and Ca(II) in a given mixture using $KMnO_4$ solution 52

Module-II : Complexometric Titration

Unit–7 : Estimation of Hardness of water 60

Unit–8 : Estimation of Ca(II) and Mg(II) in a mixture 70

Unit–9 : Estimation of Zn(II) and Mg(II) in a mixture 77

Module-III : Inorganic Preparation

Unit–10 : Preparation of Inorganic Metal Complexes 84

Module-IV : Qualitative Analysis of Organic Compounds

Unit–11 : Qualitative Analysis of Single Solid Organic Compounds 101

Module-V : Quantitative Analysis of Organic Compounds

Unit–12 : Quantitative Analysis - I 139

Unit–13 : Quantitative Analysis - II 152

Unit–13 : Quantitative Analysis - III 170

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.

(i) 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 neighbour 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

Reagents Required for Quantitative Analysis

1. Strength of Concentrated Acids and Bases :

Reagent 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 N

2. Preparation of Dilute Acids and Bases Solutions :

Reagent 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 Solution	Dissolve 111 ml of liquor NH3 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

3. Preparation of Dilute Acids and Bases Solutions :

Reagent 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%

4. Equivalent Weight of Some Common Reagents :

Reagent 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

Module-I

Estimation of Ions

Unit – 1 ❑ Estimation of Fe(II) and Fe(III) in a given mixture using $K_2Cr_2O_7$ solution

Structure

1.1 Objective

1.2 Introduction

1.3 Estimation of Ions

1.3.1 Volumetric Analysis

1.3.2 Standard substances

1.3.3 Primary standard substances

1.3.4 Secondary standard substances

1.3.5 Equivalent weights of oxidants and reductants

1.3.6 Strength of a solution

1.4 Estimation of Fe(II) and Fe(III) in a given mixture using $K_2Cr_2O_7$ solution

1.4.1 Principle

1.4.2 Chemicals Required

1.4.3 Procedure

1.4.4 Experimental Results

1.4.5 Calculation

1.5 Summary

1.6 Questions

1.1 Objective

By the end of this chapter, students should be able to–

- Understand the fundamental concepts of ion estimation, including the principles of determining ion concentrations
- Identify the Primary standard and Secondary standard substances

- Calculate the Equivalent weights of oxidants and reductants
- Determine the strength of a solution
- Perform the estimation of Fe(II) and Fe(III) in a mixture using K?Cr?O? solution with confidence and understand the theoretical concepts underpinning this analytical technique.

1.2 Introduction

The estimation of ions is a critical process in analytical chemistry, where determining the concentration of specific ions in a solution or mixture is essential for various scientific and industrial applications. Whether it's monitoring water quality, assessing environmental pollution, or conducting laboratory experiments, accurately estimating ions like sodium, calcium, chloride, and nitrate is fundamental to understanding and controlling chemical processes.

Redox titration is a type of titration based on an oxidation-reduction (redox) reaction between the analyte and the titrant. In this process, one substance (the analyte) undergoes oxidation, losing electrons, while another substance (the titrant) undergoes reduction, gaining electrons. The titration continues until the reaction reaches the endpoint, which is usually indicated by a color change in the solution, often due to an indicator or the inherent color of the titrant itself. Redox titrations are commonly used to determine the concentration of substances that can act as oxidizing or reducing agents.

This chapter provides an overview of the key methods used for estimation of Fe(II) and Fe(III) in a given mixture usingRedox titrations by K2Cr2O7 solution.

1.3 Estimation of Ions

The estimation of ions involves determining the concentration of specific ions in a solution or mixture. This process is fundamental in various fields, including chemistry, environmental science, biology, and industrial applications. Accurate ion estimation is crucial for understanding chemical reactions, ensuring environmental safety, monitoring water quality, and performing clinical diagnostics.

1.3.1. Volumetric Analysis

Quantitative analysis involves determination of the amount of element or substance present in the test sample. The amount is usually expressed either in gm/litre or in

percent. If the supplied substance is solid, it is brought into solution in an acid, a mixture of acids, an alkali, or in some other reagents. It is now reacted with a standard of a suitable reagent; the reagent is carefully selected so that the reaction is quantitative and that the completion of the reaction is indicated sharply either directly or by the addition of a suitable indicator. Then from the titre value the amount of the substance under investigation is calculated. This is called volumetric analysis.

In volumetric analysis we require burette, pipette, measuring cylinder, and measuring flask of varying size along with beaker, funnel etc. All apparatus should be cleaned carefully with distilled water.

The burette should be carefully cleaned. If it contains grease wash it with a little chromic acid solution or a mixture of alcohol and ether and then with distilled water. The pipette should also be cleaned similarly.

1.3.2 Standard substances

In volumetric analysis some chemicals are frequently used in defined concentrations reference solutions. The substances present in these solutions are called primary standard and secondary standard substances.

1.3.3 Primary standard substances

A primary standard substance should have the following requirements:

i) The substance must easily be obtained in the highly pure state from which a standard solution can be prepared by direct weighing a define amount of it followed by dissolution and dilution to a definite volume.

ii) It should neither be hygroscopic nor be oxidised by air.

iii) The substance should be readily soluble in solvents like water, the solution should be stable and its reaction with others must be quantitative and instantaneous.

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

v) It can easily be dried at 1100 - 120°C.

The substances commonly used as primary standards in different volumetric analysis are :

Acidimetry and alkalimetry : Anhydrous Na_2CO_3, borax ($Na_2B_4O_7,10H_2O$), oxalic acid ($H_2C_2O_4.2H_2O$), potassium bi-iodate, $KH(IO_3)_2$, succinic acid, etc.

Oxidimetry and Reductimetry : Oxalic acid ($H_2C_2O_4.2H_2O$), Sodium oxalate

($Na_2C_2O_4$) Potassium bi-iodate, $KH(IO_3)_2$, Potassium dichromate ($K_2Cr_2O_7$), Potassium bromate ($KBrO_3$), Potassium iodate (KIO_3), etc.

Complexometry : $ZnSO_4.7H_2O$, $Zn(CH_3COO)_2.2H_2O$ etc.

1.3.4 Secondary standard substances

A secondary standard substance is one, the strength of the solution of which can't be known by dissolving a definite weight of the substance in a known volume of the solution. Its strength can be determined by titrating against a primary standard substance. The strength of such solutions may change on standing. The substances commonly used as secondary standards in different volumetric analysis are : H_2SO_4, HC1, NaOH, $KMnO_4$, $Na_2S_2O_3.5H_2O$, $Na_2H_2EDTA.2H_2O$ etc.

1.3.5 Equivalent weights of oxidants and reductants

Oxidants gain electron(s) and get reduced while reductants give up electron(s) and get oxidised. The equivalent weight of an oxidant/reductant is the ratio of molecular weight to the change of oxidation number (O.N.) of the active element per molecule of the reactant. It may also be defined as the ratio of molecular weight to the number of electron(s) lost or gained by a molecule of the reactant.

$$\text{Equivalent weight of an oxidant/reductant} = \frac{\text{Molecular Formula weight of oxidant/reductant}}{\text{Change of oxidation number per molecule}}$$

$$= \frac{\text{Molecular Formula weight of oxidant/reductant}}{\text{No. of electron(s) lost or gained per molecule}}$$

$$\text{Equivalent weight of acid/base} = \frac{\text{Molecular weight of acid/base}}{\text{Acidity/Basicity of acid/base}}$$

Example-1 : Equivalent weight of $K_2Cr_2O_7$:

In acid medium $K_2Cr_2O_7$ acts as a strong oxidant :

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

Equivalent weight of $K_2Cr_2O_7$

$$= \frac{\text{Formula weight of } K_2Cr_2O_7}{\text{No. of electron(s) lost per molecule}} = \frac{294.18}{6} = 49.03$$

Example-2 : Equivalent weight of crystalline oxalic acid, $H_2C_2O_4.2H_2O$:

$H_2C_2O_4$ acts as a reductant : $C_2O_4^{2-} - 2e = 2CO_2$

$$\text{Equivalent weight of } H_2C_2O_4.2H_2O = \frac{\text{Molecular weight of } H_2C_2O_4.2H_2O}{\text{No. of electron(s) gained per molecule}}$$

$$= \frac{126.066}{2} = 63.033$$

1.3.6. Strength of a solution

It indicates the amount of solute in definite volume of the solution/solvent. This can be expressed as–

i) Molarity of a solution :

It is defined as the number of gram moles of a solute dissolved per litre of the solution. Thus a molar (M) solution of sulphuric acid contains 98g of H_2SO_4 per litre.

ii) Normality of a solution :

It is defined as the number of gram equivalent of a solute dissolved per litre of the solution. Thus a normal (N) solution of sulphuric acid (Molecular weight = 98) contains 98/2 = 49g of H_2SO_4 per litre [since basicity of H_2SO_4 = 2].

1.4 Estimation of Fe(II) and Fe(III) in a given mixture using $K_2Cr_2O_7$ solution

The estimation of iron in its different oxidation states, specifically Fe(II) and Fe(III), is an important analytical procedure in chemistry. This process is crucial for understanding the redox behaviour of iron in various chemical and environmental contexts, such as in metallurgical processes, water treatment, and soil analysis.

1.4.1 Principle

The estimation is done by two steps. Direct titration of the mixture with standard $K_2Cr_2O_7$ after maintaining proper condition gives the amount of Fe^{2+}. Again Fe^{3+} of the mixture is first reduced to Fe^{2+} with $SnCl_2$ adding dropwise in hot 6 (N) HCl medium followed by the addition of drop of $SnCl_2$ in excess. After cooling the solution to room temperature excess $SnCl_2$ is removed by adding $HgCl_2$ solution when a silky white precipitate appears. This ensures the completeness of the reduction.

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

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

After maintaining proper condition, this is titrated with the same standard $K_2Cr_2O_7$ solution. This titre value corresponds to the total iron [Fe^{3+} + Fe^{2+}]. The difference of the titre values will give the amount of Fe^{3+}.$Cr_2O_7^{2-}$ oxidises Fe^{2+} to Fe^{3+} in acid medium and itself gets reduced to Cr^{3+}.

Indicator : The estimation of Fe^{2+} is done by using Barium or Sodium diphenylamine sulphonate (BDS) in presence of H_3PO_4 or F^-.

1.4.2 Chemicals Required

i) Standard ~ 0.1(N)$K_2Cr_2O_7$ solution

ii) Saturated aqueous solution of Barium-diphenylaminesulphonate (BDS) indicator salt

iii) Conc HCl

iv) 15% $SnCl_2$ solution

v) 5% $HgCl_2$ solution

vi) Syrupy H_3PO_4

vii) Fe^{2+} and Fe^{3+} mixture (Unknown)

1.4.3 Procedure

i) Determination of Fe (II) :

An aliquot of 25 ml Fe^{2+} and Fe^{3+} mixture is pipetted out in a 500 ml conical flask, 100 ml 2 (N) H_2SO_4, 3 ml syrupy H_3PO_4, 4–5 drops of BDS indicator are added and titrated with the standard $K_2Cr_2O_7$ solution until the colour of the solution just changes from green to reddish-violet. The titration is repeated twice.

ii) Determination of total iron (Fe^{2+} + Fe^{3+})

An aliquot of 25 ml from the given Fe^{2+} and Fe^{3+} mixture is pipetted out in a 500 ml conical flask, 25 ml conc HCl is added, heated nearly to boiling and then reduced with SnCl2 solution adding dropwise with constant shaking until the yellow colour of the solution is just discharged. One drop of $SnCl_2$ is added in excess. The flask is rapidly cooled under tap to room temperature. 10ml 5% $HgCl_2$ solution is added at a time, shaken and allowed to stand for 5 minute when a slight silky white precipitate of Hg_2Cl_2 appears.This indicates the completeness of the reduction of Fe^{3+} to Fe^{2+}. The solution is diluted with 100ml of distilled water, 5ml syrupy H_3PO_4 and 4–5 drops of BDS indicator are added. It is then titrated with the standard $K_2Cr_2O_7$ solution until the colour of the solution just changes from green to reddish-violet. The titration is repeated twice.

1.4.4 Experimental Results

Table 1 : Estimation of Fe^{2+}

No. of Titrations	Volume of Fe^{2+} and Fe^{3+} mixutre taken in mL	Burette reading of $K_2Cr_2O_7$		Volume of $K_2Cr_2O_7$ solution required in mL	Mean volume of $K_2Cr_2O_7$ required in mL
		Initial	Final		
1					
2					
3					

Table 2 : Estimation of Fe^{2+}

No. of Titrations	Volume of Fe^{2+} and Fe^{3+} mixture taken in mL	Burette reading of $K_2Cr_2O_7$		Volume of $K_2Cr_2O_7$ solution required in mL	Mean volume of $K_2Cr_2O_7$ required in mL
		Initial	Final		
1					
2					
3					

1.4.5 Calculation

1) Let the strength of $K_2Cr_2O_7$ solution = S (N)

2) Estimation of Fe^{2+} : 25mL mixture ≡ x mL S (N) $K_2Cr_2O_7$ solution

≡ xS mL 1(N) $K_2Cr_2O_7$ solution

We have, 1000mL 1(N) $K_2Cr_2O_7$ solution? ≡ 55.847g of Fe

xS mL 1 (N) $K_2Cr_2O_7$ solution ≡ (0.055847 × x × S)g of Fe^{2+}/ 25mL mixture

≡ (0.055847 × x × S × 40)g/L of Fe^{2+}

≡ A g/L

∴ Amount of Fe^{2+} ion in the given mixture ≡ A g/L

3) Estimation of total iron (Fe^{2+} + Fe^{3+})

25mL mixture ≡ y mL S (N) $K_2Cr_2O_7$ solution

≡ yS mL 1(N) $K_2Cr_2O_7$ solution

$\therefore$ yS mL 1 (N) $K_2Cr_2O_7$ solution $\equiv$ (0.055847 × y × S)g of Fe^{2+}/25mL mixture

$\equiv$ (0.055847 × y × S × 40)g/L of total Fe

$\equiv$ B g/L

$\therefore$ Amount of total iron (Fe^{2+} + Fe^{3+}) = B g/L of the mixture

$\therefore$ Amount of Fe^{3+} ion in the given mixture = (B–A) g/L

1.5 Summary

- This chapter provides a detailed exploration of the analytical method used for estimating iron in its two common oxidation states, Fe(II) and Fe(III), using potassium dichromate ($K_2Cr_2O_2$) as the titrant.
- The estimation of Fe(II) and Fe(III) in a mixture involves two main steps.
- First, the mixture is titrated directly with a standard $K_2Cr_2O_7$ solution under proper conditions to measure the amount of Fe(II) present.
- Fe(III) is then completely reduced to Fe(II) using $SnCl_2$. After reduction, it is titrated again with the same $K_2Cr_2O_2$ solution. This titration measures the total iron content (Fe^{3+} + Fe^{2+}).
- The difference between the two titration values gives the concentration of Fe(III) in the mixture.
- The $Cr_2O_7^{-2}$ ions oxidize Fe(II) to Fe(III) in an acidic medium while being reduced to Cr^{3+}.

1.6 Questions

1. Explain the principle behind the estimation of Fe(II) and Fe(III) using K?Cr?O? solution.

Ans : see text

2. What is the role of potassium dichromate ($K_2Cr_2O_7$) in this titration method?

Ans : Potassium dichromate ($K_2Cr_2O_7$) acts as an oxidizing agent. It oxidizes Fe(II) ions to Fe(III) ions in an acidic medium. The amount of $K_2Cr_2O_7$ used in the reaction helps determine the concentration of Fe(II) and, indirectly, Fe(III) in the sample.

3. Why is it necessary to reduce Fe(III) to Fe(II) before titrating with $K_2Cr_2O_7$?

Ans : Fe(III) cannot be directly titrated with $K_2Cr_2O_7$. To measure the total iron

content, Fe(III) must be reduced to Fe(II), allowing the entire iron content (Fe^{2+} + Fe^{3+}) to be measured. This is achieved by reducing Fe(III) to Fe(II) with a reducing agent before the titration.

4. Describe the procedure for preparing the sample solution for titration.

Ans : The sample is first prepared by dissolving the mixture in a suitable solvent, typically water or acid. For Fe(III) estimation, Fe(III) is reduced to Fe(II) using a reducing agent like SnCl? in hot 6 N HCl. After reduction, the solution is cooled, and excess SnCl? is removed by adding HgCl?, which forms a precipitate to confirm the reduction is complete.

5. How do you ensure that all Fe(III) is reduced to Fe(II) during the experiment?

Ans : To ensure complete reduction, Fe(III) is treated with SnCl? in an acidic medium (6N HCl) and the reaction is performed at elevated temperatures. Excess SnCl? is then removed using $HgCl_2$. A precipitate formation confirms that all $SnCl_2$ has reacted, ensuring that the reduction of Fe(III) to Fe(II) is complete.

6. What is the purpose of adding $HgCl_2$ after reducing Fe(III) with SnCl?

Ans : $HgCl_2$ is added to remove any excess $SnCl_2$ after the reduction of Fe(III). The addition of $HgCl_2$ results in the formation of a silky white precipitate, indicating that all excess $SnCl_2$ has reacted and ensuring the completeness of the reduction process.

7. How is the endpoint of the titration identified?

Ans : The endpoint of the titration is identified by using an appropriate indicator that changes color at the end of the titration. Common indicators for this type of titration include diphenylamine or barium diphenylamine sulfonate, which change colour when all Fe(II) has reacted with the $K_2Cr_2O_7$.

8. What indicators are used in this titration, and why are they chosen?

Ans : Barium diphenylamine sulfonate are commonly used indicators. They are chosen because they exhibit a distinct colour change when the Fe(II) is completely oxidized to Fe(III), signalling the endpoint of the titration.

Unit – 2 ❑ Estimation of Fe(III) and Cu(II) in a given mixture using $K_2Cr_2O_7$ solution

Structure

2.1 Objective

2.2 Introduction

2.3 Principle

2.4 Chemicals Required

2.5 Procedure

2.6 Experimental Results

2.7 Calculations

2.8 Summary

2.9 Question

2.1 Objective

By the end of this unit, students should be able to accurately estimate the concentration of Fe(III) and Cu(II) in a mixture using $K_2Cr_2O_7$, understand the theoretical underpinnings of the method, and apply this knowledge to real-world scenarios.

2.2 Introduction

The accurate estimation of metal ions in a mixture is a cornerstone of analytical chemistry, particularly in fields such as metallurgy, environmental science, and industrial quality control. This unit focuses on the estimation of iron(III) (Fe^{3+}) and copper(II) (Cu^{2+}) ions in a given mixture using potassium dichromate ($K_2Cr_2O_7$) as the oxidizing agent.

Potassium dichromate is a versatile and powerful oxidizing agent frequently used in redox titrations. While Fe(III) is not directly titratable with $K_2Cr_2O_7$, it can be reduced to Fe(II), which is then titrated. Cu(II), on the other hand, does not directly

react with $K_2Cr_2O_7$ under standard conditions, but its presence can influence the titration process and must be accounted for separately.

In this unit, you will explore the principles behind the redox reactions involving Fe(III) and Cu(II), learn the detailed procedures for carrying out the titration, and understand how to calculate the concentrations of these metal ions in a mixture. You can use this method in real-world scenarios, such as analyzing metal content in ores, monitoring environmental pollutants, and ensuring the quality of metal products.

2.3 Principle

Both Fe^{3+} and Cu^{2+} can liberate I_2 from KI solution, but Cu^{2+} can be estimated from the mixture by complexing Fe^{3+} as $[FeF_6]^{3-}$ by adding NH_4HF_2. Due to this complex formation the formal potential of Fe^{3+}/Fe^{2+} system falls below standard reduction potential (E_0) of ½ I_2/I^- system.

$$Fe^{3+} + 3HF_{2-} = [FeF_6]^{3-} + 3H^+$$

So Fe^{3+} cannot oxidize iodide to I_2 in presence of fluoride, but Cu^{2+} quantitatively oxidize iodine to I_2 and the liberated I_2 is titrated with a standard $S_2O_3^{2-}$ solution using starch as indicator.

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

$$I_2 + S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

$\therefore$ 2 moles Cu^{2+} 1 mole I2 ? 2 moles S2O32-

or 1 mole $S_2O_3^{2-} \equiv$ 1 mole $Cu^{2+} \equiv$ 1 equivalent

$\therefore$ 1000 mL 1(N) $S_2O_3^{2-}$ solution $\equiv$ 63.546g of Cu

Fe^{3+} is first precipitated as hydrated ferric oxide $Fe_2O_3.xH_2O$ by adding aqueous ammonia. It is filtered, washed and then dissolved in hot 6(N) HCl. Fe^{3+} is reduced to Fe^{2+} by $SnCl_2$ method and Fe^{2+} is estimated by titrating with standard $K_2Cr_2O_7$ solution using Ba-diphenylaminesulphonate (BDS) as indicator.

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

$$Sn^{+2} + 2HgCl_2 = Hg_2Cl_2 \downarrow + Sn^{+4} + 2CI^-$$

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

1 mole $Cr_2O_7^{2-}$ = 6 moles + Fe^{2+}

or, 1/6 mole + $Cr_2O_7^{2-} \equiv$ 1 mole $Fe^{2+} \equiv$ 1 Equivalent

Hence, 1g equivalent of $K_2Cr_2O_7$ ≡ 55.847 g of Fe

or, 1000 ml 1(N) $K_2Cr_2O_7$ solution ≡ 55.847 g of Fe

2.4 Chemicals Required

i) Standard ~0.1 (N) $K_2Cr_2O_7$ solution

ii) Saturated aqueous solution of Barium-diphenylaminesulphonate (BDS) indicator salt

iii) Conc HCl

iv) 15 % $SnCl_2$ solution

v) 5% $HgCl_2$ solution

vi) Syrupy H_3PO_4

vii) Fe^{2+} and Fe^{3+} mixture (Unknown)

2.5 Procedure

i) Prepare 250 mL of a standard ~0.1 (N) $K_2Cr_2O_7$ solution by accurate weighing (1.225g).

ii) **Standardise the $Na_2S_2O_3$ solution (~0.1N) as follows :**

Pipette out 25mL of standard 0.1(N) $K_2Cr_2O_7$ into a 500 mL conical flask, add 25 mL 4(N) H_2SO_4 and 10 mL of 20% KI. Cover the flask and keep it in the dark for 5 minutes. Diluted with 150 mL distilled water, titrate the liberated I_2 with the ~0.1N $Na_2S_2O_3$ solution till straw yellow colour appears. 2 mL of 1% starch solution is added and the titration is continued until the blue colour just changes to light green. The titration is repeated twice.

iii) **Estimation of Cu^{2+} :**

Pipette out 25 mL of the diluted solution into a 500 mL conical flask, dilute to 100 mL with distilled water, neutralise with (1:1) NH_3 solution to obtain a permanent turbidity (avoid excess NH_3) and dissolve the same by adding 2-3g of solid NH_4HF_2. Add 10 mL 20% KI and titrate the liberated I_2 with standard 0.1(N) $Na_2S_2O_3$ solution using starch indicator till pale yellow colour appears. 2 mL of 1% starch solution is added and the titration is continued until the blue colour just disappears to white. The titration is repeated twice.

iv) **Estimation of Fe^{3+} :**

Pipette out 25 mL of the diluted solution, dilute to 100 mL with distilled water, add 1g NH_4Cl, warm and add dil (1:1) NH_3 till precipitate of hydrated ferric oxide appears (add slight excess of NH_3). Filter the precipitate using a Whatman No-1 filter paper and wash 2-3 times with 1% NH_4Cl solution containing a little of NH_3. Dissolve the precipitate in minimum volume of hot dil (1:2) HCl, re-precipitate and filter and wash as before till the washing is colourless. Dissolve the precipitate in 40 mL hot (1:1) HCl and then reduced with $SnCl_2$ solution adding drop-wise with constant shaking until the yellow colour of the solution is just discharged. One drop of $SnCl_2$ is added in excess. The flask is rapidly cooled under tap to room temperature. 10 mL 5% $HgCl_2$ solution is added at a time, shaken and allowed to stand for 5 minute when a slight silky white precipitate of Hg_2Cl_2 appears. This indicates the completeness of the reduction of Fe^{3+} to Fe^{2+}. The solution is diluted with 100 ml of distilled water, 5mL syrupy H_3PO_4 and 4-5 drops of BDS indicator are added. It is then titrated with the standard $K_2Cr_2O_7$ solution until the colour of the solution just changes from green to reddish-violet. The titration is repeated twice.

2.6 Experimental Results

Table 1 : Preparation of standard 250 mL (N/10) $K_2Cr_2O_7$ solution

Initial weight (w_1g)	Final weight (w_2g)	Initial weight taken (w_1–w_2)g	Weight have to take (g)	Strength of $K_2Cr_2O_7$ solution prepared
				= (w_1–w_2)/1.225 (N/10)

Table 2 : Standardisation of $Na_2S_2O_3$ solution Vs Standard $K_2Cr_2O_7$ solution

No. of Titrations	Volume of Standard $K_2Cr_2O_7$ solution take in mL	Burette reading of $Na_2S_2O_3$ solution		Volume of $Na_2S_2O_3$ solution required in mL	Mean volume of $Na_2S_2O_3$ solution required in mL
		Initial	Final		
1					
2					
3					

Table 3: Estimation of Cu^{2+}

No. of Titrations	Volume of diluted maxture taken in mL	Burette reading of $Na_2S_2O_3$ solution		Volume of $Na_2S_2O_3$ solution required in mL	Mean volume of $Na_2S_2O_3$ solution required in mL
		Initial	Final		
1					
2					
3					

Table 4 : Estimation of Fe^{3+}

No. of Titrations	Volume of diluted maxture taken in mL	Burette reading of $K_2Cr_2O_7$ solution		Volume of $K_2Cr_2O_7$ solution required in mL	Mean volume of $K_2Cr_2O_7$ solution required in mL
		Initial	Final		
1					
2					
3					

2.7 Calculations

i) Strength of prepared $K_2Cr_2O_7$ solution = $(w_1 - w_2)/1.225$ (N/10) = S_1 (N)

ii) Strength of $Na_2S_2O_3$ solution = $\dfrac{\text{Volume of mixture taken} \times S_1}{\text{Volume of } Na_2S_2O_3 \text{ solution required}} = S_2$ (N)

iii) Estimation of Cu^{2+}

25 mL solution ≡ x mL S_2 (N) $Na_2S_2O_3$ solution

≡ x S_2 mL 1(N) $Na_2S_2O_3$ solution

We have, 1000 mL 1 (N) $Na_2S_2O_3$ solution ≡ 63.546 g of Cu

∴ x S_2 mL 1(N) $Na_2S_2O_3$ solution ≡ $(0.063546 \times x \times S_2)$g of of Cu

≡ $(0.063546 \times x \times S_2 \times 40)$g/L of Cu

≡ A g/L

Amount of Cu^{2+} ion in the given mixture = A g/L

i) Estimation of Fe^{2+}

25 mL solution $\equiv$ y mL S_1 (N) $K_2Cr_2O_7$ solution

$\equiv$ y S_1 mL 1(N) $K_2Cr_2O_7$ solution

We have, 1000 mL 1 (N) $K_2Cr_2O_7$ solution $\equiv$ 55.847 g of Fe

$\therefore$ y S_1 mL 1(N) $K_2Cr_2O_7$ solution $\equiv$ (0.055847 $\times$ y $\times$ S_1)g of Fe

$\equiv$ (0.055847 $\times$ y $\times$ S_1 $\times$ 40)g/L of Fe

$\equiv$ B g/L

$\therefore$ Amount of Fe^{2+} ion in the given mixture = B g/L

2.8 Summary

- Both Fe^{3+} and Cu^{2+} ions can oxidize iodide (I^-) to iodine (I_2) in a KI solution. However, Fe^{3+} can be quantitatively complexed and thus separated from Cu^{2+}.
- By adding NH_4HF_2, it forms the complex $[FeF_6]^{3-}$ with Fe^{3+}. The formation of this complex lowers the formal potential of the Fe^{3+}/Fe^{2+} system below the standard reduction potential of the I_2/I^- system. As a result, Fe^{3+} cannot oxidize iodide to I_2 in the presence of fluoride. Then estimation of Cu^{2+} is done by titrating the liberated iodine with a standard thiosulfate ($S_2O_3^{2-}$) solution, using starch as an indicator.
- Fe^{3+} is first precipitated as hydrated ferric oxide ($Fe_2O_3 \cdot xH_2O$) by adding aqueous ammonia, filtered, washed, and dissolved in hot 6 N HCl. Fe^{3+} is then reduced to Fe^{2+} using $SnCl_2$. Fe^{2+} is quantified by titration with a standard $K_2Cr_3O_7$ solution using Ba-diphenylamine sulfonate (BDS) as the indicator.

2.9 Question

1. Why is potassium dichromate ($K_2Cr_2O_7$) used as the titrant for estimating Fe(III) and Cu(II) in this practical?

Ans : Potassium dichromate ($K_2Cr_2O_7$) is used as the titrant because it is a strong oxidizing agent. It reacts quantitatively with Fe^{2+} (which is reduced from Fe^{3+}) in an acidic medium, allowing for accurate estimation of Fe^{3+}. For the estimation of Cu^{2+}, it helps to determine the amount of Fe^{2+} present by back-titration if necessary, as Cu^{2+} does not directly react with $K_2Cr_2O_7$ but may interfere with the titration of Fe^{2+}.

2. Explain the role of sulfuric acid in the titration process with $K_2Cr_2O_7$.

Ans : Sulfuric acid (H_2SO_4) provides the acidic medium necessary for the dichromate ion ($Cr_2O_7^{2-}$) to act as an oxidizing agent. It ensures that Fe^{2+} is oxidized to Fe^{3+} efficiently and prevents the formation of intermediate products that could interfere with the titration. Additionally, sulfuric acid helps to maintain the stability of the dichromate solution during the titration process.

3. What is the purpose of using diphenylamine sulfonate (BDS) as an indicator in the titration of Fe^{2+} with $K_2Cr_2O_7$?

Ans : Diphenylamine sulfonate (BDS) is used as an indicator in the titration of Fe^{2+} with $K_2Cr_2O_7$ because it changes color when Fe^{2+} is completely oxidized to Fe^{3+}. The end point is detected by the appearance of a distinct color change, indicating that all Fe^{2+} has reacted with the dichromate solution.

4. How do you ensure that the Fe(III) is completely reduced to Fe(II) before titration?

Ans : To ensure complete reduction of Fe(III) to Fe(II), you add a sufficient amount of a reducing agent such as $SnCl_2$ to the solution. The reduction process is typically monitored by checking the color change or by adding excess reducing agent to ensure that all Fe(III) is reduced. Additionally, you may use a small portion of the solution to confirm that no residual Fe(III) is present before performing the titration.

5. What is the purpose of adding NH_4HF_2 in the estimation of Fe^{3+} and Cu^{2+}?

Ans : NH_4HF_2 is added to form the complex $[FeF_6]^{2-}$ with Fe^{3+}. This complex formation lowers the formal potential of the Fe^{3+}/Fe^{2+} system below the standard reduction potential of the I_2/I^- system. As a result, Fe^{3+} cannot oxidize iodide (I^-) to iodine (I_2) in the presence of fluoride. This selective inhibition allows for the accurate estimation of Cu^{2+} in the mixture by titrating the liberated iodine with thiosulfate.

Unit – 3 ❑ Estimation of Cr(VI) and Mn(II) in a given mixture using $K_2Cr_2O_7$ solution

Structure

3.1 Objective
3.2 Introduction
3.3 Principle
3.4 Chemicals Required
3.5 Procedure
3.6 Experimental Results
3.7 Calculations
3.8 Summary
3.9 Question

3.1 Objectives

By the end of this unit, students should be able to–

- Accurately estimate the concentration of Cr(VI) and Mn(II) in a given mixture using $K_2Cr_2O_7$, understand the theoretical underpinnings of the method, and apply this knowledge to real-world scenarios.
- Understand the Chemistry of Cr(VI) and Mn(II)
- Learn the procedures for sample preparation and pre-treatment for accurate estimation of Cr(VI) and Mn(II).
- Use standard calculations to express results in terms of concentration or percentage composition.

3.2 Introduction

In this unit, you will learn how to prepare samples, perform the titration using $K_2Cr_2O_2$, and calculate the concentrations of Cr(VI) and Mn(II). The process includes the preparation of standard solutions, performing the titration under acidic conditions,

and using suitable indicators to identify the endpoint. By mastering these techniques, you will be able to accurately determine the concentrations of these metals in a mixture.

3.3 Principle

From the mixture, manganese should be precipitated as MnO_2 by the treatment with sodium peroxide or $KBrO_3$ and filtered. From the filtrate portion the Cr (VI) ion can be estimated. The filtrate is evaporated to dryness, dissolve the residue in dil H_2SO_4 and add measured excess of standard Mohr's salt solution. The excess Mohr being back titrated with the standard $K_2Cr_2O_7$ solution using Ba-diphenylaminesulphonate (BDS) as indicator.

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

1 mole $Cr_2O_7^{2-} \equiv 6$ moles $+ Fe^{2+}$

or, 1 mole $Fe^{2+} \equiv 1/6$ mole $Cr_2O_7^{2-} \equiv 1/3$ mole of Cr $\equiv$ 1 Equivalent

or, 1000 ml 1(N) Mohr's salt solution $\equiv$ 49.03 g of $K_2Cr_2O_7 \equiv$ 51.996/3g of Cr

From the precipitate part Manganese ion is estimated. The precipitate containing MnO2 is dissolved in measured excess of standard Mohr's salt solution and Mn2+ can then be estimated by back titrating with standard K2Cr2O7 solution in presence of phosphoric acid using BDS as indicator.

$$3Mn^{2+} + BrO_3^- + 6H^+ = 3MnO_2 + 5Br^- + 3H_2O$$

$$MnO_2 + 2Fe^{2+} \text{ (Mohr's salt)} + 4H^+ = Mn^{2+} + 2H_2O + 2Fe^{3+}$$

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

$\therefore$ 1 mole $Mn^{2+} \equiv$ 1 mole $MnO_2 \equiv$ 2 moles of Fe^{2+}

Or, 1 mole of $Fe^{2+} \equiv$ 1/2 mole $Mn^{2+} \equiv$ 1 equivalent

$\therefore$ 1000 mL (N) Mohr's salt solution $\equiv 27.47 \times 1.01$g of Mn^{2+}

(N.B.: 1.01 is the empirical factor in this method of estimation to get accurate result)

3.4 Chemicals Required

i) Standard ~0.2 (N) $K_2Cr_2O_7$ solution

ii) ~(N/20) Mohr's salt solution

iii) Saturated aqueous solution of BDS indicator salt

iv) Sodium peroxide

v) 5% $KBrO_3$

vi) Conc H_2SO_4

vii) Syrupy H_3PO_4

viii) Whatmann No-1 filter paper

ix) Cr(VI) and Mn(II) (Unknown)

3.5 Procedure

i) Transfer the solution quantitatively into 250 ml volumetric flask and make up the volume to the mark.

ii) Prepare 250 mL of a standard ~(N/20) $K_2Cr_2O_7$ solution by accurate weighing.

iii) **Standardization of Mohr's salt solution (blank titration):**

Pipette out an aliquot of 25mL Mohr's salt solution in a 500mL conical flask, Add 25mL 2(N) H_2SO_4 3 mL syrupy H_3PO_4 and 3-4 drops of BDS indicator. Titrate the solution with the standard $K_2Cr_2O_7$ solution until the colour changes from green to reddish-violet.

iv) **Separation between two ions :**

METHOD-I : Pipette out 25 ml of this diluted solution in 250 ml beaker and dilute to 100 ml. Add sodium peroxide in small portions and shake the mixture carefully. Here all manganese should be converted to manganese dioxide. If there is no blackening on the addition of sodium peroxide in the clear supernatant liquid, it indicates that the conversion is complete. Addition of excess sodium peroxide should be avoided. Boil the whole mixture for five minutes. Filter the solution and wash the precipitate with water to free from chromate.

METHOD-II : Pipette out 25 ml of this diluted solution in 500 mL beaker. Add 10 mL 4(N) H_2SO_4 to adjust the acidity to 1(N) and then 10 mL 5% $KBrO_3$ solution is added to it. Cover the beaker with a watch glass and heat the mixture to gentle boiling for 15 to 20 minutes with occasional addition of water to make the loss to evaporation. Here all manganese should be converted to manganese dioxide. Allow the mixture to cool to room temperature. Filter the precipitate of MnO_2 through Whatman No-1 filter paper, if any turbidity appears, re-filter the first portion again

through the same filter paper. Wash the precipitate with hot water for 6-8 times using 10mL portion in each time till washing are free from BrO_3^- (test with starch-KI in acidic medium).

a) From filtrate part, estimate the Chromium ion

b) From the precipitate part, estimate Manganese ion

v) **Estimation of Chromium ion (treatment with filtrate portion) :**

Evaporate the filtrate to dryness and heat to baking in order to decompose peroxide completely. Dissolve the residue after cooling in 25 ml of distilled water and acidify with (1:4) H_2SO_4 (colour changes from yellow to orange). To the solution, add a measured excess (say 50 mL) standard N/20 Mohr's salt. Add 25 mL pf (1:1) H_2SO_4, 5 ml of syrupy H_3PO_4 and 6-8 drops of Ba-diphenyl amminesuiphonate (BDS) (0.1% an aqueous solution). Titrate the solution with the standard $K_2Cr_2O_7$ solution until the colour changes from green to reddish- violet.

vi) **Estimation of Manganese ion (treatment with Precipitate portion) :**

METHOD-I : Transfer the precipitate of MnO_2 along with the filter paper in the original beaker and add 25 mL of (1:1) H_2SO_4 followed by measured excess (say 50 mL) standard (N/20) Mohr's salt solution. Now stir well the whole mixture so that all MnO_2 reacts completely. Add 5 ml of syrupy H_3PO_4 and 4-5 drops of BDS indicator (0.1% an aqueous solution) to it. Then back titrate the excess Mohr's solution with the standard $K_2Cr_2O_7$ solution until the colour changes from green to reddish- violet. Perform a blank titration with the same amount of Mohr's solution.

METHOD-II : Transfer the precipitate of MnO_2 to the original beaker quantitatively, with 6 N hot H_2SO_4 and dissolve the precipitate by warming. Then dilute the mixture to 3N with stirring. The total volume should be Within 200 ml. Add 1 g of sodium bismuthate with stirring in portions. Filter the mixture through sintered glass crucible or asbestos bed and wash with dii. H_2SO_4. Filtration should be done in a large conical flask (500 ml) under suction taking 50 ml standard Mohr's salt solution in the conical flask. Add 25 ml of (1: 4) Add 25 mL pf (1:1) H_2SO_4, 5 ml of syrupy H_3PO_4 and 6-8 drops of BDS indicator (0.1% an aqueous solution). Titrate the solution with the standard $K_2Cr_2O_7$ solution until the colour changes from green to reddish- violet. Side by side perform one blank titration with the same amount of Mohr's solution.

3.6 Experimental Results

Table 1 : Preparation of standard 250 mL ~(N/20) $K_2Cr_2O_7$ solution

Initial weight (w_1g)	Final weight (w_2g)	Initial weight taken (w_1–w_2)g	Weight have to take (g)	Strength of $K_2Cr_2O_7$ solution prepared
			0.6128	= (w_1–w_2)/0.6128 (N/10)

Table 2 : Standardization of Mohr's solution Vs (N/20) $K_2Cr_2O_7$ solution

No. of Titrations	Volume of Mohr's salt solution taken in mL	Burette reading of $K_2Cr_2O_7$ solution		Volume of $K_2Cr_2O_7$ solution required in mL	Mean volume of $K_2Cr_2O_7$ solution required in mL
		Initial	Final		
1					
2					
3					

Table 3 : Titration of the Estimation of Chromium ion

No. of Titrations	Volume of solution maxture taken in mL	Burette reading of $K_2Cr_2O_7$ solution		Volume of $K_2Cr_2O_7$ solution required in mL	Mean volume of $K_2Cr_2O_7$ solution required in mL
		Initial	Final		
1					
2					
3					

Table 4 : Titration for the Estimation of Managanese ion

No. of Titrations	Volume of stock solution mixture + measured excess of standard Mohr's salt solution taken of mL	Burette reading of $K_2Cr_2O_7$ solution		Volume of $K_2Cr_2O_7$ solution required in mL	Mean volume of $K_2Cr_2O_7$ solution required in mL
		Initial	Final		
1					
2					
3					

3.7 Calculations

a) Strength of prepared $K_2Cr_2O_7$ solution = $(w_1 - w_2)$ / 0.6128 (N/20) = S (N)

b) **Estimation of Cr(VI) ion**

25 mL Mohr's salt solution ≡ x mL S(N) $K_2Cr_2O_7$ solution

25 mL diluted stock solution + 50 mL Mohr's salt solution ≡ y mL S(N) $K_2Cr_2O_7$ solution

Mohr consumed by Cr(VI) in 25 mL diluted stock solution ≡ (2x–y) mL S(N) $K_2Cr_2O_7$ solution

≡ [(2x–y) × S] mL 1(N) $K_2Cr_2O_7$ solution

∴ Mohr consumed by Cr(VI) in 250 mL diluted stock solution

≡ 10 × (2x–y) × S mL 1(N) $K_2Cr_2O_7$ solution

≡ 10 × (2x–y) × S mL 1(N) Mohr's salt solution

We have,

1000 mL 1(N) Mohr's salt solution ≡ 17.332g of Cr(VI)

10 × (2x–y) × S mL 1(N) Mohr's salt solution

≡ 0.01732 ×10 × (2x–y) × S g of Cr(VI)

The total amount of Cr(VI) in the supplied mixture = 0.01732 × 10 × (2x–y) × S g

a) **Estimation of Manganese ion**

25 mL Mohr's salt solution? ≡ mL S(N) $K_2Cr_2O_7$ solution

25 mL diluted stock solution + 50 mL Mohr's salt solution

≡ z mL S(N) $K_2Cr_2O_7$ solution

Mohr consumed by Mn^{2+} in 25 mL diluted stock solution

≡ (2x–z) mL S(N) $K_2Cr_2O_7$ solution

≡ [(2x–z) × S] mL 1(N) $K_2Cr_2O_7$ solution

∴ Mohr consumed by Mn^{2+} in 250 mL diluted stock solution

≡ 10 × (2x–z) × SmL 1(N) $K_2Cr_2O_7$ solution

≡ 10 × (2x–z) × SmL 1(N) Mohr's salt solution

We have, 1000 mL 1 (N) Mohr's salt solution ≡ 27.47 × 1.01g of Mn^{2+}

10 × (2x–z) × S mL 1(N) Mohr's salt solution

≡ 0.02747 × 1.01 × 10 × (2x–z) × S g of Mn^{2+}

The total amount of Mn^{2+} in the supplied mixture

= 0.02747 × 1.01 ×10 × (2x–z) × S g

3.8 Summary

- The estimation is based on the redox titration method, where potassium dichromate ($K_2Cr_2O_7$) acts as an oxidizing agent.
- For Cr(VI) : Titrate with $K_2Cr_2O_7$ in the presence of H_2SO_4.
- For Mn(II) : Oxidize Mn(II) to MnO_4^- using $K_2Cr_2O_7$, followed by titration with $Na_2S_2O_3$
- Use starch as the indicator during titration with $Na_2S_2O_3$

3.9 Question

1. What is the principle behind the estimation of Cr(VI) and Mn(II) using $K_2Cr_2O_7$?

Ans : The estimation is based on redox titration, where potassium dichromate ($K_2Cr_2O_7$) acts as a strong oxidizing agent. Cr(VI) is reduced to Cr(III), and Mn(II) is oxidized to MnO_4^-. The amount of $K_2Cr_2O_7$ used in the titration correlates with the concentration of Cr(VI) and Mn(II) in the mixture.

2. Why is sulfuric acid (H_2SO_4) used in the titration?

Ans : Sulfuric acid (H_2SO_4) is used to create an acidic environment necessary for the

redox reactions to occur efficiently. It helps in maintaining the correct oxidation states and ensures the complete reduction of Cr(VI) and oxidation of Mn(II).

3. What role does sodium thiosulfate (Na?S?O?) play in the estimation of Mn(II)?

Ans : Sodium thiosulfate ($Na_2S_2O_3$) is used to titrate the iodine liberated during the reaction. It helps in estimating the concentration of Mn(II) after it has been oxidized to MnO_4^-, which reacts with iodide ions to release iodine.

4. Why is starch used as an indicator in this titration?

Ans : Starch is used as an indicator in the titration involving sodium thiosulfate ($Na_2S_2O_3$) because it forms a deep blue complex with iodine. The disappearance of the blue color indicates the end point of the titration.

5. What is the significance of using potassium dichromate ($K_2Cr_2O_7$) as the titrant?

Ans : Potassium dichromate ($K_2Cr_2O_7$) is a primary standard with a high equivalent weight and stable composition. It acts as a strong oxidizing agent, making it ideal for accurately determining the concentration of reducing agents like Cr(VI) and Mn(II).

6. What are the oxidation states of chromium and manganese in the reaction?

Ans : In the reaction, chromium is reduced from +6 oxidation state (Cr(VI)) to +3 oxidation state (Cr(III)). Manganese is oxidized from +2 oxidation state (Mn(II)) to +7 oxidation state as permanganate ion (MnO_4^-).

7. Can you explain the role of redox reactions in this experiment?

Ans : Redox reactions involve the transfer of electrons between species. In this experiment, Cr(VI) is reduced, and Mn(II) is oxidized. These reactions allow the quantification of the analytes based on the amount of $K_2Cr_2O_7$ required to complete the reactions.s

Unit – 4 ❑ Estimation of Fe(III) and Cr(VI) in a given mixture using $K_2Cr_2O_7$ solution

Structure

4.1 Objective

4.2 Introduction

4.3 Principle

4.4 Chemicals Required

4.5 Procedure

4.6 Experimental Results

4.7 Calculations

4.8 Summary

4.9 Question

4.1 Objectives

By the end of this unit, students should be able to–

- Accurately estimate the concentration of Fe(III) and Cr(VI) in a given mixture using $K_2Cr_2O_7$, understand the theoretical underpinnings of the method, and apply this knowledge to real-world scenarios.
- Understand how Fe(III) and Cr(VI) undergo redox reactions.
- Understand the chemical reaction between Cr(VI) and $K_2Cr_2O_7$

4.2 Introduction

In this unit, we explore the crucial and detailed process of estimating the concentrations of iron(III) (Fe^{3+}) and chromium(VI) (CrO_4^{2-}) ions in a mixture using potassium dichromate ($K_2Cr_2O_7$) as the titrant.

Iron and chromium are metals of significant industrial importance, with applications ranging from steel manufacturing to pigment production and electroplating. However, their presence in the environment, particularly in their ionic forms Fe(III)

and Cr(VI), requires careful monitoring due to their potential impact on human health and ecosystems. Fe(III) ions play a crucial role in biological processes, while Cr(VI) ions are known for their toxicity and carcinogenic properties. Therefore, accurate estimation of these ions is crucial for ensuring safety in both industrial and environmental contexts.

Potassium dichromate ($K_2Cr_2O_7$) is a powerful oxidizing agent commonly used in redox titrations due to its stability and precision. In this unit, we will explore how $K_2Cr_2O_7$ facilitates the estimation of Fe(III) and Cr(VI) in a mixture through a series of redox reactions.

4.3 Principle

$Cr_2O_7^{2-}$ is directly estimated in presence of Fe^{3+} by adding measured excess of standard Mohr's salt solution, the excess Mohr being bock titrated with the standard $Cr_2O_7^{2-}$ solution using Ba-diphenylaminesulphonate (BDS)as indicator.

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

1 mole $Cr_2O_7^{2-} \equiv 6$ moles $+ Fe^{2+}$

or, 1 mole $Fe^{2+} \equiv 1/6$ mole $Cr_2O_7^{2-} \equiv$ 1/3 mole of Cr $\equiv$ 1 Equivalent

or, 1000 ml 1(N) Mohr's salt solution $\equiv$ 49.03 g of $K_2Cr_2O_7 \equiv$ 51.996/3g of Cr $\equiv$ 17.332 g of Cr

Fe^{3+} is first precipitated as hydrated ferric oxide $Fe_2O_3.xH_2O$ by adding aqueous ammonia. It is filtered, washed and then dissolved in hot 6(N) HCl. Fe^{3+} is reduced to Fe^{2+} by $SnCl_2$ method and Fe^{2+} is estimated by titrating with standard $K_2Cr_2O_7$, solution using BDS as indicator.

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

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

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

1 mole $Cr_2O_7^{2-} \equiv$ 6 moles Fe^{2+}

or, 1/6 mole $Cr_2O_7^{2-} \equiv$ 1 mole $Fe^{2+} \equiv$ 1 equivalent

Hence, 1 g equivalent of $K_2Cr_2O_7 \equiv$ 55.847 g of Fe

4.4 Chemicals Required

i) Standard ~0.2 (N) $K_2Cr_2O_7$ solution
ii) Mohr's salt solution
iii) Saturated aqueous solution of BDS indicator salt
iv) Conc H_2SO_4
v) dil (1:1) NH_3
vi) NH_4Cl solution
vii) 15% $SnCl_2$ solution
viii) 5% $HgCl_2$ solution
ix) Syrupy H_3PO_4
x) Fe(III) and Cr(VI) mixture (Unknown)

4.5 Procedure

Transfer the supplied solution *quantitatively* (25 mL)in a 250 mL volumetric flask and dilute it with distilled water up to the mark.

(a) Prepare a standard ~N/20 potassium dichromate solution to a 250 mL volumetric flask.

(b) **Standardization of Mohr's salt solution :**

Pipette out an aliquot of 25mL Mohr's salt solution in a 500mL conical flask, Add 25mL 2(N) H_2SO_4 3mL syrupy H_3PO_4 and 3-4 drops of BDS indicator. Titrate the solution with the standard $K_2Cr_2O_7$ solution until the colour changes from green to reddish- violet.

(c) **Estimation of Cr(VI) as $Cr_2O_7^{2-}$**

Pipette out an aliquot of 25 mL from the above diluted solution to a 500mL conical flask. Add a measured excess, about 50 mL, of standard ~N/20 Mohr's salt solution. Dilute to 150 mL and add 25mL 2(N) H_2SO_4, 5mL syrupy H_3PO_4 and 3-4 drops of BDS indicator. Titrate the solution with the standard $K_2Cr_2O_7$ solution until the colour changes from green to reddish- violet.

(d) **Estimation of Fe :**

Pipette out 25mL of the above diluted solution to a 500mL conical flask, dilute to 100mL with distilled water, add lg NH_4Cl, warm and precipitate hydrated ferric

oxide by adding dil (1:1) NH_3. Filter the precipitate using a Whatmann No. 1 filter paper and wash 2-3 times with 1% NH_4Cl solution containing a little of NH_3. Dissolve the precipitate to minimum volume of hot dil (1:2) HCl, filter and wash as before till the washings are colourless. Dissolve the precipitate in 40 mL hot (1 : 1) HCl and then reduced with $SnCl_2$ solution adding drop-wise with constant shaking until the yellow colour of the solution is just discharged. One drop of $SnCl_2$ is added in excess. The flask is rapidly cooled under tap water to room temperature. 10 mL 5% $HgCl_2$ solution is added at a time, shaken and allowed to stand for 5 minute when a slight silky white precipitate of Hg_2Cl_2 appears. This indicates the completeness of the reduction of Fe^{3+} to Fe^{2+}. The solution is diluted with 100 ml of distilled water. 5mL syrupy H_3PO_4 and 4-5 drops of BDS indicator are added. It is then titrated with the standard $K_2Cr_2O_7$ solution until the colour of the solution just changes from green to reddish-violet. The titration is repeated twice.

4.6 Experimental Results

Table 1 : Preparation of standard 250 mL ~(N/20) $K_2Cr_2O_7$ solution

Initial weight (w_1g)	Final weight (w_2g)	Initial weight taken (w_1–w_2)g	Weight have to take (g)	Strength of $K_2Cr_2O_7$ solution prepared
			0.6128	= (w_1–w_2)/0.6128 (N/20)

Table 2 : Standardization of Mohr's solution Vs Standard $K_2Cr_2O_7$ solution

No. of Titrations	Volume of Mohr's salt solution taken in mL	Burette reading of $K_2Cr_2O_7$ solution		Volume of $K_2Cr_2O_7$ solution required in mL	Mean volume of $K_2Cr_2O_7$ solution required in mL
		Initial	Final		
1					
2					
3					

Table 3 : Titration of the Estimation of Chromium ion

No. of Titrations	Volume of diluted maxture + Mohr's salt solution taken in mL	Burette reading of $K_2Cr_2O_7$ solution		Volume of $K_2Cr_2O_7$ solution required in mL	Mean volume of $K_2Cr_2O_7$ solution required in mL
		Initial	Final		
1					
2					
3					

Table 4 : Estimation of Fe^{3+}

No. of Titrations	Volume of diluted stock solution taken in mL	Burette reading of $K_2Cr_2O_7$ solution		Volume of $K_2Cr_2O_7$ solution required in mL	Mean volume of $K_2Cr_2O_7$ solution required in mL
		Initial	Final		
1					
2					
3					

4.7 Calculations

i) Strength of prepared $K_2Cr_2O_7$ solution = $(w_1 - w_2)/ 0.6128$ (N/20) = S (N)

ii) **Estimation of Fe^{3+}**

25 mL diluted stock solution ≡ x mL S(N) $K_2Cr_2O_7$ solution

250 mL diluted stock solution ≡ $10 \times x \times$ SmL (N) $K_2Cr_2O_7$ solution

We have, 1000 mL 1 (N) $K2Cr_2O_7$ solution ≡ 55.847 g of Fe

∴ $10 \times x \times S$ mL 1(N) $K_2Cr_2O_7$ solution ≡ $(0.055847 \times 10 \times x \times S)$g of Fe

∴ The total amount of Fe^{3+} ion in the supplied mixture = $(0.055847 \times 10 \times x \times S)$g

iii) **Estimation of Cr(VI)**

25 mL Mohr's salt solution ≡ y mL S(N) $K_2Cr_2O_7$ solution

25 mL diluted stock solution + 50 mL Mohr's salt solution

≡ z mL S(N) $K_2Cr_2O_7$ solution

Mohr consumed by Cr(VI) in 25 mL diluted stock solution

≡ (2y–z) mL S(N) $K_2Cr_2O_7$ solution

≡ [(2y–z) × S] mL 1 (N) $K_2Cr_2O_7$ solution

Mohr consumed by Cr(VI) in 250 mL diluted stock solution

≡ 10 × (2y–z) × SmL 1(N) $K_2Cr_2O_7$ solution

≡ 10 × (2y–z) × SmL 1(N) Mohr's salt solution

We have, 1000 mL 1 (N) Mohr's salt solution ≡ 17.332 g of Cr(VI)

10 × (2y–z) × S mL 1 (N) Mohr's salt solution

≡ 0.017332 ×10 × (2y–z) × S g of Cr(VI)

The total amount of Cr(VI) in the supplied mixture = 0.017332 ×10 × (2y–z)×Sg

4.8 Summary

- In the presence of Fe^{3+}, Cr(VI) in $Cr_2O_7^{2-}$ is directly estimated by adding a measured excess of standard Mohr's salt solution. The remaining Mohr's salt is then back-titrated with a standard $Cr_2O_7^{2-}$ solution, using Ba-diphenylaminesulphonate (BDS) as an indicator.
- Fe^{3+} is precipitated as hydrated ferric oxide ($Fe_2O_3 \cdot xH_2O$) by adding aqueous ammonia.
- Precipitated ferric oxide is filtered, washed, and dissolved in hot 6(N) HCl. Fe^{3+} is then reduced to Fe^{2+} using the $SnCl_2$ method, and the Fe^{2+} is titrated with a standard $K_2Cr_2O_7$ solution, again using BDS as an indicator.

4.9 Question

1. What is the principle behind the estimation of Fe(III) and Cr(VI) using $K_2Cr_2O_7$?

Ans : see text

2. Why is BDS used as an indicator in this titration?

Ans : Ba-diphenylaminesulphonate (BDS) is used as an indicator because it provides a sharp color change at the endpoint of the titration, changing from violet to green when the titration is complete. This indicates the complete reduction of $K_2Cr_2O_7$.

3. How do you prepare 500 ml 0.2 (N) $K_2Cr_2O_7$ solution for the titration?

Ans : see text

4. What is the role of SnCl? in the estimation of Fe(III)?

Ans : SnCl? (stannous chloride) is used to reduce Fe(III) to Fe(II). This reduction is necessary because $K_2Cr_2O_7$ oxidizes Fe(II) to Fe(III), allowing for the accurate estimation of Fe(III) in the original sample by measuring the amount of Fe(II) present.

5. Why is Mohr's salt used in the estimation of $Cr_2O_7^{2-}$ in the presence of Fe^{3+}?

Ans : Mohr's salt (ferrous ammonium sulfate) is used because it acts as a reducing agent, reducing $Cr_2O_7^{2-}$ to Cr^{3+}. The remaining excess Mohr's salt after the reaction is back-titrated with the K_2Cr_2O7 solution, allowing the determination of $Cr_2O_7^{2-}$ concentration.

6. What precautions should be taken while performing the titration?

Ans : Precautions include ensuring accurate measurement of reagents, avoiding contamination of solutions, maintaining a consistent temperature (especially for reactions involving Fe(III) reduction), and carefully observing the endpoint to avoid over-titration.

7. Why is Fe(III) precipitated as $Fe_2O_3 \cdot xH_2O$ before titration?

Ans : Fe(III) is precipitated as $Fe_2O_3 \cdot xH_2O$ to separate it from other interfering ions in the mixture. This ensures that the subsequent titration with $K_2Cr_2O_7$ is accurate and only measures the Fe(III) content.

8. What is the significance of using 6(N) HCl in dissolving $Fe_2O_3 \cdot xH_2O$?

Ans : 6(N) HCl is used to dissolve the $Fe_2O_3 \cdot xH_2O$ precipitate because it effectively breaks down the hydrated ferric oxide, converting it back into Fe^{3+} ions in solution, which are then reduced to Fe^{2+} for titration.

Unit – 5 ❑ Estimation of Fe(III) and Mn(II) in a given mixture using $KMnO_4$ solution

Structure

5.1 Objective

5.2 Introduction

5.3 Principle

5.4 Chemicals Required

5.5 Procedure

5.6 Experimental Results

5.7 Calculations

5.8 Summary

5.9 Question

5.1 Objective

By the end of this chapter, students should be able to–

- Precisely determine the concentration of Fe(III) and Mn(II) in a given mixture using $KMnO_4$, grasp the theoretical foundations of the method, and apply this understanding to practical, real-world situations.
- Learn how Fe(III) and Mn(II) undergo redox reactions during titration
- Familiarize with the use of potassium permanganate ($KMnO_4$) as a titrant
- Understand the role of $KMnO_4$ in redox titration.

5.2 Introduction

In this unit, we will explore the process of estimating the concentrations of iron(III) (Fe^{3+}) and manganese(II) (Mn^{2+}) ions in a given mixture using potassium permanganate ($KMnO_4$) as the titrant. Redox titration is a powerful and widely used analytical technique in chemistry, allowing for the precise determination of these ions through controlled oxidation-reduction reactions.

Iron and manganese are essential elements in various industrial and environmental contexts. Fe(III) plays a significant role in processes such as water treatment, metallurgy, and biological systems. Mn(II), on the other hand, is important in alloy production, as a catalyst in chemical reactions, and as a micronutrient in both plants and animals. Accurate estimation of these ions is critical for quality control, environmental monitoring, and research.

Potassium permanganate ($KMnO_4$) is a potent oxidizing agent, known for its ability to oxidize Fe(II) to Fe(III) and Mn(II) to Mn(VII), the latter forming MnO_4^- ions. The distinct color change associated with $KMnO_4$ makes it an ideal titrant for redox reactions, enabling clear detection of the titration endpoint.

Throughout this unit, we will delve into the theoretical principles of this redox titration, the preparation and standardization of $KMnO_4$ solution, and the step-by-step procedures for estimating the concentrations of Fe(III) and Mn(II) in a mixture.

5.3 Principle

Fe^{3+}, present in the solution, is first reduced to Fe^{2+} by $SnCl_2$ method and this is then titrated against the standard $KMnO_4$ solution in presence of zimmermann-Reinhardt solution.

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

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

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

$\therefore$ 1 mole $MnO_4 \equiv$ 5 moles of Fe^{2+}

or, 1/5 mole $MnO_4^- \equiv$ 1 moles of $Fe^{2+} \equiv$ 1 equivalent

$\therefore$ 1000 ml (N) $KMnO_4$ solution $\equiv$ 55.847 g of Fe^{2+}

Mn^{2+} can be estimated in presence iron after precipitation by the oxidation of Mn^{2+} to MnO_4^- with Na-bismuthate and filtering through sintered-glass or asbestos-pulp bed and dissolved in dil H_2SO_4 followed by addition of a measured excess of standard Mohr's salt solution, the excess Mohr's being back titrated with the standard $KMnO_4$ solution in presence of Zimmermann-Reinhardt reagent.

$$2Mn^{2+} + 5BiO_3^- + 14H^+ = 2MnO_4^- + 5Bi^{3+} + 7H_2O$$

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

$\therefore$ 2 mole Mn^{2+} ≡ 2 mole MnO_4^- ≡ 10 moles of Fe^{2+}

Or, 1 mole of Fe^{2+} ≡ 1/5 mole Mn^{2+} ≡ 1 equivalent

$\therefore$ 1000 mL (N) Mohr's salt solution ≡ 54.938/5 g of Mn^{2+}

≡ 10.9876 g of Mn^{2+}

5.4 Chemicals Required

i) Standard ~(N/20) oxalic acid solution

ii) ~(N/20) $KMnO_4$ solution

iii) Conc HCl

iv) Zimmermann-Reinhardt solution

v) Sodium bismuthate

vi) 15% $SnCl_2$ solution

vii) 5% $HgCl_2$ solution

viii) Syrupy H_3PO_4

ix) Fe(III) and Mn(II)mixture (Unknown)

5.5 Procedure

(a) Transfer the supplied solution *quantitatively* (25 mL)in a 250 mL volumetric flask and dilute it with distilled water up to the mark.

(b) Prepare 250 mL standard (N/20) oxalic acid solution by accurate weighing.

(c) **Standardise the (N/20) $KMnO_4$ solution :**

Pipette out an aliquot of 25mL standard oxalic acid solution in a 500mL conical flask, add 25 mL 4(N) H_2SO_4, heat nearly to 70°-80°C and then titrate the solution with the ~(N/20) $KMnO_4$ solution in hot condition until a faint pink colour stable for 30 sec is obtained. Record the titre value. The titration is repeated twice.

(d) **Estimation of Fe^{3+}**

Pipette out 25mL of the solution mixture in a 500 mL conical flask and add 20 mL of conc. HCl. Heat just to boiling, reduce Fe^{3+} ion with $SnCl_2$ solution adding drop wise until the yellow colour is just discharged and finally add a drop in excess. Cool under tap to room temperature. Add 10 mL 5% $HgCl_2$

solution at a time with vigorous shaking and dilute to 300mL with water. Add 25mL Zimmermann-Reinhardt solution. Titrate with the standard ~(N/20) $KMnO_4$ solution until the solution just turns light pink colour. The process is repeated twice.

Note : The reduction of Fe3+ may also be done with Al-foil in 4(N) HCl medium and then the above method is followed.

(e) **Estimation of Mn^{2+} :**

Oxidation of Mn^{2+} :

Pipette out 25 mL of the stock solution in a 500 mL conical flask, add 4-5 mL cone. H_2SO_4 and dilute to 100 mL to adjust the acidity to 3(N) and allow to cool at room temperature. Oxidise with about 0.5g of sodium bismuthate. Filter through a sintered-glass crucible or through an asbestos pulp bed fitted with a suction pump. Wash with 2(N) H_2SO_4 till the washings are colourless.

Back titration of excess Mohr's salt solution :

To the combined filtrate and washings, add a measured excess (say 50 mL) standard N/20 Mohr's salt solution so that the pink colour of permanganate is discharged. Dilute to l50mL with 2(N) H_2SO_4 and add 5 mL syrupy H_3PO_4. Titrate the solution with the standard ~(N/20) $KMnO_4$ solution until the solution just turns light pink colour stable for 30 seconds. The process is repeated twice.

5.6 Experimental Results

Table 1 : Experimental Results

Initial weight (w_1g)	Final weight (w_2g)	Initial weight taken (w_1–w_2)g	Weight have to take (g)	Strength of oxalic acid solution prepared
			0.7879	= (w_1–w_2)/0.7879 (N/20)

Table 2 : Standardization $KMnO_4$ solution Vs ~(N/20) oxalic acid solution

No. of Titrations	Volume of oxalic acid solution taken in mL	Burette reading of $KMnO_4$ solution		Volume of $KMnO_4$ solution required in mL	Mean volume of $KMnO_4$ solution required in mL
		Initial	Final		
1					
2					
3					

Table 3 : Titration of the Estimation of Fe^{3+}

No. of Titrations	Volume of solution maxture taken in mL	Burette reading of $KMnO_4$ solution		Volume of $KMnO_4$ solution required in mL	Mean volume of $KMnO_4$ solution required in mL
		Initial	Final		
1					
2					
3					

Table 4 : Estimation of Mn^{2+}

No. of Titrations	Volume of stock solution mixture + measured excess of standard Mohr's salt solution taken of mL	Burette reading of $KMnO_4$ solution		Volume of $KMnO_4$ solution required in mL	Mean volume of $KMnO_4$ solution required in mL
		Initial	Final		
1					
2					
3					

5.7 Calculations

i) Strength of prepared oxalic acid solution $= \frac{(w_1 - w_2)}{0.7879}\left(\frac{N}{20}\right) = S_1(N)$

ii) Strength of prepared $KMnO_4$ solution

$$= \frac{\text{Volume of oxalic acid solution taken} \times S_1}{\text{Volume of } KMnO_4 \text{ solution required}}(N)$$

$= S_2$ (N)

iii) Estimation of Fe^{3+}

25 mL stock solution ≡ x mL S_2 (N) $KMnO_4$ solution

∴ 250 mL diluted stock solution ≡ 10 × x × S_2 mL (N) $KMnO_4$ solution

We have, 1000 mL 1 (N) $KMnO_4$ solution ≡ 55.847g of Fe

∴ 10 × x × S_2 mL (N) $KMnO_4$ solution ≡ (0.055847 × 10 × x × S_2) g of Fe

The total amount of Fe^{3+} ion in the supplied mixture = (0.055847 × 10 × x × S_2)g

(c) Estimation of Mn^{2+}

25 mL Mohr's salt solution ≡ y mL S_2 mL (N) $KMnO_4$ solution

25 mL diluted stock solution + 50 mL Mohr's salt solution

≡ z mL S_2 mL (N) $KMnO_4$ solution

Mohr consumed by MnO_4^- in 25 mL diluted stock solution ≡ (2y–z) mL S_2mL (N) $KMnO_4$ solution

≡ [(2y–z) × S_2]mL 1(N) $KMnO_4$ solution

Mohr consumed by MnO_4^- in 250 mL diluted stock solution ≡ 10 × (2y–z) × S_2 mL 1(N) $KMnO_4$ solution

We have, 1000 mL 1(N) $KMnO_4$ solution ≡ 1000 mL (N) Mohr's salt solution

≡ 10.9876 g of Mn^{2+}

∴ The total amount of Mn^{2+} in the supplied mixture

= 0.0109876 × 10 × (2y–z) × S_2 g of Mn^{2+}

5.8 Summary

- Fe^{3+} is first reduced to Fe^{2+} using the SnCl? method.
- The reduced Fe^{2+} is titrated against a standard $KMnO_4$ solution in the presence of Zimmermann-Reinhardt solution.
- 1 mole of MnO_4^- is equivalent to 5 moles of Fe^{2+}.
- Mn^{2+} is oxidized to MnO_4^- using Na-bismuthate, then filtered through a sintered-glass or asbestos-pulp bed.
- Mn^{2+} is back titrated using Mohr's salt and standard $KMnO_4$ solution in the presence of Zimmermann-Reinhardt reagent.

5.9 Question

1. What is the principle behind the estimation of Fe(III) and Mn(II) using $KMnO_4$ solution?

Ans : see text

2. Why is SnCl? used in the estimation of Fe(III)?

Ans : $SnCl_2$ is used to reduce Fe(III) to Fe(II), which is necessary because Fe(II) is the form that can be titrated with $KMnO_4$.

3. What role does Zimmermann-Reinhardt solution play in this titration?

Ans : Zimmermann-Reinhardt solution prevents the oxidation of Fe(II) to Fe(III) by atmospheric oxygen and reduces the interference of Mn^{2}? during the titration of Fe^{2+} with $KMnO_4$.

4. What is the stoichiometric relationship between MnO_4^- and Fe^{2+} in the reaction?

Ans : The stoichiometric relationship is 1 mole of MnO_4^- is equivalent to 5 moles of Fe^{2+} in the redox reaction.

5. Why is Na-bismuthate used in the estimation of Mn(II)?

Ans : Na-bismuthate is a strong oxidizing agent used to oxidize Mn(II) to MnO_4^-, which can then be titrated or estimated using a back titration method with $KMnO_4$.

6. Why is back titration used in the determination of Mn(II)?

Ans : Back titration is used because the direct titration of Mn(II) is not feasible.

Mn(II) is first oxidized, and the excess of a known reagent (Mohr's salt) is back titrated to determine the amount of Mn(II) originally present.

7. What is the significance of the normality (N) of the $KMnO_4$ solution?

Ans : The normality (N) of the $KMnO_4$ solution indicates its concentration in equivalents per liter, which is crucial for calculating the amount of Fe(II) or Mn(II) during titration.

8. What precautions should be taken during the titration?

Ans : Precautions include ensuring the complete reduction of Fe(III) to Fe(II), preventing the exposure of the titration mixture to air to avoid oxidation, accurate measurement of reagents, and ensuring that the Na-bismuthate reaction is complete before filtration.

Unit – 6 ❑ Estimation of Fe(III) and Ca(II) in a given mixture using $KMnO_4$ solution

Structure

6.1. Objective

6.2. Introduction

6.3. Principle

6.4. Chemicals Required

6.5. Procedure

6.6 Experimental Results

6.7 Calculations

6.8 Summary

6.9 Question

6.1 Objective

By the end of this chapter, students should be able to–

- Accurately estimate the concentration of Fe(III) and Ca(II) in a given mixture using $KMnO_4$ solution, understand the theoretical underpinnings of the method, and apply this knowledge to real-world scenarios.
- Develop the skills to calculate the concentration of Fe(III) in the sample based on titration results. Study the procedure for the precipitation and separation of Ca(II) from the mixture using appropriate reagents.
- Use the appropriate method to calculate the concentration of Ca(II) after its separation from Fe(III).

6.2 Introduction

In this unit, we explore the quantitative analysis of iron (Fe^{3+}) and calcium (Ca^{2+}) ions present in a mixture, employing titration methods using potassium permanganate ($KMnO_4$) as a standard solution.

The process begins with the reduction of Fe^{3+} to Fe^{2+}, a necessary step as only Fe^{2+} can be titrated against $KMnO_4$ in acidic medium. The titration is performed in the presence of Zimmermann-Reinhardt solution, which serves to stabilize Fe^{2+} and prevent its reoxidation. The titration reaction is characterized by a distinct color change, enabling precise determination of the endpoint.

For calcium, typically less reactive in oxidation-reduction reactions, a different approach is employed. Ca^{2+} is first separated from the mixture, often through precipitation techniques, before its quantification using appropriate methods.This unit will guide you through the theoretical principles, practical techniques, and analytical calculations necessary for the successful estimation of Fe^{3+} and Ca^{2+} in mixed samples.

6.3 Principle

Iron is directly estimated first by reducing Fe^{3+} to Fe^{2+} by $SnCl_2$ method and then by titrating with a standardised $KMnO_4$ solution :

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

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

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

$\therefore$ 1 mole MnO_4^- ≡ 5 moles of Fe^{2+}

or, 1/5 mole MnO_4^- ≡ 1 moles of Fe^{2+} ≡ 1 equivalent

$\therefore$ 1000 ml (N) $KMnO_4$ solution ≡ 55.847 g of Fe^{2+}

From the mixture Ca^{2+} is precipitated as calcium oxalate, which after filtration and washing, the precipitate of calcium oxalate is dissolved in hot dil H_2SO_4 and equivalent amount of oxalic acid liberated which is titrated against the standard $KMnO_4$ solution.

$$Ca^{2+} + C_2O_4^{2-} = CaC_2O_4$$

$$CaC_2O_4 + H_2SO_4 = H_2C_2O_4 + CaSO_4$$

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

$$Ca^{2+} \equiv CaC_2O_4 \equiv H_2C_2O_4 \equiv C_2O_4^{2-} \equiv 2/5\ MnO_4^-$$

1/5 mole MnO_4^- ≡ ½ mole of Ca^{2+} ≡ 1 equivalent

$\therefore$ 1000 mL (N) $KMnO_4$ solution ≡ 20.04g of Ca

6.4 Chemicals Required

(a) ~(N/20) oxalic acid solution

(b) ~(N/20) $KMnO_4$ solution

(c) 5% $HgCl_2$ solution

(d) 15% $SnC1_2$ solution

(e) Zimmermann-Reinhardt reagent (Z.R. reagent).

(f) (1:1) NH_3

(g) Conc. HCl

(h) NH_4Cl

(i) Methyl red /Methyl orange indicator

(j) 4% ammonium oxalate solution

(k) 4(N) H_2SO_4

6.5 Procedure

(1) Transfer the supplied solution quantitatively in a 250mL volumetric flask and dilute it with distilled water up to the mark.

(2) **Prepare 250mL standard ~(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.

$\therefore$ Strength of prepared oxalic acid solution

$$= \frac{\text{Actual weight of axalic acid taken}}{0.7879}\left(\frac{N}{20}\right) = S_1\,(N)$$

(3) **Standardise the ~(N/20) $KMnO_4$ solution :**

Pipette out an aliquot of 25mL standard oxalic acid solution in a 500mL conical flask, add 25mL 4(N) H_2SO_4, heat nearly to 70°–80°C and then titrate the solution with the –(N/20) $KMnO_4$ solution in hot condition until a faint pink colour stable for 30 sec is obtained. Record the titre value. The titration is repeated twice.

(4) **Estimation of Iron :**

Iron (II) can be directly titrated with standard $KMnO_4$ solution in the following way. Pipette out 25mL of the stock solution in a 500mL conical flask. Add 20mL conc. HC1 (A. R.). Heat just to boiling and reduce Fe^{3+} ion with $SnCl_2$ solution adding dropwise until the yellow colour is just discharged and finally add a drop in excess. Cool under tap to room temperature. Add 10mL 5% $HgCl_2$ solution at a time with vigorous shaking and dilute to 300mL with water. Add 25mL Z-R reagent. Titrate with the standard ~(N/20) $KMnO_4$ solution until the solution just turns pale pink colour. Record the titre value.

(5) **Estimation of Calcium (Ca^{2+}) after the separation of iron :**

Step 1 : Separation of iron

25 ml aliquot of the stock solution is pipetted out into a 500 ml beaker1-2 ml of conc. HNO_3 is added, boiled for 3 minutes to oxidise Fe^{2+} to Fe^{3+}, diluted to 100 mL distilled water; 1-2 gms of NH_4Cl is added, heated to boiling, (1:1) NH4OH is added drop-wise with stirring by a glass-rod until the smell of ammonia persists. The precipitate of $Fe(OH)_3$ is allowed to settle on a hot asbestos board (colourless supernatant liquid indicates complete precipitation). The precipitate is filtered while hot, by a Whatman No.-41 filter paper, washed by decantation 3-4 times with hot water till free form chloride (a drop of the filtrate is to be tested with HNO_3 and $AgNO_3$). The filtrate with the washings is collected in another 500 ml beaker.

To reduce error due to adsorption double precipitation is carried out. The precipitate is dissolved in minimum volume of hot (1:1) HC1, the solution is collected in the same beaker and $Fe(OH)_3$ is reprecipitated, filtered through the same filter paper and washed with hot water till free from chloride. The filtrate and washings are collected in the previous beaker. Use the combined filtrate and washings for the estimation of calcium (N.B. Iron can also be estimated from the precipitate by dissolving the precipitate in dil HCl as usual procedure).

Step 2 : Estimation of Calcium :

The volume of the filtrate is reduced to about 150-200 mL by evaporation, 2 drops of methyl red indicator followed by 4(N) HCl are added until the solution is distinctly red (acidic). To this hot solution add about 10-15 ml of 10% ammonium oxalate solution. Then dropwise add (1:1) NH_4OH with stirring until the smell of ammonia persists. The precipitate of CaC_2O_4 is allowed to

settle (add few drops of the ammonium oxalate solution down the inclined side of the beaker to see if the precipitation is complete or not). It is then filtered, washed with cold water to free from Cl- and $C_2O_4^{2-}$. Dissolve the precipitate in a 500 mL conical flask with hot 50 ml (1: 8) H_2SO_4. The solution is diluted to 150mL with distilled water, heated on an asbestos board-to about 70°-80°C and then titrated with standard $KMnO_4$ solution adding drop-wise from a burette until pale pink colour just appears. Burette reading is noted.

Alternative method of estimation of Ca^{2+} in presence of Fe^{3+} (without separation of iron) :

Pipette out an aliquot of 25 mL from the stock solution in a 500 mL beaker, add 5 mL conc. HC1 and dilute to 50 mL by adding 20 mL distilled water Heat the solution nearly to boiling and add 100 mL of saturated ammonium oxalate solution, also in almost boiling condition, followed by 5 drops of methyl orange indicator. Add slowly drops of 1:1 aqueous NH_3 with constant stirring till the colour of the indicator is the same as that of a similar volume of standard phthalate buffer solution (pH 4) i.e. distinctly red. Ca is precipitated as CaC_2O_4 while Fe^{3+} remains in solution as oxalato complex. Allow to stand for 30 minutes in hot condition. Filter through Whatman No. 40 filter paper. Wash the beaker and the precipitate with 100 ml ice-cold water taking small portions (10 ml) at a time till the washings are free from oxalate ion (test with $CaCl_2$ solution in ammoniacal medium) and Cl (test with $HNO_3/AgNO_3$). Dissolve the precipitate in hot 50 mL 4(N) H_2SO_4 and wash with 50 mL distilled water. Heat the solution to 70° – 80°C and titrate the liberated oxalic acid with the standard KMnO4 solution until pale pink colour persist for 30 seconds.

6.6 Experimental Results

Table 1 : Preparation of 250 mL standard ~(N/20) oxalic acid solution

Initial weight (w_1g)	Final weight (w_2g)	Initial weight taken (w_1–w_2)g	Weight have to take (g)	Strength of oxalic acid solution prepared
			0.7879	= (w_1–w_2)/0.7879 (N/20)

Table 2 : Standardization $KMnO_4$ solution Vs ~(N/20) oxalic acid solution

No. of Titrations	Volume of oxalic acid solution taken in mL	Burette reading of $KMnO_4$ solution		Volume of $KMnO_4$ solution required in mL	Mean volume of $KMnO_4$ solution required in mL
		Initial	Final		
1					
2					
3					

Table 3 : Titration of the Estimation of Fe^{3+}

No. of Titrations	Volume of solution maxture taken in mL	Burette reading of $KMnO_4$ solution		Volume of $KMnO_4$ solution required in mL	Mean volume of $KMnO_3$ solution required in mL
		Initial	Final		
1					
2					
3					

Table 4 : Estimation of Ca^{2+}

No. of Titrations	Volume of stock solution taken in mL	Burette reading of $KMnO_4$ solution		Volume of $KMnO_4$ solution required in mL	Mean volume of $KMnO_4$ solution required in mL
		Initial	Final		
1					
2					
3					

6.7 Calculations

(i) Strength of prepared oxalic acid solution $= \frac{(w_1 - w_2)}{0.7879}\left(\frac{N}{20}\right) = S_1(N)$

(ii) Strength of prepared $KMnO_4$ solution

$$= \frac{\text{Volume of oxalic acid solution taken} \times S_1}{\text{Volume of } KMnO_4 \text{ solution required}}(N) = S_2\ (N)$$

(iii) **Estimation of Fe^{3+}**

25 mL diluted stock solution ≡ x mL S_2 (N) $KMnO_4$ solution

∴ 250 mL diluted stock solution ≡ 10 × x × S_2 mL (N) $KMnO_4$ solution

We have, 1000 mL 1(N) $KMnO_4$ solution ≡ 55.847 g of Fe

∴ 10 × x × S_2 mL 1(N) $KMnO_4$ solution ≡ (0.055847 × 10 × x × S_2) g of Fe

The total amount of Fe^{3+} ion in the supplied mixture = (0.055847 × 10 × x × S_2)g

Estimation of Ca^{2+}

25 mL diluted stock solution ≡ y mL S_2 (N) $KMnO_4$ solution

∴ 250 mL diluted stock solution ≡ 10 × y × S_2 mL (N) $KMnO_4$ solution

We have, 1000 mL 1(N) $KMnO_4$ solution ≡ 20.04 g of Ca^{2+}

∴ 10 × y × S_2 mL 1(N) $KMnO_4$ solution ≡ (0.02004 × 10 × y × S_2) g of Ca^{2+}

∴ The total amount of Ca^{2+} ion in the supplied mixture

= (0.02004 × 10 × y × S_2) g

6.8 Summary

- Fe^{3+} is first reduced to Fe^{2+} because only Fe^{2+} can be titrated against $KMnO_4$.
- The titration is carried out in an acidic medium with Zimmermann-Reinhardt solution, stabilizing Fe^{2+}.
- 1 mole of MnO_4^- is equivalent to 5 moles of Fe^{2+}.
- Ca^{2+} is precipitated as calcium oxalate (CaC_2O_4), which is then dissolved in dilute H_2SO_4 and the liberated oxalic acid is titrated against $KMnO_4$.
- 1 mole of MnO_4^- is equivalent to ½ mole of Ca^{2+}

6.9 Question

1. Why do we reduce Fe(III) to Fe(II) before titration?

Ans : Fe(III) is reduced to Fe(II) because only Fe(II) reacts with $KMnO_4$ in an acidic medium, making the titration possible.

2. What is the role of Zimmermann-Reinhardt solution in this titration?

Ans : Zimmermann-Reinhardt solution stabilizes Fe(II) by preventing its reoxidation to Fe(III) during the titration process.

3. What is the significance of the color change in the titration of Fe(II) with $KMnO_4$?

Ans : The color change from colorless to a faint pink indicates the endpoint of the titration, where all Fe(II) has reacted with $KMnO_4$.

4. How is Ca(II) separated from the mixture before estimation?

Ans : Ca(II) is precipitated as calcium oxalate (CaC_2O_4), which is then dissolved in dilute H_2SO_4 for further titration.

5. Why do we perform the titration of oxalic acid with $KMnO_4$ in a hot solution?

Ans : The titration is performed in a hot solution to increase the reaction rate and ensure complete oxidation of oxalic acid by $KMnO_4$.

6. Why is dilute sulfuric acid used in the titration process?

Ans : Dilute sulfuric acid is used to provide the acidic medium necessary for the $KMnO_4$ reaction and to dissolve the calcium oxalate precipitate, releasing oxalic acid for titration.

7. What is the role of potassium permanganate ($KMnO_4$) in this titration?

Ans : $KMnO_4$ acts as a strong oxidizing agent in acidic medium. It oxidizes Fe(II) to Fe(III) during the titration, and the endpoint is indicated by the appearance of a permanent pink color, signifying the presence of excess $KMnO_4$. Thus it also acts as an indicator.

8. What is the principle behind the estimation of Fe(III) using $KMnO_4$?

Ans : See text.

Module-II

Complexometric Titration

Unit – 7 ❑ Estimation of Hardness of Water

Structure

7.1 Objective

7.2 Introduction

7.3 Complexometric Titration

7.4 Principle for estimation of hardness of water

7.5 Chemicals Required

7.6 Procedure

7.7 Experimental Results

7.8 Calculations

7.9 Summary

7.10 Question

7.1 Objective

By the end of this chapter, students should be able to–

- Determine the hardness of water, grasp the theoretical foundations of the method, and apply this understanding to practical, real-world situations
- Identify the cations (primarily $Ca^{2?}$ and $Mg^{2?}$) responsible for water hardness.
- Use EDTA (Ethylenediaminetetraacetic acid) as a titrant to determine the total hardness of water.
- Use titration data to express water hardness in terms of mg/L of CaCO? equivalents.

7.2 Introduction

Water hardness is a crucial parameter that affects both industrial processes and domestic usage. It is primarily caused by the presence of dissolved calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, which can lead to the formation of scale in pipes, boilers, and other equipment, as well as reducing the effectiveness of soaps and detergents.

In this unit, we will explore the concept of water hardness, distinguishing between temporary and permanent hardness, and understand how these forms of hardness are influenced by different ions. The primary focus will be on the quantitative analysis of water hardness using titration methods, specifically with Ethylenediaminetetraacetic acid (EDTA) as the titrant. EDTA binds with calcium and magnesium ions, allowing for the precise determination of their concentration in water samples.

Through this unit, you will gain a comprehensive understanding of the theoretical principles behind water hardness estimation by Complexometric Titration.

7.3 Complexometric Titration

Complexometric titration is a type of volumetric analysis used to determine the concentration of metal ions in a solution. This method relies on the formation of a stable, soluble complex between the metal ions and a complexing agent, typically a chelating ligand like EDTA.

In a complexometric titration, the metal ions in the solution react with the EDTA to form a metal-EDTA complex. EDTA, a versatile chelating agent, binds to metal ions through its multiple donor atoms, effectively "trapping" the metal ions in a stable, ring-like structure. This reaction proceeds in a 1:1 molar ratio for most metal ions, making it possible to precisely determine the concentration of metal ions based on the volume of EDTA used.

Key Components of Complexometric Titration :

- **Chelating Agent (Titrant) :** EDTA is the most commonly used chelating agent due to its ability to form strong, stable complexes with a wide range of metal ions.
- **Indicator :** An indicator, such as Eriochrome Black T, is used to signal the endpoint of the titration. The indicator forms a weak complex with the metal ion, which is displaced by the stronger EDTA complex. The endpoint is usually marked by a distinct color change.

  pH Control : The titration is often conducted at a specific pH to ensure optimal binding between EDTA and the metal ions. For instance, a buffer solution is often used to maintain the desired pH, such as a pH of 10 for the titration of calcium and magnesium ions.

Applications of Complexometric Titration :

- Water Hardness Determination: One of the most common applications, where

the concentration of calcium and magnesium ions is measured to determine the hardness of water.

- Analysis of Metal Ions: Used in various industries, including environmental monitoring, pharmaceuticals, and metallurgy, to analyze the concentration of metal ions in solutions.
- Purity Testing of Chemicals: To assess the metal ion content in chemical samples, ensuring their purity.

7.4 Principle for estimation of hardness of water

Hardness of water is generally due to the presence of dissolved salts of calcium and magnesium in the form of bicarbonates, chlorides and sulphates. The hardness is expressed, in parts of calcium carbonate equivalent of calcium and magnesium salts, per million parts of water (ppm), by weight. The hardness of water may be estimated by titration with EDTA using Eriochrome - Black T (Solochrome - Black) indicator.

Calcium and magnesium reacts with EDTA to form stable complexes at pH 7 to 11.

$$Ca^{+2} + H_2Y^{-2} \rightleftharpoons CaY^{-2} + 2H^+$$

$$Mg^{+2} + H_2Y^{-2} \rightleftharpoons MgY^{-2} + 2H^+$$

The Calcium complex of EDTA is more stable than the Magnesium - EDTA complex. EDTA first forms a complex with Ca^{+2} ions and then with Mg^{+2} ions. The indicator forms a wine - red complex with Magnesium, which is less stable than calcium - indicator complex. So the Mg - indicator complex reacts with EDTA and the blue coloured indicator ion is set free. When hard water containing Ca^{+2} and Mg^{+2} ions is titrated with di-sodium EDTA the end point colour changes from wine - red to blue.

$$Mg^{+2} + HIn^{-2} \rightleftharpoons MgIn^- + H^+$$

$$\underset{\text{Wine-red}}{MgIn^-} + H_2Y^{-2} \rightleftharpoons MgY^{-2} + \underset{\text{Blue}}{HIn^{-2}} + H^+$$

7.5 Chemicals Required

(i) Water

(ii) Standard 0.01 (M) Zinc acetate hydrated (Mol. Wt. 219.5)

(iii) 0.01 (M) of Na_2H_2EDTA (Mol. Wt. 372.24)

(iv) Eriochrome Black T (Solochrome Black) indicator. [0.4% methanolic solution of the dyestaff solution. This is stable for 1 month. Alternatively, grind a mixture of 0.05 g of dyestaff with 5 g of A.R. NaCl or KCl or KNO_3 in a mortar and use a pinch of the indicator mixture per titration].

(v) NH_4Cl – NH_4OH Buffer solution of pH 10. [17.5 g of NH_4Cl is mixed with 142 ml of concentrated NH_3 (of sp. Gr. 0.88 – 0.90) and the mixture is made up to 250 ml with de-ionised water].

7.6 Procedure

(i) Preparation of standard 250 ml of 0.01 (M) Zinc acetate solution:

About 0.5488 g of A.R. Zn-acetate is weighed out accurately in a 250 ml volumetric flask and dissolved and diluted upto the mark with distilled water.

(ii) Standardisation of EDTA solution

Pipette out 25 ml of the standard Zn-acetate solution in 250 ml conical flask, add 2 ml of NH_4Cl – NH_4OH buffer solution, dilute the mixture to 100 ml with de-ionised water. Now add 5 ml of indicator solution or a pinch of indicator mixture and shake the mixture to obtain a wine red colour. Titrate with EDTA solution from burette until the wine-red colour changes to blue. This titration is repeated to get concordant results.

(iv) Titration of Hard water with standard EDTA solution :

Pipette out 50 ml of the hard water sample in a 250 ml conical flask, add 5 ml of NH_4Cl – NH_4OH buffer solution and 5 ml of indicator solution or a pinch of indicator mixture and shake the mixture to obtain a wine red colour. Titrate with EDTA solution from burette until the wine-red colour changes to blue. Repeat the titration three times and enter the results in table.

7.7 Experimental Results

Table - 1 : Preparation of standard 250 ml of 0.01 (M) Zinc acetate solution

Initial weight (g)	Final weight (g)	Zn-acetate taken (g)	Strength of the solution
W_1	W_2	$W = W_1 - W_2$	W/0.5488 (M/100)

Table - 2 : Standardisation of EDTA by standard Zn- acetate solution

No. of obs.	Volume of Zn-acetate (ml)	Burette reading		Volume of EDTA (ml)	Mean volume of EDTA (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

Table - 3 : Titration of Hard water with standard EDTA

No. of obs.	Volume of Hard water (ml)	Burette reading		Volume of EDTA (ml)	Mean volume of EDTA (ml)
		Initial	Final		
1.	50	0	...	...	
2.	50	...	...	...	V
3.	50	...	...	...	

7.8 Calculations

i) Strength of EDTA solution :

Volume of Zn-acetate solution = V = 25 ml

Strength of Zn-acetate solution = S = W/0.5488 (M/100)

Volume of EDTA solution = V_1 ml

Strength of EDTA solution = S_1 = ?

We know, $V \times S = V_1 \times S_1$; $\therefore S_1 = \dfrac{25 \times W}{0.5488 \times V_1}$ (M/100) = y (M/100)

ii) Hardness of water :

Molecular weight of $CaCO_3$ = 100

1000 ml of 0.01 (M) EDTA

≡ 1000 ml 0.01 (M) $CaCO_3$

≡ 1g $CaCO_3$ (since, Molecular weight of $CaCO_3$ = 100)

$\therefore$ V ml of y (M/100) EDTA $\equiv \dfrac{1 \times V \times y}{1000}$ g ofg $CaCO_3$

$\equiv V \times y \times 10^{-3}$ g of $CaCO_3$

$\therefore$ 50 parts of hard water contain $V \times y \times 10^{-3}$ g of $CaCO_3$

$\therefore$ 10^6 parts of hard water contain $V \times y \times 10^{-3} \times 10^6$ g of $CaCO_3$

$\therefore$ Total hardness of water = $V \times y \times 10^{-3} \times 10^6$ ppm

7.9 Summary

- Hardness in water is mainly due to dissolved salts of calcium (Ca^{2+}) and magnesium (Mg^{2+}), found as bicarbonates, chlorides, and sulfates. Hardness is typically measured in parts per million (ppm) as the calcium carbonate ($CaCO_3$) equivalent.
- The hardness of water is estimated through titration using Ethylenediaminetetraacetic acid (EDTA) and Eriochrome Black T as the indicator.
- Calcium and magnesium ions in the water sample react with EDTA to form stable complexes in a pH range of 7 to 11. The stability of the calcium-EDTA complex is higher than that of the magnesium-EDTA complex.
- The indicator, Eriochrome Black T, initially forms a wine-red complex with Mg^{2+} ions. This complex is less stable than the calcium-indicator complex, so it reacts with EDTA, releasing the blue-colored free indicator ion.
- When hard water containing both Ca^{2+} and Mg^{2+} ions is titrated with disodium EDTA, the endpoint of the titration is marked by a color change from wine-red to blue, indicating the complete complexation of metal ions by EDTA.

7.10 Question

1. What is water hardness, and what causes it?

Ans : Water hardness refers to the concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in water. It is caused by the presence of dissolved salts of calcium and magnesium, such as bicarbonates, chlorides, and sulfates.

2. How is water hardness expressed?

Ans : Water hardness is typically expressed in parts per million (ppm) as the equivalent concentration of calcium carbonate ($CaCO_3$) in water.

3. What is the principle behind the complexometric titration used to estimate water hardness?

Ans : see text

4. Why is EDTA used in the titration for estimating water hardness?

Ans : EDTA is used because it forms stable, soluble complexes with both calcium and magnesium ions. This allows for the accurate quantification of these ions, which contribute to water hardness.

5. What role does the Eriochrome Black T indicator play in this titration?

Ans : Eriochrome Black T acts as an indicator by forming a wine-red complex with Mg^{2}? ions in the sample. As EDTA is added, it complexes with the Mg^{2+}, freeing the indicator and causing a color change from wine-red to blue, which marks the endpoint of the titration.

6. Why is the pH of the solution important during the titration?

Ans : The pH of the solution is important because the stability of the EDTA complexes with calcium and magnesium ions depends on the pH. The titration is typically performed at a pH of 7 to 11 to ensure optimal complexation and accurate results.

7. Why is the calcium-EDTA complex more stable than the magnesium-EDTA complex?

Ans : The calcium-EDTA complex is more stable due to the stronger binding affinity of EDTA for calcium ions compared to magnesium ions. This stability difference is utilized during the titration process to ensure that calcium ions are complexed first.

8. What is complexometric titration?

Ans : Complexometric titration is a type of titration used to determine the concen-

tration of metal ions in a solution. It involves the formation of a stable complex between the metal ions and a chelating agent, such as EDTA.

9. What is the role of a chelating agent in complexometric titration?

Ans : A chelating agent, like EDTA, binds to metal ions in the solution to form stable, soluble complexes. This binding allows for the quantitative determination of the metal ions present in the solution.

10. Why is EDTA commonly used in complexometric titrations?

Ans : EDTA is widely used because it can form strong and stable complexes with a variety of metal ions. It also binds in a 1:1 molar ratio with most metal ions, making calculations straightforward.

11. What is the significance of the pH in a complexometric titration?

Ans : The pH affects the stability of the metal-EDTA complexes. Different metal ions require different pH levels for optimal binding with EDTA. For example, the titration of calcium and magnesium is typically conducted at a pH between 7 and 11.

Unit – 8 ❑ Estimation of Ca (II) and Mg (II) in a mixture

Structure

8.1 Objective

8.2 Introduction

8.3 Principle

8.4 Chemicals Required

8.5 Procedure

8.6 Experimental Results

8.7 Calculations

8.8 Summary

8.9 Question

8.1 Objective

By the end of this chapter, students should be able to–

- Grasp the theoretical background of estimating calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, including the formation of stable metal-EDTA complexes.
- Understand the function of indicators, such as Eriochrome Black T, in signaling the endpoint of the titration by changing color.
- Execute the practical steps of titrating a mixture containing Ca^{2+} and Mg^{2+} ions with EDTA, including sample preparation and measurement techniques.
- Analyze the color change at the endpoint to determine the concentration of Ca^{2+} and Mg^{2+} ions in the mixture.
- Use titration data to calculate the concentrations of Ca^{2+} and Mg^{2+} ions, expressing the results in appropriate units such as ppm (parts per million) or mg/L.

8.2 Introduction

Calcium (Ca^{2+}) and magnesium (Mg^{2+}) are two essential metal ions that signifi-

cantly impact water quality and various industrial processes. In this unit, we will focus on the estimation of Ca^{2+} and Mg^{2+} ions in a mixture using complexometric titration, a widely used analytical technique. Complexometric titration relies on the formation of stable complexes between metal ions and a chelating agent, Ethylenediaminetetraacetic acid (EDTA). EDTA effectively binds to Ca^{2+} and Mg^{2+} ions, allowing their quantification based on the amount of EDTA required to reach the endpoint of the titration.

Through this unit, you will gain a comprehensive understanding of the complexometric titration method, including the theoretical principles, practical procedures, and calculation techniques required for accurate estimation of Ca²? and Mg²? in mixtures.

8.3 Principle

Total amount of Ca^{2+} and Mg^{2+} can be estimated by titrating with standard EDTA solution at pH 10 using NH_4Cl – NH_4OH buffer solution in presence of Eriochrome Black T (EBT) indicator. Ca^{2+} in the mixture can be estimated against standard EDTA solution at pH 12.3 using Calcon or Patton- Reeder's indicator. At pH 12 Mg^{2+} being qualitatively precipitated as $Mg(OH)_2$. EDTA does not react with $Mg(OH)_2$ until all of Ca^{2+} and Ca- indicator complex form Ca- EDTA complex indicating the end point of the titration. The difference between the two titrate values gives the Mg contained in the mixture. Both Ca^{2+} and Mg^{2+} form 1 : 1 complex with EDTA.

1 mole EDTA ≡ 1 mole of $MgCO_3$ ≡ 1 mole of $CaCO_3$

∴ 1000 ml (M) EDTA solution ≡ 84.31 g of $MgCO_3$ ≡ 100.08 g of $CaCO_3$

8.4 Chemicals Required

(i) Standard 0.01 (M) Zinc acetate hydrated (Mol. Wt. 219.5)

(ii) 0.01 (M) of Na2H2EDTA (Formula wt. 372.24)

(iii) Eriochrome Black T (Solochrome Black) (EBT) indicator. [0.4% methanolic solution of the dyestaff solution. This is stable for 1 month. Alternatively, grind a mixture of 0.05 g of dyestaff with 5 g of A.R. NaCl or KCl or KNO3 in a mortar and use a pinch of the indicator mixture per titration].

(iv) Calcon or Patton- Reeder's indicator

(v) NH_4Cl – NH_4OH Buffer solution of pH 10.[17.5 g of NH_4Cl is mixed with

142 ml of concentrated NH3 (of sp. Gr. 0.88 - 0.90) and the mixture is made up to 250 ml with de-ionised water].

(vi) 10% NaOH solution

(vii) Unknown metal ion mixture

Apparatus : Burette, Pipette, 500 ml volumetric flask, 250 ml Conical flask, 250 ml beaker, Funnel, Glass rod

8.5 Procedure

(i) Transfer about 1 g of the given mixture of $CaCO_3$ and $MgCO_3$ in 250 ml beaker and dissolve with 40 ml 1 : 1 HCl solution by gentle heating on an asbestos board until a clear solution is obtained. Transfer the solution quantitatively in a 250 ml volumetric flask and make up the volume with distilled water and mix well.

(ii) **Preparation of standard 250 ml of 0.01 (M) Zinc acetate solution :**

About 0.5488 g of A.R. Zn-acetate is weighed out accurately in a 250 ml volumetric flask and dissolved and diluted up to the mark with distilled water.

(iii) **Standardisation of EDTA solution :**

Pipette out 25 ml of the standard Zn-acetate solution in 250 ml conical flask, add 1 ml of $NH_4Cl - NH_4OH$ buffer solution, dilute the mixture to 50 ml with de-ionised water. Now add 5 ml of indicator solution or a pinch of indicator mixture and shake the mixture to obtain a wine red colour. Titrate with EDTA solution from burette until the wine-red colour changes to blue. This titration is repeated to get concordant results.

(iv) **Estimation of total Ca and Mg^{2+} :**

Pipette out 25 ml of the supplied solution in 250 ml conical flask and dilute with 25 ml of distilled or de-ionised water. Add 5 ml of $NH_4Cl - NH_4OH$ buffer solution of pH 10 and a pinch of EBT indicator and titrate with standard EDTA solution until wine- red colour turns to blue. Repeat the experiment thrice and record the results.

v) **Estimation of Ca^{2+} :**

Pipette out 25 ml of the mixture in 250 ml conical flask, dilute with 25 ml deionised water. Add a drop of methyl red indicator, when red colour appears. Neutralise the mixture by adding NH_3 solution dropwise till it turns to yellow. Add 12 ml of 10% NaOH solution, shake the mixture and keep for 5 minutes at rest. $Mg(OH)_2$ will precipitate out. Titrate the resulting solution with standard EDTA solution using a pinch of Calcon or Patton- Reeder's indicator till the colour changes from wine - red to blue. This titration is repeated to get concordant results.

8.6 Experimental Results

Table–1 : Preparation of standard 250 ml of 0.01 (M) Zinc acetate solution

Initial weight (g)	Final weight (g)	Zn-acetate taken (g)	Strength of the solution
W_1	W_2	$W = W_1 - W_2$	W/0.5488 (M/100)

Table–2 : Standardisation of EDTA by standard Zn-acetate solution

No. of obs.	Volume of Zn-acetate (ml)	Burette reading		Volume of EDTA (ml)	Mean volume of EDTA (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

Table–3 : Estimation of total Ca and Mg with standard EDTA

No. of obs.	Volume of water sample (ml)	Burette reading		Volume of EDTA (ml)	Mean volume of EDTA (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

Table–4 : Estimation of Ca with standard EDTA

No. of obs.	Volume of water sample (ml)	Burette reading		Volume of EDTA (ml)	Mean volume of EDTA (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_2
3.	25	...	...	...	

8.7 Calculations

1. Strength of Zn– acetate solution = W/0.5488 (M/100) = S_1(M)

2. Strength of EDTA solution :

Volume of Zn-acetate solution = 25 ml

Strength of Zn-acetate solution = W/0.5488 (M/100) = S_1(M)

Volume of EDTA solution = V ml

Strength of EDTA solution = S_2 = ?

We know, $V \times S_2 = 25 \times S_1$; $\therefore S_2 = 25 \times S_1 / V$ (M/100) = S (M)

$\therefore$ Strength of EDTA solution = S(M)

3. Total $CaCO_3$ and $MgCO_3$ in 25ml of the supplied mixture

$\equiv V_1$ ml S (M) EDTA solution

4. Amount of $CaCO_3$ in 25 ml of the supplied mixture

$\equiv V_2$ ml S (M) EDTA solution

5. Amount of $MgCO_3$ in 25 ml of the supplied mixture $\equiv (V_1 - V_2)$ ml S (M) EDTA solution

We have, 1000 ml (M) EDTA solution $\equiv$ 84.31g $MgCO_3$

$\therefore (V_1 - V_2) \times$ S ml (M) EDTA solution $\equiv 0.08431 \times (V_1 - V_2) \times$ S g of $MgCO_3$/ 25ml mixture.

Since, 25 ml of the mixture contain $0.08431 \times (V_1 - V_2) \times$ S g of $MgCO_3$

$\therefore$ 250 ml of the mixture contain $0.08431 \times (V_1 - V_2) \times S \times 10$ g of $MgCO_3$

= W g of $MgCO_3$

We know that, 1000 ml (M) EDTA solution $\equiv$ 100.08 g $CaCO_3$

$\therefore V_2 \times$ S ml (M) EDTA solution $\equiv 0.10008 \times V_2 \times$ S g of $CaCO_3$/ 25 ml mixture

Since, 25 ml of the mixture contain $0.10008 \times V_2 \times$ S g of $CaCO_3$

$\therefore$ 250 ml of the mixture contain $0.10008 \times V_2 \times S \times 10$ g of $CaCO_3$

= W_1 g of $CaCO_3$

$\therefore$ Amount of $MgCO_3$ in the supplied mixture = W g

$\therefore$ Amount of $CaCO_3$ in the supplied mixture = W_1 g

8.8 Summary

- The total amount of Ca^{2+} and Mg^{2+} in a mixture is estimated by titrating with a standard EDTA solution at pH 10, using NH_4Cl–NH_4OH buffer solution and Eriochrome Black T (EBT) as the indicator.
- To specifically estimate Ca^{2+}, the titration is conducted at pH 12.3 using Calcon or Patton-Reeder's indicator. At this pH, Mg^{2+} precipitates as $Mg(OH)_2$, preventing its reaction with EDTA.
- The Mg^{2+} content is determined by calculating the difference between the total titration value and the value obtained from the Ca^{2+} titration. EDTA reacts with the Ca^{2+} and the Ca-indicator complex to form a Ca-EDTA complex, marking the endpoint of the titration.
- Both Ca^{2+} and Mg^{2+} form a 1:1 complex with EDTA.

8.9 Question

1. What is the principle behind the complexometric titration used to estimate Ca^{2+} and Mg^{2+} in a mixture?

Ans : see text

2. Why is the titration performed at different pH levels for Ca^{2+} and Mg^{2+}?

Ans : The titration for Ca^{2+} is performed at pH 10 to ensure accurate complexation with EDTA and to prevent Mg^{2+} from interfering. At pH 12.3, Mg^{2+} precipitates as Mg(OH)?, which allows for the selective titration of Ca^{2+}. After determining Ca^{2+}, the remaining Mg^{2+} can be calculated from the total hardness measurement.

3. What role does the Eriochrome Black T (EBT) indicator play in the titration process?

Ans : Eriochrome Black T is used as an indicator that forms a wine-red complex with Mg^{2+} ions. During the titration with EDTA, as Mg^{2+} is bound to EDTA, the indicator changes color from wine-red to blue, signaling the endpoint of the titration.

4. How does the Calcon or Patton-Reeder's indicator work for estimating Ca^{2+} at pH 12.3?

Ans : At pH 12.3, the Calcon or Patton-Reeder's indicator forms a complex with Ca^{2+} ions. The indicator changes color when all Ca^{2+} has reacted with EDTA, allow-

ing for the determination of Ca^{2+} in the mixture. This pH level also ensures that Mg^{2+} is precipitated as $Mg(OH)_2$ and does not interfere.

5. What is the importance of using NH_4Cl–NH_4OH buffer solution in this titration?

Ans : The NH_4Cl–NH_4OH buffer solution is used to maintain the pH at 10 during the titration of the total hardness, ensuring optimal conditions for the formation of EDTA-metal complexes and accurate measurement of both Ca^{2+} and Mg^{2+}.

6. Why does Mg^{2+} precipitate as $Mg(OH)_2$ at pH 12.3?

Ans : Mg^{2+} precipitates as $Mg(OH)_2$ at pH 12.3 because the higher pH increases the concentration of hydroxide ions (OH^-), leading to the formation of an insoluble $Mg(OH)_2$ precipitate, which allows for the selective titration of Ca^{2+} ions.

7. How would you handle a sample if the color change at the endpoint is not clear?

Ans : If the color change is not clear, ensure the pH is correctly maintained and check that the indicator is fresh and properly added. In case of persistent issues, consider repeating the titration or using a different indicator if suitable.

8. What are some potential sources of error in this titration method?

Ans : Potential sources of error include incorrect pH adjustment, improper indicator use, incomplete precipitation of $Mg(OH)_2$, and measurement inaccuracies. It's important to carefully follow procedure and calibrate equipment to minimize these errors.

Unit – 9 ❑ Estimation of Zn (II) and Mg (II) in a mixture

Structure

9.1 Objective

9.2 Introduction

9.3 Principle

9.4 Chemicals Required

9.5 Procedure

9.6 Experimental Results

9.7 Calculations

9.8 Summary

9.9 Question

9.1 Objective

By the end of this chapter, students should be able to–

- Understand the specific methods and conditions for estimating Zn^{2+} and Mg^{2+} ions, including the use of appropriate indicators and pH levels.
- Identify and understand the function of indicators used in the titration process, such as Eriochrome Black T and others suitable for Zn^{2+} and Mg^{2+}.
- Execute the practical steps of titrating a mixture containing Zn^{2+} and Mg^{2+} with a standard EDTA solution, including sample preparation and titration technique.
- Understand and apply the necessary pH conditions for accurate complexation and measurement of Zn^{2+} and Mg^{2+} ions

9.2 Introduction

The accurate estimation of metal ions such as zinc (Zn^{2+}) and magnesium (Mg^{2+}) is crucial in various scientific and industrial applications, including environmental monitoring, quality control, and biochemical analysis. Complexometric titration is a

widely employed analytical technique that allows for precise determination of these metal ions through the formation of stable complexes with chelating agents.

In this unit, we focus on the estimation of Zn^{2+} and Mg^{2+} ions in a mixture using complexometric titration with Ethylenediaminetetraacetic acid (EDTA) as the chelating agent. The procedure involves titrating the metal ions with a standard EDTA solution and using specific indicators to detect the endpoint of the titration. Throughout this unit, you will gain practical experience in performing complexometric titrations, understand the theoretical principles underlying the technique, and learn to calculate the concentrations of Zn^{2+} and Mg^{2+} in a mixture.

9.3 Principle

Total amount of Mg^{+2} and Zn^{+2} may be estimated by adding a measured excess of standard EDTA solution to a known volume of the mixture followed by back titrating the excess EDTA with standard Zn- acetate solution at pH 10 using Eriochrome Black T (EBT) as indicator. On stirring the above mixture with an excess of NH_4F, Mg(EDTA) 2- complex decomposes and more stable MgF_2 is formed, liberating equivalent amount of EDTA. The liberated EDTA is titrated with the same Zn- acetate solution at pH 10 using same indicator. This will give the amount of Mg^{2+} in the mixture and the difference will give the amount of Zn^{2+}.

$$Zn^{+2} + H_2EDTA^{2} \rightleftharpoons Zn(EDTA)^{-2} + 2H^{+}$$

$$Mg^{+2} + H_2EDTA^{-2} \rightleftharpoons Mg(EDTA)^{-2} + 2H^{+}$$

$$\underset{\text{Blue}}{Mg^{+2} + HIn^{-2}} \rightleftharpoons MgIn^{-} + H^{+}$$

$$\underset{\text{Wine-red}}{MgIn^{-}} + H_2EDTA^{-2} \rightleftharpoons \underset{\text{Blue}}{Mg(EDTA)^{-2}} + HIn^{-2} + H^{+}$$

$$Mg(EDTA)^{2-} + MgF_2 + 2H^{+} \rightleftharpoons MgF_2 + H_2EDTA^{-2}$$

Both Mg^{2+} and Zn^{2+} ions form 1 : 1 complexes with EDTa.

$\therefore$ 1 ml EDTA $\equiv$ 1 mole Mg^{2+} $\equiv$ 1 mole Zn^{2+}

$\therefore$ 1000 ml (M) EDTA $\equiv$ 24.31 g of Mg $\equiv$ 65.38 g of Zn

9.4 Chemicals required

(i) Standard 0.01 (M) Zinc acetate hydrated (Mol. Wt. 219.5)

(ii) 0.01 (M) of Na_2H_2EDTA (Formula wt. 372.24)

(iii) Eriochrome Black T (Solochrome Black) (EBT) indicator. [0.4% methanolic solution of the dyestaff solution. This is stable for 1 month. Alternatively, grind a mixture of 0.05 g of dyestaff with 5 g of A.R. NaCl or KCl or KNO_3 in a mortar and use a pinch of the indicator mixture per titration].

(iv) NH_4Cl – NH_4OH Buffer solution of pH 10. [17.5 g of NH_4Cl is mixed with 142 ml of concentrated NH3 (of sp. Gr. 0.88 - 0.90) and the mixture is made up to 250 ml with de-ionised water].

(v) Unknown metal ion mixture (M/100)

[Dissolve ~ 1.0 g of $MgSO_4 . 7H_2O$ and ~ 1.75 of $ZnSO_4 . 7H_2O$ in deionised water, add 2–3 drops of dil. H_2SO_4 and dilute to 1 liter.

Apparatus : Burette, Pipette, 500 ml volumetric flask, Conical flask (250 & 500ml)

9.5 Procedure

1. Preparation of standard 500 ml of 0.01 (M) Zinc acetate solution :

About 1.0957 g of A.R. Zn-acetate is weighed out accurately in a 500 ml volumetric flask and dissolved and diluted upto the mark with distilled water.

2. Standardisation of EDTA solution :

Pipette out 25 ml of EDTA solution in a 250 ml conical flask, dilute with 25 ml deionised water, add 2 ml of NH_4Cl – NH_4OH buffer solution and a pinch of Eriochrome Black T indicator (EBT) (or 4-5 drops of indicator solution). Titrate the solution with standard Zn- acetate solution until the colour of the solution changes from blue to wine red. This titration is repeated to get concordant results.

3. Estimation of total Mg^{2+} and Zn^{2+} :

Pipette out 25 ml of the supplied solution in a 500 ml conical flask. Add 5 ml of NH_4Cl – NH_4OH buffer solution, a pinch of Eriochrome Black T indicator (EBT) (or 4-5 drops of indicator solution). Now add measured excess (50 ml) of standard EDTA solution, when wine red coloured solution turns to blue. Titrate the excess EDTA with the standard Zn- acetate solution until the colour of solution changes from blue to wine red. Preserve the solution for estimation of Mg^{2+}.

4. Estimation of Mg^{2+} in the mixture :

Add ~ 2 g of NH_4F to the above titrated solution and gently stir for a minute, when the colour turns blue. Titrate the liberated EDTA (equivalent to the amount of Mg^{2+}) with same standard Zn- acetate solution until the colour of the solution changes to wine red. Repeat the experiment thrice and record the results.

9.6 Experimental Results

Table–1 : Preparation 500 ml of standard M/100 Zinc acetate solution

Initial weight (g)	Final weight (g)	Amount of Zn-acetate taken (g)	Strength of Zn-acetate
W_1	W_2	$W = W_1 - W_2$	W/0.5488 (M/100)

Table–2 : Standardisation of EDTA by standard Zn-acetate solution

No. of obs.	Volume of EDTA (ml)	Burette reading		Volume of Zn-acetate (ml)	Mean volume of Zn-acetate (ml)
		Initial	Final		
1.	25	0	...	...	x
2.	25	...	...	...	
3.	25	...	...	...	

Table–3 : Back Titration for the estimation of total Mg^{2+} and Zn^{2+}

No. of obs.	Volume of supplied Maxture + measured excess standard EDTA (ml)	Burette reading		Volume of Zn-acetate (ml)	Mean volume of Zn-acetate (ml)
		Initial	Final		
1.	25	0	...	...	V_1
2.	25	...	...	...	
3.	25	...	...	...	

Table–4 : Estimation of Mg^{2+}

No. of obs.	Volume of supplied mixture (ml)	Burette reading		Volume of EDTA (ml)	Mean volume of EDTA (ml)
		Initial	Final		
1.	25	0	...	...	z
2.	25	...	...	...	
3.	25	...	...	...	

9.7 Calculations

(i) Strength of EDTA solution :

Volume of Zn-acetate solution = V = x ml

Strength of Zn-acetate solution = S = W/1.0957 (M/100) = S_2(M)

Volume of EDTA solution = V_1 = 25 ml

Strength of EDTA solution = S_1 = ?

We know, $V \times S = V_1 \times S_1$;

$\therefore$ Strength of EDTA solution $= \dfrac{x \times W}{1.095 \times 25}$ (M/100) = S_1 (M)

$\therefore$ 25 ml S1 (M) EDTA solution ≡ x ml S_2 (M) Zn – acetate solution

(ii) 25 ml of mixture + 50 ml S_1(M) EDTA solution

≡ y ml S_2 (M) Zn- acetate solution

$\therefore$ EDTA consumed by 25 ml of (Mg^{2+} + Zn^{2+}) mixture

≡ (2x – y) ml S_2 (M) Zn- acetate solution

≡ (2x – y) × S_2 ml (M) EDTA solution

(iii) Estimation of Mg^{2+} :

25 ml of the mixture + Excess NH_4F

≡ Mg^{2+} equivalent EDTA liberated

≡ z ml S_2 (M) Zn- acetate solution

≡ z × S_2 ml (M) EDTA solution

Since, 1 ml (M) EDTA solution ≡ 0.02431 g of Mg^{2+}

$\therefore$ z × S_2 ml EDTA solution ≡ 0.02431 × z × S_2 g of Mg^{2+} / 25 ml of mixture

$\therefore$ Amount of Mg^{2+} in the supplied mixture = 0.02431 × z × S_2 × 40 g/L

iv) Estimation of Zn^{2+} :

Amount of Zn^{2+} in 25 ml of the supplied mixture ≡ $(2x - y - z) \times S_2$ ml (M) EDTA solution

Since, 1 ml (M) EDTA solution ≡ 0.06538 g of Zn^{2+}

∴ $(2x - y - z) \times S_2$ ml (M) EDTA solution ≡ $0.06538 \times (2x - y - z) \times S_2$ g of Zn^{2+} / 25 ml of the mixture

∴ Amount of Mg^{2+} in the supplied mixture $=0.06538 \times (2x - y - z) \times S_2 \times 40$g/L

9.8 Summary

- The total amounts of Mg^{2+} and Zn^{2+} in a mixture are estimated by adding an excess of standard EDTA solution to the sample. The excess EDTA is then back-titrated with a standard Zn-acetate solution at pH10, using Eriochrome Black T (EBT) as the indicator.
- When NH?F is added to the mixture, the Mg-$EDTA^{2-}$ complex decomposes, forming more stable MgF_2 and releasing equivalent amounts of EDTA. The liberated EDTA is then titrated with the Zn-acetate solution at pH 10 using the same indicator.
- The amount of Mg^{2+} is determined from the amount of EDTA liberated after the decomposition of the Mg-EDTA complex. The difference between the total amount of EDTA and the amount associated with Mg^{2+} gives the amount of Zn^{2+} in the mixture.

9.9 Question

1. What is the principle of the complexometric titration method used for estimating Zn^{2+} and Mg^{2+}?

Ans : see text

2. Why is back-titration used in this method?

Ans : Back-titration is used to measure the amount of EDTA that was not complexed with the metal ions. By reacting the excess EDTA with a standard Zn-acetate solution, the amount of EDTA initially present can be determined, allowing for the calculation of Zn^{2+} and Mg^{2+} concentrations in the mixture.

3. What role does NH_4F play in the estimation process?

Ans : NH_4F is used to decompose the $Mg(EDTA)^{2-}$ complex, converting it into a more stable MgF_2 precipitate. This reaction releases an equivalent amount of EDTA, which is then titrated with Zn-acetate solution to determine the amount of Mg^{2+} in the mixture.

4. How is the amount of Mg^{2+} and Zn^{2+} determined from the titration data?

Ans : The amount of Mg^{2+} is determined by measuring the EDTA released after reacting with NH_4F, as this EDTA was originally complexed with Mg^{2+}. The Zn^{2+} content is calculated from the difference between the total amount of EDTA used and the EDTA corresponding to the amount of Mg^{2+}.

5. Why is pH control important in this titration method?

Ans : pH control is crucial because it affects the stability of the metal-EDTA complexes and the precipitation of MgF_2. Maintaining the correct pH ensures that the complexes form and dissociate at the appropriate rates, leading to accurate titration results.

6. What indicator is used in this method, and what is its role?

Ans : Eriochrome Black T (EBT) is used as the indicator. It forms a wine-red complex with Zn^{2+} ions. During titration, when EDTA reacts with Zn^{2+}, the color changes from wine-red to blue, signaling the endpoint of the titration.

7. What are the stoichiometric relationships between EDTA, Mg^{2+} and Zn^{2+}?

Ans : In the complexometric titration, 1 mole of EDTA reacts with 1 mole of Mg^{2+} or Zn^{2+}. Therefore, the amount of EDTA used directly corresponds to the amount of metal ions in the mixture.

8. What potential sources of error could affect the accuracy of this titration method?

Ans : Potential sources of error include incorrect pH adjustments, incomplete precipitation of MgF_2, improper indicator use, and measurement inaccuracies. Ensuring proper technique and equipment calibration can help minimize these errors.

Module-III

Inorganic Preparation

Unit – 10 ❑ Preparation of Inorganic Metal Complexes

Structure

10.1 Objectives

10.2 Introduction

10.3 Inorganic Metal Complexes

10.3.1 General Steps in Preparing Inorganic Metal Complexes

10.3.2 Calculation of percentage yield

10.3.3 Characterization

10.4 Preparation of Tris (ethylenediamine) nickel(II) chloride $Ni(en)_3Cl_2$

10.5 Preparation of Ferrous ammonium sulphate (Mohr's salt); $FeSO_4(NH_4)_2SO_4.6_{H2}O$

10.6 Preparation of Potassium tris (oxalato) chromate(III) trihydrate; $K_3[Cr(C_2O_4)_3].3H_2O$

10.7 Preparation of Tetraamminecarbonatocobalt (III) nitrate; $[Co(CO_3)\ (NH_3)_4]\ NO_3$

10.8 Preparation of Potassiumbis (oxalato) cuprate(II) dihydrate $K_2[Cu(C_2O_4)_2].\ 2H_2O$

10.9 Summary

10.10 Question

10.1 Objective

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

- Learn and apply synthesis techniques to deal with different horizon of chemistry. Will correctly calculate reaction yield for relevant lab experiments.
- Allow to verify many of the fundamental concepts gathered from class room lectures

- Analyse the given procedure of an experiment and suggest or recommend improvements.

10.2 Introduction

In the previous units you have learned about the estimation techniques used in the inorganic laboratory. In this unit we will discuss about the preparation and percentage yield calculation of Complex compounds or coordination compounds. After practicing the following inorganic synthesis, you will acquire expertise in this field and will be able to perform new reaction if procedure is supplied.

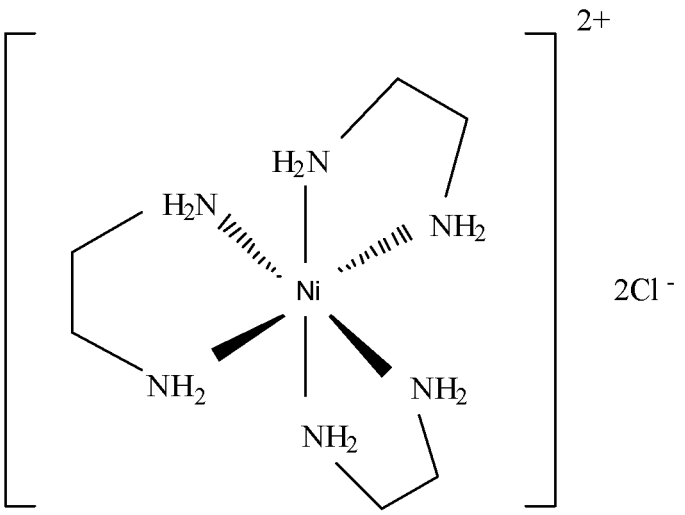
Complex compounds also known as coordination compounds are formed when molecules or ions bond to metal ions to form more complex structures. The molecules or ions that become attached to a metal ion are called ligands. Ligands must contain at least one unshared electron pair that can be donated to the metal ion to form a metal- ligand bond which is called a coordinate covalent bond.

For an example the synthesis reaction of tris (ethylenediamine) nickel(II) chloride is represented by the balanced equation :

$$NiCl_2{\cdot}6H_2O(s) + 3H_2NCH_2CH_2NH_2(aq) = [Ni(H_2NCH_2CH_2NH_2)_3]Cl_2(s) + 6H_2O(l)$$

"hydrate" ethylenediamine or "en" $Ni(en)_3Cl_2$

The equation shows that three moles of ethylenediamine, abbreviated en, are necessary to react with one mole of nickel(II) chloride hexahydrate, abbreviated hydrate, to form one mole of the complex compound, tris (ethylenediamine) nickel(II) chloride, abbreviated as $Ni(en)_3Cl_2$. The ethylenediamine (en) molecule acts as the ligand in this reaction and because it bonds to the nickel ion in two different positions, it is called a chelating ligand. The word "chelate" has Greek and Latin origins referring to a claw- like or pincer action. In this reaction each nitrogen atom (using its lone pair of electrons) in the en molecule bonds to the nickel ion; and there are three en molecules per nickel ion, forming the $Ni(en)_3^{2+}$ complex ion. The chloride ions in the solution, Cl^- (aq), form ionic bonds with the complex ion giving a purple, crystalline solid which precipitates from the solution. The structure of the complex and the ligand are shown below.



Tris (ethylenediamine) Nickel (II) chloride

10.3 Inorganic Metal Complexes

Inorganic metal complexes are coordination compounds where a central metal ion is bonded to one or more molecules or ions, known as ligands. These ligands donate electron pairs to the metal ion, forming coordinate covalent bonds. Metal complexes are prevalent in various fields, including chemistry, biology, materials science, and catalysis. The preparation of inorganic metal complexes involves combining a metal ion with ligands (molecules or ions that donate electron pairs) to form a coordination compound. These complexes are essential in various fields, including catalysis, medicinal chemistry, and material science.

10.3.1 General Steps in Preparing Inorganic Metal Complexes

(i) Selection of Metal Ion and Ligands :

Choose a metal ion (e.g., Fe^{3+}, Cu^{2+}, Ni^{2+}) and suitable ligands (e.g., ammonia, water, chloride, or organic molecules like ethylenediamine) based on the desired coordination environment and properties.

(ii) Dissolution of Starting Materials :

Dissolve the metal salt (e.g., metal chloride, nitrate, or sulfate) in water or an appropriate solvent. Dissolve the ligand in the same or a different solvent.

(iii) Mixing and Complex Formation :

Slowly add the ligand solution to the metal salt solution while stirring. The metal

ion will coordinate with the ligands, forming the desired complex. Control the pH, temperature, and stoichiometry to direct the reaction towards the desired product.

(iv) Isolation of the Complex :

Isolate the complex by precipitation, evaporation, or other methods depending on its solubility.

Filtration or centrifugation is typically used to collect the solid complex.

(v) Purification :

Purify the complex by recrystallization, washing with solvents, or using techniques like column chromatography if necessary.

(vi) Yield Calculation :

Calculate the yield by comparing the mass of the obtained complex with the theoretical yield.

10.3.2 Calculation of percentage yield

Let us consider that,

Molecular weight of starting material/limiting reagent taken = M_1

Molecular weight of final product obtained = M_2

Weight of starting material/limiting reagent taken = X

Weight of the final product obtained (Practical yield) = Y

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

$$\text{Therefore, Theoretical Yield of product} = \frac{M_2 \times x}{M_1} g$$

$$\text{Percentage yield of the product} = \frac{\text{Practical yield}}{\text{Theoretical yield}} \times 100$$

$$= \frac{Y \times M_1 \times 100}{M_2 \times X}$$

10.3.3 Characterization

Characterize the complex using various analytical techniques :

- **UV-Vis Spectroscopy :** To analyze the electronic transitions within the complex.

• **Infrared (IR) Spectroscopy :** To identify functional groups and confirm coordination.

• **NMR Spectroscopy :** For paramagnetic complexes, EPR (Electron Paramagnetic Resonance) might be more suitable.

• **X-ray Crystallography :** To determine the precise molecular structure.

• **Elemental Analysis :** To confirm the composition.

You will learn to characterize the complexes in your advanced studies. For now, let's concentrate on the synthesis of metal complexes.

10.4 Preparation of Tris(ethylenediamine)nickel(II) chloride $Ni(en)_3Cl_2$

The preparation of Tris(ethylenediamine)nickel(II) chloride, $Ni(en)_3Cl_2$, is a straightforward yet significant experiment in coordination chemistry. This complex involves the coordination of nickel(II) ions with ethylenediamine (en), a bidentate ligand that binds through its two nitrogen atoms. The resulting compound, $Ni(en)_3Cl_2$, is a violet-blue solid that showcases the octahedral geometry typical of nickel(II) complexes. This synthesis provides valuable insights into ligand coordination, complex formation, and the properties of transition metal complexes.

Principle

Tris (ethylenediamine) nickel(II) chloride is prepared by adding ethylenediamine in small portions to aqueous solution of nickel chloride :

$NiCl_2.6H_2O(s) + 3H_2NCH_2CH_2NH_2(aq) = [Ni(H_2NCH_2CH_2NH_2)_3]Cl_2(s) + 6H_2O(l)$

Chemicals required :

(a)	$NiCl_2\ 6H_2O$	: 1.2g
(b)	4.0 (M) ethylenediamine	: 8 mL
(c)	Acetone	: 30 mL
(d)	Deionised water	: 5mL

Procedure

Weigh approximately 1.2 g of $NiCl_2\ 6H_2O$ into a 100 mL beaker (Record the exact mass). Add 5 mL of deionised water, and stir to dissolve the $NiCl_2.6H_2O$. Add approximately 8 mL of 4.0 (M) ethylenediamine to the beaker (Record the exact volume used) and stir well. Add 30 mL of acetone in 10 mL increments, stirring after each addition (The product should precipitate out of solution). Cool the beaker in an

ice bath to maximize precipitation, and try scratching the wall of the beaker to initiate precipitation. Vacuum filter the product. Wash with acetone (NOTE: DO NOT USE WATER-the product is water-soluble and your product will be lost if you add water). Dry under vacuum filter until product is crystalline (4-5 minutes). Transfer the product and filter paper on a pre-weighed petri dish and air dry the product.

Yield : 1 g

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 $NiCl_2$ $6H_2O$ taken	Theoretical Yield of $Ni(en)_3Cl_2$	Weight of $Ni(en)_3Cl_2$ Obtained	Percentage yield Product

10.5 Preparation of Ferrous ammonium sulphate (Mohr's salt); $FeSO_4(NH_4)_2SO_4.6H_2O$

The preparation of Ferrous Ammonium Sulphate, commonly known as Mohr's salt $FeSO_4(NH_4)_2SO_4.6H_2O$], is an important experiment in inorganic chemistry. Mohr's salt is a double salt composed of ferrous sulfate and ammonium sulfate, crystallized together with six molecules of water. It serves as a stable source of ferrous ions (Fe^{2+}) in various analytical and industrial applications. The stability of Fe^{2+} in Mohr's salt is enhanced by the presence of ammonium sulfate, which helps prevent the oxidation of Fe^{2}? to Fe^{3}? in the presence of air. This preparation involves the careful combination of ferrous sulfate and ammonium sulfate in an aqueous solution, followed by crystallization.

Principle : When a mixture containing equimolar proportions of ferrous sulphate (FeSO4) and ammonium sulphate ($(NH_4)_2SO_4$) is crystallised from its solution, a double salt is formed. The formation of double salt may be shown as follows :

$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O \rightarrow FeSO_4.(NH_4)_2SO_4.6H_2O$$

Chemicals required :

METHOD I			**METHOD II**		
Metallic iron fillings	:	1g	Ferrous sulphate	:	7g
Ammonium Sulphate	:	2.5g	Ammonium Sulphate	:	3.5g
Conc. H_2SO_4	:	10mL	dil H_2SO_4	:	3mL
Absolute alcohol	:	q.s.	Absolute alcohol	:	q.s.

Method of Preparation :

METHOD I : Take 1g of iron filings in a 250mL beaker, add (1:6 = H_2SO_4 : H_2O) solution slowly with stirring till all of iron dissolve. Filter off the impurities and the filtrate is treated with 2.5g of ammonium sulphate dissolved in minimum volume of water. The solution is concentrated by evaporation and allow to cool when crystals of Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ are separated. Filter the light green crystals under suction, wash it with a small volume of ethyl alcohol followed by a little of acetone. Yield : 6g.

METHOD II : First take 7g ferrous sulphate 3.5g ammonium sulphate in a clean 250ml beaker. To this add about 2-3ml of dil. sulphuric acid to prevent the hydrolysis of ferrous sulphate. In another beaker, boil about 20ml of water for 5 minutes. Add the boiling hot water to the contents in the first beaker in small quantities at a time. Stir the contents of the beaker with a glass rod until the salts have completely dissolved. Filter the solution and heat the solution until its crystallisation point is reached. Then transfer the solution into a crystallising dish and keep it undisturbed. On cooling, crystals of Mohr's salt separate. Decant the mother liquor and wash the crystals with a small quantity of alcohol and then dry the crystals by placing them between filter paper pads. Find the weight of the crystals. Yield: 8g.

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 ammonium sulphate taken	**Theoretical Yield of $FeSO_4(NH_4)_2SO_4.6H_2O$**	**Weight of $FeSO_4(NH_4)_2SO_4.6H_2O$ obtained**	**Percentage yield of product**

10.6 Preparation of Potassium tris(oxalato)chromate(III)trihydrate; $K_3[Cr(C_2O_4)_3].3H_2O$

The preparation of Potassium Tris(oxalato)chromate(III) trihydrate, $K_3[Cr(C_2O_4)_3].3H_2O$, is a key experiment in coordination chemistry, involving the synthesis of a complex where a chromium(III) ion is coordinated by three oxalate ligands. This compound is a vibrant green, water-soluble complex that crystallizes with three molecules of water. The oxalate ligands act as bidentate chelating agents, forming a stable octahedral complex around the chromium ion. The synthesis involves the reaction of potassium dichromate with oxalic acid in acidic conditions, followed by the addition of potassium ions to precipitate the complex as a trihydrate.

Principle :

Potassiumtrioxalatochromate (III)trihydrate is made by adding potassium dichromate in small portions to a hot solution of oxalic acid:

$$K_2Cr_2O_7 + 7H_2C_2O_4 + 2K_2C_2O_4 = 2K_3[Cr(C_2O_4)_3] + 6CO_2 + 7H_2O$$

Chemicals required :

(a) Oxalic acid, $H_2C_2O_4.2H_2O$: 7.8g

(b) Potassium oxalate, $K_2C_2O_4.H_2O$: 3.5g

(c) $K_2Cr_2O_7$: 3.0g

(d) Absolute alcohol : q.s.

Method of Preparation :

Dissolve 7.8g oxalic acid dihydrate in 20mL warm water in a 250mL beaker. To the solution add 3.0g $K_2Cr_2O_7$ in portions. When the vigorous reaction (due to the effervescence CO_2) subsides, heat to boil for 5 minutes and then add 3.5g of potassium oxalate monohydrate to it. Allow to cool under tap to room temperature and add 10.0mL ethanol. Stir and allow stand for 20 -30 minutes. Filter through suction, wash with 50% alcohol and dry in the air.

Yield: 7.2g.

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 $K_2Cr_2O_7$ taken	Theoretical Yield of $K_3[Cr(C_2O_4)_3].3H_2O$	Weight of $K_3[Cr(C_2O_4].3H_2O$ obtained	Percentage yield of product

10.7 Preparation of Tetraamminecarbonatocobalt(III) nitrate; $[Co(CO_3)(NH_3)_4]\ NO_3$

In the complex, Tetraamminecarbonatocobalt(III) nitrate, $[Co(CO_3)(NH_3)_4]\ NO_3$, a cobalt(III) ion is coordinated by four ammonia molecules and one carbonate ion, forming a stable, octahedral structure. The synthesis involves the careful oxidation of a cobalt(II) salt in the presence of ammonia and carbonate ions, followed by the formation of the nitrate salt of the complex. This experiment demonstrates key concepts in coordination chemistry, including the stepwise coordination of ligands to a metal center, the stabilization of higher oxidation states, and the properties of cobalt(III) complexes. The resulting compound is often a bright orange or red crystalline solid, which serves as a prime example of the vivid colors and diverse structures typical of metal complexes.

Principle :

The solution of cobalt(II) nitrate and ammonium carbonate in conc. ammonia on oxidation with H_2O_2 in a hot water bath followed by cooling in ice-cold water, violet crystals of carbonatotetraamine cobalt (III) nitrate are separated.

$2Co(NO_3)_2 + 2(NH_4)_2CO_3 + 6NH_3 + H_2O_2 = [Co(CO_3)(NH_3)_4]\ NO_3 + 2NH_4NO_3 + 2H_2O$

Chemicals required :

(a) $Co(NO_3)2.6\ H_2O$: 10g
(b) $(NH_4)_2CO_3$: 25g
(c) Conc. ammonia : 50mL
(d) 10 volume or 3% H_2O_2 : 25mL
(e) Ethanol : q.s.

Method of Preparation:

Dissolve 10g of $Co(NO_3)_2.6H_2O$ in 10mL of warm water and add to it a mixture of 20g of $(NH_4)_2CO_3$ in 100mL water and 50mL conc. ammonia. Further add 25mL of 3% H_2O_2 slowly to well stirred mixture. After 10 minutes the solution is evaporated on a steam bath to a volume of 50mL. Any cobalt(II) oxide formed is filtered off while hot and further evaporation to 35mL is carried out. During the course of evaporation 5g of solid $(NH_4)CO_3$ should be added 1g portions at regular intervals. The solution is next cooled in ice, filtered by suction and the crystals are pressed well. The crystals may be washed with 8mL of alcohol and dried. Reject filtrate.

Yield: 2.5g.

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 $Co(NO_3)_2.6H_2O$ taken	Theoretical Yield of $[Co(CO_3)(NH_3)_4]NO_3$	Weight of $[Co(CO_3)(NH_3)_4]$ obtained	Percentage yield of product

10.8 Preparation of Potassiumbis(oxalato)cuprate(II)dihydrate $K_2[Cu(C_2O_4)_2].\ 2H_2O$

In Potassium bis(oxalato)cuprate(II) dihydrate, $K_2[Cu(C_2O_4)_2].\ 2H_2O$, a copper(II) ion is coordinated by two oxalate ions, forming a stable, square-planar structure. The synthesis involves the reaction of copper(II) sulfate with potassium oxalate in an aqueous solution, leading to the formation of the vibrant blue-green complex. The compound crystallizes with two molecules of water, adding to its stability. This experiment highlights important concepts such as chelation, the formation of metal-ligand complexes, and the characteristic colors of transition metal compounds.

Principle :

Potassiumbis(oxalato) cuprate(II) dihydrate is made by adding copper(II) sulphate solution in small portions to a hot solution of potassium oxalate:

$$CuSO_4.5H_2O\ (aq) + 2K_2C_2O_4.H_2O\ (aq) = K_2[Cu(C_2O_4)_2].\ 2H_2O\ (s) + K_2SO_4(aq) + 5H_2O$$

Chemicals required :

(a) $K_2C_2O_4.H_2O$: 12.3 g

(b) $CuSO_4.5H_2O$: 4.1 g

(c) Ethanol : 5mL

Procedure :

Dissolve 12.3 g potassium oxalate monohydrate ($K_2C_2O_4.H_2O$) in 35 mL distilled water and heat the solution to 90°C. Dissolve 4.1 g copper (II) sulphate pentahydrate ($CuSO_4.5H_2O$) in 8 mL distilled water, and heat the solution to 90°C. Filter the solution while still hot, and slowly with stirring, add the hot filtrate of copper(II) sulphate to the hot solution of potassium oxalate. Cool the mixture in an ice bath, filter the crystals formed and wash with cold water, followed by ethanol followed by a little of acetone. Dry the crystals in air. Record the yield of the product.

Yield: 4 g.

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 $CuSO_4.5H_2O$ taken	Theoretical Yield of $K_2[Cu(C_2O_4)_2].2H_2O$	Weight of $K_2[Cu(C_2O_4)_2].2H_2O$ obtained	Percentage yield of product

10.9 Summary

- Inorganic metal complexes are coordination compounds where a central metal ion is bonded to ligands, which are molecules or ions that donate electron pairs to form coordinate covalent bonds.
- Percentage yield of the product $= \frac{\text{Practical yield}}{\text{Theoretical yield}} \times 100$
- Preparation of Tris(ethylenediamine)nickel(II) chloride involves the coordination of nickel(II) ions with ethylenediamine (en) as a bidentate ligand, resulting in a violet-blue complex with octahedral geometry.

- Mohr's salt is prepared by crystallizing equimolar proportions of ferrous sulfate and ammonium sulfate, forming a stable double salt.
- Potassium Tris(oxalato)chromate(III) trihydrate synthesis involves reacting potassium dichromate with oxalic acid, followed by potassium oxalate to form a green, octahedral complex.
- Tetraamminecarbonatocobalt(III) nitrate complex is synthesized by oxidizing cobalt(II) nitrate in the presence of ammonia and ammonium carbonate, forming a bright orange or red crystalline complex.
- Potassium Bis(oxalato)cuprate(II) dihydrate complex is formed by reacting copper(II) sulfate with potassium oxalate, producing a blue-green complex with a square-planar structure.

10.10 Question

1. What is an inorganic metal complex?

Ans : An inorganic metal complex is a coordination compound where a central metal ion is bonded to ligands, which are molecules or ions that donate electron pairs to the metal ion, forming coordinate covalent bonds.

2. How is the percentage yield of a metal complex calculated?

Ans : The percentage yield is calculated by dividing the actual mass of the obtained complex by the theoretical mass (based on stoichiometry) and multiplying by 100%.

3. What methods can be used to characterize a metal complex?

Ans : Characterization can be done using techniques such as UV-Vis spectroscopy, IR spectroscopy, X-ray crystallography, and elemental analysis to determine the structure, composition, and properties of the complex.

4. What is the role of ethylenediamine in the preparation of $[Ni(en)_3]Cl_2$?

Ans : Ethylenediamine acts as a bidentate ligand, coordinating with the nickel(II) ion to form a stable octahedral complex.

5. What is the significance of preparing Mohr's salt in the laboratory?

Ans : Mohr's salt is a stable, double salt used as a standard in titrations and as a source of ferrous ions in various chemical reactions.

6. What is the role of oxalate ions in the preparation of $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$?

Ans : Oxalate ions act as bidentate ligands, coordinating with the chromium(III) ion to form a stable octahedral complex.

7. Why is it important to maintain acidic conditions during the preparation of $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$?

Ans : Acidic conditions prevent the hydrolysis of the chromium(III) ion and stabilize the oxalate complex.

8. What is the function of ammonia in the preparation of $[Co(CO_3)(NH_4)_4]NO_3$?

Ans : Ammonia acts as a ligand, coordinating with cobalt(III) to form the tetraammine complex, which is then stabilized by the carbonate ion.

9. Why is oxalate used as a ligand in the preparation of $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$?

Ans : Oxalate is used because it forms a stable chelate with copper(II), leading to the formation of a well-defined complex.

10. What is the typical color of $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$, and what does it indicate?

Ans : The complex is typically blue, indicating the presence of copper(II) in a d-d transition state, characteristic of its coordination environment.

Module-IV

Qualitative Analysis of Organic Compounds

Unit – 11 ❑ Qualitative Analysis of Single Solid Organic Compounds

Structure

11.1 Objective

11.2 Introduction

11.3 Systematic Qualitative Analysis of an Organic Compound

11.3.1 Physical Characteristics

11.3.2 Preliminary Test

11.3.3 Lassaigne's Test

11.3.5 Confirmatory Test:

11.3.4 Detection of Functional Groups:

11.3.6 Preparation of Corresponding Derivative

11.3.7 Conclusion

11.3.8 Chemical reactions Involve in Organic Qualitative Analysis:

11.4 Important Organic Compounds and properties of their derivatives

11.5 Summary

11.6 Questions

11.1 Objective

By the end of this unit, students should be able to–

- Understand the principles of qualitative analysis of organic compounds.
- Identify functional groups present in single solid organic compounds using chemical tests.
- Perform preliminary tests to determine physical properties such as melting point and solubility.
- Apply systematic procedures to determine the presence of special elements such as nitrogen, sulfur, and halogens in organic compounds.
- Interpret results from chemical tests to deduce the structure and identity of the organic compound.

- Develop skills in handling organic compounds and conducting laboratory tests safely and effectively.

11.2 Introduction

Practical organic chemistry may broadly be classified into three different areas :

(i) Qualitative Organic Analysis.

(ii) Quantitative Organic Analysis.

(iii) Organic Preparations.

The technique of organic analysis is somewhat different from that of the technique adopted for inorganic analysis. Most of the inorganic reactions are ionic in character and reach completion within a very short time. On the other hand organic reactions are delayed reactions and occur through several steps because they involve breaking and making of mostly covalent bonds. Therefore, requisite time, patience and manipulative skills are required to get accurate results.

The qualitative analysis of single solid organic compounds is a fundamental aspect of organic chemistry, focusing on the identification of functional groups, elements, and structural features within a compound. This unit introduces the systematic approach to analyzing and characterizing organic solids through various laboratory techniques and chemical tests. By employing qualitative analysis, chemists can deduce the functional groups present in an unknown compounds.

This unit provides a comprehensive guide to the methodologies used in the qualitative analysis of organic solids, including preliminary tests for physical properties like melting point and solubility, as well as specific chemical reactions that reveal the presence of key functional groups.

The identification or detection of organic compounds and representation in the notebook maybe based on the following procedures and guideline.

11.3 Systematic Qualitative Analysis of an Organic Compound

The systematic qualitative analysis of an organic compound involves a series of well-defined steps aimed at identifying its functional groups, and structure. Below is a general outline of the steps involved in the systematic qualitative analysis of an organic compound :

Sample No.:.....

11.3.1 Physical Characteristics :

State :

Odour :

Colour :

M.P = ... ^0C

Solubility : Take a pinch of the sample and check the solubility in the following solvents at room temperature.

Type	Water	2(N)HCl	10%NaOH	5%$NaHCO_3$	C.H_2SO_4	Division	Inference
1	✓	-	-	-	-	S	
2	x	✓	x	-	-	S_1	
3	x	x	✓	x	-	S_2	
4	x	x	✓	✓	-	S_3	
5	✓	✓	✓	✓	-	S_4	
6	x	x	x	-	✓	S_5	

✓ = Soluble; x = Insoluble; - = Not tried

Probable Functional Groups Present :

Division	Functional Groups
S	Aldehyde, ketone, Acid, phenol and poly hydroxy phenols, Poly carboxylic acid, Polyhydroxy alcohol. If N-present: Nitro phenol [NB: If the sample is soluble in water then need not try with other solvents]
S_1	Compound is basic in nature; Amine
S_2	Weak acidic in nature; Phenolic –OH, Phenolic aldehyde and ketone. If N-present: Amide, Amino phenol
S_3	Strong acidic; Phenolic acid, $–SO_3H$; –COOH
S_4	Amphoteric in nature; Amino acid, Amino Phenol
S_5	Neutral in nature; Amide, Anilide, Nitro, Aldehyde, Ketone and Ester

11.3.2.Preliminary Test

Experiment	Observation	Inference
1. Burning Test: Place little amount of the sample at the end of a flat spatula and place at the top of the flame of Bunsen burner.	1. Burns with yellow sooty flame	1. Aromatic or highly unsaturated compound present
2. Baeyer's Test: Dissolve little amount of the sample in water or acetone and then add few drops of 1%$KMnO_4$ solution	2. Rapid decolourisation of permanganate colour	2. Active unsaturated group or strong reducing group is present
3. Bromine-water: Dissolve little amount of the sample in CCl_4 and add few drops of Br_2-water	3. Reddish colour of Br_2 solution is discharged	3. Ethylenic unsaturation is present
4. Sodalime Test: Heat little amount of the sample with sodalime	4. Gas comes out with smell of NH_3	4. Amido or Imido group present

11.3.3. Lassaigne's Test : (test for N,S and halogens)

Place a freshly cut, clean and dry piece of sodium metal of the size of pea into a fusion tube. Heat the lower part of the tube gently till sodium melts to a shining globule. Then add little amount of the sample in it. Heat the tube till it becomes red hot. Now plunge it into about 5 ml of distilled water in a mortar and triturate the fused mass. Filter. Perform the following tests with the filtrate (A).

Experiment	Observation	Inference
1. Take about 1 ml of the filtrate(A) in a test tube and add a drop of $Na_2[Fe(CN)_5NO]$ solution	1. Violet or purple colouration	1. S – present
2. Place about 2ml of the filtrate(A) in a test tube, add about 30mg of $FeSO_4$ and boil the mixture. Add a drop of 1% $FeCl_3$ solution and acidify with 6(N) H_2SO_4	2. Blue or green colour or precipitate	2. N – present
3. Place 2 ml of the filtrate (A) in a test tube and add few drops of c.HNO_3 and boil the mixture gently to remove HCN. Cool the solution and then add few drops of $AgNO_3$ solution	3. (i) Curdy white precipitate (ii) Curdy light yellow (iii) Deep yellow precipitate	3. (i) Cl – present (ii) Br – present (iii) I - present

If Br or I present perform the following test

Experiment	Observation	Inference
Place about 2ml of the filtrate(A) in a test tube and diluted to 5 ml, acidified with dil. H_2SO_4. Add 2 ml of CCl_4 or CS_2 or $CHCl_3$. To this solution now add few drop of Cl_2- water with constant shaking	(i) Reddish colour in organic solvent layer (ii) Reddish colour change to violet	(i) Bromine Confirmed (ii) Iodine Confirmed

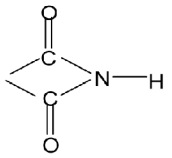
11.3.4. Detection of Functional Groups:

Experiment	Observation	Inference
1. Test for –COOH group:	1.	1.
i) Dissolve little amount of the sample in water or alcohol and transfer on a blue litmus paper	i) Blue litmus turns to red	i) –COOH or Phenolic –OH gr. Present
ii) Dissolve little amount of the sample in water or alcohol and then add few drops of saturated $NaHCO_3$ solution	ii) Effervescence of CO_2	ii)- COOH gr. Present
iii) About 0.5 g of the sample is warmed with about 2 ml of CH_3OH or C_2H_5OH and 2 drops of c.H_2SO_4. Pour the product in about 20 ml of water in a beaker	iii) Characteristic sweet smell of an ester	iii)- COOH confirmed
iv) Dissolve little amount of the sample in about 1 ml of alcohol in a test tube. Add few drops of 10% KI solution and 2-3 drops of 3% KIO_3 solution. Warm the mixture. Diluted with distilled water till a pale yellow color persists and then add 1-2 drops of freshly prepared starch solution.	iv) Blue coloration	iv) –COOH gr confirmed
2. Test for Phenolic-OH group:		2.
i) To 1 ml of the alcoholic of the sample, 2 drops of 1% $FeCl_3$ solution are added	2.	i)Phenolic –OH gr. present
ii) **Back Dye Test:** In first test tube take about 1 ml of aniline then add few drops of c.HCl. In second test tube prepare about 10% $NaNO_2$ solution. In third test tube dissolve little amount of the	i) Red, blue, green or violet coloration ii) Red or Rose red dye	ii) Phenolic -OH gr. Confirm

sample in 2 ml of 10% NaOH solution. Cool these three tubes in an ice bath. When the solutions are thoroughly chilled , transfer $NaNO_2$ solution (2) in the acidified aniline solution (1). Now transfer a drop of this diazotized mixture into the alkaline sample solution (3).		
3. **Test for Carbonyl gr.**: i)Dissolve little amount of the sample in 2 ml of CH_3OH in a dry test tube and then add few drops of 2,4 - dinotrophenylhydrazine sulphate solution [do not warm].	3. i) Red or Orange red precipitate	3. i) Carbonyl group present (Ketone or aldehyde)
ii) Little amount of the sample is warmed in a water bath with a mixture of 5 ml of Fehling's A and B solution	ii) Red precipitate of Cu_2O	ii) – CHO group present
iii)Little amount of the sample is warmed on a water bath with 5 ml of Tollens' reagent	iii) Silver mirror formed on the inner side of the test tube	iii)- CHO gr. present
iv)To the ethanoic solution of the sample, few drops of colourless Schiff's reagent is added and shaken in cold condition	iv) Pink colour of the Schiff's reagent is restored.	iv)- CHO gr. confirm

4. Test for Ester Group: i) A small quantity of the sample is hydrolyzed by a strong solution of NaOH. Cool. Acidify with dil. HCl ii) **Feigl Test** (Hydroxamic Acid Test): Take little amount of the sample in a test tube and dissolve it in 2 ml of CH_3OH and add about 0.1 g of hydroxylamine hydrochloride [or dissolve little amount of the sample in 2 ml of 5% hydroxylamine hydrochloride solution] Now add little amount of solid phenolphthaline indicator and pour drop wise saturated methanolic KOH solution until the mixture is alkaline. Add excess 5 drops of methanolic KOH. The solution is then boiled carefully and cooled. Acidify with dil. HCl then add a drop of freshly prepared 1% $FeCl_3$ solution.	4. i) White precipitate ii) A wine red colouration	4. i)Ester gr. present ii)Ester gr. Confirm
5. **Test for Alcoholic –OH gr**: i) **Ceric ammonium nitrate test**: Dissolve little amount of the sample in water or CCl_4 and then add a drop of Ceric nitrate Solution.	5. i) Amber red colouration	5. i) Alcoholic –OH group present

6. Test for Primary Amine Group: **i) Dye Test:** Take three test tubes. a) In first tube take little amount of the sample add few drops of water(if sample is solid) then add 2-3 drops of c.HCl. b) In second test tube prepare 1ml 10% $NaNO_2$ solution. c) In third test tube dissolve 30 mg β – naphthol in 5 ml 10% NaOH. Place the three mixtures in an ice bath. When the solutions are thoroughly chilled, transfer $NaNO_2$ solution (b) into acidified sample solution (a). Now pour a drop of this diazotized mixture to alkaline sodium β - naphthoxide solution. **ii) Carbylamine Test:** Place little amount of the sample in a dry test tube then add 1 ml of $CHCl_3$ and a bead of KOH. Boil the mixture gently.	6. i) A red dye will form ii) Smell of iso-cyanide comes out	6. i) Aromatic primary – NH_2 present ii)Presence of $-NH_2$ confirm
7. Test for Amido Group: i) Place little amount of the sample in a test tube and add 2 ml of 10% NaOH solution. Boil the mixture gently. ii) Place little amount of the sample in a test tube and dissolve in water or alcohol and now add few drops of cold solution of	7. i) Gas comes out with smell of NH_3 which • Produces white dense fume in contact of c. HCl moist glass rod. • Turns red litmus paper into blue. • Turns Nesseler's Reagent moist paper into black ii) N_2 gas evolves.	7. i) $-CONH_2$ present ii) $-CONH_2$ present

HNO_2 (obtained by the reaction between $NaNO_2$ and HCl). iii) **Hydroxylamine hydrochloride Test:** Take about 0.1 g of the sample and about 0.1 g of hydroxyl amine hydrochloride in a test tube. Dissolve the mixture in about 5 ml of alcohol and boil gently for 2-3 minutes. Cool, and then pour few drops of freshly prepared 1% $FeCl_3$ solution.	iii) Bluish red colouration	iii) – $CONH_2$ present
8. **Test for Imido Group:** Place little amount of the sample in a test tube and add 2 ml of 10% NaOH solution. Boil the mixture gently. (**Note:** Amido gr. must absent)	8. i) Gas comes out with smell of NH_3	8. i) Imide present 
9. **Test for Nitro Group:** i) A small quantity of the sample is boiled 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 20 mg. of β – naphthol in 5 ml 10% NaOH. Place the three mixtures in an ice bath. When the solutions are thoroughly chilled, transfer $NaNO_2$ solution into reduced sample solution. Now pour a drop of this diazotized mixture to alkaline sodium β - naphthoxide solution.	9. i) Red or orange red dye	9. i)-NO_2 gr. Present
ii) **Mulliken-Barker Test:** A small quantity of the sample is boiled in a water bath with Zn-dust and NH_4Cl in aqueous alcoholic medium for 5 minutes. The solution is filtered. Few drops of Tollen's reagent is	ii) Greyish black precipitate	ii)Ar-NO_2 group present.

added to the 5 ml of filtrate and wormed.		
10. Test for Anilido Group:	10.	10.
i) A small quantity of the sample is warmed by adding 3 ml dil. HCl for 2 minutes, cool, perform the dye test with this cold solution.	i) Rose red dye	i)-C_6H_5-NHCO group present.
ii) **Tafel's Test:** Take little amount of the sample in a dry test tube, pour 1 ml of conc. H_2SO_4, shake the mixture. Now add a small crystal of $K_2Cr_2O_7$	ii) Rose red colouration changes to green on standing	ii)Anilide gr. present

** Perform the tests for nitrogen containing functional group only if indication for nitrogen obtained in the Lassaigne's Test. In absence of nitrogen do not perform the tests for nitrogen containing functional group.

11.3.5. Confirmatory Test:

Experiment	Observation	Inference

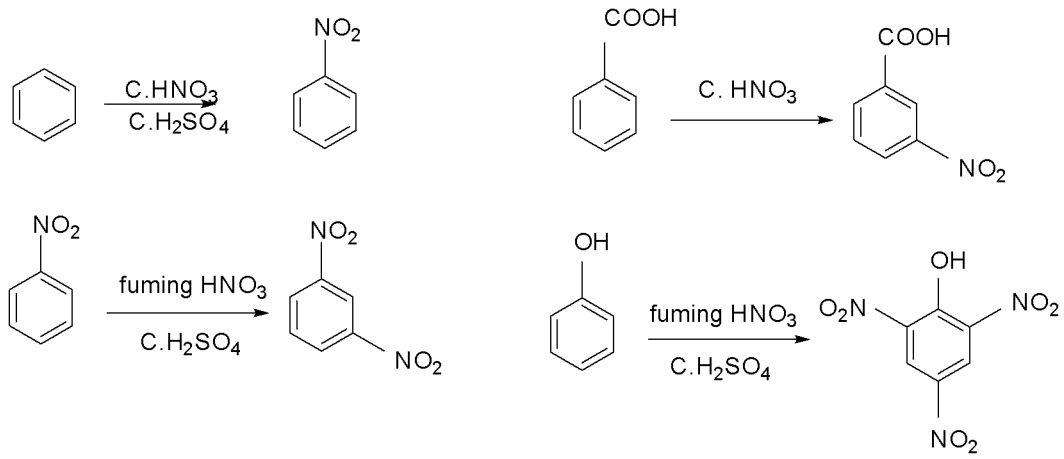
** Write again the confirmatory tests for the functional groups which was found positive during the Detection of Functional Groups

11.3.6 Preparation of Corresponding Derivative

1. Preparation of Nitro, Poly-Nitro derivative :

Dissolve about 1 g of the sample in 5 ml of conc. H_2SO_4 in a 100 ml dry conical flask. Cool the solution and keep the mixture in an ice bath. Now add 5 ml ice cooled HNO_3 drop by drop with constant shaking of the mixture. Keep in mind that during addition temperature should not rise above 10°C. After complete addition, warm the mixture at about 70°C placing over steam bath for 15-20 minutes. Cool the reaction product and pour it into 25 ml ice- cold water. Separate the precipitate of nitro compound by filtration and recrystallized from alcohol. Dry and determine the melting point of the derivative.

If a poly nitro derivative is to be prepared, fuming HNO_3 (sp. gr. 1.42) and conc. H_2SO_4 (sp. gr. 1.98) are to be used depending upon the nature of the compound.



2. Preparation of Benzoyl Derivative : (Schotten-Baumann Reaction) [for Ph–OH. $-NH_2$ grs.]

Dissolve about 1 g of the sample in minimum volume of acetone in a conical flask fitted with cork. Add 2 ml of benzoyl chloride and 30 ml of 20% NaOH solution to the flask. Shake the content vigorously until the odour of benzoyl chloride just disappears (if required little more NaOH solution may be added) and a precipitate is formed.

Filter the solid and wash first with cold dil HCl then with water and recrystallize the product from alcohol. Determine the m.p.

3. Preparation of Amide Derivative: [for –COOH gr.]

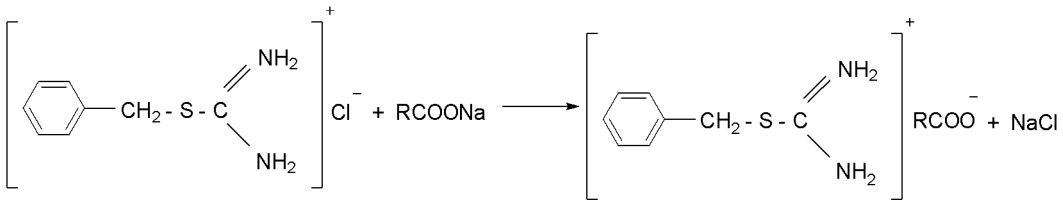
Place 0.5 g of the sample in a dry mortar with 2 g of PCl_5 and triturate it with a pestle inside of a fume cupboard until it is converted to a liquid. Add about 10 ml of liquor NH3, little at a time. When vigorous reaction has ceased, stir, cool and pour into little amount of ice-cool water and filter. Dry and determine the m.p.

4. Preparation of Anilide Derivative: [for –COOH gr.]

Place 0.5 g of the sample in a dry mortar with 2 g of PCl_5 and triturate it with a pestle inside of a fume cupboard until it is converted to a liquid. Dissolve it in 2 ml acetone and pour in a 100 ml flask. Add 1 ml freshly distilled aniline and cool. Add 20 ml NaOH solution, shake well, filter the precipitate, wash the solid with cold water, crystallize from alcohol, dry and determine the melting point of the anilide derivative.

5. Preparation of S-Benzylisothiouronium salts (SBT) Derivative: [for – COOH gr.]

S-Benzylisothiouronium chloride reacts with the Na and K salt of organic acids to for crystalline S-Benzylthiouronium salts.Dissolve or suspend about 0.2 g of the sample in ml of warm water. Adjust pH of this solution to almost neutral with 0.1 (N) NaOH solution using phenolphthalein as indicator. Add few drops of 0.1 (N) HCl solution and solution of 1 g S-benzylthiouronium chloride in 5 ml of water or alcohol. Cool the mixture in an ice bath. Filter;crystallize from dilute alcohol or hot water.



6. Preparation of Acid Derivative: [for $-CONH_2$ gr.]

Reflux 0.5 g of the sample with 20 ml of 10% NaOH solution and add 5-6 beads of NaOH in a 100 ml conical flask for 15-20 minutes, till the evolution of NH3 gas is ceased (test with litmus paper). Cool the mixture in an ice bath and acidify with c. HCl. Filter the precipitate, wash with water and crystallize from aqueous ethanol. Determine the m.p. of the derivative.

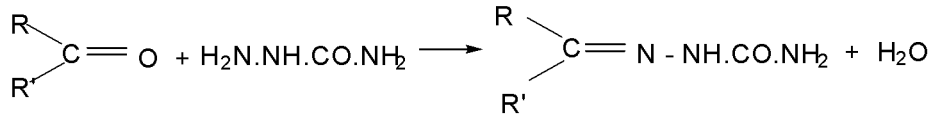
7. Preparation of 2,4-dinitro phenylhydrazone Derivative: [for =C=O gr.]

Take about 0.5 g of the given sample and dissolve it in methanol in a dry test tube. Add few drops of conc. HCl and about 5 ml of 1% 2,4-dinitro phenylhydrazine solution and heat the mixture for few minutes by immersing in boiling water. Add little amount of water till the turbidity appears. Again warm the mixture till it becomes clear, cool, a solid precipitate of 2,4- dinitro phenylhyrdazone derivative separates. Filter, dry and determine the melting point of the derivative.

[Note: addition of conc. HCl is not required if 2,4- dinitro phenylhydrozine sulphate reagent is used instead of 2,4-dinitro phenylhydrazine]

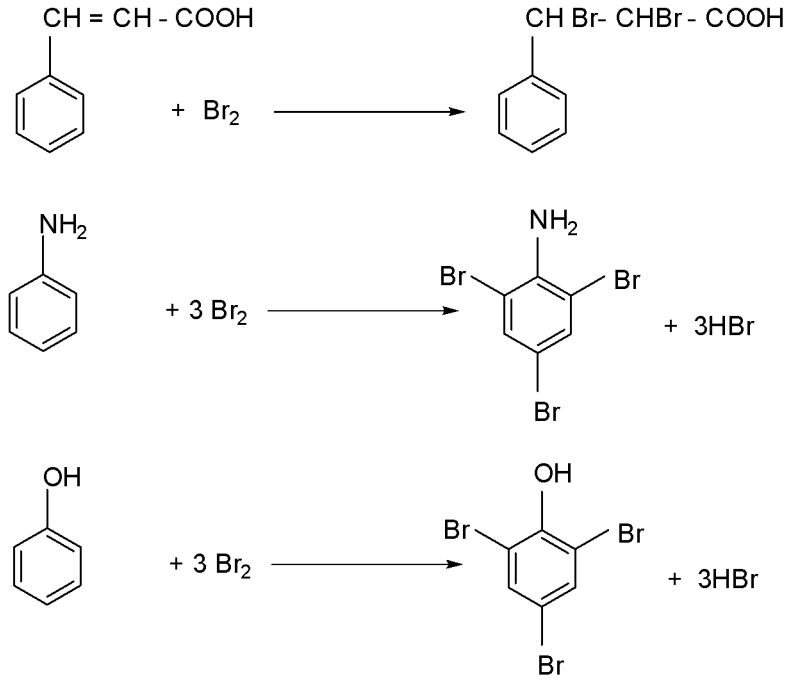
8. Preparation of Semicarbazide Derivative: [for =C=O gr.]

Take 0.5 g of the sample in a RB flask and dissolve it in 5 ml of 50% alcohol by warming. Dissolve about 0.5 g of semicarbazide hydrochloride and about 1 g of anhydrous sodium acetate in minimum volume of water. Reflux the mixture for 5 minutes under low flam with constant shaking. Cool the mixture, pour it in into 20 ml of cold water and stir with a glass rod when solid semicarbazone separates. Filter, dry and recrystallise from alcohol or acetic acid. Determine the melting point of the dried derivative.



9. Preparation of Bromo Derivative: [for Ph-OH, Ph-NH_2, Ph-C=C-COOH]

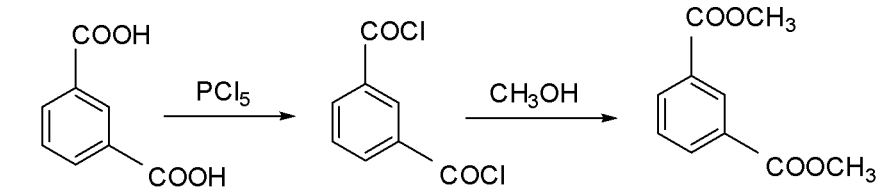
Dissolve 0.5 g of the sample in about 2 ml of glacial acetic acid in a dry test tube. Now add drop by drop Br_2 solution with constant shaking (prepared by add 1 ml liquid Br_2 in 3 ml of glacial acetic acid) till slight yellow color persists in the solution. Warm the mixture for few minutes over a steam bath. Cool, pour the reaction product of the test tube into about 20 ml of cold water taken in a beaker. Bromo derivative will separate out. Filter, wash with cold water, recrystallised from alcohol and determine the m.p. of the derivative.



10. Preparation of Methyl Ester Derivative :

Place 0.5 g of the sample in a dry mortar with 2 g of PCl_5 and triturate it with a pestle inside of a fume cupboard until it is converted to a liquid. Add about 5 ml of methanol and stir. Allow to stand the mixture for 10-15 minutes and then add 10

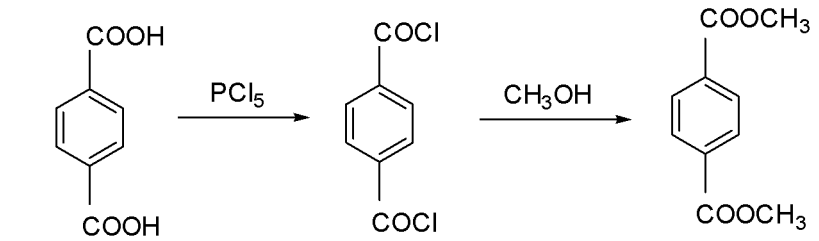
ml of water. Filter, wash the solid with little cold water. Crystallize from aqueous methanol and determine the m.p. of the derivative.



Iso-phthalic acid

MP 113^{0}C

MP 64^{0}C



Terephthalic acid

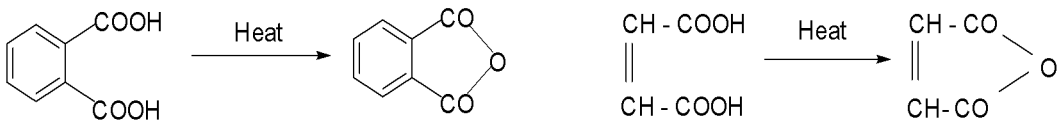
Sublime

MP 140^{0}C

11. Preparation of Anhydrides of Carboxylic acids: [for dibasic acid]

Few dibasic acids, like succinic acid and phthalic acid etc., on heating readily yield their anhydride which may be treated as their derivatives for identification.

Take about 1 g of the sample in a small porcelain basin and place the basin on a sand bath. Place a long stemmed inverted funnel, plugged with cotton, to cover the material. Heat the basin rapidly, cool , and collect the sublimed product from the funnel and determine the m.p. of the product.



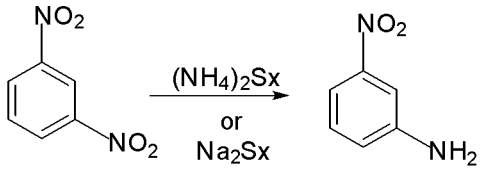
12. Preparation of Derivatives by Reduction :

Aromatic compounds containing one or more than one nitro group(s) can be reduced to amine group completely or partly by using sodium polysulphide.

a) Reduction by Sodium Sulphide or Ammonium Polysulphide:

Take 2 g of pure $Na_2S.\ 9H_2O$, 0.5 g of powdered sulphur and 10 ml of distilled water and heat in a 100 ml beaker till a clear solution is obtained. Dissolve 1 g of

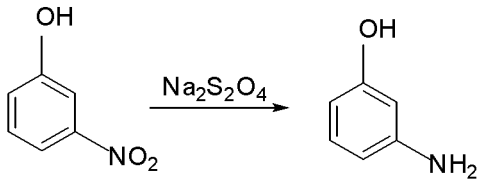
the sample in about 10 ml of alcohol in a 100 ml conical flask, heat to boiling. Now add drop by drop the prepared polysulphide solution to the sample solution at boiling condition with constant stirring for 10-15 minutes. Keep the mixture at boiling condition through out process. Cool, filter under suction and wash with cold water. Collect the solid and dissolve in dil. HCl (warm if necessary) and then filter off to remove excess sulphur or unreacted starting material if any present. Alkaline the filtrate with excess NH_4OH solution to precipitate amino- compound. Filter, recrystallise from boiling water and determine the m.p. of the product.



b) Reduction by Sodium Hyposulphide:

(This reduction is best for nitro phenols.)

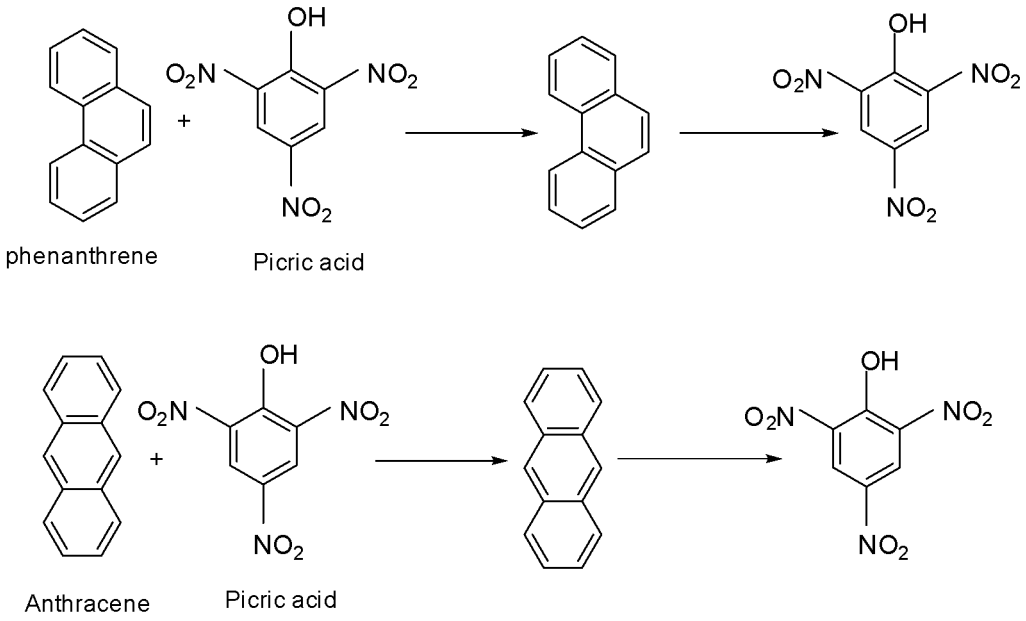
Take about 1 g of the sample, 15 ml of distilled water and 5 g of $NaHSO_3$ in a round bottomed flask. Heat the mixture and zinc- dust in such a way that the solution begins to boil and pour 1 ml of HCl. If no yellow colouration is obtained after placing a drop of the solution on a filter paper indicate the completion of the reduction. Filter the mixture at hot condition and cool the filtrate. The solid is then filtered, recrystallised from hot water and determine the m.p. of the product.



13. Preparation of Picrate Derivative:

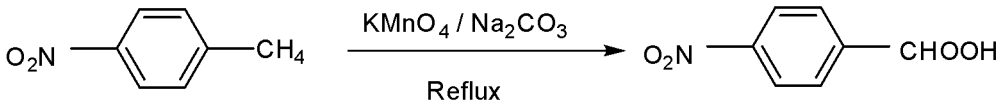
Prepare about 2 ml of saturated solution of picric acid and mix with saturated solution of 0.5 g of sample in benzene and shake the mixture. Allow to stand the mixture for few minutes. Filter, wash the precipitate with few drops of benzene. Dry the precipitate on blotting paper and determine the m.p. of the derivative.

[NB: Alcohol or glacial acetic acid may be employed but protic solvents tend to dissociate picrates]



a) Oxidation by Alkaline $KMnO_4$:

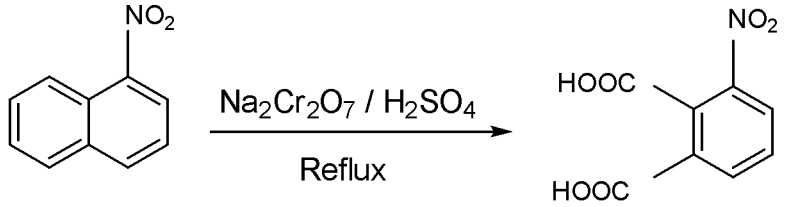
Take about 0.5 g of the sample, 1 g of Na_2CO_3, 2 g finely powdered $KMnO_4$ in 100 ml R.B flask fitted with condenser. Add about 50 ml of water and reflux for about 1 hour until the pink colour of $KMnO_4$ has been discharged. (If required excess $KMnO_4$ can be removed by $NaHSO_3$). Cool the mixture and acidify with dil H_2SO_4. Filter the solid under suction, wash with cold water till acid free. Recrystallise from alcohol- water mixture, dry and determine the m.p. [This oxidation can be carried out using NaOH instead of Na_2CO_3 and acidify with conc. HCl at cold condition].



b) Oxidation by Chromic Acid:

Take about 0.5 g of the sample, 1.5 g of $Na_2Cr_2O_7$ and about 5 ml of water in a round bottomed flask (R.B) fitted with a condenser. Add dropwise 3 ml of conc. H_2SO_4 to the suspension of the mixture in RB flask. Reflux the mixture for about 30 minutes. Cool and filter the product under suction. Purify the product after dis-

solution in aqueous Na_2CO_3 solution and then acidify with H_2SO_4 to precipitate the acid product. Filter, recrystallise from dil. Alcohol and determine the m.p.



11.3.7 Conclusion:

Hence the given sample(No.....) N, S, Cl, Br, I is/are present/absent as characteristic element/s and contains ..... functional group(s).

The probable compound is ..... (from literature)

11.3.8 Chemical reactions Involve in Organic Qualitative Analysis:

A. Lassaingne's test :

When an organic compound containing N, S or X (halogens) is fused with sodium metal, the compound decomposes and the elements are converted into sodium salt of CN^-, SCN^-, S^{-2} and X^- (Cl^-, Br^- and I^-).

$$\text{C, H, O, N, S, X (Haloges)} \xrightarrow{\text{Fusion with sodium metal}} \text{NaCN, NaSCN, } Na_2S\text{, NaX}$$

$$Na + C\ N = NaCN$$

$$Na + C + N + S = NaSCN$$

$$2Na + S = Na_2S$$

$$Na + X\ (cl, Br, I) = NaX$$

$$2Na + 2H_2O = 2NaOH + H_2$$

1. Test for Nitrogen:

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4$$

$$Fe(OH)_2 + 2NaCN = Fe(CN)_2 + 2NaOH$$

$$FeSO_4 + 2NaCN = Fe(CN)_2 + Na_2SO_4$$

$$Fe(CN)_2 + 4NaCN = Na_4[Fe(CN)_6]$$

$$3Na_4[Fe(CN)_6] + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 12NaCl$$

2.

3. Test for Sulphur:

$$Na_2S + (CH_3COO)_2Pb = PbS + 2CH_3COONa$$

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

4.

5. **Test for Nitrogen and Sulphur present together:**

$$Fe^{+3}\ SCN^{-} = [Fe(SCN)]^{+2}$$

Blood red colour

6.

7. Test for Haloges:

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

$$AgCl + 2\,NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2\,H_2O$$

$$NaBr + AgNO_3 \longrightarrow AgBr + NaNO_3$$

$$AgBr + 2\,NH_4OH \longrightarrow [Ag(NH_3)_2]Br + 2\,H_2O$$

$$NaI + AgNO_3 \longrightarrow AgI + NaNO_3$$

$$AgI + NH_3 \longrightarrow \text{Insoluble}$$

B. Reactions of Non-nitrogenous Functional Groups:

1. Test for Carboxylic acid group: (–COOH)

i) $NaHCO_3$ Test:

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2 + H_2O$$

ii) Esterification Test:

$$R - \overset{\overset{O}{\|}}{C} - OH + C_2H_5 - OH \longrightarrow R - \overset{\overset{O}{\|}}{C} - OC_2H_5 + H_2O$$

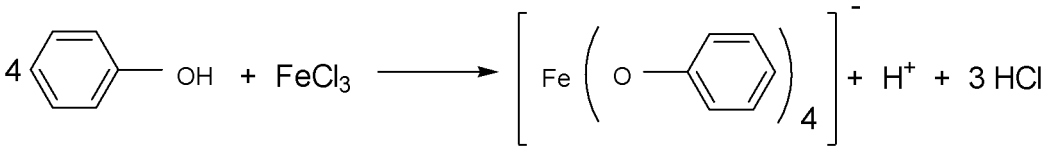
iii) Potassium iodate-iodide test:

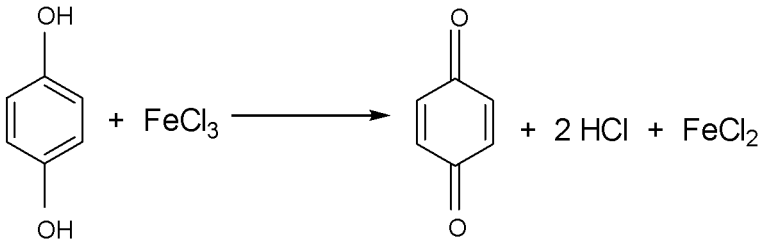
$$6\,Ph\text{-}COOH + 5\,KI + KIO_3 \longrightarrow 3\,I_2 + 6\,Ph\text{-}COOK + 3\,H_2O$$

$$Starch + I_2 \longrightarrow \text{Blue colouration}$$

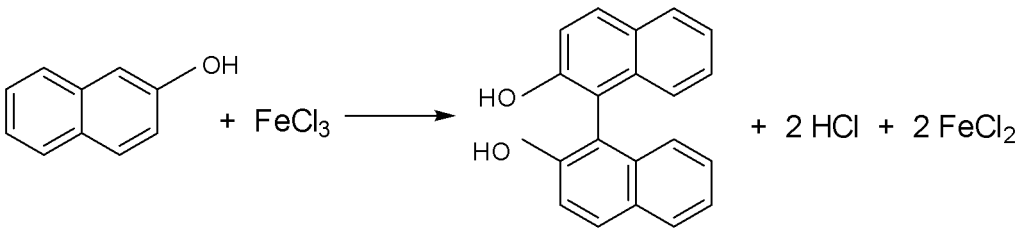
2. Test for Phenolic – OH group :

i) $FeCl_3$ Test :



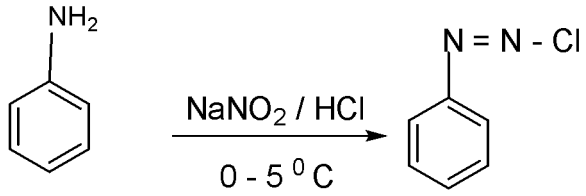


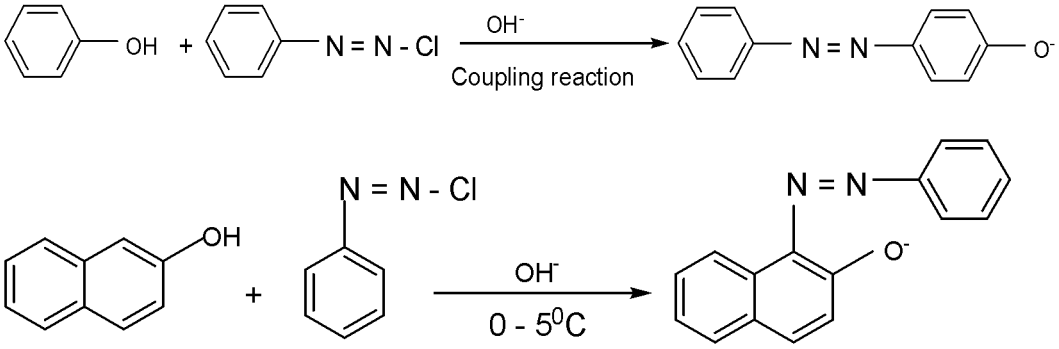
Hydroquinol (Quinol) Benzoquinone



β-Dinaphthol (Green)

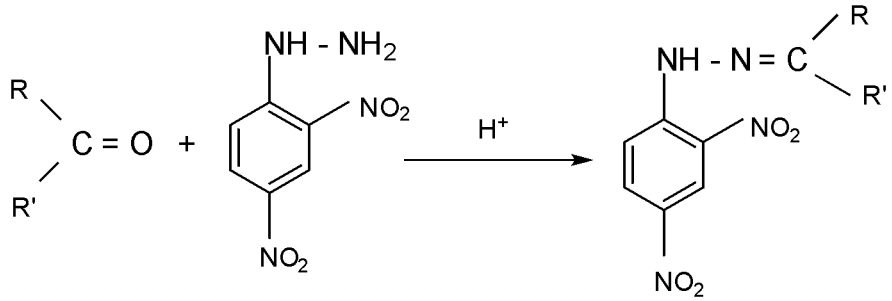
ii) Back Dye Test:





3. Test for Carbonyl group:

i) 2,4 - Dinitrophenyl hydrazine Test:



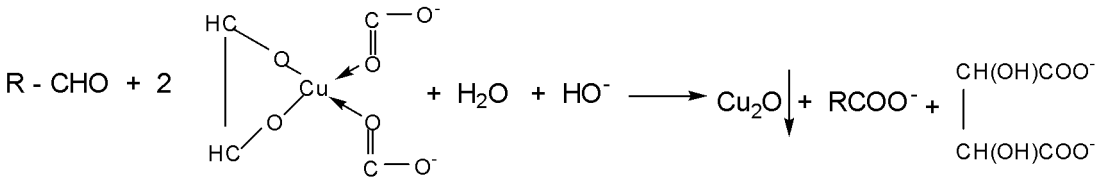
2,4- Dinitrophenyl hydrazone

$Cu_2O + \downarrow RCOOH$

4. Test for Aldehyde group:

i) Fehling's solution Test:

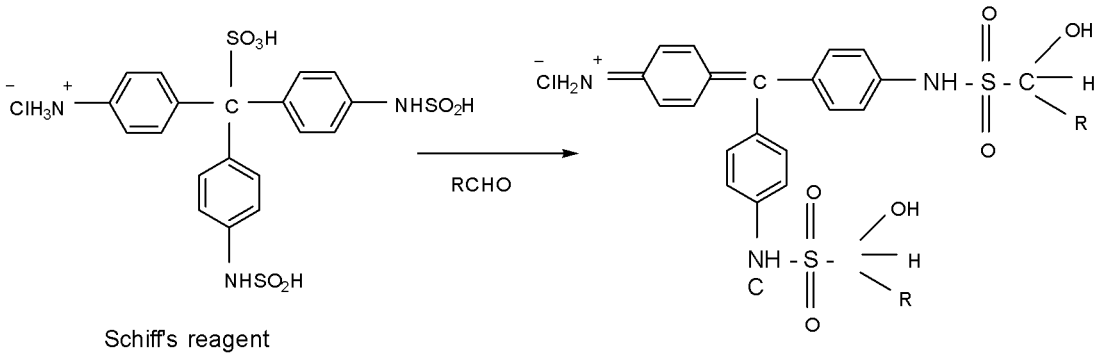
$$RCHO + 2CuO = Cu_2O + \downarrow RCOOH$$



ii) Tollen's Reagent Test:

$$R - CHO + 2\ [Ag(NH_3)_2]OH = 2Ag + RCOONH_4 + H_2O + 3NH_3$$

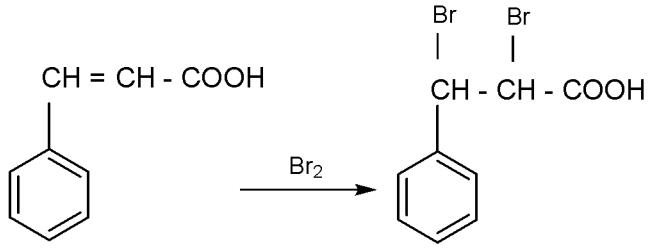
ii) Schiff's Reagent Test :



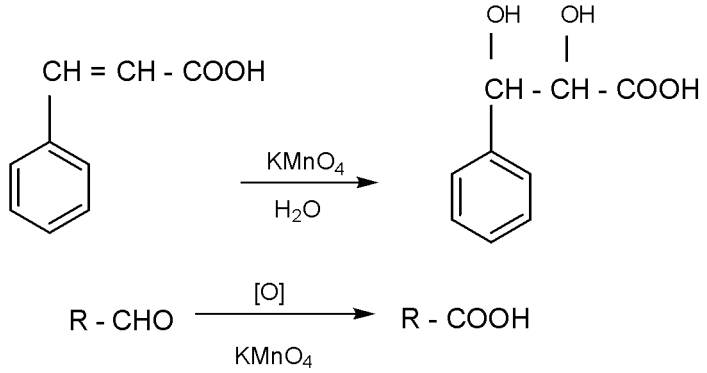
Schiff's reagent

5. Test for Active Unsaturation or Strong Reducing group :

i) Br_2 – water Test;



ii) Baeyer's Test;

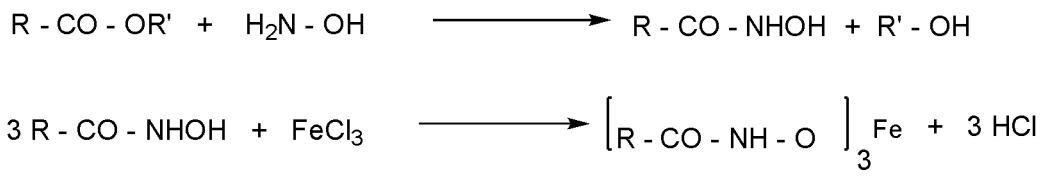


6. Test for Ester group:

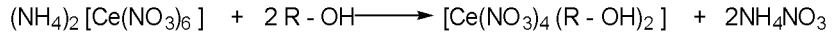
i) Hydrolysis test :

$$Ph - CO - OR + H_2O \rightleftharpoons Ph - CO = OH + R - OH$$

ii) Feigl Test (Hydroxamine test):



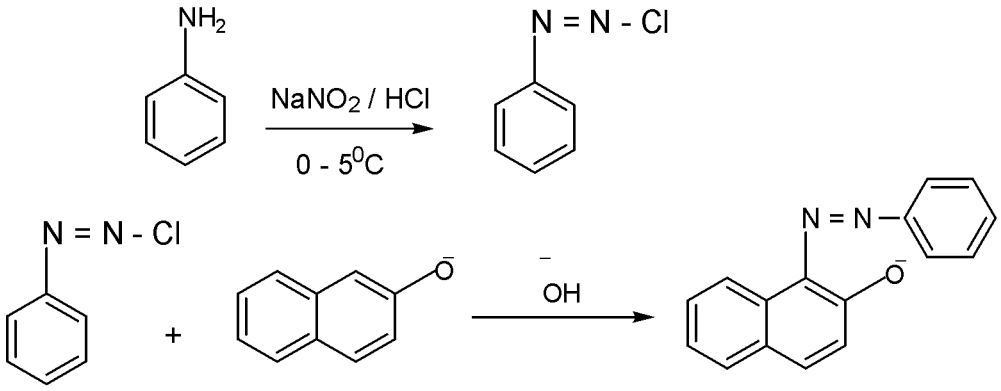
7. Test for Alcoholic –OH group : (Ceric ammonium nitrate test):



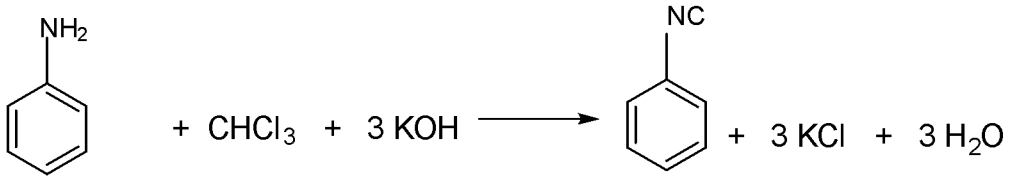
C. Reactions of Nitrogenous Functional Groups:

1. Test for Primary Amine:

i) Dye test:

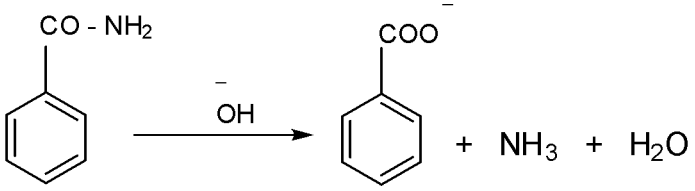


ii) Carbylamine Test:



2. Test for Amido group:

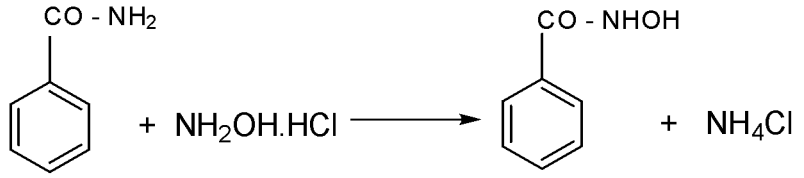
i) Hydrolysis test:

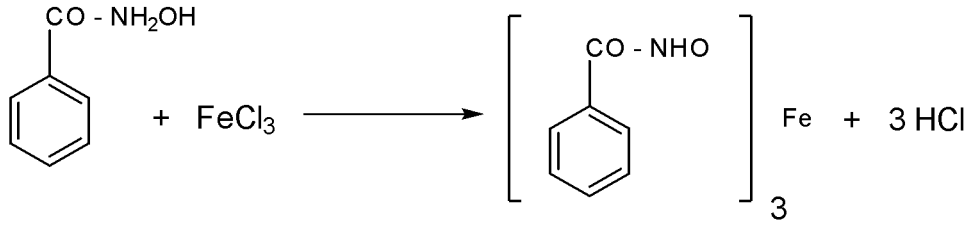


ii) Nitrous acid test:

$$C_6H_5 - CO - NH_2 + HO - N = O \rightarrow C_6H_5 - COOH + N_2 + H_2O$$

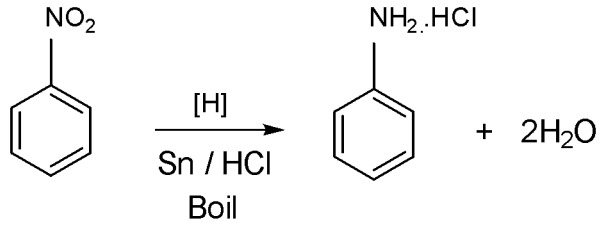
iii) Hydroxylamine hydrochloride test:

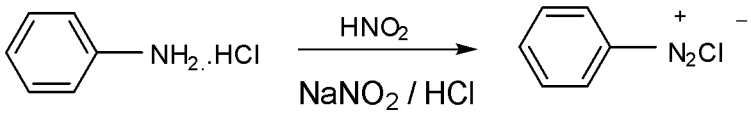


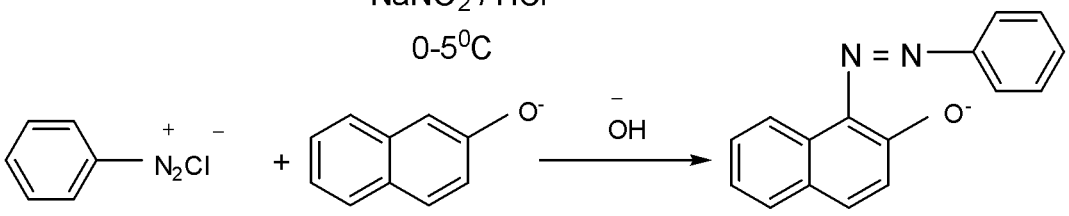


3. Test for Nitro group:

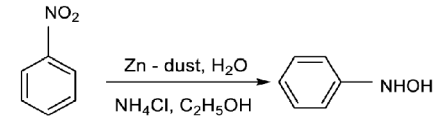
i) Reduction test:

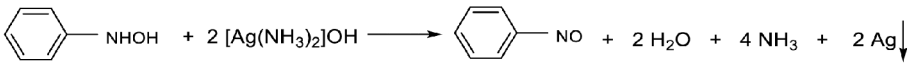






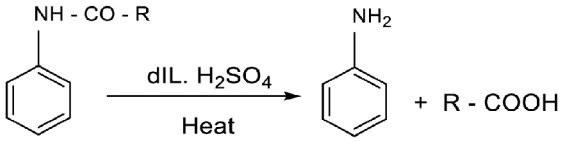
ii) Mulliken - Barker test:





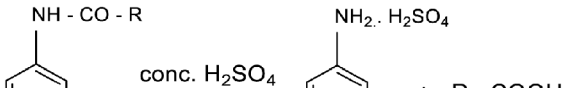
4. Test for Anilido group:

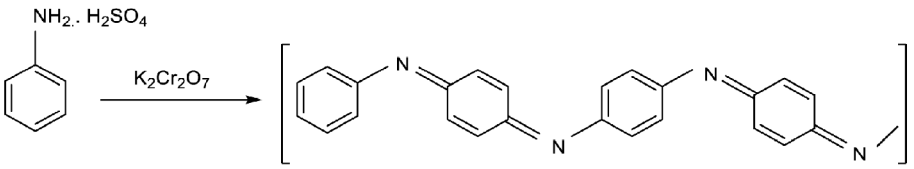
i) Dye test after hydrolysis:



[Same as dye test of aniline]

ii) Tafel's test:

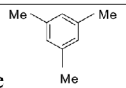




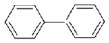
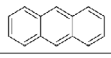
11.4. Important Organic Compounds and properties of their derivatives

A. Hydrocarbon and halogen compounds:

Liquid

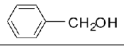
B.P^{0}C	Name of the Compound	Properties and derivatives
80	Cyclohexane 	On addition to the fuming HNO_3 yields adipic acid, M.P. 149^{0}C
142	o-Xylene 	On oxidation with alkaline $KmnO_4$ yields phthalic acid, M.P. 195^{0}C
146	Styrene	On oxidation with alkaline $KmnO_4$ yields benzoic acid, M.P. 121^{0}C
164	 Mesitylene	On oxidation yields trimesic acid , M.P. 300^{0}C ; methyl ester M.P. 143^{0}C , ethyl ester M.P. 133^{0}C

Solid

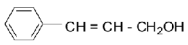
M.P^{0}C	Name of the Compound	Properties and derivatives
70	Diphenyl 	On oxidation by chromic acid in glacial acetic acid yields benzoic acid, M.P. 1210C
216	Anthracene 	Oxidised to anthraquinine M.P. 2720C ; Picrate M.P. 1380C
80	Naphthalene 	Oxidised to phthalic acid M.P. 1950C ; Picrate M.P. 1490C

B. Alcohol

Liquid

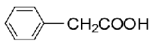
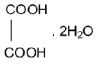
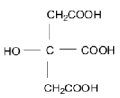
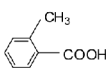
B.P0C	Name of the Compound	Properties and derivatives
160	Cyclohexanol (Hexalin) 	On addition to the fuming HNO3 yields adipic acid, M.P. 1490C
205	Benzoyl alcohol 	Oxidation with acidic or alkaline KMnO4 yields bezoic acid M.P. 1210C

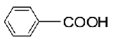
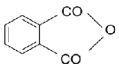
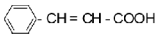
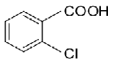
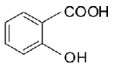
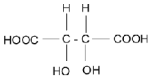
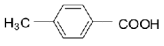
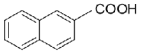
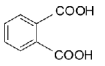
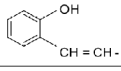
Solid

M.P^{0}C	Name of the Compound	Properties and derivatives
33	Cinnamyl alcohol 	Oxidised to cinnamic acid M.P. 133^{0}C
166	D-manitol	Hexabenzoate M.P. 124^{0}C ; on heating with PCl_5 yields hexachlorohexane M.P. 137^{0}C

C. Carboxylic acid

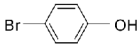
Solid

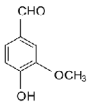
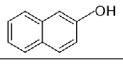
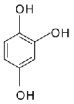
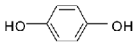
M.P^{0}C	Name of the Compound	Properties and derivatives
76	Phenylacetic acid 	SBT M.P. 165^{0}C; Amide M.P. 154^{0}C ; Anilide M.P. 118^{0}C Oxidation with alkaline $KMnO_4$/NaOH yields benzoic acid M.P. 121^{0}C
100	o-Methoxybenzoic acid 	Amide M.P. 128^{0}C ; Anilide M.P. 131^{0}C
101	Oxalic acid 	SBT M.P 195 (d) ; Dianilide M.P. 246^{0}C
100	Citric acid 	Tri - amide M.P 210^{0}C ; Tri- anilide M.P 192^{0}C ; Methyl ester M.P. 79^{0}C
104	o-Toluic acid 	SBT M.P. 145^{0}C ; Amide M.P. 142^{0}C ; Anilide M.P. 125^{0}C Oxidation with alkaline $KMnO_4$ yields Phthalic acid M.P. 195^{0}C

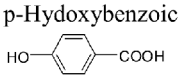
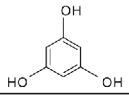
121	Benzoic acid 	SBT M.P. 167^0C ; Amide M.P. 128^0C ; Anilide M.P. 164^0C
131	Phthalic anhydride 	Reflux with acetic acid and urea yields Phthalimide M.P. 238^0C
133	Cinnamic acid 	SBT M.P. 175^0C ; Anilide M.P. 153^0C
137	o-Chlorobenzoic acid 	Amide M.P. 139^0C ; Anilide M.P. 114^0C
150	o-Bromobenzoic acid 	SBT M.P. 171^0C ; Amide M.P. 155^0C ; Anilide M.P. 141^0C
155	Salicylic acid 	SBT M.P. 146^0C ; Amide M.P. 139^0C ; Anilide M.P. 134^0C
162	α- Naphthoic acid 	SBT M.P. 135^0C ; Amide M.P. 205^0C ; Anilide M.P. 205^0C
170	(+) Tartaric acid 	Diamide M.P. 195^0C (d) ; Dianilide M.P. 264^0C
180	p- Toluic acid 	SBT M.P. 185^0c ; Amide M.P. 162^0C ; Anilide M.P. 168^0C
185	Succinic acid 	SBT M.P. 154^0C ; Diamide M.P. 260^0C ; Dianilide M.P. 228^0C
185	β- Naphthoic acid 	Amide M.P. 192^0C ; Anilide M.P. 170^0C
195 (d)	Phthalic acid 	SBT M.P 157^0C ; Ahydride M.P. 131^0C ; Diamide M.P. 220^0C ; Phthalimide M.P. 231^0C
207	o-Coumaric acid 	Amide M.P. 209^0C (d) ; Acetyl M.P. 149^0C

D. Phenol

Solid

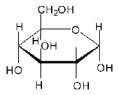
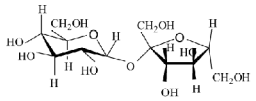
M.P^{0}C	**Name of the Compound**	**Properties and derivatives**
63	p-Bromophenol 	Benzoyl M.P. 102^0C ; With Br_2-water yields tribromophenol M.P. 95^0C
	s-Trichlorophenol	

67		Benzoyl derivative M.P. 70^0C
80	Vanillin 	Oxime M.P. 117^0C Benzoate M.P. 178^0C DNP M.P. 270^0C
94	α- Naphthol 	Benzoate M.P. 56^0C Picrate M.P. 189^0C
104	Catechol 	Dibenzoate M.P. 84^0C
110	Resorcinol 	Dibenzoate M.P. 117^0C
122	β- naphthol 	Benzoate M.P. 107^0C ; Picrate M.P. 156^0C
133	Pyrogallol 	Tribenzoate M.P. 89^0C Triacetate M.P. 165^0C
140	Hydroxyhydroquinone 	Tribenzoate M.P. 120^0C Triacetate M.P. 96^0C
155	Salicylic acid 	SBT M.P. 146^0C Amide M.P. 139^0C Anilide M.P. 134^0C Acetyl M.P. 135^0C
169	Hydroquinol (Quinol) 	Benzoate M.P. 205^0C On mild oxidation yields Benzoquinone (Yellow) M.P. 116^0C and/or Quinohydrone (Green) M.P. 171^0C

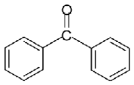
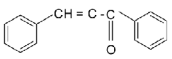
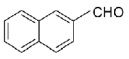
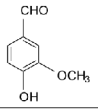
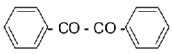
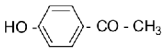
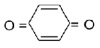
M.P^{0}C	**Name of the Compound**	**Properties and derivatives**
213	p-Hydoxybenzoic acid 	Red colour in $FeCl_3$ test. SBT M.P. 143^0C Anilide M.P. 197^0C
218	Phloroglucinol 	Benzoate M.P. 185^0C Diacetate M.P. 104^0C

E. Carbohydrate

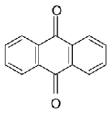
Solid

M.P^{0}C	Name of the Compound	Properties and derivatives
146	D-Glucose 	To the small quantity of the aqueous sample solution, add a few drops of $(CH_3COO)_2Pb$ solution, heat and add 2 ml of dil. NH_4OH solution. Heat again, a rose pink colouration. On oxidation by HNO_3 yields saccharic acid M.P. 125^{0}C Oxime M.P 137^{0}C Phenylosazone M.P. 205^{0}C
169	Sucrose 	No reaction with Fehling's and Tollen's reagents. On oxidation by HNO_3 yields saccharic acid M.P. 125^{0}C

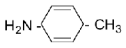
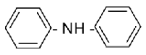
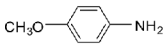
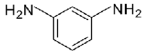
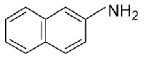
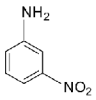
F. Aldehyde , Ketone and Quinine

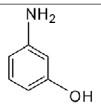
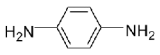
M.P^{0}C	Name of the Compound	Properties and derivatives
48	Benzophenone 	Phenylhydrazone M.P. 137^{0}C Semicarbazone M.P. 164^{0}C 2,4 – Dinitrophenylhydrazone M.P. 229^{0}C
58	Chalcone 	Phenylhydrazone M.P. 118^{0}C Semicarbazone M.P. 168^{0}C 2,4 – Dinitrophenylhydrazone M.P. 244^{0}C
60	β- Naphthaldehyde 	On mild oxidation yields β- Naphthoic acid M.P. 121^{0}C Semicarbazone M.P. 245^{0}C 2,4 – Dinitrophenylhydrazone M.P. 245^{0}C
80	Vanillin 	Oxime M.P. 117^{0}C Benzoate M.P. 178^{0}C 2,4-DNP M.P. 270^{0}C
95	Benzil 	On oxidation with alkaline $KMnO_4$ yields benzoic acid M.P. 121^{0}C
109	p- hydroxyacetophenone 	Semicarbazone M.P. 199^{0}C 2,4 – Dinitrophenylhydrazone M.P. 261^{0}C Benzoate M.P. 134^{0}C
115	p-Benzoquinone 	2,4 – Dinitrophenylhydrazone M.P. 186^{0}C
117	p-Hydroxybenzaldehyde	Phenylhydrazone M.P. 178^{0}C Semicarbazone M.P. 223^{0}C 2,4 – Dinitrophenylhydrazone M.P. 280 ^{0}C

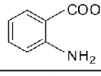
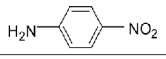
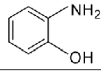
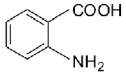
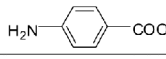
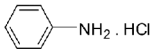
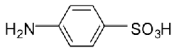
	HO-  -CHO	

M.P^{0}C	Name of the Compound	Properties and derivatives
125	1,4 – Naphthaquinone 	Semicarbazone M.P. 247^{0}C 2,4 – Dinitrophenylhydrazone (mono) M.P. 278 ^{0}C
284	Anthraquinone 	KOH fusion yields Benzoic acid M.P. 121^{0}C On reduction with Sn/HCl yields Anthrone M.P. 155^{0}C

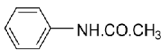
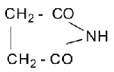
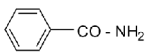
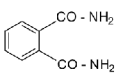
G. Amines (Amine, Aminophenol, Aminoacid, Nitroamine)

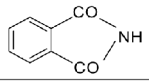
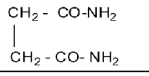
M.P^{0}C	Name of the Compound	Properties and derivatives
45	p- Toluidine 	Benzoyl M.P. 158^{0}C Picrate M.P. 169^{0}C
50	α- Naphthylamine 	Benzoyl M.P. 161^{0}C Picrate M.P. 161^{0}C
53	Diphenylamine 	Benzoyl M.P. 180^{0}C Picrate M.P. 182^{0}C
57	p- Anisidine 	Benzoyl M.P. 154^{0}C Picrate M.P. 117^{0}C
63	m- Phenylenediamine 	Brown precipitate with $NaNO_2$/HCl Dibenzoyl M.P. 240^{0}C
71	o- Nitroaniline 	Benzoyl M.P. 94^{0}C
102	o- Phenylenediamine 	Dibenzoyl M.P. 301^{0}C
111	β- Naphthylamine 	Benzoyl M.P. 162^{0}C Picrate M.P. 195^{0}C
114	m- Nitroaniline 	Benzoyl M.P. 155^{0}C
	m- Aminophenol	Monobenzoyl M.P. 174^{0}C

122		Dibenzoyl M.P. 153^{0}C
140	p- Phenylenediamine 	Boiling with dil. $FeCl_3$ or H_2SO_4/MnO_2 yields Benzoquinone M.P. 115^{0}C Picrate M.P. 202^{0}C

M.P^{0}C	Name of the Compound	Properties and derivatives
147	Anthranilic acid 	Benzoyl M.P. 182^{0}C Amide M.P. 108^{0}C Anilide M.P. 126^{0}C
147	p- Nitroaniline 	Benzoyl M.P. 199^{0}C
174	o- Aminophenol 	Dark brown precipitate with $FeCl_3$ Dibenzoyl M.P. 184^{0}C
174	m- Aminobenzoic acid 	Amide M.P. 75^{0}C Anilide M.P. 129^{0}C Acetyl M.P. 250^{0}C
186	p- Aminobenzoic acid 	Benzoyl M.P. 278^{0}C Amide M.P. 183^{0}C
198(d)	Aniline hydrochloride 	Benzoyl M..P. 163^{0}C Picrate M.P.. 165^{0}C
~300 (d)	Sulphanilic acid 	With Br_2 – water yields 2,4,6 – Tribromoaniline M.P. 119^{0}C

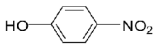
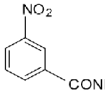
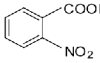
H. Anilides, Amides and Imides

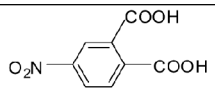
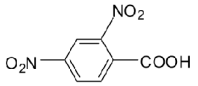
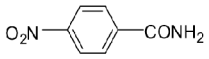
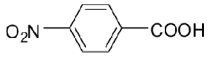
M.P^{0}C	Name of the Compound	Properties and derivatives
114	Acetanilide 	On nitration with c. HNO_3 / c. H_2SO_4 yields p-Nitroaniline M.P. 147^{0}C
125	Succinamide 	On hydrolysis with HCl yields Succinic acid M.P. 185^{0}C
128	Benzamide 	On hydrolysis yields benzoic acid M.P. 121^{0}C
219 (d)	Phthalamide 	On heating yields Phthalimide M.P. 231^{0}C On hydrolysis yields Phthalic acid M.P. 195^{0}C

233	Phthalimide 	On hydrolysis with NaOH yields Phthalic acid M.P. 195^{0}C
242	Succinamide 	On heating yields Succinimide M.P. 125^{0}C On hydrolysis with NaOH yields Succinic acid M.P. 185^{0}C

I. Nitro Compunds

Nitro – Acids, Phenols, Halides, Aldehydes and Ketones.

M.P^{0}C	Name of the Compound	Properties and derivatives
44	o-Nitrobenzaldehyde 	On oxidation with $KMnO_4$ yields o-Nitrobenzoic acid M.P. 144^{0}C Phenylhydrazone M.P. 156^{0}C Semicarbazone M.P. 256^{0}C 2,4- Dinitrophenylhydrazone M.P. 192^{0}C
45	o-Nitrophenol 	Benzoate M.P. 142^{0}C Reduction by boiling with Zn-dust and $CaCl_2$ solution yields o-Aminophenol M.P. 174^{0}C
52	p-nitrotoluene 	Oxidation by $KMnO_4$ or $K_2Cr_2O_7$ yields p-Nitrobenzoic acid M.P. 241^{0}C
80	m-Nitroacetophenone 	Semicarbazone M.P. 261^{0}C 2,4- Dinitrophenylhydrazone M.P. 233^{0}C
90	m-Dinitrobenzene 	Boling with alkaline $K_3Fe(CN)_6$ yields 2,4-Dinitrophenol M.P. 114^{0}C Reduction with NH_4SH yields m-Nitroaniline M.P. 114^{0}C
97	m-Nitrophenol 	Reduction with Zn-dust and $CaCl_2$ solution yields m-Aminophenol M.P. 122^{0}C Benzoate M.P. 95^{0}C
114	p-Nitrophenol 	Benzoate M.P. 142^{0}C
143	m-Nitrobenzamide 	On hydrolysis with dilute NaOH yields m-Nitrobenzoic acid M.P. 140^{0}C
146	o-Nitrobenzoic acid 	Reduction with Sn/HCl yields Anthranilic acid M.P. 144^{0}C Amide M.P. 176^{0}C Anilide M.P 155^{0}C
	4-Nitrophthalic acid	Anilide M.P. 192^{0}C

165		Amide M.P. 200^0C (d)
183	2,4-Dinitrobenzoic acid 	Amide M.P. 203^0C
201	p-Nitrobenzamide 	On hydrolysis with dilute NaOH yields p-Nitrobenzoic acid M.P. 241^0C
241	p-Nitrobenzoic acid 	Amide M.P 201^0C Anilide M.P. 211^0C Methyl ester M.P. 96^0C

11.5 Summary

- Initial examination involves observing physical properties such as color, state, odor, and determining the melting point, which helps narrow down possible identities of the compound.
- The solubility of the compound in water, organic solvents, acids, and bases provides insights into its polarity and possible functional groups.
- Tests like Lassaigne's test are used to detect the presence of elements such as nitrogen, sulfur, and halogens in the compound.
- Specific chemical tests are conducted to identify functional groups, including tests for alcohols, aldehydes, ketones, carboxylic acids, amines, phenols, and esters.
- Additional tests are performed to confirm the presence of specific functional groups, ensuring the accuracy of the analysis.
- Derivatives of the compound may be prepared to confirm the functional groups and aid in identifying the compound.
- All data from physical observations, solubility tests, elemental analysis, and functional group identification are compiled to deduce the structure and identity of the compound.

11.6 Question

1. For what purpose Leissanigene's test is used?

Ans: To dedect the presence of nitrogen, sulphur and halogens in organic compound.

2. Can, potassium or calcium or magnesium be used in place of sodium metal in Leissanigene's test?

Ans: No; potassium is too reactive and hence dangerous whereas calcium and magnesium are less reactive.

3. Why dry fusion tube is used in Leissanigene's test?

Ans: If water present in fusion tubes it will then react with sodium metal and make it inactive.

$2\ Na + 2\ H_2O = 2\ NaOH + H_2$

4. What is Baeyer's reagent?

Ans: 1% alkaline $KMnO_4$ solution is known as Baeyer's reagent.

5. What is the use of Baeyer's reagent in qualitative organic analysis?

Ans: Baeyer's reagent is used to detect the unsaturation or presence of easily oxidisable group in organic compound.

6. Is there any test common to both alcohol and phenol?

Ans: Yes; ceric ammonium nitrate test - alcohols produce amber red colour while phenols give greenish brown colour or precipitate.

7. What is Fehling's solution?

Ans: Fehling's solution is the mixture of two solutions.

Fehling - A : 7% $CuSO_4$ solution

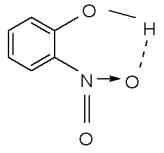
Fehling - B : Rochelle salt (sodium potassium tartarate) in 10% NaOH solution

8. What reaction happen when Fehling's solution is treated with aldehyde?

Ans: $R\text{-}CHO + 2\ Cu(OH)_2 = R\text{-}COOH + Cu_2O \downarrow + 2\ H_2O$

9. Why o–Nitro phenol dose not give $FeCl_3$ test for phenolic group?

Ans: Because o-Nitro phenol dose not have free phenolic group due to the formation of strong intramolecular hydrogen bonding between nitro group ($-NO_2$) and phenolic (-OH) group.



10. Why is the solution finally acidified for the detection of nitrogen in Leissanigene's test?

Ans: Prussian blue is stable in acid medium but decomposed to brown precipitate of $Fe(OH)_3$ in alkaline medium.

$$\underset{\text{Blue}}{Fe_4[Fe(CN)_6]_3} + 12\,NaOH \longrightarrow \underset{\text{Brown}}{4\,Fe(OH)_3} + \underset{\text{Colourless}}{3\,Na_4[Fe(CN)_6]}$$

11. Why is blood red colouration sometimes obtained on addition of $FeCl_3$ solution to sodium extract?

Ans: NaCNS is produced, if inadequate sodium metal is used during fusion process, which then reacts with $FeCl_3$ solution as follows;

$$3\,NaCNS + FeCl_3 \longrightarrow 3\,NaCl + Fe(CNS)_3$$

$$Fe(CNS)_3 + 3\,NaCNS \longrightarrow Na_3[Fe(CNS)_6]$$

$$Na_3[Fe(CNS)_6] + FeCl_3 \longrightarrow 3\,NaCl + \underset{\text{(Red)}}{Fe[Fe(CNS)_6]}$$

12. Why the decolourisation of Br_2-water dose not necessarily mean the presence of unsaturation in compound?

Ans: The colour of Br_2-water may disappear due to substitution in the aromatic ring containing strong +R group eg., –OH. $-NH_2$ etc.

13. Why dose benzoin response to Tollen's test?

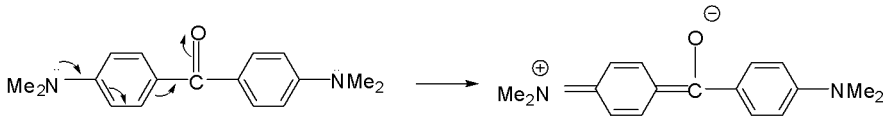
Ans: The –CO. CHOH – group present in benzoin shows reducing properties like –CHO group.

14. Why the violet colur of iodine disappear during further addition of excess Cl_2 – water in Leissanigene's test?

Ans: Excess chlorine reacts with iodine to produce colourless ICl, iodine monochloride, an interhalogen compound.

15. Why Mischler's ketone does not response to D.N.P. test?

Ans: Due to extensive delocalisation of electron pair diminishes the reactivity of the = C=O group.



16. Why a green coloured solution sometimes obtained in the Leissanigene's test for nitrogen?

Ans: This is due to the incomplete sodium fusion and combination of yellow colour of Fe^{+3}.

17. Why is some time black coloured solution obtained on addition of $FeSO_4$ solution to sodium extract?

Ans: If S is present in the sample, during sodium fusion it prodeces Na_2S which then on reaction with $FeSO_4$ produces black precipitate of FeS.

$$Na_2S + FeSO_4 = FeS + Na_2SO_4$$

18. Why a violet colour is observed during chlorine water test for iodine containing organic samples?

Ans: NaI formed liberates I_2 is dissolved in organic layer giving violet colouration.

$$2\ NaI + Cl_2 = 2\ NaCl + I_2\ (violet)$$

as the liberated iodine has greater solubility in CCl_4 layer than in water.

19. What test do you suggest for nitroanilides and nitroanilines?

Ans: Mulliken and Barker's test.

Module-V

Quantitative Analysis of Organic Compounds

Unit – 12 ❑ Quantitative Analysis – I

Structure

12.1 Objective
12.2 Introduction
12.3 Estimation of Glycine by Sorensen Formal Method
12.3.1 Principle
12.3.2 Chemicals Required
12.3.3 Procedure
12.3.4 Experimental Results
12.3.5 Calculation
12.4 Estimation of Glucose by Titration using Fehling's Solution
12.4.1 Principle
12.4.2 Chemicals Required
12.4.3 Procedure
12.4.4 Experimental Results
12.4.5 Calculation
12.5 Estimation of Sucrose by Titrating Using Fehling's Solution
12.5.1 Principle
12.5.2 Chemicals Required
12.5.3 Procedure
12.5.4 Experimental Results
12.5.5 Calculation
12.6 Summary
12.7 Question

12.1 Objective

By the end of this chapter, students should be able to–

- Understand the principle behind Sörensen's formal method for glycine estimation.

- Grasp the principle of Fehling's solution in estimating glucose concentration. Learn the method of using Fehling's solution to estimate sucrose indirectly through glucose.
- Perform the titration process and Analyze the titration results to calculate the concentration of the organic molecules in solutions

12.2 Introduction

Quantitative analysis of organic compounds is a crucial aspect of chemistry that involves determining the amount or concentration of specific organic substances within a sample. This unit explores the principles, methods, and techniques used to quantify organic compounds, providing essential insights into their chemical composition and purity.

In this unit, students will delve into various titrimetric methods, which are commonly employed in both academic research and industrial applications to estimate the concentrations of organic molecules. By the end of this unit, students will be equipped with the knowledge and skills necessary to perform quantitative analysis of organic compounds, making them proficient in an essential area of chemical science that underpins many advancements in fields ranging from pharmaceuticals to food chemistry.

12.3 Estimation of Glycine by Sorensen Formal Method

The Sorensen formaldehyde method is a classical method used for the estimation of amino acids, particularly glycine. This method relies on the reaction between formaldehyde and the amino group of the amino acid, which forms a Schiff base, effectively neutralizing the amino group. The amount of free amino acid can then be determined by titration. It is to note that, amino acids contain a secondary amine group (-NH group)suchasProline and Hydroxyproline do not respond in the estimation of glycine by the Sorensen formaldehyde method due to their secondary amine structure.

12.3.1 Principle

Amino acids are amphoteric character in aqueous solution because they exist in equilibrium in both the cationic and anionic forms. This dipolar ion is known as Zwiter ion. For this reason amino acids cannot be titrated directly with alkali.

$$H_2N - CHR - COOH \rightleftharpoons^{H_2O} H_3N^{\oplus} - CHR - COO^{\ominus}$$

So glycine is first treated with formaldehyde to produce N-methylene glycine. Thus the basic character of glycine is lost and the product is now only acidic in nature, which can be titrated with standard alkali solution directly.

$$H_2N - CH_2 - COOH + HCHO \longrightarrow H_2C = N - CH_2 - COOH + H_2O$$

Glycine N-methylene glycine

$$H_2C = N - CH_2 - COOH + NaOH \longrightarrow H_2C = N - CH_2 - COONa + H_2O$$

1000 ml (N) NaOH solution ≡ 1 g equivalent of glycine ≡ 75 g of glycine

Molarity of NaOH × Volume of NaOH used = Moles of glycine

Mass of glycine = Moles of glycine × Molar mass of glycine (75.07 g/mol)

12.3.2. Chemicals Required

(i) Standard ~ 0.1 (N) oxalic acid solution

(ii) ~ 0.1 (N) NaOH solution (0.4 g in 100 ml of distilled water)

(iii) Formalin solution (40% aqueous solution of formaldehyde)

(iv) Phenolphthalein indicator

(v) Glycine solution (Unknown) [Dissolve 15 g of glycine in 100 ml of distilled water and supply 4–6 ml to each student].

12.3.3. Procedure

1. Preparation of 250 ml 0.1 (N) Standard Oxalic Acid Solution :

Weigh out accurately ~ 1.5758 g of oxalic acid and dissolve it in 250 ml of volumetric flask with distilled water.

∴ Strength of Oxalic acid = Weight taken (w)/ 1.5758(N/10) = S (N)

2. Standardization of NaOH solution :

Standardize the NaOH solution with the standard oxalic acid solution using phenolphthalein indicator.

3. Preparation of glycine solution :

Make up the volume of given unknown solution of glycine to 100 ml in a volumetric flask.

4. Estimation of glycine :

Take 10 ml ,of formalin solution in a 250 ml conical flask, add 25 ml of distilled water and 1-2 drops of phenolphthalein indicator. Neutralize with standard NaOH solution, adding drop by drop from burette till pink colour appears. Ignore the titre value.

Pipette out 25 ml of the supplied glycine solution in another 250 ml of conical flask, add 1-2 drops of phenolphthalein indicator and titrate with standard NaOH solution by adding drop by drop from burette till pink colour appears. Ignore the titre value and fill the burette with same NaOH solution to the zero mark.

Now transfer the above neutralised formalin solution to the above glycin solution and then titrate with standard NaOH solution until the solution just turns to pink colour.

12.3.4. Experimental Results

Table-1 : Preparation of 0.1 (N) Standard Oxalic Acid Solution :

Initial weight (g)	Final weight (g)	Weight taken (g)
W_1	W_2	$W = W_1 - W_2$

Table - 2 : Standardisation of NaOH solution

No. of obs.	Volume of oxalic acid (ml)	Burette reading		Volume of NaOH (ml)	Mean volume of NaOH (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

Strength of NaOH solution : $25 \text{ ml} \times S(N) = V_1 \text{ ml} \times S_1$

$\therefore S_1 = 25 \times S / V_1 \text{ (N)}$

Table - 3 : Estimation of Glycine

No. of obs.	Volume of glycine acid (ml)	Burette reading		Volume of NaOH (ml)	Mean volume of NaOH (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_2
3.	25	...	...	...	

12.3.5 Calculation

Strength of NaOH solution = S_1 (N)

25 ml glycine solution ≡ V_2 ml S_1 (N) NaOH solution

≡ $V_2 \times S_1$ ml (N) NaOH solution

We have, 1000 ml (N) NaOH solution ≡ 75 g of glycine

$\therefore$ $V_2 \times S_1$ ml (N) NaOH solution ≡ $0.075 \times V_2 \times S_1$ g of glycine / 25 ml

≡ $0.075 \times V_2 \times S_1 \times 40$ g of glycine / 1000 ml

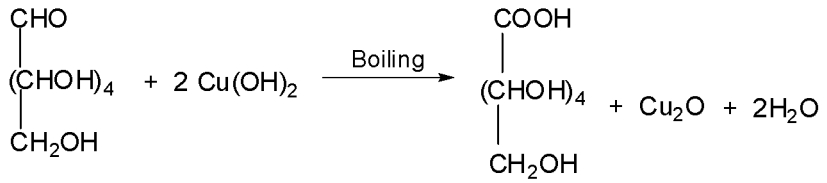
$\therefore$ Amount of glycine in supplied solution = $0.075 \times V_2 \times S_1 \times 40$ g / lit.

12.4 Estimation of Glucose by Titration using Fehling's Solution

The estimation of glucose using Fehling's solution is a classic method in analytical chemistry, particularly useful in educational settings for demonstrating the principles of redox titration. Fehling's solution is a mixture of two solutions: Fehling's A (copper(II) sulfate solution) and Fehling's B (alkaline tartrate solution). The method relies on the reducing property of glucose, which reduces copper(II) ions (Cu^{2+}) in Fehling's solution to copper(I) oxide (Cu_2O), a red precipitate.The amount of glucose can be determined by titrating it with a known concentration of Fehling's solutions.

12.4.1. Principle

Glucose oxidised to gluconic acid by Fehling's solution under boiling condition and Fehling's solution itself reduced to red cuprous oxide.



The Fehling's solution is first standardised by tritrating with standard glucose solution using methylene blue as indicator.

The unknown glucose solution is then estimated by using this standardised Fehling's solution.

12.4.2. Chemicals Required

(i) Standard glucose solution

(ii) Fehling's solution – A

(iii) Fehling's solution – B

(iv) Methylene blue indicator

(v) Glucose solution [Dissolve 55 g of glucose in 100 ml of distilled water and supply 9 - 12 ml to each student]

12.4.3. Procedure :

1. Preparation of Fehling's solution – A :

Dissolve 17.32 g $CuSO_4.5H_2O$ in 250 ml of distilled water in a volumetric flask.

2. Preparation of Fehling's solution – B :

Dissolve about 8.65 g of Rochelle salt (sodium potassium tartarate) and about 25 g of NaOH in a 250 ml volumetric flask, dilute up to the mark with distilled water and mix uniformly.

3. Preparation of glucose solution :

Make up the volume of given unknown solution of glucose to 250 ml in a volumetric flask.

4. Preparation of Standard Glucose Solution :

Weigh out accurately ~ 1.25 g of A.R glucose in 250 ml volumetric flask, dissolve and diluted up to the mark with distilled water.

5. Standardisation of Fehling's solution :

Pipette out 10 ml of Fehling's solution – A and Fehling's solution – B separately in a clean 250 ml conical flask. Add 20 ml of distilled water. Boil the mixture on a wire-gauge. Place 1-2 pieces of glass beads as anti bumping. Add standard glucose solution dropwise in the boiling condition from a burette till the colour of the supernatant liquid appears pale blue. Add 3-4 drops of methylene blue indicator and continue the titration keeping the solution in boiling condition till the blue colour discharged with simultaneous settling down of a bright red precipitate of cuprous oxide.

6. Estimation of supplied glucose solution with the standardised Fehling's solution :

Wash the burette with distilled water after removing the glucose solution and then rinse with the supplied glucose solution. Fill the burette with suppled glucose solution and follow the procedure mentioned above.

[Note : Without using methylene blue the titration may be carried out.]

12.4.4. Experimental results

Table - 1 : Preparation of Standard Glucose Solution :

Initial weight (g)	Final weight (g)	Weight taken (g)
W_1	W_2	$W = W_1 - W_2$

Table - 2 : Standardisation of Glucose solution

No. of obs.	Volume of Fehling's solution (ml)	Burette reading		Volume of Glocose solution (ml)	Mean volume of Standard glucose solution (ml)
		Initial	Final		
1.	20	0	...	...	
2.	20	...	...	...	V
3.	20	...	...	...	

Table - 3 : Estimation of Supplied Glucose Solution

No. of obs.	Volume of Fehling's solution (ml)	Burette reading		Volume of NaOH (ml)	Mean volume of NaOH (ml)
		Initial	Final		
1.	20	0	...	...	
2.	20	...	...	...	V_1
3.	20	...	...	...	

12.4.5 Calculation

20 ml Fehling's solution ≡ V ml of standard glucose solution

250 ml standard glucose solution ≡ W g of glucose

V ml of standard glucose solution ≡ $W \times V/250$ g of glucose

$\therefore$ V_1 ml of the supplied glucose solution ≡ V ml of standard solution

≡ $W \times V/250$ g of glucose

$\therefore$ 1000 ml of supplied glucose solution ≡ $(W \times V/V_1) \times 4$ g of glucose

$\therefore$ Amount of glucose present in supplied solution = $(W \times V/V_1) \times 4$g

$\therefore$ % of glucose present in supplied solution = $(W \times V/ V1) \times 0.4$ g

Note :

The entire titration should be completed within 3-4 minutes.

The solution should be shaken before use.

Titration should be done under boiling condition to prevent the backward aerial oxidation.

12.5 Estimation of Sucrose by Titrating Using Fehling's Solution

Estimating sucrose using Fehling's solution involves a few additional steps compared to the direct titration of reducing sugars like glucose. This is because sucrose is a non-reducing sugar, meaning it does not react directly with Fehling's solution. To estimate sucrose, it must first be hydrolysed into its constituent reducing sugars, glucose, and fructose, which can then be titrated using Fehling's solution. This method can be used in laboratories for the analysis of sugar content in various food products.

12.5.1 Principle

Sucrose is non-reducing sugar, so it can be estimated by converting it into two reducing sugars by hydrolysis viz. D-(+)- glucose and D-(–)- fructose by boiling with dilute HCl.

$$C_{12}H_{22}O_{11} \quad H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

$\therefore$ 342 g of sucrose = 360 g of inverted sugar

These inverted sugars are titrated with standard Fehling's solution using methylene blue as indicator.

Amount of sucrose (g)

$$= \frac{\text{Volume of sucrose solution (mL)} \times \text{Molarity of Fehlings solution (M)}}{\text{Molecular weight of sucrose (342.30g/mol)}}$$

12.5.2 Chemicals Required

(i) Standard glucose solution

(ii) Fehling's solution – A

(iii) Fehling's solution – B

(iv) Supplied sucrose solution [Dissolve 55 g of sucrose in 100 ml of distilled water and supply 9 – 12 ml to each student]

(v) Methylene blue indicator

12.5.3 Procedure

1. **Preparation of standard glucose solution :**

   Weigh out accurately about 1.25 g of A.R. glucose and dissolve in distilled water in 250 ml volumetric flask.

2. **Preparation of Fehling's solution – A :**

   Dissolve 17.32 g $CuSO_4.5H_2O$ in 250 ml of distilled water in a volumetric flask.

3. **Preparation of Fehling's solution – B :**

   Dissolve about 8.65 g of Rochelle salt (sodium potassium tartarate) and about 25 g of NaOH in a 250 ml volumetric flask, dilute up to the mark with distilled water and mix uniformly.

4. **Preparation of sucrose solution :**

   Make up the volume of given unknown solution of sucrose to 100 ml in a volumetric flask.

5. **Standardisation of Fehling's solution with standard glucose solution :**

   Pipette out 10 ml of Fehling's solution - A and Fehling's solution - B separately in a clean 250 ml conical flask. Add 20 ml of distilled water. Boil the mixture on a wire-gauge. Place 1-2 pieces of glass beads as anti bumping. Add standard glucose solution dropwise in the boiling condition from a burette till the colour of the supernatant liquid appears pale blue. Add 3-4 drops of methylene blue indicator and continue the titration keeping the solution in boiling condition till the blue colour discharged with simultaneous settling down of a bright red precipitate of cuprous oxide.

6. **Estimation of supplied sucrose solution with the standardised Fehling's solution:**

   Pipette out 25 ml of the supplied sucrose solution in a 250 ml conical flask and dilute to 100 ml with distilled water. Add 5 ml of conc. HCl and heat to about 60 – 70°C on a steam bath for 15 - 20 minutes. The inversion takes place, cool the solution. Neutralise with 30% NaOH solution using methyl red (or orange) as indicator. Transfer the solution quantitatively in a 250 ml volumetric flask and then diluted with distilled water up to the mark.

   Pipette out 10 ml of Fehling's solution - A and Fehling's solution - B separately in a clean 250 ml conical flask. Add 20 ml of distilled water. Boil the mixture on a wire-gauge. Place 1-2 pieces of glass beads as anti bumping. Add standard glucose solution dropwise in the boiling condition from a burette till the colour of the supernatant liquid appears pale blue. Add 3-4 drops of methylene

blue indicator and continue the titration keeping the solution in boiling condition till the blue colour discharged with simultaneous settling down of a bright red precipitate of cuprous oxide.

12.5.4 Experimental Result

Table – 1 : Preparation of Standard Glucose Solution :

Initial weight (g)	Final weight (g)	Weight taken (g)
W_1	W_2	$W = W_1 - W_2$

Table – 2 : Standardisation of Glucose solution

No. of obs.	Volume of Fehling's solution (ml)	Burette reading		Volume of Glocose solution (ml)	Mean volume of Standard glucose solution (ml)
		Initial	Final		
1.	20	0	...	...	
2.	20	...	...	...	V
3.	20	...	...	...	

Table – 3 : Estimation of Supplied Glucose Solution

No. of obs.	Volume of Fehling's solution (ml)	Burette reading		Volume of supplied Sucrose (ml)	Mean volume of supoplied Sucrose (ml)
		Initial	Final		
1.	20	0	...	...	
2.	20	...	...	...	V_1
3.	20	...	...	...	

12.5.5 Calculation

250 ml standard glucose solution = W g of glucose

20 ml Fehling's solution ≡ V ml of the standard glucose solution ≡ V_1 ml of Inverted sugar

∴ V_1 ml of Inverted sugar ≡ V ml of the standard glucose solution ≡ W × V / 250 g of glucose.

∴ 250 ml of the Inverted sugar solution ≡ 25 ml supplied sucrose solution

≡ (250 × W × V) / (V_1 × 250) g of glucose

≡ (W × V) / V_1 g of glucose

Since, 360 g glucose ≡ 360 g of Inverted sugar ≡ 342 g of sucrose

∴ (W × V) / V_1 g of glucose ≡ (342 × W × V) / (360 × V_1) g of sucrose in 25 ml of the supplied solution

∴ Amount of sucrose present in the supplied solution

= (342 × W × V × 40) / (360 × V_1) g in 1 lit.

= (38 × W × V) / V_1 g / lit.

Note :

1. The entire titration should be completed within 3-4 minutes.
2. The solution should be shaken before use.
3. Titration should be done under boiling condition to prevent the backward aerial oxidation.

12.6 Summary

- For the estimation of glycine by Sorensen Formal method, Glycine is reacted with formaldehyde in the presence of the indicator, and the mixture is titrated with a standard alkali until the endpoint is reached.
- Fehling's A Solutionis a blue solution of copper(II) sulfate ($CuSO_4$).
- Fehling's B Solution is a clear solution containing potassium sodium tartrate(Rochelle salt) and a strong alkali, usually sodium hydroxide (NaOH).
- Glucose reduces Fehling's solution, converting cupric ions to cuprous oxide, which precipitates out. The amount of glucose is determined by titration.
- Sucrose is hydrolyzed to glucose and fructose, which then reduces Fehling's solution. The amount of sucrose is calculated based on the titration.

12.7 Question

1. What is the Sorensen Formal Method?

Ans: The Sorensen Formal Method is a titration technique used to estimate the concentration of amino acids, such as glycine, by reacting the amino group with formaldehyde and then titrating the remaining carboxylic acid group with a standard alkali.

2. Why is formaldehyde used in the Sorensen Formal Method?

Ans: Formaldehyde reacts with the amino group of glycine to form a Schiff base, effectively blocking the amino group. This allows the carboxylic acid group to be titrated without interference from the amino group.

3. Which indicator is used in the Sorensen Formal Method, and why?

Ans: Phenolphthalein is used as the indicator because it changes color at the pH range where the titration of the carboxylic acid group occurs, signaling the endpoint of the titration.

4. What is the principle behind the estimation of glucose using Fehling's solution?

Ans: The principle is based on the reduction of copper(II) ions in Fehling's solution by glucose to form a red precipitate of copper(I) oxide (Cu_2O). The amount of glucose is proportional to the volume of Fehling's solution reduced.

5. What are the components of Fehling's solution?

Ans: Fehling's solution is composed of Fehling's A (copper(II) sulfate solution) and Fehling's B (a solution of potassium sodium tartrate and sodium hydroxide).

6. Why is it important to titrate the glycine solution immediately after adding formaldehyde?

Ans: It is important to titrate immediately to ensure that the reaction between glycine and formaldehyde is complete and that the Schiff base is fully formed, allowing for accurate titration of the carboxylic acid group.

7. Can Sorensen Formal Method be used for other amino acids? Why or why not?

Ans: Yes, this method can be used for other amino acids that have a free amino group and a carboxylic acid group. However, the specific reaction conditions may vary depending on the amino acid's properties.

8. What is the role of the Schiff base in Sorensen Formal Method?

Ans: The Schiff base is formed when formaldehyde reacts with the amino group of glycine. It effectively neutralizes the amino group, allowing the carboxylic acid group to be titrated without interference, making the estimation of glycine possible.

9. What is the principle behind the estimation of sucrose using Fehling's solution?

Ans: The principle involves the hydrolysis of sucrose into glucose and fructose, both of which are reducing sugars that can reduce Fehling's solution to form a red

precipitate of copper(I) oxide. The amount of sucrose is then determined by titration.

10. Why is hydrolysis of sucrose necessary before titration?

Ans: Sucrose itself is a non-reducing sugar, so it must be hydrolyzed into glucose and fructose, which are reducing sugars that can react with Fehling's solution.

11. What chemicals are required for the estimation of sucrose using Fehling's solution?

Ans: The chemicals required include sucrose solution, hydrochloric acid (for hydrolysis), sodium hydroxide (for neutralization), and Fehling's A and B solutions.

12. What is the role of potassium sodium tartrate in Fehling's solution?

Ans: Potassium sodium tartrate acts as a complexing agent, keeping the copper(II) ions in solution and preventing their precipitation as hydroxide in the strongly alkaline medium.

13. Why is Fehling's solution specifically used for estimating glucose and not non-reducing sugars like sucrose?

Ans: Fehling's solution is used for glucose because glucose is a reducing sugar that can reduce copper(II) ions to copper(I) oxide. Non-reducing sugars like sucrose do not have free aldehyde or ketone groups and cannot reduce Fehling's solution unless they are first hydrolyzed into their reducing sugar components.

Unit – 13 ❑ Quantitative Analysis – II

Structure

13.1 Objective
13.2 Introduction
13.3 Estimation of Vitamin-C (Reduced)
13.3.1 Principle
13.3.2 Chemicals Required
13.3.3 Procedure
13.3.4 Experimental Results
13.3.5 Calculation
13.4 Estimation of Aniline by Bromination (Bromate-Bromide) Method
13.4.1 Principle
13.4.2 Chemicals Required
13.4.3 Procedure
13.4.4 Experimental Results
13.4.5 Calculation
13.5 Estimation of Phenol by Bromination (Bromate-Bromide) Method
13.5.1 Principle
13.5.2 Chemicals Required
13.5.3 Procedure
13.5.4 Experimental Results
13.5.5 Calculation
13.6 Summary
13.7 Questions

13.1 Objective

By the end of this chapter, students should be able to–

- Learn about the iodimetric titration and use it for Vitamin C estimation

- Understand the principles of redox titration and its application in Vitamin C estimation.
- Learn the step-by-step procedure for the bromate-bromide method for estimating aromatic amines and phenol.
- Calculate the concentration of aniline in a sample using bromate-bromide method.
- Learn the detailed procedure for estimating phenol using the bromate-bromide method.

13.2 Introduction

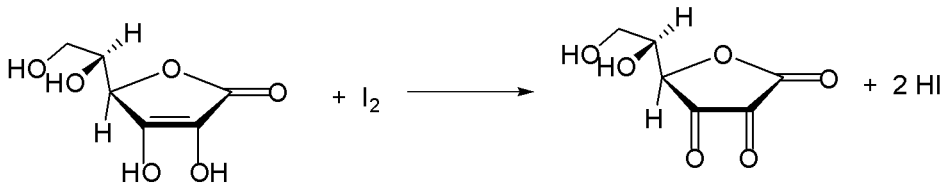
Quantitative analysis is fundamental in analytical chemistry, enabling precise determination of substance concentrations in various samples. In this unit, we examine three key techniques for estimating organic compounds, each vital in chemistry, pharmaceuticals, environmental science, and industrial quality control. Mastery of these methods is essential for accurately measuring active ingredients, pollutants, and other chemical species. This unit will equip you with the skills to perform reliable estimations across a range of scientific and industrial applications.

13.3 Estimation of Vitamin-C (Reduced)

Vitamin C (ascorbic acid) is an essential nutrient known for its antioxidant properties and its role in maintaining overall health. Accurate estimation of Vitamin C is crucial for assessing the nutritional content of food and the potency of pharmaceutical products. **Iodometry** is an indirect titration method where iodine (I_2) is liberated by a redox reaction, and this iodine is then titrated with a standard solution of sodium thiosulfate ($Na_2S_2O_3$). On the other hand, **Iodimetry** is a direct titration method where iodine is used as the titrant to determine the concentration of reducing agents. Iodometry generally deals with oxidizing agents, while iodimetry is used for reducing agents.Both methods are based on the redox chemistry of iodine, and they are essential techniques for quantitative analysis in various fields. Now, we will use the iodimetric titration technique forestimation of Vitamin-C (Reduced). This method is particularly significant in quality control processes in the food and pharmaceutical industries.

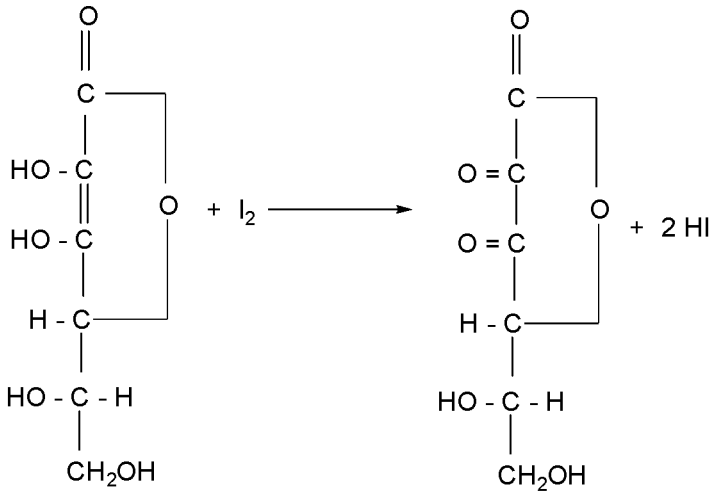
13.3.1 Principle

The estimation of vitamin C i.e., L-ascorbic acid depends upon the quantitative oxidation of ascorbic acid to dehydro-L- ascorbic acid with iodine solution in acid medium.



L-Ascorbic acid Dehydro-L- ascorbic acid

Or



L-Ascorbic acid Dehydro-L- ascorbic acid

According to the molecular formula :

$$C_6H_8O_6 + I_2 \longrightarrow C_6H_6O_6 + 2\,HI$$

L-ascorbic acid Dehydro-L-ascorbic acid

This reaction forms the basis of iodimetric estimation of ascorbic acid. A known value of an aqueous solution of Vitamin C (reduced) is treated with measured excess of standard iodine solution. After the reaction is over the excess iodine is back titrated with a standard solution sodium thiosulphate. The difference in the titre of thisulphate gives the amount of iodine consumed and hence the amount of vitamin C.

According to the iodimetry, we have

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

Thus, 1 mole of $C_6H_8O_6$ ≡ 1 mole of I_2 ≡ 2 moles of $Na_2S_2O_3$

Or, 2 moles of $Na_2S_2O_3$ ≡ 1 mole of $C_6H_8O_6$

Or, 1 mole of $Na_2S_2O_3 \equiv \frac{1}{2}$ mole of $C_6H_8O_6$

$\therefore$ 1000 ml of (N) $Na_2S_2O_3$ solution $\equiv \frac{176.2}{2}$ g of vitamin C = 88.1 g of vitamin C

$\therefore$ 1 ml of (N) $Na_2S_2O_3$ solution ≡ 0.0881 g of vitamin C = 88.1 mg of vitamin C

13.3.2 Chemicals Required

(i) Standard (N/20) $K_2Cr_2O_7$ solution

(ii) ~ (N/20) I_2 in KI solution.

(iii) ~ (N/20) sodium thiosulphate solution

(iv) 10% KI solution

(v) 1% starch solution

(vi) Vitamin C solution (supplied)

[Dissolve 4.405 g of vitamin C in 100 ml of volumetric flask and supply 8-11 ml to each student].

13.3.3 Procedure

1. **Preparation of 250 ml of ~ (N/20) standard $K_2Cr_2O_7$ solution :**

   Weigh out accurately ~ 0.6129 g of $K_2Cr_2O_7$ in a 250 ml volumetric flask, dissolve in distilled water, and make up to the mark, and mix uniformly.

2. **Preparation of 250 ml ~ (N/20) I_2 in KI solution :**

   Dissolve ~ 1.6 g of iodine in a solution of 2 g of KI dissolved in 20 ml of distilled water and dilute to 250 ml with distilled water.

3. **Preparation of 250 ml of ~ (N/20) sodium thiosulphate solution :**

   Dissolve ~ 3 g of $Na_2S_2O_3.5H_2O$ in 250 ml of distilled water and mix uniformly.

4. **Preparation of 250 ml of 10% KI solution :**

   Dissolve 25 g of KI in 250 ml of distilled water.

5. Preparation of vitamin C solution:

Dilute the supplied vitamin C solution with distilled water in a 100 ml volumetric flask up to the mark.

6. Standardisation of (N/20) sodium thiosulphate solution against standard $K_2Cr_2O_7$ solution :

Pipette out 25 ml of $K_2Cr_2O_7$ solution in 500 ml conical flask and add 10 ml of 5 ml conc. HCl and 2 g KI. Cover the mouth of the flask with watch glass, shake well and keep in a dark place for about 5 minutes. Add 175 ml of distilled water and titrated with thiosulphate solution from the burette until the colour turns to straw yellow. Add 2 ml of 1% starch solution and continue the titration until the blue colour turns to green. Note the burette reading and repeat the experiment thrice.

7. Standardisation of iodine solution against standard thiosulphate solution:

Take an aliquot 25 ml of the ~ (N/20) I_2 in KI solution in a 500 ml conical flask, dilute to 100 ml with distilled water and titrate with the standard thisulphate solution from burette until the colour turns to pale yellow. Add 2 ml of 1% starch solution and continue the titration until the blue colour is just discharged and repeat the experiment thrice.

8. Estimation of vitamin C solution :

Pipette out 25 ml of the diluted vitamin C solution in a 500 ml conical flask, dilute with 25 ml of distilled water. Add 1 ml of 4(N) H_2SO_4 to maintain the acidity ≤ 0.1 (N). Add a measured (25/50/75 ml say $25 \times x$ *ml*) of standard ~ (N/20) iodine solution using pipette so that the colour of iodine persists in the solution, allow to stand for 30 seconds. Add 2 ml of 1% starch solution, the mixture turns to blue. Titrate quickly with the standardised thiosulphate solution till the blue colour is just discharged.

13.3.4 Experimental Result

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

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of $K_2Cr_2O_7$ solution
W_1	W_2	$W = W_1 - W_2$	0.6129	250	W/06129 (N/20) = S(N)

Table - 2 : Standardisation of thiosulphate solution against standard $K_2Cr_2O_7$ solution :

No. of obs.	Volume of $K_2Cr_2O_7$ (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

Table - 3 : Standardisation of I_2 solution against standard thiosulphate solution :

No. of obs.	Volume of I_2 (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_2
3.	25	...	...	...	

Table - 4 : Estimation of Vitamin C :

No. of obs.	Volume of vitamin C (ml)	Volume of I_2 solution (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
			Initial	Final		
1.	25	*x* 25	0	...	...	
2.	25	*x* 25	...	...	...	V_3
3.	25	*x* 25	...	...	...	

13.3.5 Calculation

Strength of $K_2Cr_2O_7$ solution = S (N)

25 ml of S (N) $K_2Cr_2O_7$ solution ≡ Iodine ≡ V_1 ml of thiosulphate solution

∴ Strength of thiosulphate solution = $25 \times S/V_1$ (N) = S_1(N)

25 ml of I_2 – solution $\equiv V_2$ ml of S_1(N) thiosulphate solution

$\therefore$ (25 ml $\times$ x) ml iodine solution $\equiv$ x V_2 ml of S_1 (N) thiosulphate solution

Now, (25 $\times$ x) ml I2 – solution $\equiv$ (25 ml vitamin C solution + V_3 ml of S_1(N) thiosulphate solution)

$\therefore$ 25 ml of vitamin C solution $\equiv$ (x $V_2 - V_3$) ml of S_1 (N) thiosulphate solution

Since, 1 ml of (N) thiosulphate solution $\equiv$ 88.1 mg of vitamin C

Since, 25 ml of vitamin C solution $\equiv$ (x $V_2 - V_3$) ml of S_1(N) thiosulphate solution

$\equiv 88.1(x\ V_2 - V_3) \times S_1$ mg of vitamin C

$\therefore$ 1 ml of vitamin C solution $\equiv 88.1(x\ V_2 - V_3) \times S_1/25$ mg of vitamin C

$\therefore$ Strength of the vitamin C solution $= 88.1(x\ V_2 - V_3) \times S_1 \times 1000/25$mg/lit.

$= 88.1\ (x\ V_2 - V_3) \times S_1 \times 40$ mg/lit.

Or, $= 88.1\ (x\ V_2 - V_3) \times S_1 \times 100/25$ mg%

$= 88.1\ (x\ V_2 - V_3) \times S_1 \times 4$ mg %

13.4 Estimation of Aniline by Bromination (Bromate–Bromide) Method

Aniline, an aromatic amine, is a compound widely used in the production of dyes, drugs, and polymers. Accurate estimation of aniline is important for quality control in industrial processes and environmental monitoring due to its potential health hazards. The bromination (bromate-bromide) method is an effective analytical technique for this purpose.

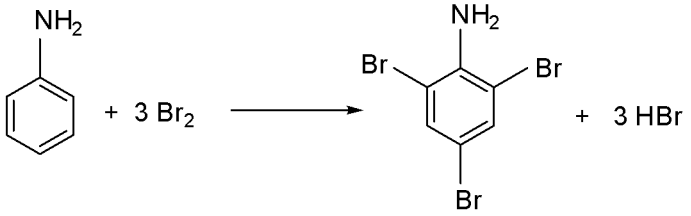
13.4.1. Principle

The bromination method relies on the reaction of aniline with bromine. In this technique, bromate ions (from potassium bromate) react with bromide ions (from potassium bromide) to generate bromine in situ. Aniline can be estimated by the reaction with measured excess of standard $KBrO_3$–KBr solution in presence of acid. The bromine so liberated reacts quantitatively with aniline to form 2,4,6- tribromo aniline.

The excess bromine is made to reacts with KI to liberate iodine which is then titrated with standard sodium thiosulphate solution using starch as indicator. The

reactions are as follow–

$$KBrO_3 + 5KBr + 6HCl \longrightarrow 3Br_2 + 6KCl + 3H_2O$$



$$Br_2 + 2KI = I_2 + 2KBr$$

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

$\therefore$ $KBrO_3 = 3Br_2 = C_6H_5NH_2 = 3I_2 = 6Na_2S_2O_3$

$\therefore$ 1 mole $Na_2S_2O_3 \equiv$ 1/6 mole $C_6H_5NH_2 \equiv$ 1 equivalent

i.e., 1 g equivalent of $Na_2S_2O_3 \equiv$ 1/6 mole $C_6H_5NH_2$

$\therefore$ 1000 ml (N) $Na_2S_2O_3$ solution $\equiv$ 93.066/6 g of $C_6H_5NH_2$

= 15.511 g of $C_6H_5NH_2$

13.4.2 Chemicals Required

(i) 0.2 (N) $KBrO_3$ – KBr solution :

(ii) 10% KI solution

(iii) 0.1 (N) $Na_2S_2O_3$. $5H_2O$ solution.

(iv) Starch solution

(v) Aniline solution (Supplied)

[Mix 2.5 g of distilled aniline with 3 ml of conc. HCl and diluted with distilled water in a 250 ml volumetric flask upto the mark and supply 4 – 7 ml to each student]

13.4.3 Procedure

1. Preparation of 0.1 (N) $KBrO_3$ – KBr solution :

Dissolve 0.6958 g of $KBrO_3$ and 5 g KBr in 250 ml volumetric flask and dilute upto the mark with distilled water.

2. Preparation of 10% KI solution:

Dissolve 10 g of KI in 100 ml of distilled water.

3. Preparation of 0.1 (N) $Na_2S_2O_3$. $5H_2O$ solution:

Dissolve ~ 6.25 g of $Na_2S_2O_3$. $5H_2O$ in 250 ml distilled water.

4. Preparation of aniline solution :

Dilute the supplied aniline solution with distilled water in a 100 ml volumetric flask up tothe mark.

5. Standardisation of $Na_2S_2O_3$ solution :

Pipette out 25 ml of the $KBrO_3$ – KBr solution in 500 ml conical flask. Add 10 ml of distilled water, 10 ml conc. HCl and 15 ml of 10% KI solution and shake the mixture. Dilute the mixture with 180 ml of distilled water [keeping the acidity of the solution is about 0.5 (N)] and titrate the liberated I_2 with $Na_2S_2O_3$ solution, till pale yellow colour appears. Then add 2 ml of starch solution and continue the titration until the blue colour just disappears. Repeat the process thrice.

6. Estimation of aniline solution :

Pipette out 25 ml supplied aniline solution in 500 ml conical flask. Add 50 ml of of $KBrO_3$ – KBr solution and 10 ml of conc. HCl. Shake the solution to mix the components intimately. Add 10 ml of 10% KI solution and 150 ml of distilled water [to keep the acidity of the solution is about 0.5 (N)]. Titrate the liberated I_2 with standard $Na_2S_2O_3$ solution, till pale yellow colour appears. Then add 2 ml of starch solution and continue the titration until the blue colour just disappears. Repeat the process three times.

13.4.4 Experimental Results

Table-1 : Preparation of Standard $KBrO_3$ – KBr Solution :

Initial weight (g)	Final weight (g)	Weight taken (g)
W_1	W_2	$W = W_1 - W_2$

Table - 2 : Standardisation of $Na_2S_2O_3$ solution against standard $KBrO_3$–KBr solution :

No. of obs.	Volume of $KBrO_3$ –KBr (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V
3.	25	...	...	...	

Table - 3 : Estimation of Aniline :

No. of obs.	Volume of Aniline solution + $KBrO_3$ – KBr (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
		Initial	Final		
1.	25 + 50	0	...	...	
2.	25 + 50	...	...	...	V_1
3.	25 + 50	...	...	...	

13.4.5 Calculation

Strength of $KBrO_3$ – KBr solution ≡ W / 0.6958 (N/10)

The reaction in acid medium is

$$BrO_3^- + 6\ H^+ + 6e = Br^- + 3H_2O$$

∴ Equivalent weight of KBrO3 ≡ M. Wt./6 = 167/6 = 27.8333

Thus, 1000 ml (N) $KBrO_3$ solution contain 27.8333 g of $KBrO_3$

∴ 250 ml 0.1 (N) ... ... 27.8333/40 = 0.6958 g of $KBrO_3$

Srength of $Na_2S_2O_3$ = S (N)

[Applying the formula; $V_1 \times S_1 = V_2 \times S_2$ i.e., $25 \times W/0.6958\ (N/10) = V \times S_2$

∴ $S_2 = (25 \times W) / (0.6958 \times V \times 10)\ (N) = S\ (N)$

25 ml $KBrO_3$ – KBr solution ≡ V ml S (N) $Na_2S_2O_3$ solution

25 ml aniline + 50 ml $KBrO_3$ – KBr solution ≡ V_1 ml S (N) $Na_2S_2O_3$ solution

∴ 25 ml aniline solution ≡ $(2V - V_1)$ ml S (N) $Na_2S_2O_3$ solution

Since, 1000 ml of (N) $Na_2S_2O_3$ solution ≡ 93.066/6 g of Aniline

∴ $(2V - V_1)$ ml S (N) $Na_2S_2O_3$ solution ≡ $0.093066 \times (2V - V_1) \times S/6$ g of Aniline in 25 ml solution

∴ The amount of Aniline in supplied sample solution ≡ $0.093066 \times (2V - V_1) \times S \times 40/6$ g in 1000 ml

$= 0.62044 \times (2V - V_1) \times S$ g / lit.

13.5 Estimation of Phenol by Bromination (Bromate- Bromide) method

Phenol is a significant organic compound used in the manufacturing of pharmaceuticals, disinfectants, and other industrial products. Its accurate estimation is crucial for quality control and environmental monitoring due to its potential toxicity. The bromination method using bromate and bromide is an effective technique for quantifying phenol.

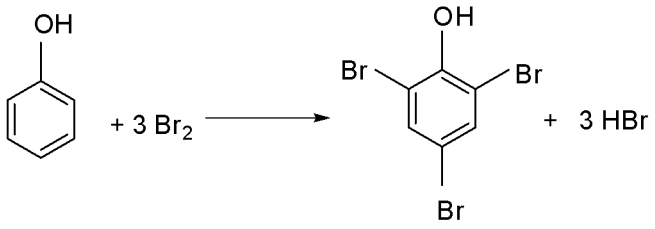
13.5.1 Principle

The bromination method for estimating phenol involves the generation of bromine in situ using a bromate-bromide mixture. Thus, phenol can be estimated by the reaction with measured excess of standard $KBrO_3$ – KBr solution in presence of acid.

The bromine so liberated reacts quantitatively with phenol to form 2,4,6- tribromo phenol.

The excess bromine is made to reacts with KI to liberate iodine which is then titrated with standard sodium thiosulphate solution using starch as indicator. The reactions are as follow–

$$KBrO_3 + 5KBr + 6HCl \rightarrow 3Br_2 + 6KCl + 3H_2O$$



$$Br_2 + 2\ KI = I_2 + 2\ KBr$$

$$2\ Na_2S_2O_3 + I_2 = 2\ NaI + Na_2S_4O_6$$

$\therefore$ $KBrO_3 = 3\ Br_2 = C_6H_5OH = 3\ I_2 = 6\ Na_2S_2O_3$

$\therefore$ 1 mole $Na_2S_2O_3 \equiv 3$ moles $Br_2 \equiv 3$ mole $I_2 \equiv 1$ equivalent

$\therefore$ 1000 ml (N) $Na_2S_2O_3$ solution $\equiv$ 94.112 g of phenol

In acid medium BrO_3^- react as

$$BrO_3^- + 6H^+ + 6e \rightleftharpoons Br^- + 3H_2O$$

$\therefore$ Equivalent weight of $KBrO_3$ = M. Wt./6 = 167/6 = 27.8333

Thus, 1000 ml (N) KBrO3 solution contain 27.8333 g of $KBrO_3$

$\therefore$ 250 ml 0.1 (N) $KBrO_3$ solution contain 27.8333/40 = 0.6958 g of $KBrO_3$

13.5.2 Chemicals Required

(i) 0.1 (N) $KBrO_3$ – KBr solution :

(ii) 10% KI solution

(iii) 0.1 (N) $Na_2S_2O_3$. $5H_2O$ in 250 ml of distilled water.

(iv) Starch solution

(v) Phenol solution (Supplied)

[Dissolve 2.5 g of Phenol in distilled water in a 250 ml volumetric flask upto the mark and supply 9 - 11 ml to each student]

13.5.3 Procedure

1. Preparation of 0.1 (N) $KBrO_3$ – KBr solution :

Dissolve 0.6958 g of $KBrO_3$ and 5 g KBr in 250 ml volumetric flask and dilute upto the mark with distilled water.

2. Preparation of 10% KI solution :

Dissolve 10 g of KI in 100 ml of distilled water.

3. Preparation of 0.1 (N) $Na_2S_2O_3$. $5H_2O$ solution :

Dissolve ~ 6.25 g of $Na_2S_2O_3$. $5H_2O$ in 250 ml distilled water.

4. Preparation of phenol solution :

Diluted the supplied phenol solution with distilled water in a 100 ml volumetric flask upto the mark.

5. Sandardisation of $Na_2S_2O_3$ solution :

Pipette out 25 ml of the $KBrO_3$ – KBr solution in 500 ml conical flask. Add 10 ml of distilled water, 10 ml conc. HCl and 15 ml of 10% KI solution and shake the mixture. Dilute the mixture with 180 ml of distilled water [keeping the acidity of the solution is about 0.5 (N)] and titrate the liberated I_2 with $Na_2S_2O_3$ solution, till pale yellow colour appears. Then add 2 ml of starch solution and continue the titration until the blue colour just disappears. Repeat the process three times.

6. Estimation of phenol solution :

Pipette out 25 ml supplied aniline solution in 500 ml conical flask. Add 50 ml of of $KBrO_3$ – KBr solution and 10 ml of conc. HCl. Shake the solution to mix the

components intimately. Add 10 ml of 10% KI solution and 150 ml of distilled water [to keep the acidity of the solution is about 0.5 (N)] . Titrate the liberated I2 with standard $Na_2S_2O_3$ solution, till pale yellow colour appears. Then add 2 ml of starch solution and continue the titration until the blue colour just disappears. Repeat the process three times.

13.5.4. Experimental Results

Table-1 : Preparation of standard $KBrO_3$ – KBr Solution :

Initial weight of $KBrO_3$ (g)	Final weight of $KBrO_3$ (g)	Amount of $KBrO_3$ taken (g)
W_1	W_2	$W = W_1 - W_2$

Table - 2 : Standardisation of $Na_2S_2O_3$ solution against standard $KBrO_3$–KBr solution

No. of obs.	Volume of $KBrO_3$ –KBr (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V
3.	25	...	...	...	

Table - 3 : Estimation of Aniline :

No. of obs.	Volume of Phenol solution + $KBrO_3$ – KBr (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
		Initial	Final		
1.	25 + 50	0	...	...	
2.	25 + 50	...	...	...	V_1
3.	25 + 50	...	...	...	

13.5.5 Calculation

Strength of $KBrO_3$ – KBr solution ≡ W / 0.6958 (N/10)

Strength of $Na_2S_2O_3$ solution = S (N), say

Applying the formula; $V_1 \times S_1 = V_2 \times S_2$ i.e., $25 \times W/0.6958\ (N/10) = V \times S_2$

∴ $S_2 = (25 \times W)/ (0.6958 \times V \times 10)\ (N) = S\ (N)$

25 ml $KBrO_3$ – KBr solution ≡ V ml S (N) $Na_2S_2O_3$ solution

25 ml phenol + 50 ml $KBrO_3$ – KBr solution ≡ V_1 ml S (N) $Na_2S_2O_3$ solution

∴ 25 ml phenol solution ≡ $(2V - V_1)$ ml S (N) $Na_2S_2O_3$ solution

Since, 1000 ml of (N) $Na_2S_2O_3$ solution ≡ 93.066/6 g of Phenol

∴ $(2V - V_1)$ ml S (N) $Na_2S_2O_3$ solution ≡ $0.093066 \times (2V - V1) \times S /6$ g of Phenol in 25 ml solution

∴ The amount of Phenol in supplied sample solution

≡ $0.093066 \times (2V - V_1) \times S \times 40 /6$ g in 1000 ml

= $0.62044 \times (2V - V1) \times S$ g / lit.

Note : During the estimation of Aniline and Phenol the flask always be stopped after the addition of reagents to prevent the loss of bromine due to its high volatility.

13.6 Summary

- Iodometry is indirect, involves the titration of iodine released from the reaction with the analyte, whereas iodimetry is direct, and involves titration with iodine.
- Iodometry generally deals with oxidizing agents, while iodimetry is used for reducing agents.
- Vitamin C (ascorbic acid) is estimated through its reaction with iodine in a direct titration process. Iodine oxidizes Vitamin C to dehydroascorbic acid, and the amount of iodine consumed is measured.
- The Bromate-Bromide method is a quantitative analytical technique used for the estimation of various substances, including aromatic amines and phenols. This method involves the generation of bromine in situ, which then reacts with the target compound. The amount of bromine consumed in the reaction is used to determine the concentration of the analyte.
- In Bromate-Bromide method , as soon as the reagents are added and mixed, promptly stopper the flask. This prevents the escape of bromine vapors and

maintains the integrity of the reaction mixture.

- To use the Bromate-Bromide method for quantitative analysis, a standard solution of potassium bromate (KBrO?) and potassium bromide (KBr) is required. This solution will generate bromine in situ when mixed in an acidic medium.
- Aniline is estimated by its reaction with bromine generated from a bromate-bromide mixture. The bromine reacts with aniline, and the extent of bromine consumption is used to quantify aniline.
- Phenol is estimated using its reaction with bromine, generated from a bromate-bromide solution. The amount of bromine consumed by phenol indicates its concentration in the sample.

13.7 Question

1. What is iodimetry, and how does it differ from iodometry?

Ans: Iodimetry is a type of volumetric analysis where iodine (I_2) is used as a titrant to determine the concentration of reducing agents. In iodimetry, iodine reacts directly with the analyte. Iodometry, on the other hand, involves the use of a reducing agent to convert iodine to iodide ions, and then the iodine or iodide is titrated with a standard solution. Essentially, iodimetry is focused on titrating with iodine, while iodometry often involves a two-step process where iodine is first generated and then titrated.

2. What is the principle behind the iodimetric estimation of Vitamin C?

Ans: see text.

3. What is the role of potassium iodide in the iodimetric titration?

Ans: Potassium iodide (KI) is used to form a stable iodine solution. It reacts with iodine to produce iodide ions, which helps in the formation of iodine molecules in the solution. This also ensures that the iodine remains in solution and is available for the titration process.

4. Why is starch used as an indicator in the titration for estimation of Vitamin C?

Ans: Starch is used as an indicator because it forms a blue complex with iodine, which helps in detecting the end point of the titration. As iodine is reduced to iodide ions during the titration with sodium thiosulfate, the blue color disappears, indicating that the titration is complete.

5. Why is iodine used in estimation of Vitamin C, and what is its role?

Ans: Iodine is used as the oxidizing agent in the iodimetric method. Vitamin C reduces iodine to iodide ions, and the amount of iodine consumed in this reaction is proportional to the amount of Vitamin C present. The iodine serves as a direct reagent for the titration process.

6. Why is it important to use a fresh solution of iodine in this method?

Ans: Fresh iodine solutions are crucial because iodine can evaporate or degrade over time, which would affect the accuracy of the titration. Using a fresh solution ensures that the concentration of iodine is known and consistent, leading to more reliable results.

7. What precautions should be taken to avoid errors in this method?

Ans: To avoid errors, ensure that the Vitamin C solution is freshly prepared and free of oxidation, perform the titration quickly to minimize iodine evaporation, and use freshly prepared iodine and sodium thiosulfate solutions. Additionally, conduct the titration in a dimly lit area to prevent light-induced decomposition of iodine.

8. How does the bromination method work for estimating aniline?

Ans: In the bromination method, bromine is generated in situ from a bromate-bromide mixture in an acidic medium. The generated bromine reacts with aniline to form a brominated product. The amount of bromine consumed is proportional to the concentration of aniline in the sample. The unreacted bromine is then titrated with sodium thiosulfate to determine the amount of bromine that reacted with aniline.

9. What role does sulfuric acid play in the bromination process?

Ans: Sulfuric acid is used to create an acidic environment necessary for the generation of bromine from the bromate-bromide mixture. The acid also helps to maintain the stability of the bromine and facilitates its reaction with the aniline.

10. What is the principle of estimating phenol using the bromination method?

Ans: see text

11. How do you handle bromine to prevent loss and ensure accurate results?

Ans: Handle bromine carefully by promptly stoppering the flask after mixing reagents to prevent bromine loss. Perform the reaction and titration quickly to minimize the exposure of bromine to the air. Use appropriate personal protective equipment and work in a well-ventilated area or under a fume hood.

12. What are the potential sources of error in the Bromate-Bromide method and how can they be minimized?

Ans: Potential sources of error include:

Loss of bromine : Minimize exposure to air and ensure the flask is stoppered immediately after mixing.

Inaccurate concentration of solutions : Use precisely measured amounts of reagents and standardize solutions accurately.

Incomplete reaction : Ensure thorough mixing and proper reaction conditions (e.g., adequate acidification).

13. What is ascorbic acid?

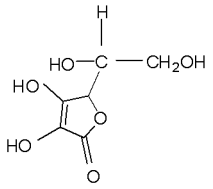
Ans: Ascorbic acid is vitamin C, which is water soluble vitamin.

14. What are the natural sources of ascorbic acid?

Ans: In juice of fresh fruits and vegetables.

15. Does ascorbic acid molecule contain free carboxylic acid group?

Ans: Ascorbic acid molecule does not contain a free carboxylic acid group, because this carboxylic acid group reacts with its hydroxyl group eliminating a water molecule to form a ring compound.



16. What are the uses of ascorbic acid?

Ans: Ascorbic acid is good reducing agent. It is added to the processed foods as a preservative, as an antioxidant, it prevents oxidation of other food compounds. This reducing property of ascorbic acid is considered to prevent cancer in the body.

17. What is the brominating agent generally used in volumetric analysis ?

Ans: A mixture of $KBrO_3$ and KBr in acid medium is used for liberation of Br_2.

$$KBrO_3 + 5\ KBr + 6\ HCl = 3\ Br_2 + 6\ KCl + 3\ H_2O$$

18. Can we employ diazotisation reaction to estimate aniline ?

Ans: Yes, we can estimate aniline by dissolving aniline in HCl and titrating against standard $NaNO_2$ solution using starch indicator externally.

19. Electron transfer per molecule of $KBrO_3$ is 5. But equivalent weight in case of aniline estimation is calculated by dividing the molecular weight by 6– why ?

Ans: The liberated Br_2 (in the 'zero' oxidation state) after bromination it reduced to Br^- (–1, oxidation state), so net electron transfer becomes 6. For this reason equivalent weight = molecular weight / 6.

$$KBrO_3 + 5\ KBr + 6\ HCl = 3\ Br_2 + 6\ KCl + 3\ H_2O$$

20. What is the advantage of dichromatometry?

Ans: $K_2Cr_2O_7$ is a primary standard as such it does not require standardisation.

21. How $K_2Cr_2O_7$ is used in iodometry and iodimetry?

Ans: The strength of thiosulphate solution is determined against the standard $K_2Cr_2O_7$ solution.

22. Why in iodometric titration freshly prepared starch solution used?

Ans: An old starch solution does not produce blue colour, it produces reddish-violet colour. This colour is decolourised slowly by thiosulphate (hypo) solution, so sharp end point is not achieved.

23. How starch acts as an indicator?

Ans: Starch is a mixture of amylose and amylopectin. $I_3^- \left(I^- + I_2 \rightleftharpoons I_3^-\right)$ is adsorbed by amylose gives the blue colour. When all the iodine is exhausted during titration the blue colour disappears giving the original colour of the solution.

24. Why starch solution is added nearly the end point of a iodometric titration?

Ans: Starch can adsorb iodine when the concentration iodine is high. This iodine is not released completely during titration with $S_2O_3^=$ solution as such starch is added near the end point to avoid the trapping of the iodine in such a way.

25. Any indicator other than starch that can be used in iodometry and iodimetry?

Ans: Sodium starch glycollate can be used. It is soluble in hot water and stable for months. With excess of iodine its colour is green. With decrease in concentration of iodine colour changes to blue and at the end point colour is intense blue. The end point is very sharp. (so it is recommended for better results).

26. why standardised sodium sulphite is not used in Iodometry?

Ans: Sodium sulphite in solution rapidly oxidised to sodium sulphate. Which has no reducing property? The equivalence of sulphite is not established stoichiometrically, because it is not available in the higher state of purity and the solution is oxidised constantly

Unit – 14 ❑ Quantitative Analysis – III

Structure

14.1 Objective
14.2 Introduction
14.3 Estimation of Formaldehyde (Formalin)
- **14.3.1 Principle**
- **14.3.2 Chemicals Required**
- **14.3.3 Procedure**
- **14.3.4 Experimental Results**
- **14.3.5 Calculation**

14.4 Estimation of Acetic Acid in Commercial Vinegar
- **14.4.1 Principle**
- **14.4.2 Chemicals Required**
- **14.4.3 Procedure**
- **14.4.4 Experimental Results**
- **14.4.5 Calculation**

14.5 Estimation of Urea by Hypobromite Method
- **14.5.1 Principle**
- **14.5.2 Chemicals Required**
- **14.5.3 Procedure**
- **14.5.4 Experimental Results**
- **14.5.5 Calculation**

14.6 Estimation of Saponification Value of Oil/ Fat/ Ester
- **14.6.1 Principle**
- **14.6.2 Chemicals Required**
- **14.6.3 Procedure**
- **14.6.4 Experimental Results**
- **14.6.5 Calculation**

14.7 Summary
14.8 Question

14.1 Objective

By the end of this chapter, students should be able to–

- Understand the chemical reactions involved in the estimation of formaldehyde and learn the method to accurately quantify formaldehyde in various samples.
- Master the techniques for determining the concentration of acetic acid in vinegar. This method can be applied to evaluate the quality and concentration of commercial vinegar through accurate analysis.
- Gain knowledge of the hypobromite method for urea estimation. Perform the titration and calculation to determine urea concentration in samples.
- Learn the principles behind saponification and its measurement. Apply the saponification value measurement to evaluate the chemical characteristics of fats and oils in different industries.

14.2 Introduction

Unit 14 explores the principles and practical applications of various quantitative estimation techniques, which are essential for analyzing organic compounds and mixtures. These methods are vital in both industrial and laboratory settings, as they provide accurate measurements that are crucial for product quality, regulatory compliance, and research advancements.

We will examine methods to accurately estimate the concentration of formaldehyde, ensuring its safe and effective use. Additionally, using the titration method-a straightforward and reliable approachwill be discussed for determining acetic acid levels. The hypobromite method is also highlighted in this unit for its effectiveness in estimating urea concentration. Furthermore, the importance of determining the saponification value of Oil/Fat/Esterwill be explained, particularly in the contexts of soap production, biodiesel manufacturing, and food industry applications.

14.3 Estimation of Formaldehyde (Formalin)

Formaldehyde, a simple yet highly reactive aldehyde, is commonly used in its aqueous solution form known as formalin. Formalin is widely utilized in various industries, including preservation, disinfection, and manufacturing, due to its strong preservative and anti-bacterial properties. Understanding the precise concentration of

formaldehyde in formalin is essential for maintaining product quality, complying with safety regulations, and preventing overexposure, which could lead to harmful effects.

The iodometric method is a widely used technique for the estimation of formaldehyde (formalin) due to its precision and reliability. This method is based on the oxidation-reduction reaction between formaldehyde and iodine, where formaldehyde is oxidized, and iodine is reduced.

14.3.1 Principle

In the iodometric estimation, the formaldehyde (HCHO) solution is oxidised quantitatively to formic acid by iodine in alkaline medium. The oxidation is caused actually by sodium hypoiodite generating from the reaction iodine and NaOH. The excess alkali neutralises the formic acid thus formed. The excess hypoiodite reacts with HCl to liberate iodine which is titrated with standard sodium thiosulphate solution, where iodine oxidised the thiosulphate to tetrathionate ($S_4O_6^{-2}$).

$$I_2 + 2\,NaOH = NaOI + NaI + H_2O$$

$$HCHO + NaOI + NaOH = HCOONa + NaI + H_2O$$

$$HCHO + I_2 + 3\,NaOH = HCOONa + 2\,NaI + 2\,H_2O$$

$$NaOI^{(excess)} + NaI + 2\,HCl = 2\,NaCl + I_2 + H_2O$$

$$I_2 + 2\,Na_2S_2O_3 = Na_2S_4O_6 + 2\,NaI$$

$\therefore$ $I_2 + 2\,S_2O_3^{-2} = 2^{I-} + S_4O_6^{-2}$

$\therefore$ $HCHO \equiv I_2 \equiv 2\,S_2O_3^{-2}$

$\therefore$ $S_2O_3^{-2} \equiv \frac{1}{2}\,HCHO \equiv 1$ equivalent

$\therefore$ 1000 ml of (N) thiosulphate solution $\equiv$ 15 g of HCHO

Or, 1 ml of (N) thiosulphate solution $\equiv$ 0.015 g of HCHO

14.3.2 Chemicals Required

(i) 0.1 (N) $K_2Cr_2O_7$ solution,

(ii) 0.1 (N) I_2 solution,

(iii) 0.1 (N) $Na_2S_2O_3$ solution,

(iv) 1% Starch solution

(v) Iodate-free KI,

(vi) Conc. HCl

(vii) 10% NaOH solution

(viii) Formalin solution (supplied).

[Dissolve 12.5 ml of formalin with distilled water in a 250 ml volumetric flask upto the mark and supply 9 – 12 ml to each student]

14.3.3 Procedure

1. Preparation of 250 ml ~(N/10) $K_2Cr_2O_7$ solution:

Weight approximately 1.2257 gm of $K_2Cr_2O_7$ and dissolve it in 250 ml distilled water. Note the accurate weight of $K_2Cr_2O_7$ taken.

2. Preparation of 0.1 (N) iodine solution:

Dissolve 1.27g of I2 and 2.5 g KI in 250 ml volumetric flask and dilute upto the mark with distilled water.

3. Preparation of 0.1 (N) $Na_2S_2O_3$ solution:

Dissolve 12.5 g of $Na_2S_2O_3$ in 500 ml of distilled water.

4. Preparation of formalin solution:

Diluted the supplied Formalin solution with distilled water in a 100 ml volumetric flask upto the mark.

5. Standardisation of 0.1 (N) $Na_2S_2O_3$ solution against standard $K_2Cr_2O_7$ solution:

Pipette out 25 ml of K_2Cr_2O7 solution in 500 ml conical flask and add 10 ml of 5 ml conc. HCl and 2 g KI. Cover the mouth of the flask with watch glass, shake well and keep in a dark place for about 5 minutes. Add 175 ml of distilled water and titrated with thiosulphate solution from the burette until the colour turns to straw yellow. Add 2 ml of 1% starch solution and continue the titration until the blue colour turns to green. Note the burette reading and repeat experiment thrice.

6. Estimation of Formaldehyde:

Take 25 ml of the formalin solution in a 500 ml conical flask followed by addition of 50 ml of I_2 solution. Add 10% NaOH solution slowly until the colour of the solution changes from brown to pale yellow stable for at least 15 minutes. After standing for 15 minutes the solution is acidify by adding 2(N) HCl and keep the flask in dark for 5 minutes. Then titrate with standard $Na_2S_2O_3$ solution using starch as indicator as usual.

14.3.4 Experimental Results

Table – 1 : Preparation of 250 ml ~(N/10) $K_2Cr_2O_7$ solution:

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of $K_2Cr_2O_7$ solution
W_1	W_2	$W = W_1 - W_2$	1.2257	250	W/1.2257 (N/10) = S(N)

Table - 2 : Standardisation of $Na_2S_2O_3$ solution against standard $K_2Cr_2O_7$ solution:

No. of obs.	Volume of $K_2Cr_2O_7$ (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

Table - 3 : Standardisation of I_2 solution against standard $Na_2S_2O_3$ solution :

No. of obs.	Volume of I_2 solution (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_2
3.	25	...	...	...	

Table - 4 : Back titration for estimation of formalin solution :

No. of obs.	Volume of formalin solution (ml)	Volume of I_2 solution (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
			Initial	Final		
1.	25	50	0	...	...	
2.	25	50	...	...	...	V_3
3.	25	50	...	...	...	

14.3.5. Calculation

$I_2 \equiv NaOI \equiv 2\ Na_2S_2O_3 \equiv HCHO \equiv 30$ g HCHO

2×1000 ml (N) $Na_2S_2O_3$ solution $\equiv$ 30 g HCHO

1 ml (N) $Na_2S_2O_3$ solution $\equiv 30 / (2 \times 1000) = 0.015$ g of HCHO

Strength of $K_2Cr_2O_7$ solution = S (N)

Now, 25 ml of S (N) $K_2Cr_2O_7$ solution $\equiv V_1$ ml of S_1 (N) $Na_2S_2O_3$ solution

$\therefore$ Strength of $Na_2S_2O_3$ solution = $S_1 = 25 \times S / V_1$ (N)

25 ml of I_2^- solution $\equiv V_2$ ml of S_1(N) $Na_2S_2O_3$ solution

$\therefore$ 50 ml of I_2^- solution $\equiv 2\ V_2$ ml of S_1(N) $Na_2S_2O_3$ solution

$\therefore$ Back titration value $\equiv$ 25 ml of formalin solution + 50ml of I_2^-solution

$\equiv V_3$ ml of S_1 (N) $Na_2S_2O_3$ solution

$\therefore$ 25 ml of sample diluted formalin solution

$\equiv (2V_2 - V_3)$ of S_1 (N) $Na_2S_2O_3$ solution

$\equiv (2V_2 - V_3) \times S_1$ ml of (N) $Na_2S_2O_3$ solution

Since, 1 ml (N) $Na_2S_2O_3$ solution $\equiv$ 0.015 g of HCHO

$\therefore$ 25 ml of sample diluted formalin solution $\equiv (2V_2 - V_3) \times S_1$ ml of (N) $Na_2S_2O_3$ solution

$\equiv 0.015 \times (2V_2 - V_3) \times S_1$ g of HCHO

$\therefore$ 100 ml of sample diluted formalin solution $\equiv 4 \times 0.015 \times (2V_2 - V_3) \times S_1$ g of HCHO

$\therefore$ 1000 ml of sample diluted formalin solution

$\equiv 40 \times 0.015 \times (2V_2 - V_3) \times S_1$ g of HCHO

$\therefore$ The amount of Formalin in supplied sample solution

$= 40 \times 0.015 \times (2V_2 - V_3) \times S_1$ g/lit.

14.4 Estimation of Acetic Acid in Commercial Vinegar

Acetic acid is the primary component responsible for the characteristic sour taste of vinegar. The accurate estimation of acetic acid concentration in commercial vinegar is essential for ensuring product quality and consistency. This titrimetric method is widely employed in quality control processes within the food industry to ensure that vinegar meets the required standards for acetic acid content, thereby ensuring consistency and consumer satisfaction.

14.4.1 Principle

Acetic acid is a weak acid and produced in vinegar by fermentation of ethyl alcohol or molasses by acetobacter aceti. Commercial vinegar contains alcohol ester, acetic acid and tartatic acid.

The estimation of acetic acid in vinegar is based on an acid-base titration, where acetic acid (a weak acid) is titrated with a strong base, usually sodium hydroxide (NaOH). Thus, a measured quantity of vinegar is diluted to a definite volume and an aliquot is titrated with a standard NaOH solution using phenolphthalein indicator as it is a titration of a weak acid and stong base. Acetic acid (CH_3COOH) reacts with sodium hydroxide (NaOH) to form sodium acetate (CH_3COONa) and water (H_2O).

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

$$\text{Concentration of Acetic Acid (mol/L)} = \frac{V_b \times C_b}{V_s}$$

where

- V_b = volume of NaOH solution used (in liters)
- C_b = Concentration of NaOH solution (in mol/L)
- V_s = Volume of vinegar sample used (in liters)

Percentage of Acetic Acid

$$= \left(\frac{\text{Concentration of Acetic Acid} \times \text{Molar Mass of Acetic Acid} \times \text{Dilution Factor}}{\text{Density of Vinegar}} \right)$$

14.4.2 Chemicals Required

(i) Standard ? (N/20) oxalic acid

(ii) (N/20) NaOH solution

(iii) Vinegar solution (Unknown)

(iv) Phenolphthalein indicator

14.4.3 Procedure

1. Preparation of 250 ml standard ~ (N/20) oxalic acid solution:

Weight approximately 0.7875 gm of oxalic acidand dissolve it in 250 ml distilled water. Note the accurate weight taken.

2. Preparation of ~ (N/20) NaOH solution:

Dissolve about 0.5 g of NaOH in 250 ml of distilled water uniformly.

3. Preparation of Vinegar solution:

Take 10 ml of the commercial vinegar in 250 ml volumetric flask and the volume is made up to the mark with distilled water. Shake to mix the solution uniformly.

4. Standardisation of NaOH solution:

Pipette out 25 ml of the standard oxalic acid solution in 250 ml conical flask and titrate with (N/20) NaOH solution using phenolphthalein as an indicator till the solution turns to pink.

5. Estimation of acetic acid in vinegar solution:

Pipette out 25 ml of the vinegar solution in 250 ml conical flask and titrate with standard (N/20) NaOH solution using phenolphthalein as an indicator till the solution turns to pink. The titration is repeated thrice.

14.4.4 Experimental Results

Table – 1 : Preparation of 250 ml standard ~(N/20) oxalic acid solution:

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of oxalic acid solution
W_1	W_2	$W = W_1 - W_2$	0.7875	250	W/1.2257 (N/10) = S(N)

Table - 2 : Standardisation of NaOH solution against standard (N/20) oxalic acid:

No. of obs.	Volume of oxalic acid solution (ml)	Burette reading		Volume of NaOH solution (ml)	Mean volume of NaOH solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

Table - 3 : Estimation of Acetic Acid against standard NaOH solution :

No. of obs.	Volume of vinegar solution (ml)	Burette reading		Volume of NaOH solution (ml)	Mean volume of NaOH solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_2
3.	25	...	...	...	

14.4.5 Calculation

Strength of NaOH solution:

Volume of oxalic acid solution = 25 ml,

Strength of oxalic acid solution = S(N)

Volume of NaOH solution = V_1 ml

Strength of NaOH solution = S_1 = ?

We have, 25 ml × S (N) = V_1 ml × S_1

$\therefore$ $S_1 = 25 \times S / V_1$ (N)

Reaction :

$CH_3COOH + NaOH = CH_3COONa + H_2O$

i.e. 40 g NaOH $\equiv$ 60 g $CH_3COOH \equiv$ 1 equivalent

Since, 1000 ml (N) NaOH solution contain 1 g equivalent of NaOH

$\therefore$ 1000 ml (N) NaOH solution $\equiv$ 60 g of CH_3COOH

Thus, 1000 ml S_1 (N) NaOH solution $\equiv 60 \times S_1$ g of acetic acid

$\therefore$ V_2 ml S_1 (N) NaOH solution $\equiv 60 \times S_1 \times V_2 / 1000$ g of acetic acid

$\therefore$ $60 \times S_1 \times V_2 / 1000$ g of acetic acid present in 25 ml of the diluted vinegar solution

Thus, 25 ml of the vinegar solution contain $60 \times S_1 \times V_2 / 1000$ g of acetic acid

$\therefore$ 250 ml of the vinegar solution contain $60 \times S_1 \times V_2 \times 250 / 1000 \times 25$g of acetic acid

$\therefore$ 1000 ml of the vinegar solution contain $60 \times S_1 \times V_2 \times 250 \times 1000$ /

$1000 \times 25 \times 250$ g of acetic acid

$= 60 \times S_1 \times V_2$ / 25 g of acetic acid

$= 60 \times 25 \times S \times V_2/25 \times V_1$ g of acetic acid

$= 60 \times S \times V_2 / V_1$ g of acetic acid

$\therefore$ Amount of acetic acid present in the commercial vinegar

$= 60 \times S \times V_2 / V_1$ g/lit.

14.5. Estimation of Urea by Hypobromite Method

Urea, a vital nitrogen-containing compound, is extensively used in agriculture, pharmaceuticals, and chemical industries. The estimation of urea concentration is crucial in various applications, including the analysis of fertilizers and clinical samples. The hypobromite method is a widely used technique for estimating urea due to its simplicity and effectiveness.

14.5.1 Principle

The hypobromite method is based on the reaction of urea with sodium hypobromite, which results in the decomposition of urea into nitrogen gas (N_2), carbon dioxide (CO_2), and water (H_2O). The volume of nitrogen gas evolved is directly proportional to the amount of urea present in the sample, and this is used to determine the concentration of urea.

Urea is treated with measured excess of standardised alkaline hypobromite solution it is oxidised to nitrogen:

$$CO(NH_2)_2 + 3OBr^- + 2OH^- = N_2 + CO_3^{=} + 3Br^-$$

Unreacted hypobromite is estimated by adding excess of KI, followed by acidification with dilute H_2SO_4 and liberated iodine is back titrated with the standard sodium thiosulphate solution using starch as indicator.

$$OBr^- + 2I^- + 2H^+ = I_2 + Br^- + H_2O$$

$$I_2 + 2S_2O_3^{=} = 2I^- + S_4O_6^{=}$$

$\therefore$ $CO(NH_2)_2 \equiv 3\ OBr^- \equiv 3I_2 \equiv 6\ S_2O_3^{=}$

Or, $S_2O_3^{=} \equiv 1/6\ CO(NH_2)_2 \equiv 1$ equivalent

$\therefore$ 1000 ml (N) $S_2O_3^{=}$ solution $\equiv$ 60/6 or 10 g of urea.

Since hypobromite is very unstable when prepare directly by the reaction between Br2 and alkali. So it is advantageous to produce hypobromite in situ by adding excess bromide to the solution of hypochlorite.

$$OCl^- + Br^- = OBr^- + Cl^-$$

$$\text{Mole of urea} = \frac{\text{Volume of } N_2 \text{(inliters)}}{\text{Molar volume of gas at STP}}$$

$$\text{Concentration of Urea (mol/L)} = \frac{\text{Moles of urea}}{\text{Volume of sample (L)}}$$

14.5.2 Chemicals Required :

(i) Standard ? (N/20) $K_2Cr_2O_7$ solution

(ii) ~(N/20) $Na_2S_2O_3$ solution

(iii) 10% KI solution

(iv) 1% starch solution

(v) ~(N/20) NaOCl solution

(vi) ~(N/20) KBr solution

(vii) Supplied urea solution (Unknown)

∴ [Dissolve 3.125 g of urea in distilled water in a 250 ml volumetric flask upto the mark and supply 9 – 11 ml to each student]

14.5.3 Procedure

1. **Preparation of 250 ml ~(N/10) $K_2Cr_2O_7$ solution:**

   Weight approximately 1.2257 gm of $K_2Cr_2O_7$ and dissolve it in 250 ml distilled water. Note the accurate weight of $K_2Cr_2O_7$ taken

2. **Preparation of 250 ml of ~ (N/20) $Na_2S_2O_3$ solution:**

   Dissolve about 4 g of $Na_2S_2O_3$ solution in 250 ml of distilled water.

3. **Preparation of 500 ml of (N/20) NaOCl solution:**

   Dissolve 0.931 g of NaOCl in 500 ml of 2 (N) NaOH solution.

4. **Preparation of 500 ml of (N/20) KBr solution:**

   Dissolve 1.4888 g of KBr in 500 ml of distilled water.

5. Preparation of Urea solution:

Diluted the supplied Urea solution with distilled water in a 250 ml volumetric flask upto the mark.

6. Standardisation of (N/20) $Na_2S_2O_3$ solution:

Pipette out 25 ml of $K_2Cr_2O_7$ solution in 500 ml conical flask and add 10 ml of 5 ml conc. HCl and 2 g KI. Cover the mouth of the flask with a watch glass, shake well and keep it in a dark place for about 5 minutes. Add 175 ml of distilled water and titrated with thiosulphate solution from the burette until the colour turns to straw yellow. Add 2 ml of 1% starch solution and continue the titration until the blue colour turns to green. Note the burette reading and repeat the experiment thrice.

7. Standardisation of (N/20) NaOBr solution:

Pipette out an aliquot of 25 ml of hypobromite solution in a 500 ml of conical flask, add 5 ml of conc. HCl and 10 ml of 10% KI solution. Cover the mouth of the flask with a watch glass and keep in dark place for about 5 minutes. Titrate the liberated iodine with standard (N/20) $Na_2S_2O_3$ solution till straw yellow colour appears. Add 2 ml of 1% starch solution and continue the titration until the blue colour just disappears. Note the burette reading and repeat the experiment thrice.

8. Estimation of Urea (supplied):

Pipette out 25 ml of the supplied urea solution in 500 ml of conical flask, add 50 ml of the hypobromite solution, 2 ml conc. HCl and 10 ml of 10% KI solution. Cover the mouth of the flask with a watch glass and keep in dark place for about 5 minutes. Titrate the liberated iodine with standard (N/20) $Na_2S_2O_3$ solution till straw yellow colour appears. Add 2 ml of 1% starch solution and continue the titration until the blue colour just disappears. Note the burette reading and repeat the experiment thrice.

14.5.4. Experimental Result

Table – 1 : Preparation of 250 ml of (N/20) $K_2Cr_2O_7$ solution:

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of $K_2Cr_2O_7$ solution
W_1	W_2	$W = W_1 - W_2$	0.6129	250	W/0.6129 (N/10) = S(N)

Table - 2 : Standardisation of $Na_2S_2O_3$ solution against standard $K_2Cr_2O_7$ solution:

No. of obs.	Volume of hypobromite solution (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_3
3.	25	...	...	...	

Table - 3 : Standardisation of Hypobromite solution against standard $Na_2S_2O_3$ solution :

No. of obs.	Volume of $K_2Cr_2O_7$ (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_2
3.	25	...	...	...	

Table - 4 : Back titration for the estimation of Urea solution :

No. of obs.	Volume of Urea soln. (ml)	Volume of hypobromite soln. (ml)	Burette reading		Volume of $Na_2S_2O_3$ solution (ml)	Mean volume of $Na_2S_2O_3$ solution (ml)
			Initial	Final		
1.	25	50	0	...	...	
2.	25	50	...	...	...	V_4
3.	25	50	...	...	...	

14.5.5. Calculation

Standardisation of $Na_2S_2O_3$ solution:

Strength of $K_2Cr_2O_7$ solution = S_1 (N)

Volume of $K_2Cr_2O_7$ solution = V_1 ml = 25 ml

Strength of $Na_2S_2O_3$ solution = S_2 (N) = ?

Volume of $Na_2S_2O_3$ solution = V_2 ml

$\therefore$ $25 \times S_1 = V_2 \times S_2$

or, $S_2 = 25 \times S_1 / V_2 = S$ (N) (say)

Estimation of urea solution :

25 ml of NaOBr solution $\equiv$ V_3 ml of S (N) $Na_2S_2O_3$ solution

25 ml urea solution + 50 ml of NaOBr solution

$\therefore$ V_4 ml of S (N) $Na_2S_2O_3$ solution

$\therefore$ 25 ml urea solution $\equiv (2V_3 - V_4)$ ml of S (N) $Na_2S_2O_3$ solution

$\equiv (2V_3 - V_4) \times S$ ml of (N) $Na_2S_2O_3$ solution

We have, 1000 ml of (N) $Na_2S_2O_3$ solution $\equiv$ 10 g of urea

$\therefore$ $(2V_3 - V_4) \times S$ ml of (N) $Na_2S_2O_3$ solution

$\equiv 0.01 \times (2V_3 - V_4) \times S$ g of urea /25 ml

25 ml urea solution contain $0.01 \times (2V_3 - V_4) \times S$ g of urea

$\therefore$ 1000 ml urea solution contain $0.01 \times (2V_3 - V_4) \times S \times 40$ g of urea

Hence the amount of urea present in supplied solution

$= 0.01 \times (2V_3 - V_4) \times S \times 40$ g/lit.

14.6 Estimation of Saponification Value of Oil/ Fat/ Ester

The saponification value is a crucial parameter in the analysis of oils, fats, and esters, representing the amount of potassium hydroxide (KOH) required to saponify one gram of the substance. This value provides insights into the average molecular weight (or chain length) of the fatty acids present in the oil or fat, which is essential in industries such as soap making, biodiesel production, and food processing.

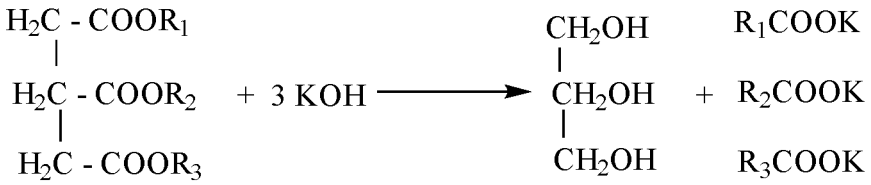
14.6.1. Principle

Oils and fats are all glyceride esters of higher fatty acids. Those are liquid at ordinary condition are known as oils and those are solid at room temperature known as fats. Glycerides when refluxed with alcoholic KOH, hyrolised to produce glycerol and Na / K salt of corresponding fatty acids. This process is known as saponification.

The number of milligram (mg) of KOH required to saponify 1 g of fat or oil defines as the saponification value.

The saponification value is determined by reacting a known quantity of oil, fat, or ester with an excess of alcoholic potassium hydroxide (KOH) solution. The mixture

is heated to ensure complete saponification of the triglycerides present. The unreacted KOH is then titrated with a standard acid solution, usually hydrochloric acid (HCl). The saponification value is calculated based on the amount of KOH that reacted with the sample.



Calculate the saponification value using the formula:

$$\text{Saponification Value} = \frac{(B - S) \times N \times 56.1}{W}$$

Where:

- B = Volume of HCl used in the blank titration (in mL)
- S = Volume of HCl used in the sample titration (in mL)
- N = Normality of the HCl solution
- W = Weight of the sample (in grams)
- 56.1 = Molar mass of KOH (in g/mol)

14.6.2. Chemicals Required

(i) ~(N/2) Standard oxalic acid solution
(ii) Oil (supplied)
(iii) ~(N/2) KOH solution
(iv) ~(N/2) HCl solution
(v) Phenolphthalein indicator

14.6.3. Procedure :

1. Preparation of 100 ml standard ~ (N/2) oxalic acid solution:

Weight approximately 3.1516gm of oxalic acidand dissolve it in 100 ml distilled water. Note the accurate weight taken

2. Preparation of 250 ml of (N/2) KOH solution:

Dissolve about 7.0 g of KOH in 250 ml of alcohol.

3. Preparation of 250 ml of (N/2) HCl solution:

Dissolve conc. HCl in 250 ml of distilled water with 1:5 ratio.

4. Standardisation of KOH solution against standard (N/2) oxalic acid solution:

Pipette out 10 ml of the alcoholic KOH solution in 250 ml conical flask and titrate with standard (N/2) oxalic acid solution using phenolphthalein as an indicator till the solution turns from pink to colourless. Repeat the titration thrice.

5. Standardisation of (N/2) HCl solution against standard (N/2) alcoholic KOH solution:

Pipette out 10 ml of the standard alcoholic KOH in 250 ml conical flask and titrate with (N/2) HCl solution using phenolphthalein as an indicator till the solution turns from pink to colouless. Repeat the titration thrice.

6. Back titration of excess alkali:

Weigh out accurately about 1 g of the supplied oil sample (mustard oil) in 250 ml conical flask fitted with a condenser. Add 25 ml of ~(N/2) alcoholic KOH solution to it by a pipette. Reflux the mixture on a steam bath till the oil is completely saponified (no oily matter will remain). Cool the solution to bring at room temperature. Now titrate the excess KOH solution by the standard ?(N/2) HCl solution using phenolphthalein as indicator till the solution turns from pink to colourless. Record the titrate value (V5 ml).

7. Blank titration:

Pipette out 25 ml of the standard ~(N/2) alcoholic KOH solution in 250 ml conical flask and titrate with standard ~(N/2) HCl solution using phenolphthalein as an indicator till the colour of the solution turns from pink to colourless. Record the titrate value (V4 ml).

14.6.4. Experimental Result:

Table – 1 : Preparation of 100 ml of (N/2) oxalic acid solution:

Initial weight (g)	Final weight (g)	Weight taken (g)	Weight required (g)	Volume to be made (ml)	Strength of oxalic acid solution
W_1	W_2	$W = W_1 - W_2$	3.1516	100	$W/3.1516$ (N/2) $= S_1$(N)

Table - 2 : Standardisation of KOH solution against standard (N/2) oxalic acid:

No. of obs.	Volume of KOH solution (ml)	Burette reading		Volume of oxcilic acid solution (ml)	Mean volume of oxalic acid solution (ml)
		Initial	Final		
1.	10	0	...	...	
2.	10	...	...	...	V_1
3.	10	...	...	...	

Table - 3 : Standardisation of HCl solution against standard KOH solution:

No. of obs.	Volume of KOH solution (ml)	Burette reading		Volume of HCl solution (ml)	Mean volume of HCl solution (ml)
		Initial	Final		
1.	10	0	...	...	
2.	10	...	...	...	V_3
3.	10	...	...	...	

Table - 4 : Weight of oil

Initial weight (g)	Final weight (g)	Weight taken (g)
W_3	W_4	$W_5 = W_3 - W_4$

Table - 5 : Back titration of escess alkali :

No. of obs.	Volume of KOH solution (ml)	Burette reading		Volume of HCl solution (ml)	Mean volume of HCl solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_5
3.	25	...	...	...	

Table - 6 : Blank titration of KOH solution:

No. of obs.	Volume of KOH solution (ml)	Burette reading		Volume of HCl solution (ml)	Mean volume of HCl solution (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_4
3.	25	...	...	...	

14.6.5. Calculation:

1. Standardisation of alcoholic KOH solution against standard oxalic acid solution:

Volume of oxalic acid = V_1

Strength of oxalic acid solution = S_1(N)

Volume of KOH solution = V_2 ml = 10 ml

Strength of KOH solution = S_2 = ?

We have, V_1 ml × S_1 (N) = V_2 ml × S_2

i.e., V_1 ml × S_1 (N) = 10 ml × S_2

$S_2 = V_1 \times S_1 / 10$ (N)

2. Standardisation of HCl solution against standard alcoholic KOH solution:

Volume of HCL solution = V_3 ml

Strength of HCl solution = S_3 = ?
Volume of KOH solution = V_2 ml = 10 ml
Strength of KOH solution = S_2 (N)

We know, $V_2 \times S_2 = V_3 \times S_3$ i.e., 10 ml $\times$ S_2 (N) = V_3 ml $\times$ S_3
$\therefore$ $S_3 = 10 \times S_2 / V_3$ (N)

3. Blank titre value (25 ml KOH solution) $\equiv$ V_4 ml S_3 (N) HCl solution
W_5 g oil + 25 ml KOH solution $\equiv$ $(V_4 - V_5)$ ml S_3 (N) HCl solution
$\equiv$ $(V_4 - V_5) \times S_3$ ml (N) HCl solution
$\equiv$ $(V_4 - V_5) \times S_3$ ml (N) KOH solution

We have, 1000 ml (N) KOH solution $\equiv$ 56.1 g of KOH
$\equiv$ $(V_4 - V_5) \times S_3$ ml (N) KOH solution
$\equiv$ $0.0561 \times (V_4 - V_5) \times S_3$ g of KOH

Or, W_5 g of oil $\equiv$ $0.0561 \times (V_4 - V_5) \times S_3$ g of KOH
$\equiv$ $56.1 \times (V_4 - V_5) \times S_3$ mg of KOH

$\therefore$ 1 g oil $\equiv$ $56.1 \times (V_4 - V_5) \times S_3 / W_5$ mg of KOH

$\therefore$ The saponification value of the given oil = $56.1 \times (V_4 - V_5) \times S_3/W_5$ mg

14.7 Summary

- Formaldehyde (HCHO) is quantitatively oxidized to formic acid by iodine in an alkaline medium. The oxidation is facilitated by sodium hypoiodite, generated from the reaction of iodine with sodium hydroxide (NaOH). Excess sodium hypoiodite reacts with hydrochloric acid (HCl) to release iodine. The liberated iodine is titrated with a standard sodium thiosulfate solution.
- Commercial vinegar contains acetic acid, alcohol ester, and tartaric acid.
  Acetic acid (a weak acid) is titrated with a strong base, typically sodium hydroxide (NaOH). Phenolphthalein is used as an indicator to signal the end-point of the titration.
- Hypobromite method is used for quantifying urea. The hypobromite method involves reacting urea with sodium hypobromite, leading to the decomposition of urea into nitrogen gas (N_2), carbon dioxide (CO_2), and water (H_2O).
- The volume of nitrogen gas evolved is proportional to the amount of urea in

the sample, which is used to determine urea concentration.

- Sodium hypobromite is unstable when prepared directly from bromine (Br_2) and alkali. It is preferable to produce hypobromite in situ by adding excess bromide to a solution of hypochlorite.
- The number of milligram (mg) of KOH required to saponify 1 g of fat or oil defines as the saponification value.
- Oils and fats are glyceride esters of higher fatty acids. Glycerides are hydrolyzed by refluxing with alcoholic potassium hydroxide (KOH). This reaction produces glycerol and the Na/K salts of the fatty acids. The saponification value is calculated based on the amount of KOH that reacted with the sample.
- The saponification value is critical in industries like soap making and biodiesel production.

14.8 Question

1. Why standardisation of $Na_2S_2O_3$ solution is done by $K_2Cr_2O_7$ solution ?

Ans: $K_2Cr_2O_7$ is used as primary standard and it is obtained in higher state of purity and has high molecular weight. It is cheap compare to KIO_3, $KBrO_3$, etc.

2. Why saponification value of oil is determined?

Ans: The determination of saponification value indicates the rancidity of the oil as well as its purity.

3. What is saponification reaction?

Ans: Discussed in principle.

4. Why alcoholic KOH is used for determination of saponification value?

Ans: Alcohol makes the medium homogeneous and KOH asserts hydrolysis of soap which may consume HCl during titration.

5. What do you mean by rancidity of oil?

Ans: The oil on keeping, develops bad odour we say the oil become rancid. The bad odour is due to the formation of lowed fatty acids due to hydrolysis of oil by moisture or enzymatic.

6. Why rancid or old oils show abnormally high saponification value ?

Ans: The rancid oil contain higher proportion of lower fatty acids. So consumption of mg KOH/g of oil is high. That is why the rancid or old oils show abnormally high saponification value.

7. What is the difference between oils and fats ?

Ans: Oil is liquid containing mainly glycerides of unsaturated fatty acids and fat is solid containing mainly glycerides of saturated fatty acids.

8. How the acid base indicator changes its colour?

Ans: Acid-base indicators are either weak acids or bases. They exist in more than one tautomeric forms. Tautomerism is generally between benzenoid and quinoid forms.

$$\underset{\text{Benzenoid form}}{HIn} \rightleftharpoons \underset{\text{Quinoid form}}{HIn} \rightleftharpoons H^+ + In^-$$

In acid medium, the equilibrium shifts to left i.e. to undissociated HIn. After neutralisation in slight alkaline medium the equilibrium shifts to right gives the colour of ionised quinoid form of indicator.

9. Why is hypobromite prepared in situ instead of directly from bromine and alkali?

Ans: Hypobromite is prepared in situ because it is unstable when prepared directly from bromine and alkali. Producing it in situ by adding bromide to a hypochlorite solution ensures stability and consistent reactivity.

10. What is the saponification value and how is it determined?

Ans: The saponification value is the number of milligrams of potassium hydroxide (KOH) required to saponify one gram of oil, fat, or ester. It is determined by reacting a known quantity of the sample with excess alcoholic KOH, heating the mixture, and then titrating the unreacted KOH with a standard acid solution, usually hydrochloric acid (HCl).

11. Why is it necessary to heat the mixture during saponification?

Ans: Heating is necessary to ensure complete saponification of the triglycerides present in the oil, fat, or ester. The heat facilitates the hydrolysis reaction, allowing all the ester bonds to break and react with KOH.

Reference

- Svehla, G. Vogel 's Qualitative Inorganic Analysis, Pearson Education, 2012. Mendham, J. Vogel 's Quantitative Chemical Analysis, Pearson, 2009.
- Vogel, A.I., Tatchell, A.R., Furnis, B.S., Hannaford, A.J. & Smith, P.W.G., Text-book of Practical Organic Chemistry, Prentice-Hall, 5th edition, 1996.
- Mann, F.G. & Saunders, B.C. Practical Organic Chemistry Orient-Longman, 1960.
- Nad, A. K., Mahapatra, B. Ghoshal, A. An Advanced Course in Practical Chem-istry , Paperback, 2011.
- Dutta, S, B. Sc. Honours Practical Chemistry, Bharati Book Stall.
- Bhattacharyya, R. C, A Manual of Practical Chemistry.
- Khosla, B. D.; Garg, V. C. & Gulati, A. Senior Practical Physical Chemistry, R. Chand & Co.: New Delhi (2011).
- Ahluwalia, V.K. & Aggarwal, R. Comprehensive Practical Organic Chemistry,Universities Press.